I CARBANION- AND FREE RADICAL-TYPE REARRANGEMENTS IN HOMOALLYLIC SYSTEMS

II NUCLEAR MAGNETIC RESONANCE IN CYCLOPROPANES

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Merlin E. H. Howden

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ABSTRACT

I. CARBANION- AND FREE RADICAL-TYPE REARRANGEMENTS IN HOMOALLYLIC SYSTEMS

A study was made of the Grignard and free-radical reactions of vinyl-and phenyl-substituted allyl-carbinyl derivatives. Cyclopropylcarbinyl products were obtained in both types of reactions for the (γ -vinylallyl)-carbinyl and (γ , γ -diphenylallyl)-carbinyl systems, and evidence was obtained bearing on the intermediates involved in some of these rearrangements.

II. NUCLEAR MAGNETIC RESONANCE IN CYCLOPROPANES

Analysis of the nuclear magnetic resonance spectra of a number of cyclopropanes yielded data in the form of spin-spin coupling constants and chemical shifts. This information was correlated with existing theories on molecular structure and on the electronic structure of cyclopropanes. The chemical shifts for several cyclopropane hydrocarbons were interpreted in part in terms of a cyclopropane ring-current effect.

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PART I

Introduction

In view of the mounting body of evidence testifying to the remarkable lability towards interconversion of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl derivatives in carbonium ion (1), and, in some cases, free-radical (2) and carbanion-type (3) reactions, which are believed to involve intermediates of an exciting and unusual type, it was of considerable interest to determine whether rearrangements of appropriately substituted allylcarbinyl derivatives would occur in carbanion and free-radical reactions. Part I of this thesis is concerned with rearrangements of the latter type in phenyl- and vinyl-substituted allylcarbinyl systems and with attempts to elucidate the nature of the intermediates involved. Before discussing this work in detail, it is desirable to provide a theoretical framework for discussion of earlier results with unsubstituted systems.

Calculations of the Stabilities of Intermediates in Cyclopropylcarbinyl-Cyclobutyl-Allylcarbinyl Interconversions.

The systems studied were assumed to consist of three p-orbitals which overlapped in a manner determined by the geometry of the intermediate. Overlap was increased by decreasing the distance between carbon atoms bearing the p-orbitals, accomplished by compressing alternate bond angles. In the procedure used (4, 5) a total energy (TE) minimum is found by balancing electronic delocalization energy (DE) calculated by the simple LCAO molecular-orbital method (6) against strain-energy due to bond-angle bending. With regard to the calculations themselves several points need to be clarified. Firstly, Simonetta and Winstein (5) assumed that (as illustrated for the homoallyl cation I) the angles, θ and θ', between the "bent" σ-bonds at C_3, C_4 and C_2 and the internuclear C_3-C_4 and C_2-C_3 lines were equal, and that the p-orbitals at C_2 and C_4 were perpendicular to the bent bonds rather than to the internuclear lines. This effectively increases 2,4-overlap over the case in which the p-orbitals are taken to be perpendicular to the internuclear lines. Although there is some justification for this approach, the assumption that $\theta = \theta'$ may well be a poor one, particularly for small compressions of the C_2-C_3-C_4 angle. Accordingly, in the present work, as in that of Woods, Carboni and Roberts (4), the p-orbitals involved are assumed to be perpendicular to the adjacent internuclear line. The most realistic delocalization energies available from the present treatment would probably lie between those calculated here and those obtained using Simonetta and Winstein's assumptions.

In previous papers (4, 5), strain energies (SE) were calculated by means of the equation,

$$\text{SE per angle} = 2B\left[0.996 - \frac{(0.5+1.5\cos\alpha/2)(0.577+2^{1/2}\cos\alpha/2)}{4}\right] \quad (1)$$

where B is the normal C-C bond energy and α is the angle of bending from the normal value of 109° 28' for a given bond angle. This equation applies to bonds which can be considered to involve $\underline{sp}^2$ orbitals on one carbon and $\underline{sp}^3$ orbitals on the other carbon. Values of B of 59 and 66.6 kcal./mole were used. These values have been superseded by the much higher currently accepted figure of 82.6 kcal./mole (7). Accordingly the calculations of Woods, Carboni and Roberts (4) on the 7-dehydronorbornyl cation II, and of Simonetta and Winstein (5) on the homoallyl system I, were corrected for this change. Total energies were also calculated for the 7-dehydronorbornyl radical and are given in Table I. The anion was found to have a DE of zero in all cases, while the DE for the radical is always half that for the cation. The unperturbed state is now calculated to be the most stable for the cation and radical, and the configuration with R_{27} = 2.0 A, which gave the maximum stabilization for the cation in the calculations of Woods, Carboni and Roberts, now appears to have a lower-TE value. The outstanding

Table I

Summary of Calculations for the 7-Dehydronorbornyl System.[a]

R_{27}, A	-DE, cation	-DE, radical	net SE	-TE, cation	-TE, radical
2.296	7.7	3.9	0	7.7	3.9
2.200	10.8	5.4	4.5	6.3	0.9
2.000	18.4	9.2	11.1	7.3	-0.9
1.800	25.1	12.5	21.9	3.2	-9.4

[a] All energies are in kcal./mole.

feature of the 7-dehydronorbornyl cation is its high calculated stabilization for the unperturbed state. Appreciable stability is also predicted for the radical in the unperturbed configuration, but this is lost as R_{27} is decreased, by the rapid increase in SE.

In the remaining calculations to be described, a simple formula obtained by Dauben (8) was also used to calculate strain energies and the results were compared with those obtained using Equation 1.

$$\text{SE per angle} = \frac{1}{2}\,\underline{A}\,\alpha^2 \qquad (2)$$

where $\underline{A}$ is the apparent bending force constant and α is the bond angle deformation. Here $\underline{A}$ is allowed to vary with α in the manner shown in

Figure 1. A remains almost constant at 0.0240 kcal. degree^{-2} mole^{-1} up to an α of about 20° and thereafter it follows the line made by the points for cyclobutane (0.024), diphenylene (0.0176) and cyclopropane (0.0060). In this way an approximate strain-energy formula is obtained in which Dauben (8) considers that all factors except for "torsional strain" have been lumped together in the A values for highly-strained systems. Equation 2 is also believed to hold for angle-bending at an sp^2 center (8). A comparison of the strain energies per angle calculated from Equations 1 and 2 is made in Figure 2. Up to $\alpha = 30°$ the curves for the two equations follow each other fairly closely. Thereafter they show quite different behavior in that the curve for Equation 1 continues to rise monotonically, while the graph for Equation 2 reaches a maximum of 9.3 kcal./mole at an α of 40°, then the strain energy rapidly decreases as α is further increased. The results of the calculations for the homoallyl system (1,4-overlap neglected) are summarized in Table II. Since of the two lowest orbitals one is bonding and the other is non-bonding, the DE's for the homoallyl cation, radical and anion are identical in simple MO theory, which neglects interelectronic repulsion. The effect of using Equation 1 or 2 for the calculation of SE, on the TE for the homoallyl system is shown in Figure 3 in which $-TE_{11}$ and $-TE_{12}$ from Table II are plotted against R_{24}. The variation of TE with R is seen to be quite different for the

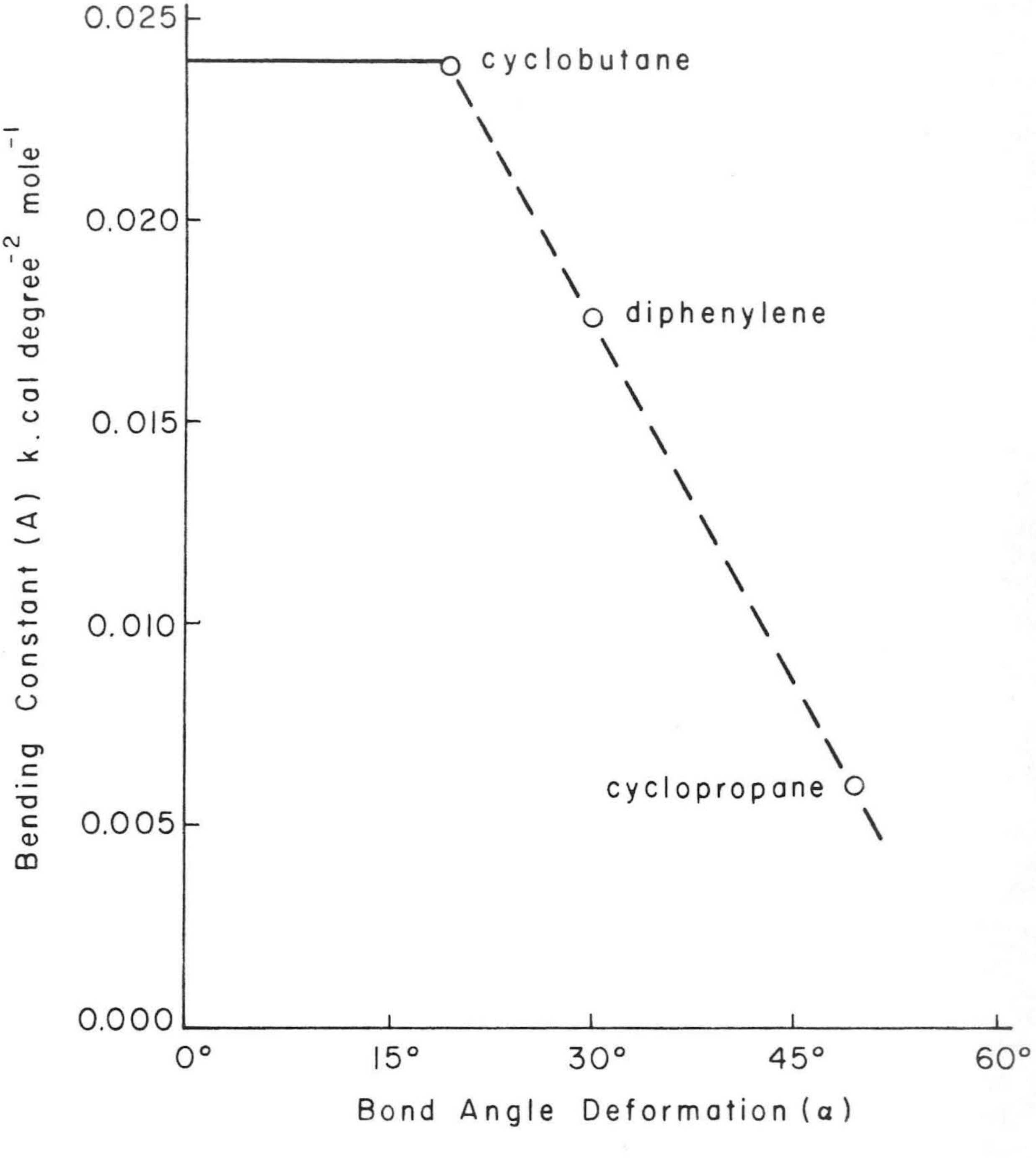


Fig. 1.— Relation between the apparent bending constant (A) and bond-angle deformation (α), according to Dauben (8).

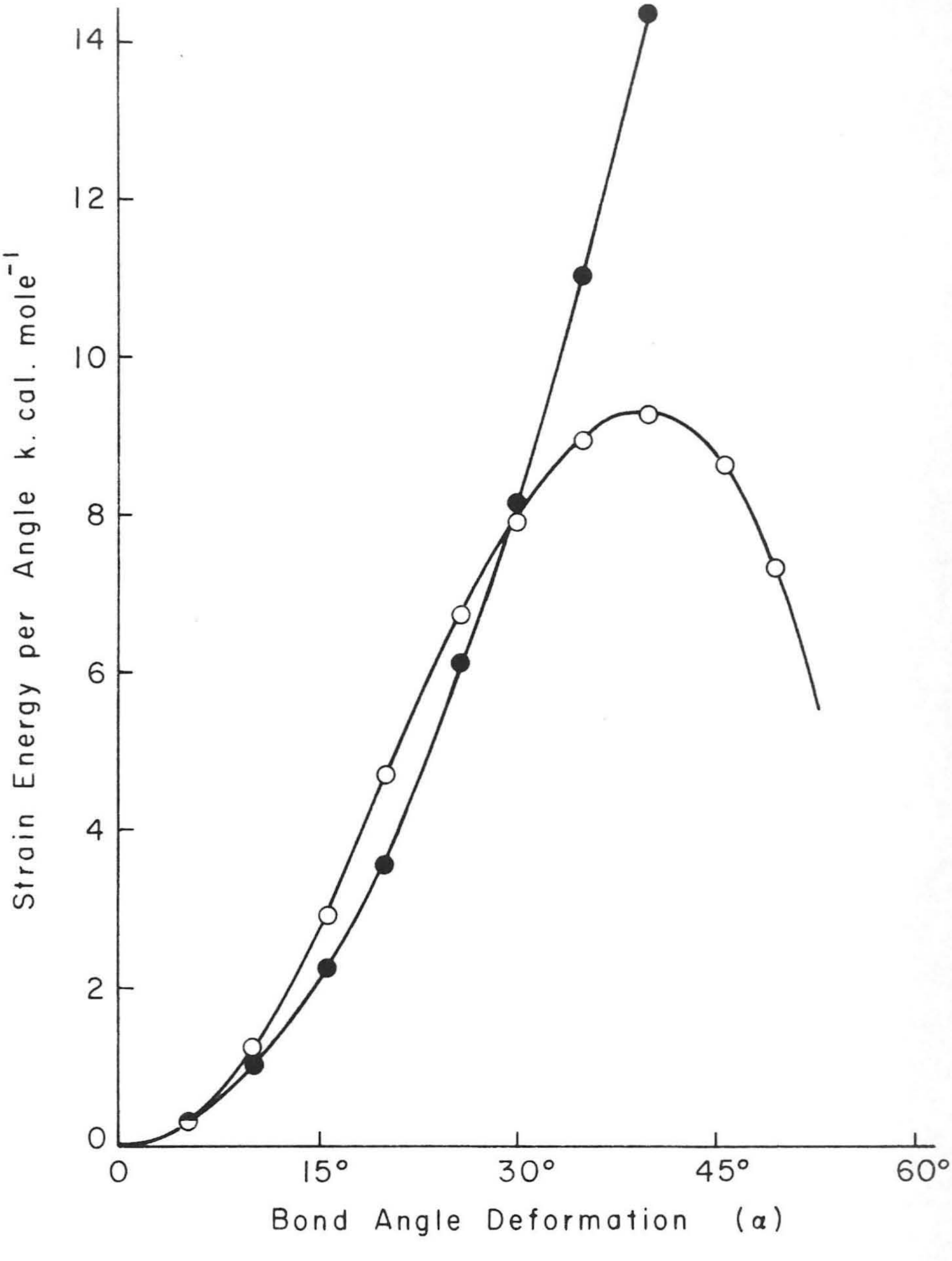


Fig. 2.— Comparison between the strain energies per angle calculated from Equation 1 (shaded circles) and from Equation 2 (open circles).

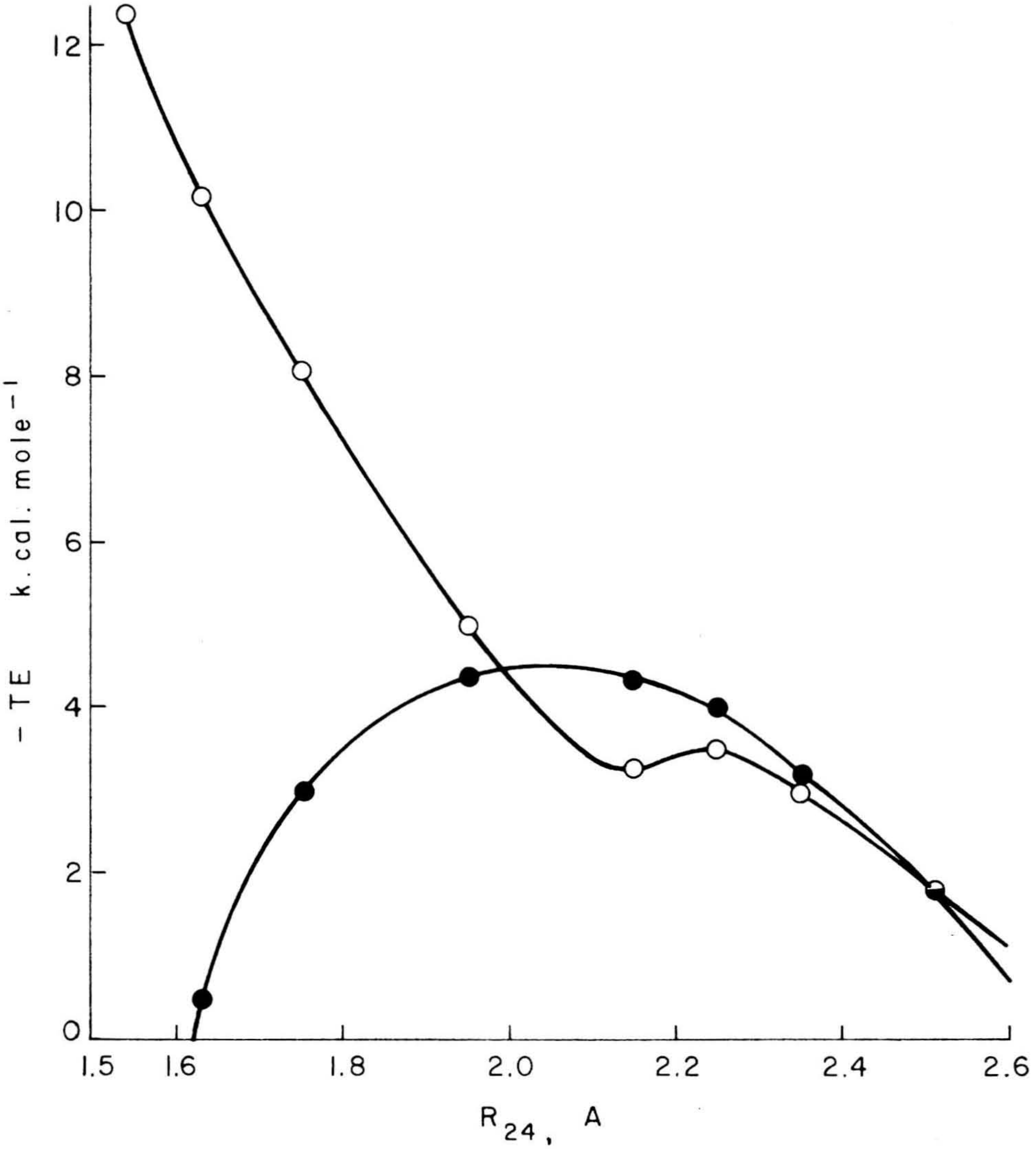


Fig. 3.— Comparison of the total energies for the homoallyl system in which strain energies were calculated using Equation 1 (shaded circles) or Equation 2 (open circles).

Table II

Summary of Calculations for the Homoallyl System.[a]

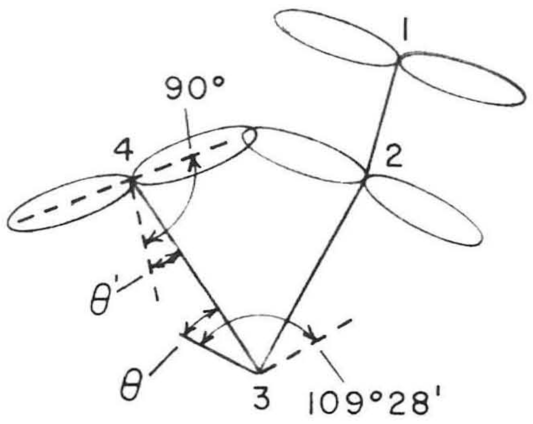
R_{24}, A	$-DE_1$ ref. 5	$-DE_2$ this work	SE_1 Eqn. (1)	SE_2 Eqn. (2)	$-TE_{11}$ $(-DE_1-SE_1)$	$-TE_{12}$ $(-DE_1-SE_2)$	$-TE_{21}$ $(-DE_2-SE_1)$	$-TE_{22}$ $(-DE_2-SE_2)$
2.51	1.8	1.8	0.0	0.0	1.8	1.8	1.8	1.8
2.35	4.2	3.3	1.0	1.2	3.2	3.0	2.3	2.1
2.25	6.4[b]	5.0	2.3	2.9	4.0	3.5	2.8	2.1
2.15	8.3	6.8	4.1	5.0	4.3	3.3	2.7	1.7
1.95	13.2	10.8	8.8	8.2	4.4	5.0	2.1	2.7
1.75	17.4	15.1	14.4	9.3	3.0	8.1	0.6	5.8
1.63	18.8	17.2	18.3	8.6	0.5	10.2	-1.2	8.5
1.54	19.7	18.5	21.4	7.3	-1.7	12.4	-3.0	11.1

[a] All energies are in kcal./mole (β_{12} assumed to be 20 kcal./mole).

[b] Value calculated in this work.

two cases. When Equation 1 is used, a single maximum -TE value of 4.5 kcal./mole is obtained at an R of 2.05 A. When R is further decreased -TE also decreases monotonically. On the other hand, use of Equation 2 leads to a subsidiary maximum in -TE of 3.5 kcal./mole for an R of 2.25 A. When R is further decreased, -TE decreases slightly at first, then rises, and continues to rise monotonically. The latter behavior is due to the fact that Equation 2 predicts SE to decrease for small values of R. It is difficult to tell which equation most correctly predicts the energy of the system in the critical region of R_{24} equal to 1.8 to 2.5 A. There may well be more than one -TE maximum for the actual intermediates. The C-C bond energy correction now reduces the $-TE_{11}$ value for the homoallyl system to 27% of the delocalization energy of the allyl system. The corresponding figure for $-TE_{21}$ is 17%, considerably lower than the value of 40% originally calculated by Simonetta and Winstein (5).

The tricyclobutonium cation III has frequently been considered (9) as an intermediate in carbonium ion-type interconversions of cyclopropylcarbinyl, cyclobutyl and allylcarbinyl derivatives since it accounts very economically for the high degree of isotope-position rearrangement observed in reactions with the ^{14}C-labelled compounds. Recent results (1,10) suggest that the tricyclobutonium ion is more properly regarded as a "way-point" or transition state in the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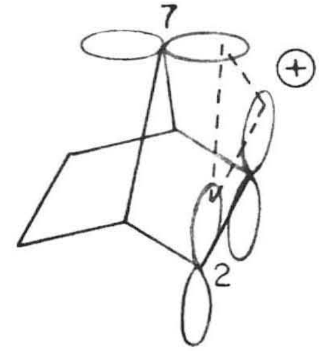
I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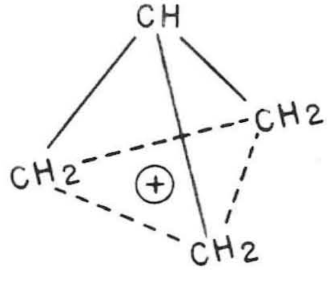
II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CH2
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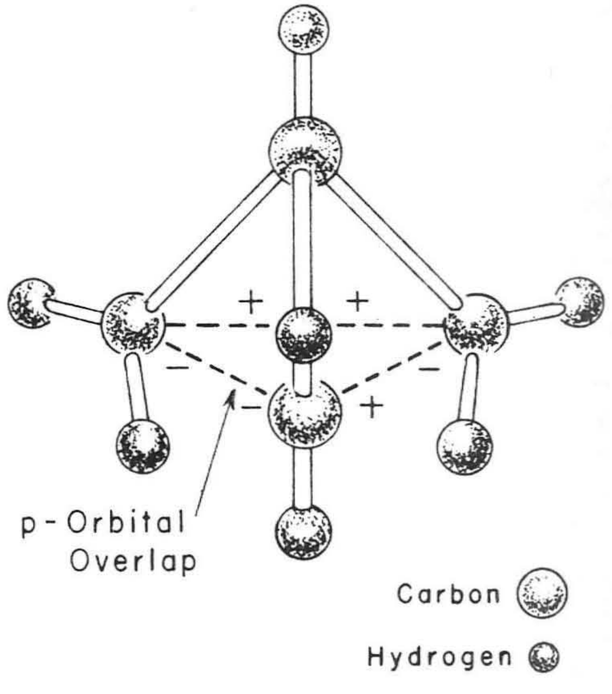
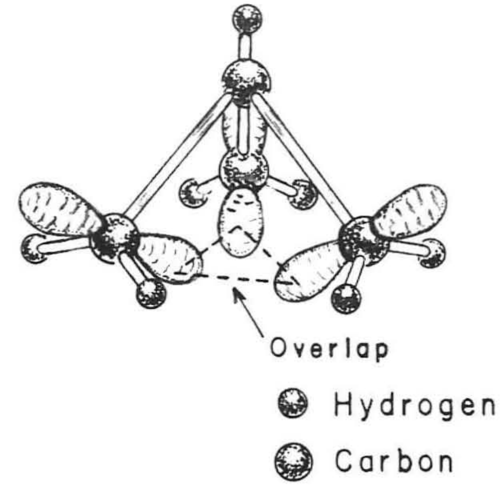
CH2

III


+
+
−
−
−
+
p-Orbital Overlap
Carbon
Hydrogen

IV

rapid, but not instantaneous, interconversion of three unsymmetrical bicyclobutonium ions (vide infra), which are currently the most fashionable intermediates for these reactions. Calculations of the total energies of the tricyclobutonium cation, radical and anion were carried out for two conformations IV (1) and V, assuming a $CH-CH_2$ bond length of 1.50 A. As the signs for the p-orbital wave-functions indicate, IV is destabilized by anti-bonding overlap between two of the methylene groups. A similar situation arises in the 7-norbornadienyl cation VI, and may in part explain why this cation appears to exist in the configuration VII (11). Simple MO calculations (12) indicate however that VI is considerably more stable than VII in the unperturbed state despite the anti-bonding overlap. For IV and V overlap was increased by compressing the three C-C bonds together in a symmetrical manner. This procedure leads to high SE's since three angles are being bent simultaneously. In V, p-orbital overlap was assumed, although Roberts and Mazur (9) originally postulated sp^3 overlap for this configuration. The calculations for the cation IV indicate that it is an extremely unstable system electronically, since its energy diagram (vide infra) is inverted relative to a cyclopropenium cation. The DE was found to be always positive for the cation (5.6 kcal./mole for R, the C-C distance between CH_2 groups, equal to 1.6 A), and with strain energy added, IV would seem to be a very poor



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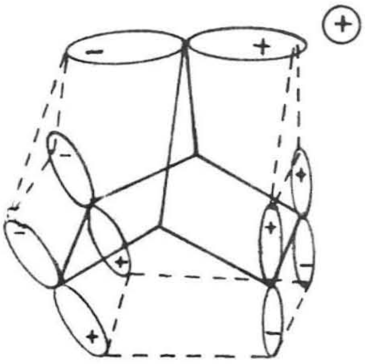
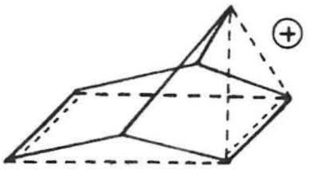
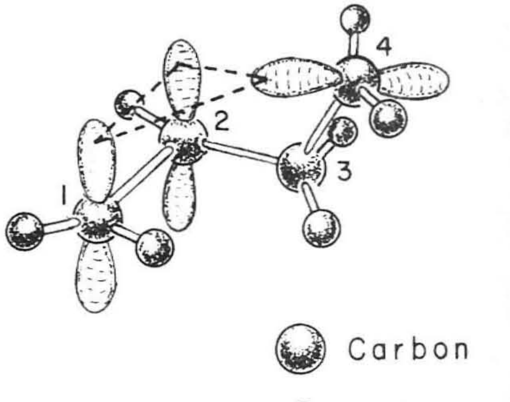


VI



VII



VIII

configuration indeed for the cation. Since the cation has two electrons available for the two lowest degenerate orbitals, IV might be expected to be a triplet state for the cation.

The situation in IV is improved somewhat for the radical and particularly the anion, although at no configuration does the SE_1 permit a net negative TE. These calculations are summarized in Table III. Total energies are not given since these are nearly all large and positive.

Table III

Summary of Calculations for the Tricyclobutonium Conformation IV.[a]

R, A	β'/β[b]	-DE, radical	-DE, anion	SE_1, Eqn. (1)	SE_2, Eqn. (2)
2.45	0.2980	-22.1	-16.2	0	0
2.37	0.3418	-19.5	-12.7	0.9	0.9
2.30	0.3784	-17.3	- 9.7	2.7	3.2
2.20	0.4327	-14.0	- 5.4	6.3	8.2
2.10	0.4942	-10.4	- 0.5	11.8	14.8
2.00	0.5598	- 6.4	4.8	18.3	20.1
1.92	0.6152	- 3.1	9.2	24.5	23.7
1.85	0.6656	- 0.1	13.3	30.0	25.9
1.70	0.7789	6.7	22.3	43.8	27.7
1.60	0.8592	11.6	28.7	53.8	26.3

[a] All energies are in kcal./mole

[b] β' is the exchange integral for the <u>p</u>-overlap in terms of β, the integral for overlap in ethylene.

The anti-bonding overlap impasse encountered in IV is avoided in V. The calculations for this case are presented in Table IV,

Table IV

Summary of Calculations for the Tricyclobutonium Conformation V.[a]

R, A	β'/β[b]	-DE, cation	-DE, radical	$-TE_1$ (DE cation $-SE_1$)	$-TE_2$ (DE cation $-SE_2$)
2.30	0.3316	-13.5	-20.1	-16.2	-16.6
2.20	0.4114	- 7.1	-15.3	-13.4	-15.3
2.10	0.4999	0.0	-10.0	-11.8	-14.8
2.00	0.5917	7.3	- 4.5	-11.0	-12.8
1.92	0.6658	13.3	- 0.1	-11.2	-10.4
1.85	0.7307	18.5	3.8	-11.5	- 7.5
1.7	0.8624	29.0	11.7	-14.8	1.3
1.6	0.9408	35.3	16.5	-18.5	9.0

[a] All energies are in kcal./mole; SE's are the same as in Table III.

[b] See footnote to Table III.

where the SE's are the same as in Table III. TE values for the radical and anion and DE values for the anion are not given in Table IV, since these are all large and positive. From Table IV, the maximum value of $-TE_1$ for V is seen to be -11.0 kcal./mole at R equal to 2.0 A. Thus this conformation is also calculated to be very unstable for the cation, and a fortiori for the radical and anion. Matters are not helped by the fact that in V, with R equal to 2.0 A, hydrogen atoms on the methylene groups are only 1.78 A apart, so that V is also destabilized by substantial H-H non-bonded repulsions. These would be alleviated to a certain extent by using $\underline{sp}^3$ hybridization as suggested by Roberts and Mazur (9). The outlook for tricyclobutonium ions as intermediates or even transition states in these interconversion reactions appears very dim from the viewpoint of the above calculations. The main reasons for this are that the strong ethylenic 1, 2-overlap has been destroyed in the tricyclobutonium system, and that high-strain energies are encountered since three bond-angles are being compressed simultaneously.

Representative calculations were also made for bicyclobutonium cations, radicals and anions using the conformation VIII. The bicyclobutonium system differs from the homoallyl case (I) in that 1, 4-overlap is taken into account. The geometry of VIII is rather complicated and structural parameters were measured from an accurately-scaled mechanical model. Angles between p-orbitals and internuclear lines, and skew angles between p-orbitals were measured with a bevel protractor and are considered to be accurate to ± 1°. Internuclear distances were obtained using calipers and were reproducible to ±0.005 A. The C_1-C_2 distance was fixed at 1.34 A and the C_2-C_3 and C_3-C_4 lengths were assumed to 1.54 A. The geometric measurements and calculated exchange integrals are presented in Tables V and VI, and the corresponding delocalization, strain and total energies are given in Table VII. The roots of the cubic equations were obtained from the tables of Salzer (13).

Table V

Structural Parameters for the Bicyclobutonium System VIII.

Calcn. No.	$\alpha°$	$\beta°$	$\gamma°$	$\delta°$	$\theta°_1$	$\theta°_2$	$\theta°_{41}$	$\theta°_{42}$	$\epsilon°_{14}$	$\epsilon°_{24}$
1	109	102	26	66	61.0	56.0	60.5	55.6	36.2	0
2	109	102	26	85.5	61.0	56.0	45.7	50.8	19.1	26.2
3	109	102	26	102	61.0	56.0	35.0	52.5	0	46.9
4	120	99.5	20	87.5	61.5	53.8	42.5	49.7	20.8	21.8
5	110	99.5	20	90.5	59.3	53.9	44.0	48.6	21.8	24.9
6	100	99.5	20	92.5	56.8	53.0	45.4	48.5	23.6	27.5
7	90	99.5	20	93.5	53.6	52.9	48.4	50.0	24.5	28.9
8	80	99.5	20	91.5	51.0	53.1	54.4	48.8	26.3	26.9
9	110	109.5	20	88	62.8	58.1	49.6	53.4	17.8	22.3
10	110	89.5	20	94.5	56.0	50.0	37.5	44.2	28.0	33.8
11	110	79.5	20	99.5	52.0	45.8	30.8	39.1	35.0	43.6
12	110	69.5	20	105.5	49.9	41.2	24.3	36.0	52.7	56.0
13	110	60	20	110	48.6	34.2	20.3	33.8	73.5	68.3
14	115	74.5	20	101.5	51.6	43.2	26.2	36.0	44.9	44.8
15	115	74.5	35	90.5	53.2	49.5	31.6	35.2	42.6	47.8
16	120	92.5	20	92	57.0	48.9	36.9	44.3	23.2	30.2

Key to Table V:

$\alpha = C_1$-C_2-C_3 angle.

$\beta = C_2$-C_3-C_4 angle.

γ measures the angle between the C_2-C_3-C_4 plane and the C_1-C_2-C_3 plane. It increases in the counter-clockwise direction as an observer looks along the C_3-C_2 bond, and is 0° when C_3-C_4 is coplanar with the C_2-C_3 bond and the p-orbital at C_2. It is 90° when C_3-C_4 lies in the C_1-C_2-C_3 plane.

δ measures the angle between the plane defined by the p-orbital at C_4 and the C_3-C_4 bond, and the C_2-C_3-C_4 plane. It is 90° when the p-orbital at C_4 is coplanar with C_2-C_3-C_4 and increases in the counter-clockwise direction for an observer looking along the C_4-C_3 bond.

θ_1, θ_2 are the angles between the p-orbitals at C_1, C_2 and the C_1-C_4, C_2-C_4 internuclear lines respectively.

θ_{41}, θ_{42} are the angles between the p-orbital at C_4 and the C_1-C_4, C_2-C_4 internuclear lines respectively.

$\epsilon_{14}, \epsilon_{24}$ are the angles between the p-orbitals at C_1 and C_4, and at C_2 and C_4, as seen by an observer looking along the C_1-C_4 and C_2-C_4 internuclear lines respectively.

Table VI

Internuclear Distances and Exchange Integrals for the Bicyclobutonium System VIII.

Calcn. No.	R_{14}, A	R_{24}, A	β_{14}/β	β_{24}/β
1	2.730	2.380	0.1414	0.3686
2	2.730	2.380	0.1802	0.3743
3	2.730	2.380	0.1980	0.3419
4	2.900	2.335	0.0868	0.4176
5	2.755	2.325	0.1624	0.4247
6	2.585	2.330	0.2670	0.4242
7	2.428	2.338	0.3654	0.4144
8	2.255	2.328	0.4486	0.4231
9	2.953	2.495	0.0443	0.2899
10	2.555	2.145	0.2978	0.5576
11	2.340	1.955	0.4695	0.7052
12	2.130	1.730	0.5996	0.8443
13	1.920	1.528	0.7046	0.9253
14	2.290	1.845	0.4995	0.7973
15	2.100	1.845	0.5870	0.7457
16	2.760	2.210	0.1776	0.5270

Table VII

Summary of Calculations for the Bicyclobutonium System VIII.

Calcn. No.	-DE ⊕	-DE ⊙	-DE ⊖	SE_1 (Eqn.1)	SE_2 (Eqn. 2)	$-TE_1$ ⊕	$-TE_1$ ⊙	$-TE_1$ ⊖	$-TE_2$ ⊕	$-TE_2$ ⊙	$-TE_2$ ⊖
1	4.7	2.9	1.1	1.8	2.1	2.9	1.1	-0.8	2.7	0.8	-0.9
2	5.5	3.2	0.8	1.8	2.1	3.6	1.3	-1.0	3.4	1.1	-1.2
3	5.2	2.8	0.4	1.8	2.1	3.3	0.9	-1.4	3.1	0.7	-1.6
4	4.8	3.6	2.4	1.0	1.2	3.8	2.6	1.3	3.6	2.4	1.2
5	6.1	3.8	1.5	2.1	2.4	4.0	1.7	-0.6	3.7	1.4	-0.9
6	8.0	4.3	0.5	4.6	5.9	3.4	-0.3	-4.1	2.1	-1.6	-5.4
7	9.8	4.9	0.1	9.2	9.1	0.6	-4.3	-9.1	0.7	-4.2	-9.0
8	11.7	5.8	0.0	15.4	10.5	-3.7	-9.6	-15.4	1.2	-4.7	-10.5
9	2.2	1.7	1.2	1.0	1.2	1.1	0.6	0.2	1.0	0.5	0.0
10	11.5	6.5	1.6	4.6	5.9	6.9	1.9	-3.1	5.6	0.6	-4.4
11	18.9	10.2	1.6	9.2	9.1	9.7	1.0	-7.6	9.8	1.1	-7.5
12	25.6	13.8	2.1	15.4	10.5	10.2	-1.6	13.3	15.1	3.3	-8.4
13	30.4	16.4	2.4	22.5	8.5	7.9	-6.1	-20.1	21.8	7.8	-6.2
14	21.9	12.3	2.6	11.3	9.2	10.6	0.9	-8.7	12.7	3.0	-6.6
15	22.7	11.8	0.9	11.3	9.2	11.4	0.5	-10.5	13.5	2.6	-8.4
16	8.4	5.5	2.6	2.7	3.5	5.7	2.8	-0.1	4.9	2.0	-0.9

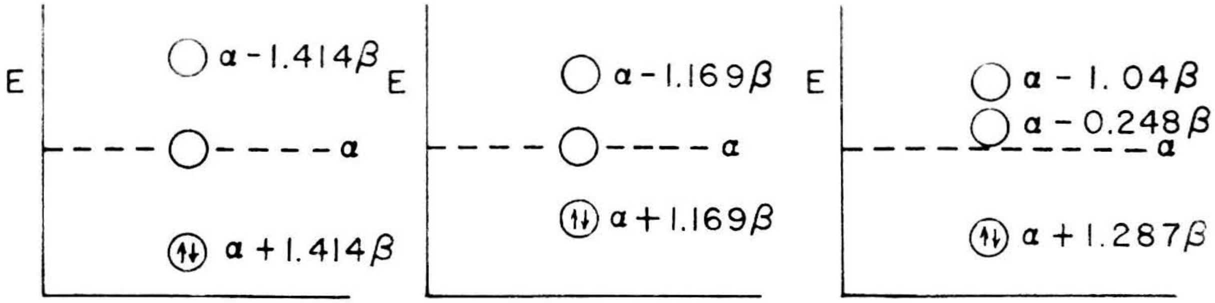
Key to Table VII:

The symbols ⊕ , ⊙ and ⊖ refer to the cation, radical and anion respectively. All energies are in kcal./mole. The calculation numbers correspond to those in Table V. TE_1 and TE_2 denote total energies obtained by adding strain energies calculated in Equations 1 and 2 respectively to the delocalization energies.

The strain energy in VIII is determined in these calculations only by the angles α and β. Since Dauben (8) had found that Equation 2 applied equally well to bending at an $\underline{sp}^2$ center, this was assumed for Equation 1 also, although Equation 1 was not originally derived for this case. This assumption for Equation 1 is probably a reasonably good one for the small compressions of α present in the most stable configurations found in Table VII. Discussions of TE values for VIII will be confined to those for TE_1 since these are most easily compared with corresponding figures for the homoallyl and 7-dehydronorbornyl cases. Calculations 1-3 correspond in geometry to the 2-dehydronorbornyl system. The β_{14} value in Calc. 1 indicates that 1,4-overlap is appreciable in the unperturbed system. In 1 and 3 the p-orbitals at C_2 and C_4 and C_1 and C_4 respectively are eclipsed, while in 2 the plane formed by the C_3-C_4 bond and the p-orbital at C_4 approximately bisects C_1-C_2. Thus the calculations 1 to 3 represent conditions of increasing 1,4-overlap in which strain-energy does not change. Table VII shows that the stabilization of the anion decreases along this series while the cation and radical are more stable with the C_4 p-orbital in the central position. The cation gains more by increased 1,4-overlap than the radical. These results are independent of strain-energy considerations, and the result for the radical is particularly interesting since it indicates that, for a system where the arrangement of the orbitals is already determined by the molecular geometry, some stabilization due to 1,4-overlap can be expected. In the remaining calculations, the plane formed by the C_3-C_4 bond and the p-orbital at C_4 was made for simplicity to bisect the C_1-C_2 bond. Calculations 4 to 8, and 9 to 13 with 5, represent two swathes cut through the energy surfaces for this system in which first β was held constant at an intermediate value and α was varied, then α was fixed and β was varied, respectively. Table VII shows that the stabilization of the cation increases slightly for the first 10° decrease in α, then decreases rapidly as α is further diminished. In contrast, the compression of β is seen to have a highly beneficial effect on the stability of the cation. The reason for this difference in behavior is that in varying α only, R_{24} remains constant (see measured values in Table VI), and the 2,4-overlap barely changes, while when β is decreased both 1,4- and 2,4-overlap increase markedly. Using the results of Calculations 4 to 13 rough energy surfaces were constructed for the cation and radical and values of α and β for the positions of the estimated minima were obtained. The surfaces appeared to fall smoothly to a single minimum, although the series of surfaces which would be obtained if α, β, γ and δ were allowed to vary independently might well show more complex topography. Calculation 14 represents the minimum estimated for the cation with γ at 20°. When γ was increased so that 1,4-overlap increased, further stabilization of the cation resulted but the stability of the radical and anion decreased. Calculation 16 corresponds to the minimum estimated for the radical.

The maximum value, 11.4 kcal./mole, of the net stabilization energy calculated for the bicyclobutonium cation is thought to be close to the actual maximum obtainable from this treatment. Comparison with Table II indicates that the bicyclobutonium cation is calculated to be more stable than the "homoallylic" cation by a factor of four. The effect of 1,4-overlap is therefore very powerful. The high stability calculated for the bicyclobutonium cation is in accord with enhanced solvolytic reactivity found for cyclopropylcarbinyl and cyclobutyl derivatives (14). The configuration at which maximum stabilization is attained for the cation is seen from Tables V and VI to be an unsymmetrical one in which 1,4- and 2,4-overlap are comparable but not equal. Very little bending (5°) of α has occurred while β has been strongly compressed (by 35°). If the tricyclobutonium cation was to be considered as a transition state for interconversion of bicyclobutonium cations, then reference to Tables IV and VII shows that the calculated enthalpy of activation for this process is 22.4 kcal./mole. Unless large entropy differences of the correct sign are to be invoked, this barrier would seem to be too imposing for the rapid interconversion envisaged (1b) for bicyclobutonium cations. The validity of this comparison between the calculated total energies of the two structures is doubtful however, since their σ-bond systems are quite different and the strong ethylenic overlap in the bicyclobutonium intermediate is no longer present in the tricyclobutonium case. Also the stability of V would probably be considerably greater with $\underline{sp}^3$ rather than $\underline{p}$ overlap since the $\underline{sp}^3$ overlap integrals greatly exceed those for $\underline{p}$ overlap (15). Recent results of Borcic and Sunko (16) on deuterium-isotope effects in the solvolysis of ring-deuterated cyclopropylcarbinylbenzenesulfonate indicate the non-equivalence of C_3 and C_4 in the transition state for the solvolysis.

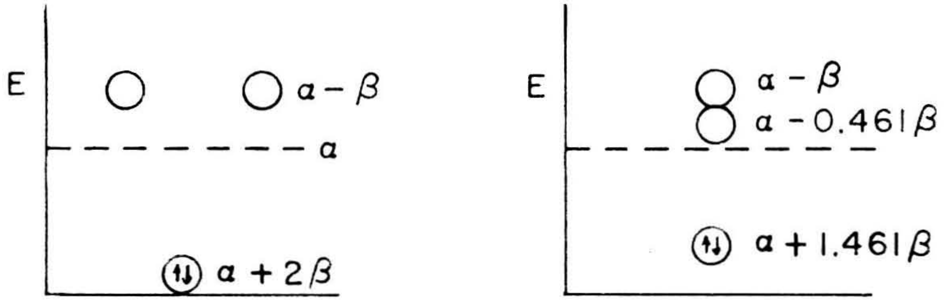
Comparison of Tables VII and II shows that in no instance is the net stabilization energy for the bicyclobutonium radical or anion calculated to be greater than that for the most stable homoallyl case. The results therefore predict that pure 2,4- or "homoallylic" overlap leads to the most stable radicals and anions. This result is vindicated by earlier work (17, 2,3,18) and this thesis (vide infra) in which it was found that cyclobutyl compounds were not interconverted with cyclopropylcarbinyl or allylcarbinyl derivatives in reactions involving free-radical or carbanion-type intermediates. Although the stabilities calculated for the homoallyl intermediates are much lower than for the bicyclobutonium cation, non-classical structures for the former are not ruled out. A qualitative picture of the reasons for the decrease in stability of the radical and anion with increasing 1,4-overlap is obtained by consideration of the MO energy diagrams shown in Figure 4. Data are given for the homoallyl, bicyclobutonium and 7-dehydronorbornyl systems with approximately the same values for the 2,4- or 2,7-



Allyl

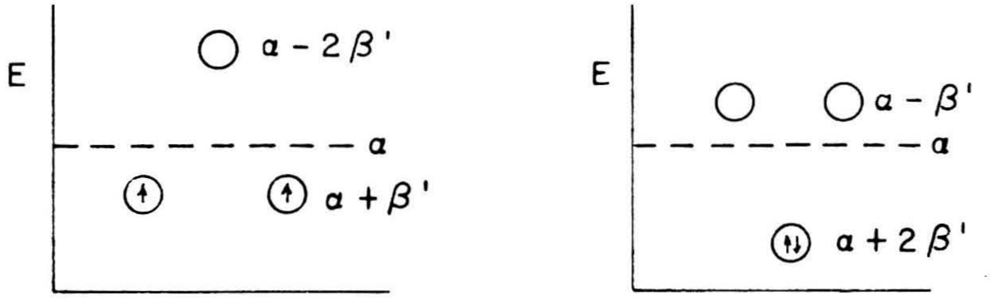
Homoallyl ($\beta_{24} = 0.607\beta$)

Bicyclobutonium ($\beta_{24} = 0.558\ \beta$)



Cyclopropenium

bis-homocyclopropenyl (7-dehydronorbonyl with $\beta_{24} = 0.580\beta$)



Tricyclobutonium IV

Tricyclobutonium V

Fig. 4.– Simple MO energy diagrams for p-overlap in various three-orbital two-electron systems.

exchange integral. It is seen that in passing along this series the energy of the lowest bonding orbital decreases, so that the stability of the cation increases. However, the non-bonding orbital in the homoallyl diagram becomes a weakly antibonding orbital in the bicyclobutonium diagram. The energy lost by the bonding orbital relative to the homoallyl case is more than offset by the energy gained by the antibonding orbital, and as a result the radical, and especially the anion, are calculated to be less stable electronically in the bicyclobutonium than in the homoallyl configuration.

The electron distribution in the most stable configuration (Calculation 15) found for the bicyclobutonium cation was obtained by calculating the coefficients of the atomic orbitals in the bonding molecular orbital. The net atomic charges thus obtained for C_2, C_1 and C_4 were in the ratio 1: 1.34: 2.05 and correspond to the percentage contributing resonance structures given in IX. This distribution appears to disagree with experiment since the proportions of products corresponding to nucleophilic attack on these positions are about 10: 10: 1 (1b). The calculated values predict far too much charge on C_4. This may be due to the fact that changes in hybridization at the various carbon atoms as overlap increases have not been taken into account. Another possibility is that the experimental product ratios do not accurately represent the charge distributions in the isolated intermediate, and that stereoelectronic and other factors are important in determining the product ratios.

The highly approximate nature of the preceding calculations cannot be overemphasized. No allowance has been made for hybridization changes nor for interelectronic repulsion. The latter would be expected to lead to increased stabilization of radical intermediates relative to anions and of the cations relative to the radicals. Approximate ways of estimating the effect of electron repulsion have been discussed by Streitweiser (19). The strain-energy estimations are also very crude since there is no reliable way of knowing which equation to use and over what range it is valid. Also non-bonded repulsions, although likely to be important, have not been explicitly considered. Despite the approximations implicit in the treatment, it is gratifying to note that most of the major predictions of the calculations are borne out by experiment.

Rearrangements of Allylcarbinyl Grignard Reagents.

The foregoing calculations are of little use in predicting the proportions of allylcarbinyl and cyclopropylcarbinyl products from reactions involving carbanion-type intermediates. A number of experimental results (concerned with rearrangements of Grignard reagents) bearing on this problem have been discussed in detail by Nordlander (3) and will be mentioned briefly here. It was found by Roberts and coworkers by nuclear magnetic resonance (n-m-r) and product studies, that:

(i) The Grignard reagent from cyclopropylcarbinyl or allylcarbinyl halides is predominantly the allylcarbinyl Grignard reagent and affords allylcarbinyl products.

(ii) The Grignard reagent from cyclobutyl halides is predominantly the cyclobutyl Grignard reagent and yields cyclobutyl products.

(iii) The Grignard reagent from 5-endo-dehydronorbornyl or nortricyclyl halides exists predominantly as the nortricyclyl Grignard reagent and gives nortricyclyl products.

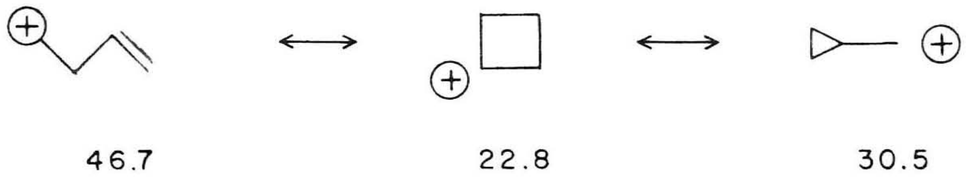
(iv) The 1- and 2-positions in allylcarbinyl Grignard reagents are slowly interconverted at room temperature as measured by isotope-position rearrangements (18).

Apart from the well-known lability of allylic Grignard reagents (20, 3), rearrangements in the tritylmethyl system (21) and the examples of phenyl migration recently reported by Grovenstein (22) and Zimmerman, et al. (23), the above represent the only well-documented examples of structural rearrangement of the carbon fragments in carbanion-type reactions. The mechanism of the interconversion (iv) is not known, although a plausible intermediate is the cyclopropylcarbinyl Grignard reagent X, which by opening the ring in two ways can lead to equilibration of the 1- and 2-positions. In X, and elsewhere in this thesis, the X group attached to magnesium is unspecified since some doubt still exists as to the structure of Grignard reagents (3). The kinetics of rearrangement of the 1-deuterium-labelled allylcarbinyl

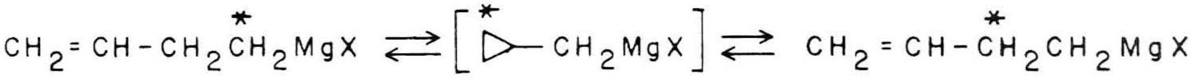
Grignard reagent have been followed by Shafer, et al. (18) by n-m-r spectroscopy. Although a first-order rate law is indicated, the molecularity of the rearrangement in Grignard reagent was not established since both uni- and bimolecular processes should give a first-order rate law (24).

In the present work, a study was made of the reactions of 3- and 4-substituted allylcarbinyl Grignard reagents. It was anticipated that phenyl- or vinyl-substitution at these positions might facilitate rearrangement by stabilization of the negative charge in the rearranged Grignard reagent and that this would be manifested by formation of cyclobutyl or cyclopropylcarbinyl products. It was found that carbonation of the Grignard reagent from (β-phenylallyl)-carbinyl chloride XI gave a 61% yield of (β-phenylallyl)-acetic acid. No 1-phenylcyclobutanecarboxylic acid was obtained. Thus even when tempted with a well-placed phenyl group the allylcarbinyl Grignard reagent cannot be induced to give cyclobutyl products. This is in accord with the observation (3) that the cyclobutyl Grignard reagent itself does not rearrange. The above result does not disallow the possibility that some 1-phenylcyclobutyl Grignard reagent is present in equilibrium with the open-chain form prior to reaction with carbon dioxide.

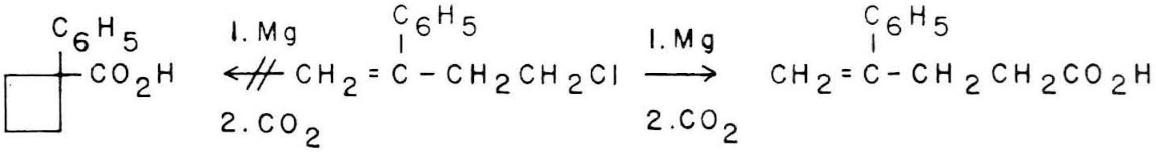
Another system investigated was the Grignard reagent from 1-bromo-3,5-hexadiene, a vinyl 4-substituted allylcarbinyl halide. Here, by analogy with X, there is the possibility of an equilibrium



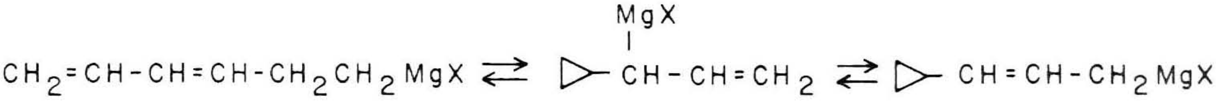
IX



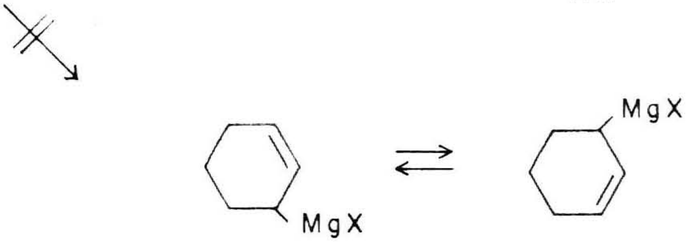
X



XI

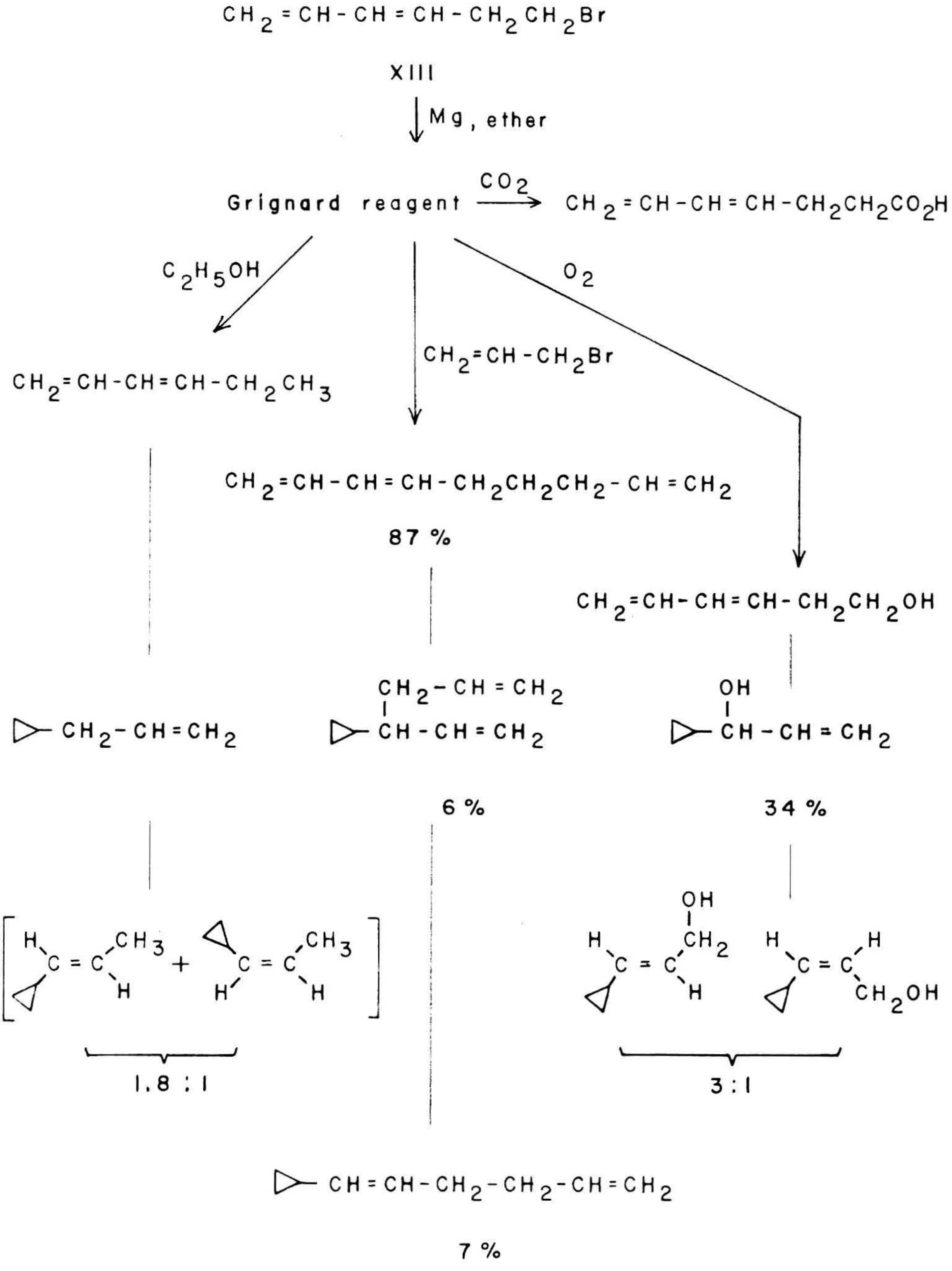


XII



XIV

with the cyclopropylallyl Grignard reagent XII, which,like the butenyl Grignard reagent (25), would probably exist as a rapidly equilibrating mixture of the α- and γ-cyclopropylallyl forms. Unless special ability to stabilize negative charge is attributed to the cyclopropyl group, the latter equilibrium is expected, on the basis of the results with the butenyl Grignard reagent, to lie very far in favor of the γ-cyclopropylallyl form. This does not imply, however, that nearly quantitative rearrangement of the (γ-vinylallyl)-carbinyl Grignard reagent to the γ-cyclopropylallyl Grignard reagent would necessarily occur. The products isolated from reactions of the Grignard reagent from 1-bromo-3,5-hexadiene XIII with carbon dioxide, allyl bromide, ethanol and oxygen, are shown on the following page. Carbonation afforded exclusively 4,6-heptadienoic acid as the only carboxylic acid product. The reaction with ethanol gave about 77% 3,5-hexadiene, 10% allylcyclopropane and 13% of what was tentatively identified as a mixture of cis- and trans-propenylcyclopropane with one of the isomers predominating by a factor of 1·8. These percentages and those given in the chart apply to the relative proportions of compounds in the separated product mixture, and for the ethanol reaction are very rough due to difficulties in achieving satisfactory vapor-phase chromatography (v-p-c) resolution. No cyclohexene was found in the product indicating that the alternative, and quite plausible, rearrangement to the cyclohexenyl Grignard reagent XIV does not occur to a


CH2=CH-CH=CH-CH2CH2Br
XIII
Mg, ether
Grignard reagent
CO2
CH2=CH-CH=CH-CH2CH2CO2H
C2H5OH
O2
CH2=CH-CH2Br
CH2=CH-CH=CH-CH2CH3
CH2=CH-CH=CH-CH2CH2CH2-CH=CH2
87 %
CH2=CH-CH=CH-CH2CH2OH
CH2-CH=CH2
CH2-CH=CH2
CH-CH=CH2
6 %
OH
CH-CH=CH2
34 %
H
CH3
H
+
CH3
H
H
1.8 : 1
OH
H
CH2
H
H
H
H
CH2OH
3 : 1
CH=CH-CH2-CH2-CH=CH2
7 %

detectable extent. The reaction of the Grignard reagent from 1-bromo-3,5-hexadiene with allyl bromide yielded 87% of the normal product nona-1,3,8-triene, and rearranged products, 3-cyclopropyl-1,5-hexadiene (6%) and 1-cyclopropyl-1,5-hexadiene (7%). The cyclopropylallyl coupling products are thus formed in comparable amounts, as has also been found by Young, et al. (26) for the reaction of the butenyl Grignard reagent with allyl bromide (1:1 ratio of secondary to primary isomers).

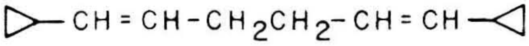
With oxygen, the Grignard reagent formed 34% of vinylcyclopropylcarbinol and 66% of other products consisting of the unrearranged 3,5-hexadien-1-ol and a mixture of *cis*- and *trans*-γ-cyclopropylallyl alcohol in which one stereoisomer predominates by a factor of three. *V-p-c* resolution was not sufficiently good to obtain accurate proportions for all the products, but over 50% of the mixture consisted of rearranged alcohols. The much higher proportion of rearrangement observed in the reaction with oxygen than with the other substrates may be due to mechanistic factors operative in the oxygenation reactions of Grignard reagents in general, which have not yet been elucidated. Walling and Buckler (27) picture the formation of alcohols from oxygen and Grignard reagents as simply arising from reaction of excess Grignard reagent with a hydroperoxy Grignard reagent produced in an unspecified manner by combination with oxygen. The details of the mode of formation of the hydroperoxy Grignard reagent have not been elucidated. Hock, et al. (28) have emphasized the possibility of free-radical character in this reaction.

One may conclude from the above results with ethanol, carbon dioxide and allyl bromide that either the Grignard reagent exists almost exclusively in the (γ-vinylallyl)-carbinyl form and the rearranged products are formed by a cyclic mechanism related to that for the butenyl Grignard reagent (3), or that the Grignard reagent exists partially in the cyclopropylallyl form XII which is the precursor of the rearranged products. The absence of rearranged products in the reaction with carbon dioxide requires, for the second explanation, either that open-chain carboxylic acid is formed from cyclopropylallyl Grignard reagent by a direct (cyclic) reaction or that carbon dioxide reacts much more rapidly with the (γ-vinylallyl)-carbinyl than with the cyclopropylallyl form. All of the latter could be converted to the former as the former is removed by reaction with carbon dioxide, provided that the rate of rearrangement of the cyclopropylallyl Grignard reagent was much faster than its reaction with carbon dioxide. The question of whether appreciable amounts of the cyclopropylallyl form are present in the Grignard solution might be resolved by *n-m-r*, if rearranged hydrocarbon coupling products (*vide infra*) could be removed. It is interesting to note that carbon dioxide affords exclusively the α-methylallyl product (29), while alcohols (30) and allyl bromide (26) yield considerable amounts of crotyl products as well, in reactions of the butenyl Grignard reagent. Although the present results do not allow one to distinguish between the above mechanisms, it is at least apparent that the desired stabilization of rearranged intermediates by the vinyl group has been achieved. The results also constitute the first examples of rearranged products obtained from a non-allylic acyclic halide via Grignard reactions.

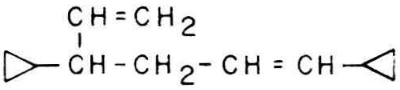
Carbonation of an ether solution of the Grignard reagent from 1-bromo-3,5-hexadiene which had been refluxed for 24 hr. afforded a 42% yield (based on bromide) of 4,6-heptadienoic acid and a 33% yield of a hydrocarbon fraction. This fraction consisted mainly of 1,6-dicyclopropyl-1,5-hexadiene XV and 1,4-dicyclopropyl-1,5-hexadiene XVI in the ratio 62:35, some allylcyclopropane and 3,5-hexadiene (which could have been formed in part by reaction of a little water on the solid carbon dioxide with the Grignard reagent) and very small amounts of other low-boiling products. The cyclopropylallyl coupling products XV and XVI were the only high-boiling materials observed in this fraction, and no cyclopropylallyl-(γ-vinylallyl)-carbinyl coupling products were isolated. Qualitative evidence was obtained (see Experimental) which may indicate that these hydrocarbons were formed during reaction of the bromide with magnesium rather than in the reaction of the Grignard reagent with carbon dioxide. Very little is known about the mechanism of formation of Grignard reagents from magnesium and halides in ether (31). It is of course a surface reaction and may be rather complex and sensitive to impurities in the magnesium. Just as in other dissolving-metal reactions, free-radical-type processes might well be important. If the reaction of 1-bromo-3, 5-hexadiene with magnesium could lead in part to the formation of (γ-vinylallyl)-carbinyl free radicals, then these might be expected to rearrange to cyclopropylallyl radicals, since the enthalpy difference between them is calculated by a thermodynamic cycle method (see next section) to be -16 kcal. / mole. Coupling of the resultant stabilized cyclopropylallyl radicals (or of resonance-stabilized non-classical radicals of the type XVIII) could then give XV and XVI. However, definite proof should be obtained that the latter are not formed during reaction of the Grignard reagent with substrates before the above scheme is accepted.

When the Grignard reagent from 1-bromo-3, 5-hexadiene was refluxed for 72 hr. (three times as long as in the first reaction), then carbonated, there was obtained only a 26% yield (based on bromide) of 4, 6-heptadienoic acid (compared with 42% previously), but a 45% yield of hydrocarbon fraction (cf. 33% before) consisting largely of the dienes XV and XVI in the ratio 51: 31. It is difficult to tell whether these results are meaningful. Certainly the decreased yield of carboxylic acid could be attributed to polymerization and other side-reactions of the Grignard reagent. The increased yield of hydrocarbon fraction could conceivably be within the natural range of variation of the hydrocarbon yield. If it is not, however, and the difference between the hydrocarbon yields is significant, then one might conclude that the Grignard reagent slowly decomposes with formation of the coupling products. This type of decomposition was observed by Cason and Fessenden (32) for the dibutenyl cadmium reagent which afforded octadiene coupling products in refluxing ether. Clearly this cannot be the means of formation of the bulk of the hydrocarbons, since a 48 hr. reflux only gives an additional 12% yield and a 24 hr. reflux is thus expected to give only a 6% yield, whereas the observed figure for 24 hr. reflux is 33%. A pathway for formation of the dienes XV and XVI by a coupling with rearrangement of the Grignard reagent with unreacted 1-bromo-3,5-hexadiene also seems unlikely since only 13% of rearranged products (relative to unrearranged product) were obtained in the reaction of the Grignard reagent with allyl bromide. On reaction of the Grignard reagent with ethanol and allyl bromide, the coupling products were isolated in amounts comparable to that obtained in carbonation, while the yield was much higher in the reaction with oxygen. This may indicate that in the latter case they are formed in part during reaction of the Grignard reagent with oxygen.

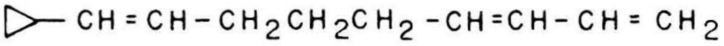
When 1-bromo-3,5-hexadiene was added to magnesium and cobaltous chloride in ether, a reaction which generates alkyl free radicals from the halide (33), there was obtained a 41% yield (based on bromide) of a hydrocarbon fraction which consisted mainly of XV, XVI and a compound characterized by its spectra as 1-cyclopropylnona-1,6,8-triene XVII, in the ratio 40 : 29 : 7.5, as well as other unidentified



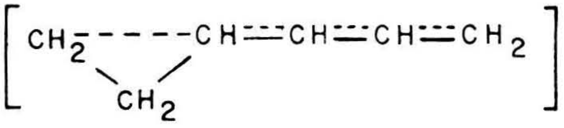
XV



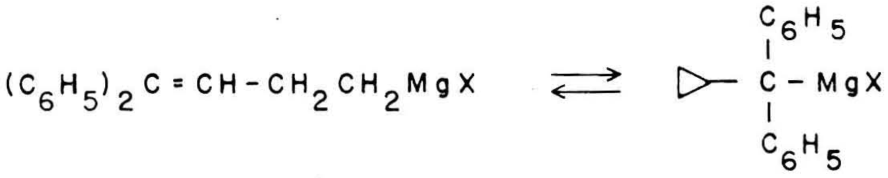
XVI



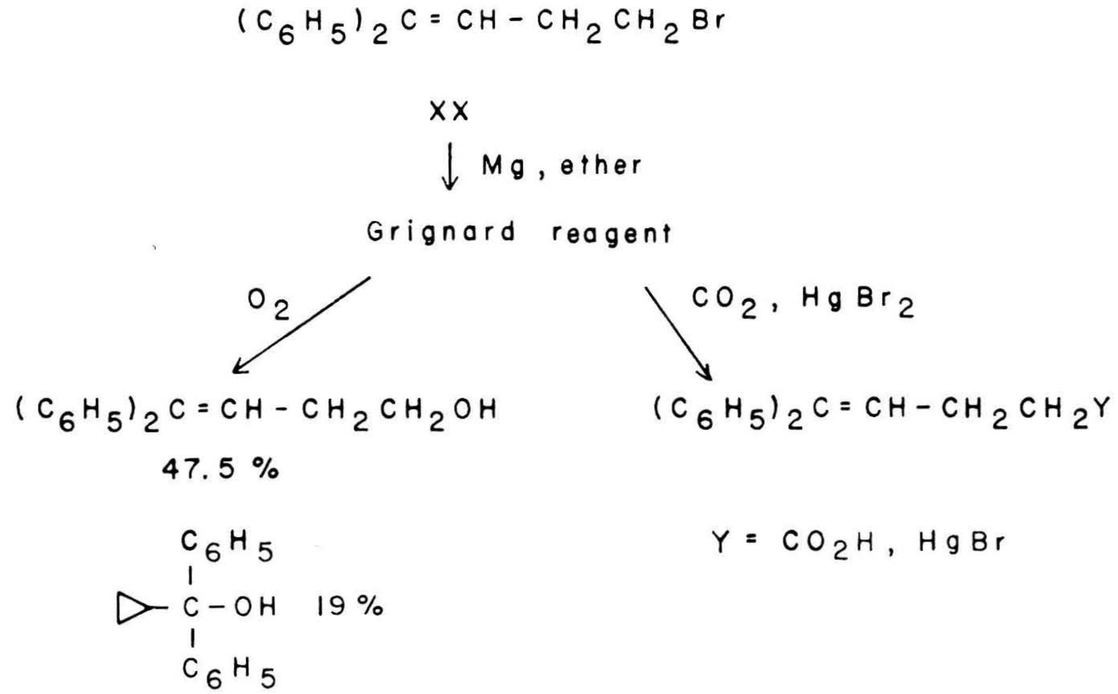
XVII



XVIII



XIX



lower-boiling compounds. The ratio of XV to XVI decreased somewhat relative to previous mixtures, and XVII is a new product composed of coupled γ-cyclopropylallyl and (γ-vinylallyl)-carbinyl fragments. Except for XVII, the products are essentially the same as in the hydrocarbon fractions discussed earlier, providing some measure of support for the concept of free-radicals as precursors of the coupling products XV and XVI. The hydrocarbon XVII may arise because of a higher local concentration of (γ-vinylallyl)-carbinyl free radicals generated in the solution, not all of which have time to rearrange before coupling.

A system studied in some detail was the Grignard reagent from (γ, γ-diphenylallyl)-carbinyl bromide XX. In this case there is the possibility of an equilibrium XIX between the (γ, γ-diphenylallyl)-carbinyl and the diphenylcyclopropylcarbinyl forms of the Grignard reagent. Negative charge in the diphenylcyclopropylcarbinyl form would be expected to be strongly stabilized by the two phenyl groups, although steric crowding on the carbinyl carbon atom may work against this. In the synthesis of (γ, γ-diphenylallyl)-carbinyl bromide results were obtained which contradict the conclusions made from earlier work by Lipp, et al. (34). Treatment of diphenylcyclopropylcarbinol with phosphorus tribromide was found to afford exclusively (γ, γ-diphenylallyl)-carbinyl bromide, whose structure was firmly established. No diphenylcyclopropylcarbinyl bromide was formed. This is in accord with other carbonium-type rearrangements of cyclopropylcarbinyl derivatives and with the fact that, despite determined efforts, Silver (35) was unable to prepare even methylcyclopropylcarbinyl bromide under mild conditions. The paper by Lipp, et al. (34), which is better known for its description of heroic attempts to prepare cyclopropanone, states that treatment of diphenylcyclopropylcarbinol with phosphorus tribromide yielded only diphenylcyclopropylcarbinyl bromide. No details of structure proof for the latter, or for the corresponding iodide or chloride which were also described, were given. In the light of the present results, most of the diphenylcyclopropylcarbinyl structures given in Lipp's paper should now be changed to (γ, γ-diphenylallyl)-carbinyl structures. A similar pitfall seems to have caught Bennett and Bunce (36) who stated that the product of the reaction of phenylcyclopropylcarbinol with phosphorus tribromide was unrearranged phenylcyclopropylcarbinyl bromide, since the product showed cyclopropyl infrared bands near 3000 and 3085 cm^{-1} and did not react with potassium permanganate. Their insistence that the product was unrearranged is all the more surprising since their paper contains a reference to the work of Close (37), who showed conclusively that the sole isolable product from the reaction of phenylcyclopropylcarbinol with phosphorus trichloride was (γ-phenylallyl)-carbinyl chloride, and that in authentic phenylcyclopropylcarbinyl compounds the cyclopropyl infrared bands from 3000 to 3100 cm^{-1} were obscured by phenyl absorption.

The reaction of the Grignard reagent from (γ, γ-diphenylallyl)-carbinyl bromide XX with carbon dioxide or mercuric bromide afforded exclusively unrearranged products. However, the reaction with oxygen gave a mixture of 19% (based on bromide) of diphenylcyclopropylcarbinol XXI and 47.5% of (γ, γ-diphenylallyl)-carbinol. Lipp, et al. (34) also isolated diphenylcyclopropylcarbinol from the reaction of the Grignard reagent from their bromide with oxygen. Again the reaction with oxygen leads to considerable rearrangement, just as with the Grignard reagent from 1-bromo-3,5-hexadiene, and one may tentatively conclude that the mechanism for reaction of oxygen with Grignard reagents differs markedly from that for other reactants. The fact that no rearranged products were obtained in the reactions with carbon dioxide or mercuric bromide does not necessarily imply that appreciable quantities of the diphenylcyclopropylcarbinyl form of the Grignard reagent are not present in the Grignard solution, as pointed out previously for the (γ-vinylallyl)-carbinyl case.

In order to gain more information on the structure of the Grignard reagent, the n-m-r spectrum of the Grignard reagent from 4,4-diphenyl-1-bromo-3-butene-1,1-$\underline{d}_2$ was studied. The n-m-r spectrum of the bromide is shown in Figure 6 and is seen to contain a small amount of an impurity, which did not affect the interpretation of the spectra of the derived Grignard reagent. The n-m-r spectra of two preparations of the Grignard reagent are shown in Figures 5 and 7. It is not known

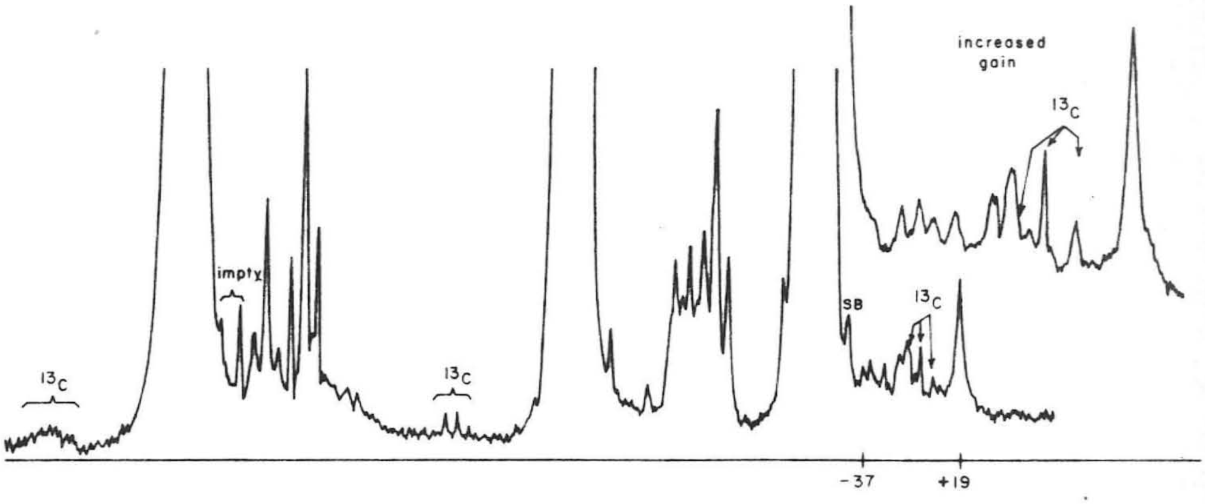


Fig. 5.— Proton n-m-r spectrum of the Grignard reagent from 4,4-diphenyl-1-bromo-3-butene-1,1-d$_2$ in ether. Chemical shifts are in c.p.s. relative to the internal standard, tetramethylsilane (not shown). Signals designated ^{13}C are satellites due to naturally abundant ^{13}C in the ether and phenyl groups. SB denotes a spinning side-band.

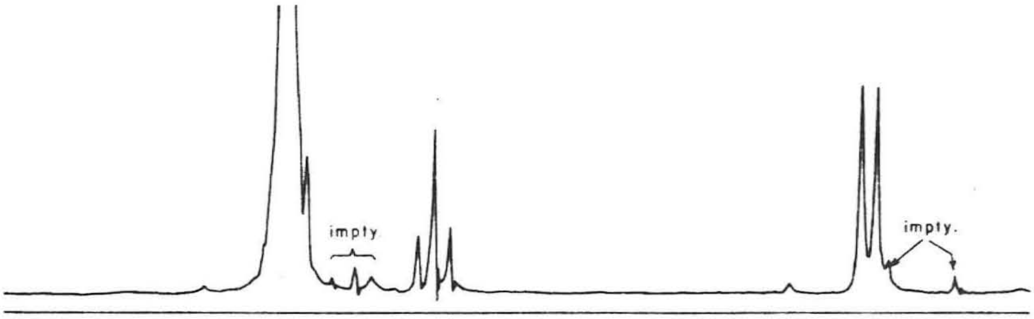


Fig. 6.— Proton n-m-r spectrum of 4,4-diphenyl-1-bromo-3-butene-1,1-d$_2$. The off-scale peak is due to phenyl hydrogens. Peaks due to an impurity are noted.

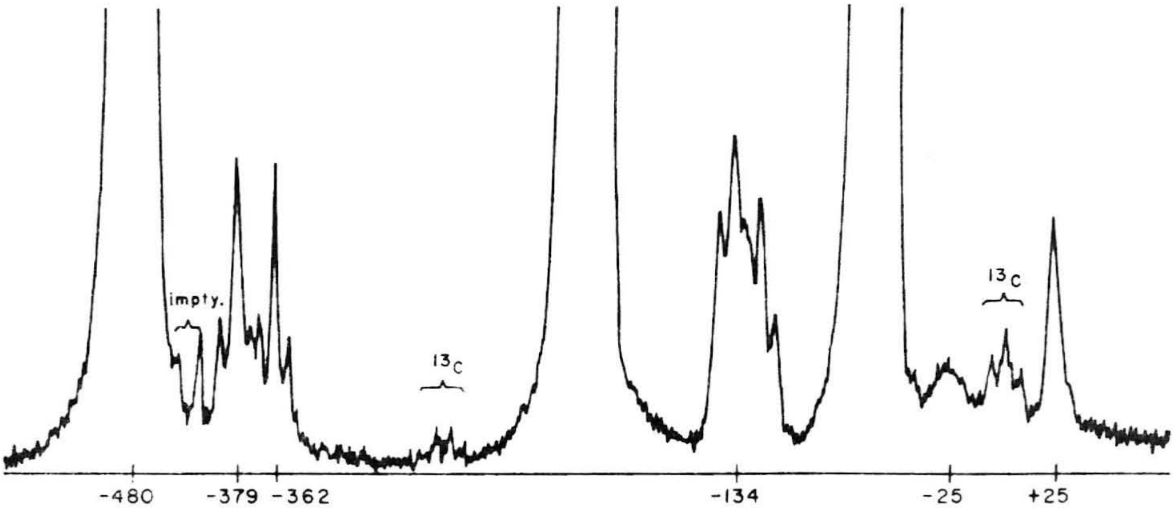


Fig. 7.— Proton *n-m-r* spectrum of the Grignard reagent from 4,4-diphenyl-1-bromo-3-butene-1,1-d_2 in ether. Chemical shifts are in c. p. s. relative to the internal reference, tetramethylsilane (not shown). Signals designated ^{13}C are satellites due to naturally abundant ^{13}C in the ether.

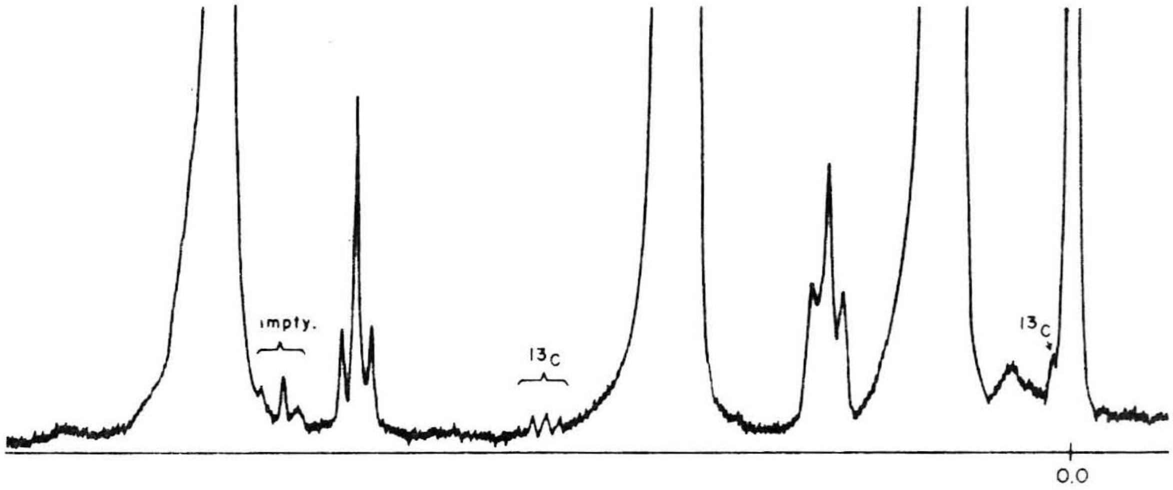
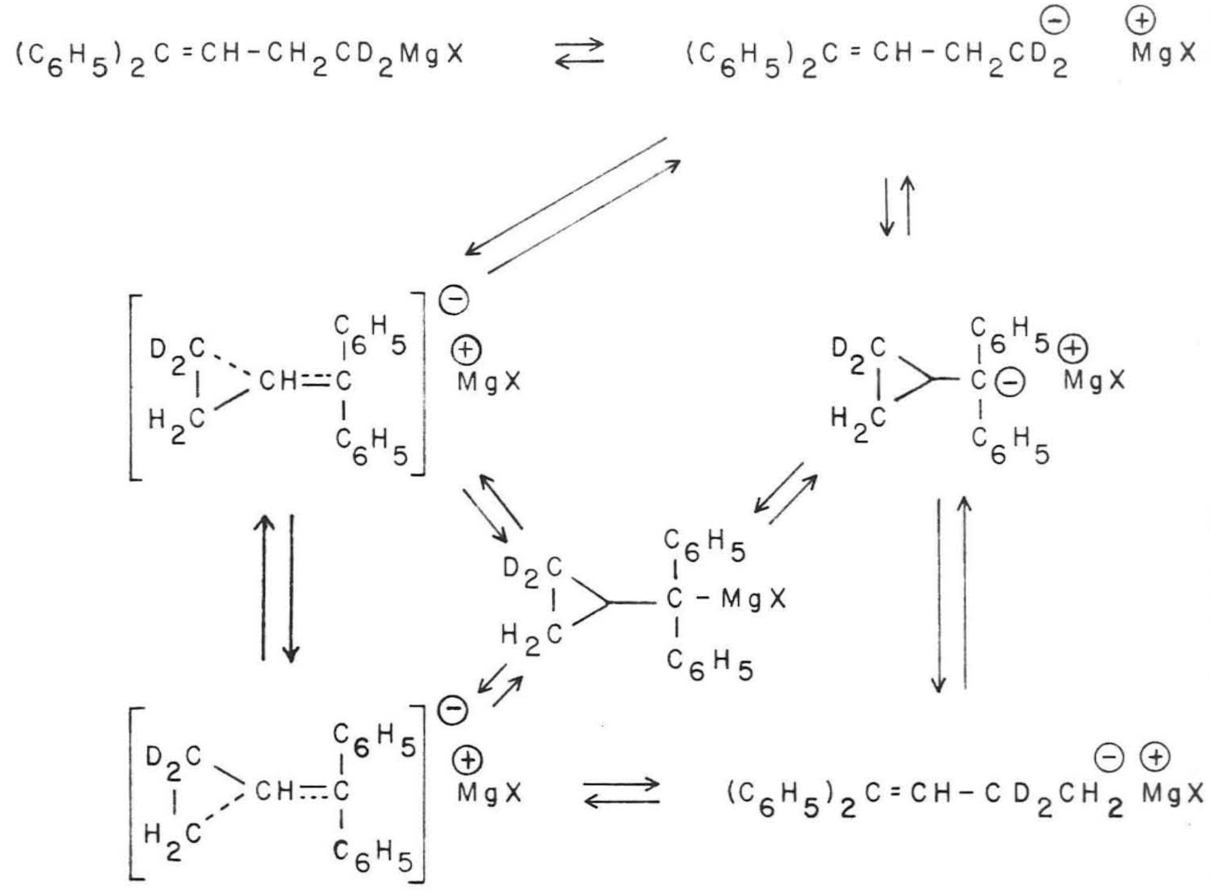


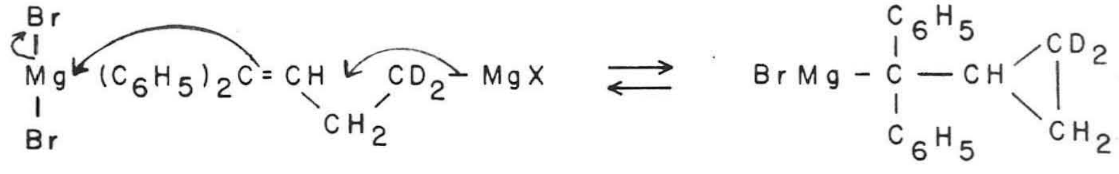
Fig. 8.— Proton *n-m-r* spectrum of the product of reaction of the *n-m-r* sample of Grignard reagent corresponding to Fig. 7 with methanol. Tetramethylsilane is internal reference. Peaks due to an impurity and ^{13}C-satellites from the ether solvents are marked.

why the latter differ slightly in detail. The n-m-r spectrum of the Grignard reagent was taken 5 hr. after the start of its preparation at 20° and did not change with time. This fact and the presence of a sizeable α-methylene singlet at high-field indicated that equilibration of the α- and β-positions in the Grignard reagent was already complete by the time the first spectrum was taken. This equilibration is much faster than for the unsubstituted allylcarbinyl Grignard reagent for which the half-time is 30 hr. at 27° (18). These results are accommodated by a mechanism XXII involving ionization of the carbon-magnesium bond in the (γ, γ-diphenylallyl)-carbinyl Grignard reagent to give the (γ, γ-diphenylallyl)-carbinyl carbanion within an ion pair. This could then rearrange to the diphenylcyclopropylcarbinyl carbanion (in an ion pair) or to a delocalized homoallylic carbanion. Collapse of the resulting ion pair may then give the diphenylcyclopropylcarbinyl Grignard reagent. Opening of the latter, or the ion pair, by the reverse process then can lead to equilibration of the α- and β-positions in the open-chain Grignard reagent. If the rate-determining step in this mechanism is the ring closure of the (γ, γ-diphenylallyl)-carbinyl carbanion then the equilibration of the α- and β-positions would be expected to be faster than in the unsubstituted case, due to stabilization of the transition state by the phenyl groups. Unless one invoked special type of bonding of magnesium to the phenyl groups, a mechanism XXIII for the equilibration, suggested by Nordlander (3), in which rearrangement is initiated by electrophilic attack of magnesium halide on the terminal vinylic carbon atom leading directly to the cyclopropylcarbinyl Grignard reagent, would not be expected to lead to a much faster rate for the diphenyl case. The results appear to rule out this mechanism and to support the scheme XXII, but do not give specific information as to the intermediates involved.

It was therefore of interest to determine whether evidence for the presence of the diphenylcyclopropylcarbinyl form of the Grignard reagent could be gleaned from its n-m-r spectrum. The best criterion for the latter is likely to be the cyclopropyl methylene peaks which generally occur at high-field above methyl resonances (38). Figures 5 and 7 show that there are indeed sizeable peaks upfield of the methyl resonance of the ether, having the expected chemical shifts. However, the spectra are complicated by the presence of an extraneous vinyl triplet and midfield methylene absorptions which are attributed to deuterated 1,1-diphenylbutene. They are very unlikely to be due to unreacted bromide since the Grignard reagent was prepared under conditions in which no bromide was recovered from preparative reactions. The above conclusion is supported by the n-m-r spectrum (Fig. 8) of the product obtained when the n-m-r sample of the Grignard reagent used in Figure 7 was treated with methanol. Drastic simplification of the spectrum resulted, due to formation of 1,1-diphenylbutene. No separate resonances for the β-methylene or vinyl hydrogens of unreacted bromide are evident in Figure 8. However, a small peak just to the


(C6H5)2C=CH-CH2CD2MgX
(C6H5)2C=CH-CH2CD2 ⊖ ⊕ MgX
D2C, H2C, CH, C, C6H5, C6H5 ⊖ ⊕ MgX
D2C, H2C, C6H5, C ⊖, C6H5 ⊕ MgX
D2C, H2C, C6H5, C-MgX, C6H5
D2C, H2C, CH, C, C6H5, C6H5 ⊖ ⊕ MgX
(C6H5)2C=CH-CD2CH2 ⊖ ⊕ MgX

XXII


Br
Mg
Br
(C6H5)2C=CH
CH2
CD2-MgX
BrMg-C-CH
C6H5
C6H5
CD2
CH2

XXIII

low-field side of the tetramethylsilane resonance is present, and is attributed to the cyclopropyl methylene hydrogens of diphenylcyclopropylmethane XXVII. Area measurements indicate that the relative proportion of the latter is 7%, in fair agreement with the value of 5% isolated in preparative reactions (vide infra). The n-m-r spectrum of the product of treatment of the n-m-r sample of Grignard reagent with bromine still showed small peaks in the cyclopropyl region similar to those in Figure 5. These are probably due to diphenylcyclopropylmethane, since the reaction with bromine is not likely to lead to diphenylcyclopropylcarbinyl bromide. One may conclude from the above results that (i) the Grignard reagent exists predominantly in the allylcarbinyl form, (ii) 1,1-diphenylbutene (and probably diphenylcyclopropylmethane) are formed during reaction of the bromide with magnesium, or less likely by decomposition of the Grignard reagent and (iii) cyclopropyl methylene peaks are present in the n-m-r spectrum which are due to diphenylcyclopropylmethane or the diphenylcyclopropylcarbinyl form of the Grignard reagent, or both. If the hydrocarbons could be removed from the solution of Grignard reagent, the n-m-r spectrum would provide a definite answer to the question of whether detectable amounts of diphenylcyclopropylcarbinyl Grignard reagent are present. In Figure 7, areameasurements on the broad peak at -25 c.p.s. attributed to cyclpropyl resonances and on the α-methylene peak at +25 c.p.s. due to the Grignard reagent, indicated that the molar ratio of diphenylcyclopropylcarbinyl compounds to (γ, γ-diphenylallyl)-carbinyl Grignard reagent was 1: 3.74, assuming that the cyclopropyl resonance arises from two hydrogens per molecule. Since this ratio seems too high (on the basis of preparative reactions) to be due solely to diphenylcyclopropylmethane, there is a distinct possibility that part of the resonances on the high-field side of the ether methyl absorption arise from cyclopropyl methylene hydrogens in the diphenylcyclopropylcarbinyl Grignard reagent.

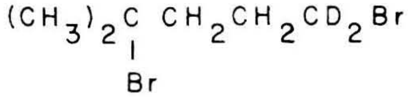
The n-m-r spectra of unlabelled Grignard reagent from (γ, γ-diphenylallyl)-carbinyl bromide and chloride were taken by Nordlander (39). The resolution was not as good as obtained with the deuterated Grignard reagent so that detection of the cyclopropyl peaks was more difficult, although twice as many hydrogens would be giving rise to these peaks. Only small broad peaks were observed in the cyclopropyl region. A significant feature of these spectra was the appearance of part of the methyl triplet of 1,1-diphenylbutene just to the high-field side of the ether methyl resonance.

An attempt to prepare 1-bromo-4,4-dimethyl-3-butene-1,1-$\underline{d}_2$ XXIV by elimination of hydrogen bromide from 1,4-dibromo-4-methylpentane-1,1-$\underline{d}_2$ XXV was complicated by concurrent elimination involving one of the methyl groups, and the bromide XXIV could not be isolated in a pure state. On the basis of the results with the diphenyl analog and bearing in mind that methyl groups destabilize carbanion centers (40), equilibration of the α- and β-positions in the Grignard reagent from XXIV is expected to proceed more slowly than with the allylcarbinyl Grignard reagent itself. A study of what effect changing the metal from magnesium to, say, lithium has on the rate of equilibration of the α- and β-positions in the allylcarbinyl system would be of interest.

At this point it is appropriate to describe the reactions of active hydrogen compounds with the Grignard reagent from (γ, γ-diphenylallyl)-carbinyl bromide, and abnormal products isolated from reactions of the latter. Substantial yields of hydrocarbon fractions were isolated from reactions of the Grignard reagent with oxygen, carbon dioxide and mercuric bromide. These were found to consist of mixtures of 1,1-diphenylbutene XXVI and diphenylcyclopropylmethane XXVII, with the former predominating, plus similar amounts of polymeric residues which could not be distilled. Diphenylcyclopropylmethane was also present in the products of active hydrogen compounds with the Grignard reagent. In the reaction with carbon dioxide, the hydrocarbon mixture was still formed when oxygen was rigorously excluded from the system at all times. The results of these experiments are summarized in Table VIII. It should be emphasized that the results in Table VIII were obtained under widely different conditions for preparation and reaction of the Grignard reagent as recorded in the Experimental, and any conclusions drawn from the data must be tempered by this fact. For the non-active hydrogen compounds the relative percent of diphenylcyclopropylmethane shows very little change, while the variation in hydrocarbon yield is somewhat greater. For the active hydrogen compounds,

$(CH_3)_2C=CH-CH_2CD_2Br$

XXIV

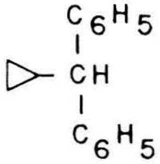


$(CH_3)_2CBrCH_2CH_2CD_2Br$

XXV

$(C_6H_5)_2C=CH-CH_2CH_3$

XXVI



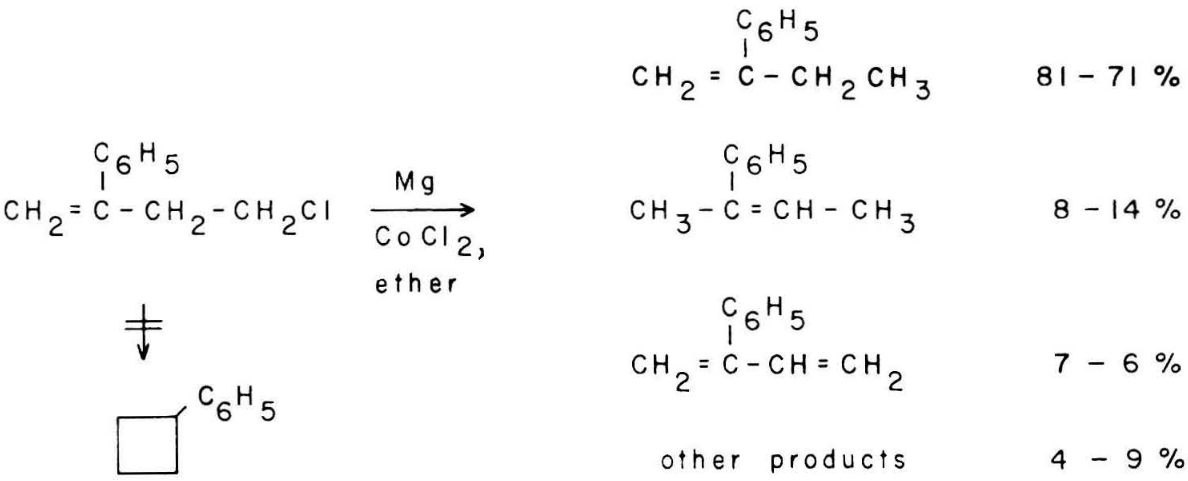
XXVII

$$2RMgX + CoX_2 \longrightarrow 2MgX_2 + CoR_2$$

$$\longrightarrow Co + 2R\cdot \text{ (or } R-R\text{)}$$

$$Co + 2R'X \longrightarrow CoX_2 + 2R\cdot \text{ (or } R-R\text{)}$$

XXVIII



XXIX

Table VIII

Hydrocarbons from Reactions of the Grignard Reagent from (γ, γ-Diphenylallyl)-carbinyl Bromide.

Reactant	% Yield of Hydrocarbons[a]	% of Diphenylcyclopropylmethane[b]
Carbon dioxide	14.3	21.5
Carbon dioxide	10.1	28.5
Carbon dioxide (absence of oxygen)	22.0	26.3±1.1[c]
Mercuric bromide	17.9	26
Oxygen	18.9	23
Ammonium chloride solution	90.5	4
Methanol	86.6	5
Hydrogen chloride (gas)	89.5	9
Phenylacetylene	90.5	10
Cobaltous chloride (catalytic amount)	35.1	35

[a] After distillation, based on bromide.

[b] The percentages given refer to diphenylcyclopropylmethane relative to diphenylcyclopropylmethane plus 1,1-diphenylbutene and were measured by *v-p-c*.

[c] The standard deviation for the *v-p-c* measurement is cited.

the variation in percent of diphenylcyclopropylmethane is considerable, although it is difficult to tell how much significance to attach to this. If the hydrocarbons obtained from the first five reactions in Table VIII have been formed during reaction of the bromide with magnesium (as seems to be the case, judging from the n-m-r results discussed earlier) and if reaction of the active hydrogen compounds with the Grignard reagent afforded exclusively 1, 1-diphenylbutene, then the average percent of diphenylcyclopropylmethane in the isolated products of the latter reactions is calculated to be 5%. This figure agrees with the observed values for reactions with methanol and ammonium chloride solution, but is about half those for hydrogen chloride and phenylacetylene. This may imply that about 4% of the diphenylcyclopropylmethane is being formed from the Grignard reagent with the latter reactants. On the whole the results in Table VIII are consistent with the hypothesis that XXVI and XXVII are formed during reaction of the bromide with magnesium rather than during reaction of the Grignard reagent with substrates. It seems likely that the formation of hydrocarbons during reactions of halides with magnesium (or other metals) may be much more general than indicated here. particularly where the radicals from the halides are resonance-stabilized. Careful examination of neutral fractions isolated from carbonations of a range of Grignard reagents would establish whether this was so. In this connection it is interesting to note that Zimmerman and Zweig (23a) isolated in over 50% yield a neutral fraction consisting of 19% of rearranged 1, 2-diphenylpropane and 81% of 2, 2-diphenylpropane from carbonation of the product of reaction of lithium with 1-chloro-2, 2-diphenylpropane in ether after 3 hr. at reflux. The major acidic product was 2-methyl-2, 3-diphenylpropionic acid, formed by phenyl migration. The authors attributed the unrearranged 2, 2-diphenylpropane to β-proton abstraction by 2, 2-diphenylpropyllithium from the ether, and the 1, 2-diphenylpropane as arising from rearranged lithium reagents due to incomplete exclusion of moisture on carbonation. Since the yield of acids was only 42% the carbon dioxide used must have been very wet indeed for this explanation to be tenable. A reinvestigation of this reaction might well show that the hydrocarbons are mainly formed at an earlier stage, possible during reaction of the halide with lithium. A free-radical precursor for the rearranged 1, 2-diphenylpropane is feasible since Curtin and Hurwitz (41) observed quantitative phenyl migration in the decarbonylation of (2, 2-diphenylpropyl)-carboxaldehyde. The neutral fraction isolated by Zimmerman and Zweig from reaction of bis-(2, 2-diphenylpropyl)-mercury with lithium in ether (8 hr. at 0°) followed by carbonation was stated to consist of 97% 2, 2-diphenylpropane. The composition of the neutral fraction obtained when this reaction mixture was refluxed for 3 hr. prior to carbonation, was not given. On carbonation of 2, 2-diphenylpropylmagnesium chloride they obtained a substantial yield of hydrocarbon product, which was stated to be essentially pure 2, 2-diphenylpropane.

When (γ, γ-diphenylallyl)-carbinyl bromide was treated with lithium for 4 hr. at room temperature in ether, then carbonated, no carboxylic acid was isolated. The sole products were a 27% yield of a mixture consisting of 41% diphenylcyclopropylmethane and 59% 1, 1-diphenylbutene, and a large amount of polymeric material. Part of the latter could have arisen from 1, 1-diphenylbutadiene formed by attack of the lithium reagent on unreacted bromide. It is unlikely that the bulk of the diphenylcyclopropylmethane and 1, 1-diphenylbutene was formed by cleavage of the solvent by lithium reagent, since the half-life for the related n-butyllithium in ether is 153 hr. at 25° (42). There is no obvious interpretation for the above results and more work needs to be done to unravel the details of the mechanism. The proportion of diphenylcyclopropylmethane is notably higher than that obtained in the Grignard reactions. In order to make a different point of entry into this system, the metalation of diphenylcyclopropylmethane with n-butyllithium was attempted, but without success. Bennett and Bunce (36) were similarly unable to metalate phenylcyclopropylmethane with butyllithium or amylsodium.

Two reactions were studied which would be expected to generate (γ, γ-diphenylallyl)-carbinyl free radicals. The results of the reaction of the Grignard reagent from (γ, γ-diphenylallyl)-carbinyl bromide with a catalytic amount of cobaltous chloride are shown in Table VIII. Part of the hydrocarbon product was probably derived from the reaction of the bromide with magnesium. Unreacted Grignard reagent was removed by carbonation. The proportion of diphenylcyclopropylmethane in the product is seen to be slightly higher than in the first five reactions in Table VIII. A procedure similar to that of Urry and Nicolaides (43) in which (γ , γ -diphenylallyl)-carbinyl chloride was added to ethylmagnesium bromide and cobaltous chloride in ether, afforded a 60% yield of hydrocarbons consisting largely of a mixture of 11% of diphenylcyclopropylmethane, and 89% of 1, 1-diphenylbutene. The reason for the much lower proportion of rearranged hydrocarbon obtained in this reaction is not clear. That the same products, in similar proportions, are obtained from these free-radical-type reactions as in the Grignard reactions is gratifying and lends some support to the idea that the diphenylcyclopropylmethane and 1, 1-diphenylbutene may be formed in the Grignard reactions through hydrogen abstraction from the diethyl ether used as solvent by radicals derived from reaction of (γ , γ -diphenylallyl)-carbinyl halide with magnesium. The nature of these radicals is the topic of the following section.

Cason and Fessenden (32) observed that treatment of the butenyl Grignard reagent with cadmium chloride in refluxing ether yielded directly a mixture of octadiene coupling products. They attributed this result to free radical decomposition of the butenyl cadmium reagent. Comparison of bond dissociation energies given by Cottrell (7) indicates that D_{CH_2-Cd} for dicrotylcadmium is probably only about 18 kcal./mole, and that for di-(α -methylallyl)-cadmium should be even lower. Cason and Fessenden's results are thus not as surprising as they may at first appear. When the Grignard reagent from (γ , γ -diphenylallyl)-carbinyl bromide was treated with cadmium chloride in ether, the cadmium reagent formed as evidenced by a negative test for Grignard reagent. The cadmium derivative was refluxed for 24 hr., and on hydrolysis a vigorous reaction occurred indicating that most of the reagent was intact. The product was a 91.6% yield of pure 1,1-diphenylbutene. The fact that no diphenylcyclopropylmethane was detected by v-p-c is puzzling since some is expected to have been produced during formation of the Grignard reagent. It was apparent however that the cadmium reagent, unlike the lithium reagent, was stable under the reaction conditions.

Rearrangements of Allylcarbinyl Free Radicals

In order to clarify certain anomalous reactions which appeared to occur during formation of Grignard reagents and to involve free radical-type processes, a study was made of the bona fide free radical (and related) reactions of substituted allylcarbinyl systems. Most of the work was confined to the (γ , γ -diphenylallyl)-carbinyl case. The subject of free-radical rearrangements in general, and in small-ring systems in particular, has been exhaustively reviewed by Shuster (2), and earlier work will be mentioned only where it has a direct bearing on the discussion at hand.

It was shown in the previous section that only allylcarbinyl, and no cyclobutyl, products were obtained from carbonation of the Grignard reagent from (β -phenylallyl)-carbinyl chloride. It was of interest therefore to determine whether cyclobutyl products were produced in free-radical reactions of the (β -phenylallyl)-carbinyl system. The method chosen to generate (β -phenylallyl)-carbinyl radicals was the Kharasch reaction of the corresponding Grignard reagent with cobaltous chloride (31). The mechanism for this reaction has been discussed by Walling (33) who favored the scheme XXVIII. When (β -phenylallyl)-carbinyl chloride was added to magnesium and cobaltous chloride in ether a 53-63% yield of hydrocarbons was obtained consisting of a mixture of 2-phenyl-1-butene, 2-phenyl-2-butene (identified by its n-m-r spectrum), 2-phenyl-1,3-butadiene and small amounts of the other lower-boiling products in the proportions shown in XXIX. Phenylcyclobutane definitely was not, and 1-phenylcyclobutene probably was not, a product of the reactions. Thus, as in the Grignard reactions, the (β -phenylallyl)-carbinyl system appears to have no propensity to rearrange to the 1-phenylcyclobutyl structure in a free-radical reaction despite the stabilization of the radical center offered by the pheny group in the arranged structure. The products in XXIX are more or less those expected of disproportionation of, and hydrogen abstraction from, solvent by (β-phenylallyl)-carbinyl radicals. The 2-phenyl-2-butene may arise by hydrogen abstraction from 2-phenyl-1-butene.

Before discussing free radical reactions in the (γ, γ-diphenylallyl)-carbinyl system, it is appropriate to mention briefly some related reactions in which rearrangement was found to occur. It was found that diphenylcyclopropylcarbinol was quantitatively dehydroxylated by Raney nickel containing absorbed hydrogen in refluxing ethanol. The product consisted of 59% of diphenylcyclopropylmethane, 36% of 1,1-diphenylbutane (identified by <u>n</u>-<u>m</u>-<u>r</u> spectrum) and 5% of an unidentified compound. Extensive rearrangement occurred, in contrast to the work of Bonner (44) who detected no phenyl migration in the Raneynickel dehydroxylation of 1,2,2-triphenyl-ethanol-1-^{14}C. Very little is known concerning the mechanism of these dehydroxylation reactions and no conclusions can yet be made about the intermediates involved. Similar results were obtained in the hydrogenation of diphenylcyclopropylcarbinol in ethanol-acetic acid catalyzed by 10% palladium-on-carbon. The product was composed of 58% diphenylcyclopropylmethane and 42% of 1,1-diphenylbutane. Here carbonium ion intermediates are a distinct possibility since some acetic acid was necessary to make the reduction go.

Another reaction which led to rearrangement was the reduction of (γ , γ -diphenylallyl)-carbinyl bromide by triphenyltin hydride. The products were triphenyltin bromide and a mixture consisting of 14% of diphenylcyclopropylmethane and 86% of 1,1-diphenylbutene. When hexane was used as solvent and the triphenyltin hydride was added slowly to the bromide, the proportion of diphenylcyclopropylmethane (12.5%) was essentially unchanged. Reductions of other alkyl and alkenyl bromides hydrocarbons by triphenyltin hydride have been reported by Noltes andKerk (45). The occurrence of homoallylic rearrangements in reductions by metal hydrides is not without precedent, and Gaylord (46) has summarized several examples where 3,5-cyclo-cholestanes were obtained in lithium aluminum hydride reductions of cholesteryl tosylates. Karrer and Asmis (47) have postulated without supporting evidence that the rearrangement step involves carbonium ion intermediates. The mechanisms of reductions by triphenyltin hydride are not known, but it may be relevant to the present discussion that triphenyltin hydride adds in the anti-Markovnikov sense to styrene (and other olefins) and gives triphenyl-(2-phenylethyl)-tin (48). On the basis of this result a possible formulation for the production of diphenylcyclopropyl methane from (γ , γ -diphenylallyl)-carbinyl bromide is XXX. The departure of the bromide ion might be assisted by the triphenyltin group.

We now turn to a discussion of free-radical reactions of (γ, γ-diphenylallyl)-carbinyl and diphenylcyclopropylcarbinyl derivatives. Treatment of diphenylcyclopropylmethane with slightly more than one equivalent of N-bromosuccinimide in refluxing carbon tetrachloride in the presence of an initiator led to recovery of a considerable amount of unreacted starting material and to formation of (γ, γ-diphenylallyl)-carbinyl bromide and polybrominated open-chain products. At the time this work was done, the fugitive nature of diphenylcyclopropylcarbinyl bromide was not fully appreciated. Most, if not all, of the open-chain bromide could have been formed by a carbonium ion-type rearrangement of diphenylcyclopropylcarbinyl bromide within ion-pairs. The results therefore do not yield any information as to the stability of intermediate radicals. Bennett and Bunce (36) claim to have prepared phenylcyclopropylcarbinyl bromide in 42% yield by reaction of phenylcyclopropylmethane with N-bromosuccinimide. This result must be regarded with suspicion in view of the criticism levelled against Bennett and Bunce's work in the previous section. Kuivala, et al. (49) studied the reaction of N-bromosuccinimide with 1-phenyl-2-isopropylcyclopropane, but the open-chain product was abnormal in that it appeared to result from addition of the elements of bromine at the 1- and 2-positions. The structure of the dibromide was not proved conclusively and it is possible that the open-chain product resulted from rearrangement of 2-phenyl-dimethylcyclopropylcarbinyl radicals and further reactions.

The α, α'-azoisobutyronitrile-initiated autoxidation of diphenylcyclopropylmethane (alone or in the presence of sodium carbonate) in refluxing benzene afforded negligible yields of hydroperoxide, since no alcohols were obtained on catalytic reduction of the product and most of the starting material was recovered. Low yields of hydroperoxides have also been reported for the autoxidation of other benzylhydryl-type hydrocarbons (33). A study of the rate of the autoxidation of diphenylcyclopropylmethane by the method of Hammond, et al. (50) showed inhibition at an early stage. The reason for this is not clear. The initial rate of oxygen uptake was found to be 7.65×10^{-2} ml./min., compared with the figure 8.85×10^{-2} ml./min. determined for cumene under the same conditions (51). Using the equations deduced by Hammond and coworkers (52), the ratio $k_p / k_t^{1/2}$ of the rate constant for the propagation step (3) to the square root of the rate constant for the termination step (4), was calculated to be 3.1×10^{-3} $\ell^{1/2}$ mole$^{-1/2}$sec$^{-1/2}$ for diphenycyclopropylmethane. In Equations 3 and 4, RH corresponds to diphenylcyclopropylmethane and

$$R'O_2\cdot + R\text{-}H \xrightarrow{k_p} R'O_2H + R'\cdot \qquad (3)$$

$$R'O_2\cdot + R'O_2\cdot \xrightarrow{k_t} \text{products} \qquad (4)$$

$R'^{\cdot}$ denotes rearranged or unrearranged radicals derived from RH. The above ratio compares with the higher figure, 9.5×10^{-3} for tetralin (same units) obtained under the same conditions. Since k_t might be expected to be only weakly dependent on the structure of R' in most cases, these ratios probably reflect the rates of the propagation step (3) and may correlate with the stability of $R'^{\cdot}$. The structures of tetralin and diphenylcyclopropylmethane differ too much for one to be able to draw conclusions from these rates about the effect of the cyclopropyl group on an adjacent radical center. In this regard, a comparison of the rates of autoxidation of cumene and phenyldicyclopropylmethane may be worthwhile.

The difficulties encountered in finding suitable ways of generating free radicals from diphenylcyclopropylmethane suggested that attack of the problem from the (γ , γ -diphenylallyl)-carbinyl end might prove more fruitful. The first approach tried was unorthodox and turned out to be singularly unsuccessful. The cleavage of alkylmercuric bromides by hydrogen bromide in glacial acetic acid generally yields alkanes and mercuric bromides. Keller (53) found that this reaction had the earmarks of a free-radical chain process in that it was accelerated by benzoyl peroxide and inhibited by hydroquinone. No mechanism was suggested for the reaction, but the following hypothetical chain fits the observed facts and each propagation step is expected to be strongly exothermic.

$$\left.\begin{aligned} \mathrm{Br}^{\cdot} + \mathrm{RHgBr} &\longrightarrow \mathrm{R}^{\cdot} + \mathrm{HgBr}_2 \\ \mathrm{R}^{\cdot} + \mathrm{HBr} &\longrightarrow \mathrm{RH} + \mathrm{Br}^{\cdot} \end{aligned}\right. \quad \text{propagation} \qquad (5)$$

With (γ, γ-diphenylallyl)-carbinylmercuric bromide and hydrogen bromide in acetic acid, the products were 1, 1-diphenylethylene (82%), 1, 1-diphenylbutene (14%) and 4% of unidentified materials (which did not include diphenylcyclopropylmethane). The formation of 1, 1-diphenylethylene is unusual and probably arises (54) by addition of hydrogen bromide to the double bond of the organomercurial, followed by a fragmentation of the resulting molecule, related to those studied by Grob (55), which is initiated by attack of bromide ion. This sequence is shown in XXXI.

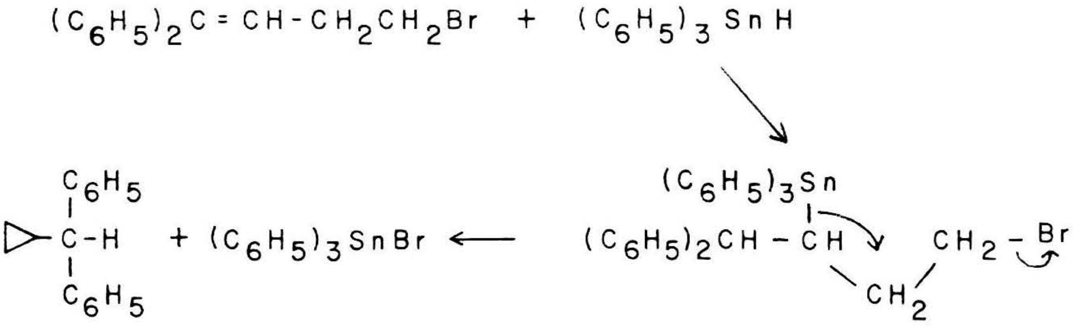
The attempted di-t-butylperoxide catalyzed decarbonylation of (γ, γ-diphenylallyl)-acetaldehyde XXXII also proved to be a barren source of (γ, γ-diphenylallyl)-carbinyl radicals, although for quite different reasons. The free-radical decarbonylation of aldehydes has been discussed in detail by Schuster (2). The main products are hydrocarbons and carbon dioxide formed according to the following chain.

$$\begin{aligned} R\dot{C}O &\longrightarrow R^{\cdot} + CO \\ R^{\cdot} + RCHO &\longrightarrow RH + R\dot{C}O \end{aligned} \qquad \text{propagation} \qquad (6)$$

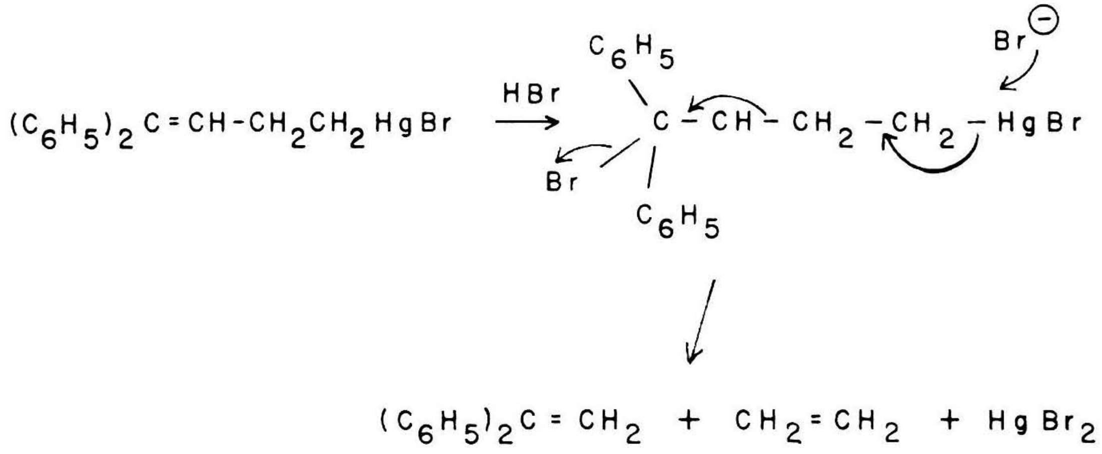
Negligible yields of 1,1-diphenylbutene or diphenylcyclopropylmethane were obtained from attempted decarbonylations of (γ,γ-diphenylallyl)-acetaldehyde under a variety of conditions. This is ascribed to the diversion of $R^{\cdot}$ radicals from the chain propagation to addition to the double bond of the aldehyde and to hydrogen abstractions at the allylic position. Addition to the double bond is expected to be particularly facile because of the stabilization of the adduct radical by two phenyl groups. Another factor which could stop the chains would be if rapid rearrangement of (γ,γ-diphenylallyl)-carbinyl radicals to the diphenylcyclopropylcarbinyl or a related non-classical radical occurred. Hydrogen abstraction from the aldehyde by this species might be endothermic by as much as 20 kcal./mole, making this a very unfavorable propagation step.

It was apparently desirable to produce (γ,γ-diphenylallyl)-carbinyl free radicals in a non-chain reaction, and the thermal decomposition of *t*-butyl (γ,γ-diphenylallyl)-peracetate was a logical candidate. The thermal decompositions of a range of *t*-butyl peresters have been studied by Bartlett and Hiatt (56). The decomposition affords the alkyl radical, carbon dioxide and the *t*-butoxy radical. Several preliminary decompositions of *t*-butyl (γ, γ-diphenylallyl)-peracetate were run in the presence of common hydrogen donors. Low yields of 1, 1-diphenylbutene and diphenylcyclopropylmethane were obtained, with the relative proportion for the latter being 8-14% for cumene, 5% for benzylhydrol and 0% for tetralin. Thus significant rearrangement had occurred, particularly with cumene. These experiments were plagued by side reactions, for a full account of which the Experimental Section should be consulted. Tributyltin hydride proved to be a much more powerful hydrogen donor (57) and satisfactory yields of the desired hydrocarbons were obtained using it.

In view of the formation of diphenylcyclopropylmethane in free radical reactions of the (γ, γ-diphenylallyl)-carbinyl system it was of considerable interest to try to determine the nature of the precursor of this rearranged product. The diphenylcyclopropylmethane could be formed from the diphenylcyclopropylcarbinyl radical or from a non-classical homoallylic radical, intermediate in structure between the former and the (γ, γ-diphenylallyl)-carbinyl radical. The latter possibility carries important theoretical implications in organic chemistry, since, although non-classical intermediates appear to be well established in certain carbonium ion reactions (1, 58), it can fairly be stated that no unequivocal evidence for a non-classical free radical has yet been published. The formulation of rearrangements observ-



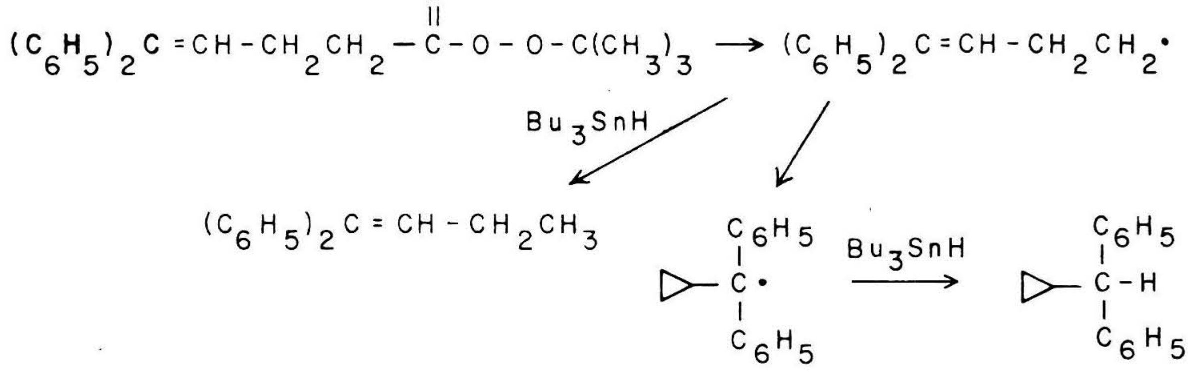
XXX



XXXI

$(C_6H_5)_2C=CH-CH_2CH_2CHO$

XXXII



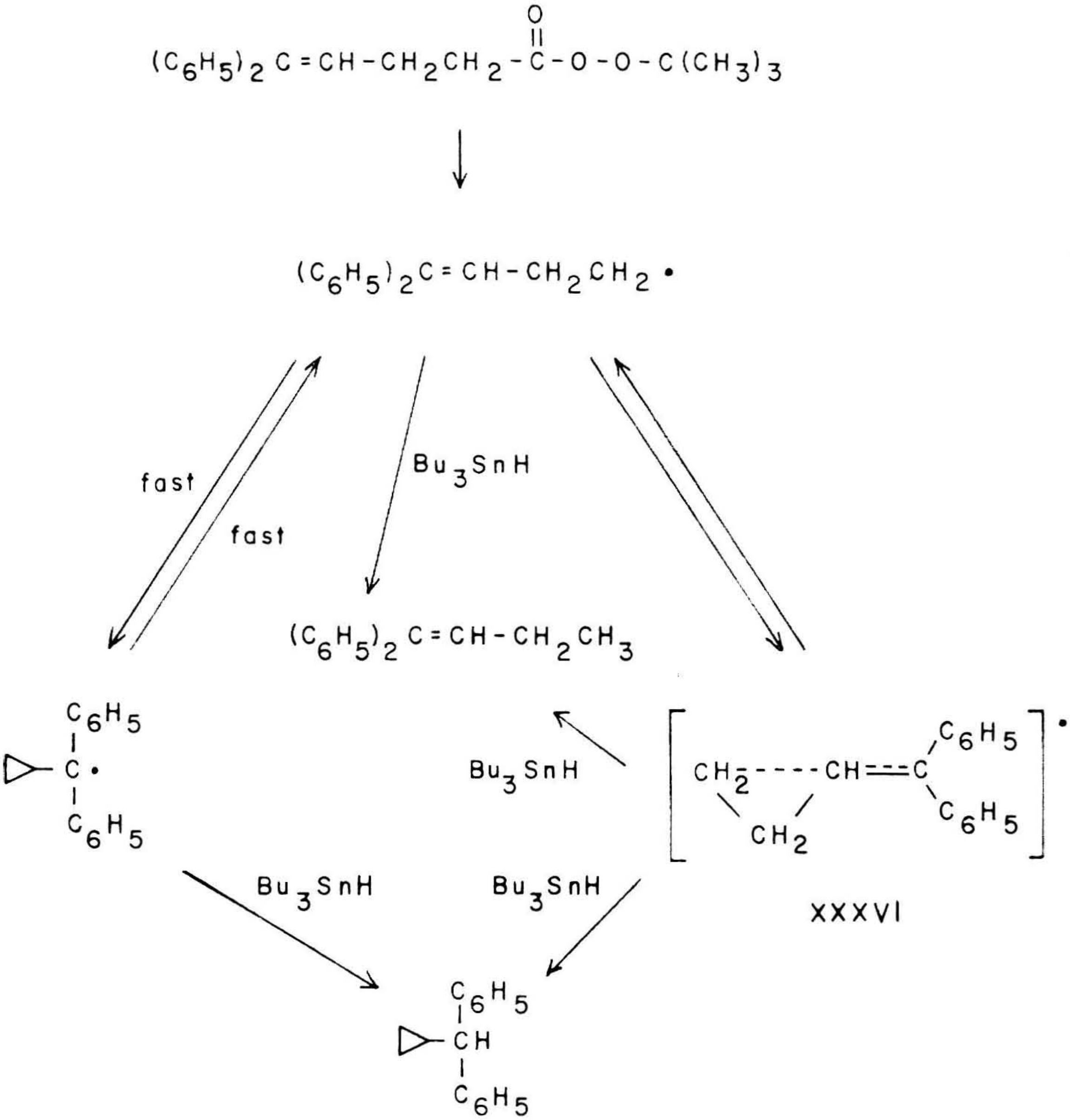
XXXIII

ed by Schuster (2) in the decarbonylations of small-ring aldehydes, in terms of non-classical delocalized species is attractive but the available data are equally compatible with classical structures.

A product study was made of the decomposition of *t*-butyl (γ , γ -diphenylallyl)-peracetate in chlorobenzene in the presence of tributyltin hydride. The initial concentration of perester and the bath temperature (110°) was the same in each run, but the concentration of hydrogen donor was varied from .0.56 to 0.56 M. These and other results to be discussed are summarized in the Experimental Section. It was found that for a 10-fold decrease in tributyltin hydride concentration the relative proportion of diphenylcyclopropylmethane to diphenylcyclopropylmethane plus 1,1-diphenylbutene was essentially unchanged (a slight *decrease* from 6 to 4.5% was observed). On the basis of the discussions given by Seubold (59) and Cristol, et al. (60), this implies that the hydrocarbon products are formed from a single radical or from two or more radicals in rapid equilibrium. The kinetic equations supporting this conclusion have been developed by Cristol, et al. (60). Thus a mechanism XXXIII, in which the diphenylcyclopropylcarbinyl radical is formed irreversibly from the (γ , γ -diphenylallyl)-carbinyl radical or in which the reverse step is slow compared with rate of reaction of the former with tributyltin hydride, is ruled out. The remaining plausible alternatives are that the diphenylcyclopropylmethane and 1.1-diphenylbutene are formed from a single non-classical radical which is attacked by tributyltin hydride at either reactive end, or from (γ, γ-diphenylallyl)-carbinyl and diphenylcyclopropylcarbinyl radicals which are in rapid equilibrium.

A study was made of the kinetics of decomposition of *t*-butyl (γ, γ-diphenylallyl)-peracetate and of the saturated analog, *t*-butyl 5, 5-diphenylperpentanoate, in order to determine the nature of the radical species formed in the rate-determining step of decomposition of the former perester. Bartlett and Hiatt (56) found that a series of *t*-butyl peresters undergo thermal decomposition at rates parallel to the stability of the radical $R^\cdot$ in the formula $RCO_3C(CH_3)_3$, and presented evidence that the decomposition of these esters involved simultaneous rupture of an O-O and C-C bond with the formation of carbon dioxide in the primary step. From Bartlett and Hiatt's results, it is expected that if a resonance-stabilized non-classical radical is formed in the rate-determining step of decomposition of *t*-butyl (γ, γ-diphenylallyl)-peracetate, then the rate of decomposition would be considerably greater than for *t*-butyl 5, 5-diphenylperpentanoate, in which the γ, δ-double bond is absent and no stabilization of the incipient radical center by the phenyl groups is possible. The rates of decomposition of the two peresters were followed at 109.7° in chlorobenzene solution in the presence of excess iodine, to prevent induced decomposition. Complications were encountered with the rates for t-butyl (γ , γ -diphenylallyl)-peracetate in that, although a good first-order plot was found for the first 60% or so of reaction, a wide scatter of points was obtained after this stage. This behavior is discussed more fully in the Experimental Section. The rate constants were calculated from expanded plots of the early points and the average value was $k_1 = 7.7 \times 10^{-5}$ sec^{-1}. This is only slightly greater than the average value 5.3×10^{-5} sec^{-1}, for t-butyl peracetate at 110° in chlorobenzene in the absence of iodine, obtained by Hiatt (61). The average rate constant found for the decomposition of t-butyl 5,5-diphenylperpentanoate was $k = 5.5 \times 10^{-5}$ sec^{-1}. Thus the thermal decomposition of t-butyl (γ , γ -diphenylallyl)-peracetate is faster than that of t-butyl 5,5-diphenylperpentanoate by a factor of only 1.4. This increase seems too modest to ascribe it to the formation of a resonance-stabilized radical in the primary step for decomposition of t-butyl (γ , γ -diphenylallyl)-peracetate, especially in view of the large rate accelerations observed by Bartlett and Hiatt (56) for concerted perester decompositions. The results are accommodated by the formation of the (γ , γ -diphenylallyl)-carbinyl radical in the initial step.

A distinction has now to be made between the mechanisms XXXIV and XXXV involving, on the one hand, a fast equilibrium between (γ , γ -diphenylallyl)-carbinyl and diphenylcyclopropylcar-



XXXVI

XXXIV

XXXV

binyl radicals and, on the other hand a single non-classical radical, intermediate in structure between them and written tentatively as XXXVI (delocalization of the electron involving the phenyl rings understood, but not shown). Other equilibria in XXXIV and XXXV, such as between the non-classical radical XXXVI and the diphenylcyclopropylcarbinyl radical, are possible but are not included in the chart. It is interesting to note that in the *n-m-r* spectrum of the Grignard reagent from 4, 4-diphenyl-1-bromo-3-butene-1, 1-$\underline{d}_2$ (Fig. 5 and 7) discussed earlier, *both* vinyl triplets present show a large central component due to a superimposed vinyl singlet. The latter corresponds to the (γ, γ-diphenylallyl)-carbinyl species with deuterium in the 2-position. One of the vinyl multiplets was shown to be due to 1, 1-diphenylbutene, which is possibly formed by a free-radical process during reaction of the bromide with magnesium. If this is true then the 1-and 2-positions in the radical must be equilibrated faster than the rate of its reaction with solvent. This requirement is accommodated by a mechanism of the type XXXIV, and by XXXV if the non-classical radical XXXVI is assumed to be in equilibrium with a similar radical in which the other CH-CH_2 ring-bond is partially broken.

The effect of temperature variation on the ratio of diphenylcyclopropylmethane to 1, 1-diphenylbutene obtained in the thermal decomposition of *t*-butyl (γ, γ-diphenylallyl)-peracetate in the presence of tributyltin hydride provided a possible way of distinguishing between XXXIV and XXXV. The initial concentrations of tributyltin hyrdride and perester were held constant, and it was found that for a decrease in temperature of 40° the ratio of diphenylcyclopropylmethane to 1, 1-diphenylbutene was essentially unchanged, although there was a slight trend in the direction of an increase. The interpretation of this lack of temperature effect requires an estimate of the enthalpy difference (Δ H) between the (γ , γ -diphenylallyl)-carbinyl and the diphenylcyclopropylcarbinyl radicals. Δ H values for this and other substituted allycarbinyl-cyclopropylcarbinyl free radical interconversions were calculated by a thermodynamic cycle method using bond dissociation energies given by Walling (33), Cottrell (7) and Szwarc (62), and heats of formation from tables (63) and elsewhere in the literature. Table IX summarizes the results. It was assumed that the cyclopropyl group stabilized a radical center to the same extent as a methyl group, although greater stabilization by cyclopropyl is conceivable (2).

The ΔH value for the γ -vinyl case is in accord with the isolation of cyclopropylallyl coupling products almost exclusively from the reaction of the Grignard reagent from 1-bromo-3, 5-hexadiene with cobaltous chloride (see preceeding section). For the phenyl-substituted

TABLE IX

Calculated Enthalpies for Free-Radical Allycarbinyl-Cyclopropylcarbinyl Interconversions

System	Δ H, kcal./mole
(γ, γ-diphenylallyl)-carbinyl →diphenylcyclopropylcarbinyl	−24.5
(γ-vinylallyl)-carbinyl →vinylcyclopropylcarbinyl	−16
(γ-phenylallyl)-carbinyl →phenylcyclopropylcarbinyl	−15
(γ, γ-dimethylallyl)-carbinyl →dimethylcyclopropylcarbinyl	− 3
allylcarbinyl → cyclopropylcarbinyl	+ 16.5

system the calculated Δ H value indicates that the phenylcyclopropylcarbinyl radical should be much more stable than the open-chain radical.

Bennett and Bunce (36) unwittingly provided confirmation of this point when they isolated a 33% yield of 1,2-dicyclopropyl-1,2-diphenylethane from the reaction of ethylmagnesium bromide and cobaltous chloride with, what they considered to be, phenylcyclopropylcarbinyl bromide (now postulated to be γ-phenylallyl)-carbinyl bromide, see previous Section). The small Δ H value calculated for the corresponding dimethyl structures indicates that this is a nicely-balanced system which might give either (γ , γ -dimethylallyl)-carbinyl or dimethylcyclopropylcarbinyl products depending on the conditions. This conclusion is in agreement with the results of Schuster (2) who found that the product of decarbonylation of dimethylcyclopropylacetaldehyde alone was 2-methyl-2-pentene, but that a 42 :9 mixture of 2-methyl-2-pentene and isopropylcyclopropane was produced in the presence of benzyl mercaptan. The high positive value of Δ H calculated for the unsubstituted allylcarbinyl case is indicative of much higher stability for the allycarbinyl than for the cyclopropylcarbinyl free radical. Experimental confirmation for this prediction is found in the decarbonylation of cyclopropylacetaldehyde (2) which gives 1-butene as the only isolable hydrocarbon product. In the photochemical chlorination of methylcyclopropane (17), where the radicals are attacked by the very reactive chlorine molecule, rearrangement is not complete and a 50% mixture of allylcarbinyl chloride and cyclopropylcarbinyl chloride results (accompanied by a number of side-products).

The large negative ΔH calculated for the (γ , γ -diphenylallyl)-carbinyl→diphenylcyclopropylcarbinyl free-radical rearrangement indicates that a hypothetical equilibrium involving these two species should lie very far in favor of the diphenylcyclopropylcarbinyl radical, or that a non-classical radical of the type XXXVI should closely resemble the diphenylcyclopropylcarbinyl radical in structure. Either of these situations would not necessarily be reflected in the observed hydrocarbon product ratios since the hydrogen abstraction reaction leading to 1, 1-diphenylbutene is expected to be more facile than that generating diphenylcyclopropylmethane in both cases.

We are now in a position to attempt to interpret the lack of temperature effect on the ratio of the hydrocarbons isolated from decomposition of t-butyl (γ , γ -diphenylallyl)-peracetate in the presence of tributyltin hydride. The activation energies for free-radical hydrogen abstraction reactions are relatively small and generally lie in the range 5-10 kcal. / mole (64). Thus the difference in activation energy between the reaction of the diphenylcyclopropylcarbinyl and the (γ , γ -diphenylallyl)-carbinyl radicals with tributyltin hydride is expected to be small; probably no more than two or three kcal. / mole. Since mechanism XXXIV requires that the equilibrium between the radicals be fast, one might conclude that the difference in activation energy between the reactions leading from the (γ , γ -diphenylallyl)-carbinyl radical to 1, 1-diphenylbutene and diphenylcyclopropylmethane is mainly determined by the enthalpy difference between the diphenylcyclopropylcarbinyl and (γ , γ -diphenylallyl)-carbinyl radicals. In view of the high calculated ΔH of -24.5 kcal. /mole, a marked temperature effect on the ratio of hydrocarbon products is expected.

Since the observed temperature effect is negligible, one is forced to the conclusion that XXXIV cannot be the predominant operative mechanism. Granting the validity of the above argument, XXXV emerges as the only plausible mechanism which is consistent with the experimental results. This requires that the non-classical free radical XXXVI be the major precursor for the 1, 1-diphenylbutene and diphenylcyclopropylmethane formed. The present results do not firmly establish the existence of the intermediate XXXVI, but only provide indirect evidence for it. Further work will be required to prove rigorously that the scheme XXXV is operative.

PART II

Introduction

The structure and reactivity of cyclopropanes has intrigued organic chemists back to the time of Baeyer and his Strain Theory (65). The unique geometry, symmetry and bonding properties of the cyclopropane ring confer it with special qualities that are unlike those of any other ring system. Many physical and chemical techniques have been applied to cyclopropanes in probing these properties, and as a result the gross features of the ring have been revealed. The rapid development of nuclear magnetic resonance spectroscopy (66) provides a new tool for investigating some of the more subtle aspects of the structure of cyclopropanes. This Part is concerned with an empirical study of the *n-m-r* spectra of selected cyclopropanes and with attempts to correlate the results with existing theories.

Spin-Spin Coupling Constants in Cyclopropanes.

N-m-r proton-proton spin coupling constants (J, ref. 38) appear to be very sensitive to the spatial disposition of the nuclei involved and to the electronic structure of the molecule to which the nuclei are attached. In particular, a dependence of $J_{\underline{gem}}$ on H-C-H angle in methylene groups was predicted theoretically by valence-bond calculations of Gutowsky, et al. (67) and experimental results were in reasonable agreement with the calculated angular dependence. Gutowsky's theoretical curve is shown in Figure 9. It predicts that $J_{\underline{gem}}$ should decrease with decreasing H-C-H angle, become zero at an angle of 125°, then change sign. Banwell and Sheppard (68) replotted the experimental data using only points for which $J_{\underline{gem}}$ and H-C-H angle had been measured in the same molecule. They proposed on this basis a linear relation (see Fig. 9) between $J_{\underline{gem}}$ and H-C-H angle. Several measurements have been made (69) of the H-C-H angle in cyclopropane, and the most acceptable appears to be 118°. The only other H-C-H angles that have been measured in cyclopropanes are 114.6° in cyclopropyl chloride and 115.6° in cyclopropyl cyanide (69). The range 114.5-118° therefore seems reasonable for this angle in cyclopropanes. The theoretical curve of Gutowsky, et al. predicts positive geminal coupling constants of about 4.5-7 c.p.s., while the experimental line of Banwell and Sheppard indicates values in the range 0-5 c.p.s. for cyclopropanes. The geminal cyclopropane coupling constants found in the present work are summarized in Table X. Two of these were from 1,1,2,2-tetrasubstituted cyclopropanes, for which the analysis of the AB spectrum is straightforward (66). Most of the remainder were obtained by analysis of the proton ^{13}C-satellite spectra of sym-1,1-disubstituted cyclopropanes (vide infra) and are considered accurate

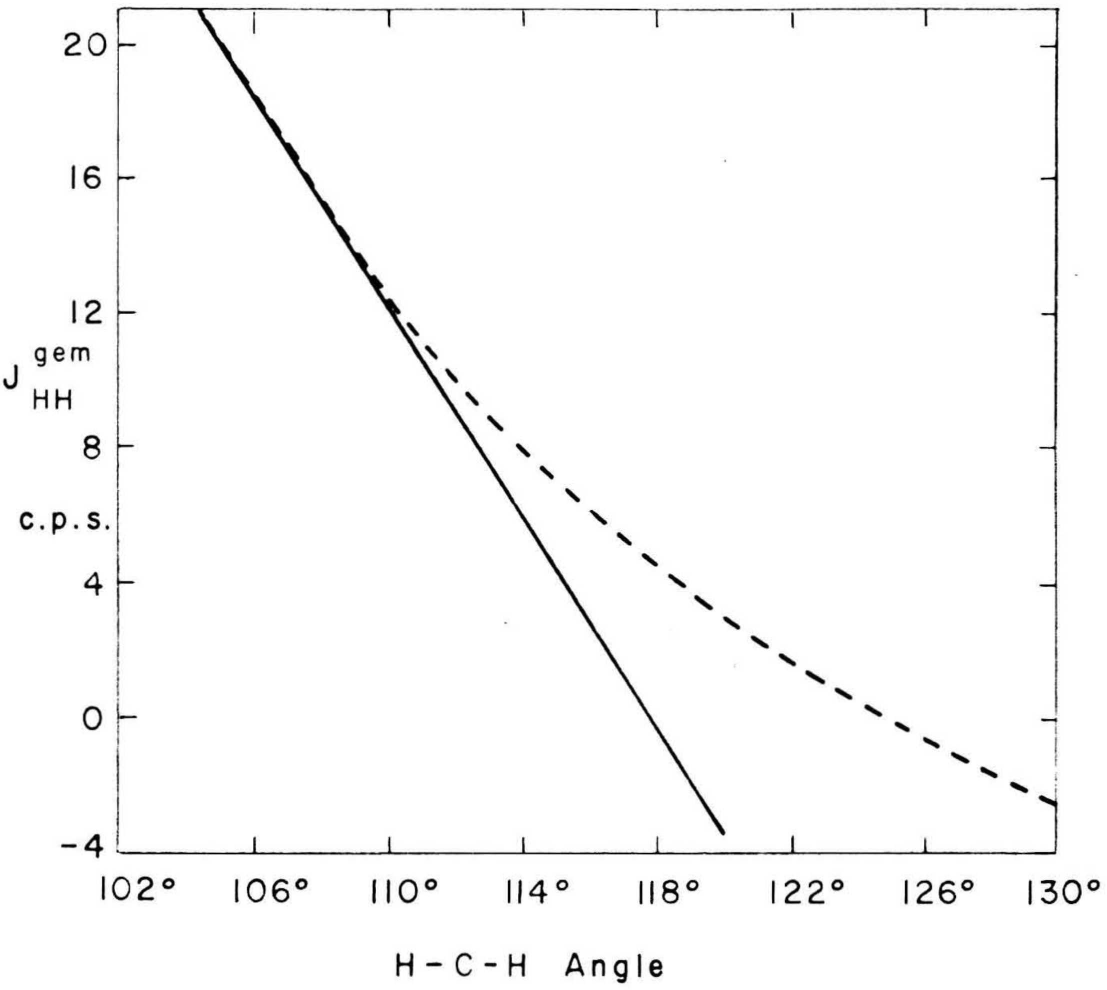


Fig. 9.— Relation between the geminal proton-proton spin-spin coupling constant and the H-C-H angle. The dashed line is the theoretical curve of Gutowsky, et al. (67); the solid line is due to Banwell and Sheppard (68).

to ±0.4 c.p.s. Also included in Table X are some approximate values given in the literature. The latter were deduced directly from ABX spectra and are seen to be somewhat larger than the other values. The coupling constants found in the present work lie in the range 2.3 to 4.2 c.p.s., which is considerably lower than the range predicted by the theoretical curve in Figure 9, but is embraced by the linear relation of Banwell and Sheppard. The *gem*-coupling constant, at least for 1,1-dichlorocyclopropane, has the same sign as the vicinal coupling constants since computation showed that small negative values did not fit the observed ^{13}C-satellite spectra (see next section), although -15 c.p.s. also gave good agreement. Such large negative constants are very unlikely however (67). The values for cyclopropanes may be compared with J_{gem} = 5.8 ± 0.5 c.p.s. found by Reilly and Swalen (72) for substituted epoxides. The latter are generally higher than those found for cyclopropanes consistent with the slightly smaller H-C-H angle in ethylene oxide relative to cyclopropane (69).

Of particular interest are the relative magnitudes of the vicinal coupling constants in cyclopropanes. The valence-bond calculations of Karplus (73) predict a dependence of the vicinal proton-proton coupling constant in ethanes and ethylenes on the dihedral angle between the C-H bonds. For sp^3 hybridization the calculated values were fitted approximately by the equations,

TABLE X

Geminal Coupling Constants in Cyclopropanes

Compound	$J_{\underline{gem}}$, c.p.s.	Ref.
1,3,4,5-Tetramethyl-2-methylenebicyclo[3.1.0]hex-3-ene	3.1	this thesis
Dimethyl 1,2-dimethylcyclopropane-cis-1,2-dicarboxylate	4.2	" "
Dimethyl 1-methylcyclopropane-trans-1,2-dicarboxylate	4.2[a]	" "
1,1-Dichlorocyclopropane	2.3	" "
1,1-Dimethylcyclopropane	2.5	" "
Spiropentane	2.7	" "
Spirohexane	3.0	" "
Chlorospiropentane	5	70
1-Nitrocyclopropane-cis-1,2-dicarboxylic anhydride	6.4	71

[a] from numerical analysis of ABX spectrum, only considered accurate to ±0.5 c.p.s.

$$J_{HH'} = 8.5 \cos^2\phi - 0.28 \text{ (c.p.s.)} \qquad 0^\circ \leq \phi \leq 90^\circ$$

$$\text{and} \quad J_{HH'} = 9.5 \cos^2\phi - 0.28 \text{ (c.p.s.)} \qquad 90^\circ \leq \phi \leq 180^\circ \tag{1}$$

where ϕ is the dihedral angle. Conroy (74) has calculated a similar angular dependence for *sp*^{3} hybridization using a molecular-orbital method, and the results were in excellent agreement with quoted experimental values. The theoretical curves for the calculations of Karplus and Conroy are shown in Figure 10. They are seen to follow each other fairly closely, but differ mainly in that the Karplus treatment predicts slightly negative coupling constants near $\phi = 90^\circ$ and leads to J values somewhat smaller than calculated by Conroy, for the range 90-180°. In this connection, it should be noted that Conroy used a scaling factor which affects the height, but not the general shape, of the curve to give a better fit to his experimental coupling constants in this range of ϕ.

For the measured H-C-H angles of 114.5-118° for cyclopropanes cited previously the range of ϕ is calculated to be 131-134° for *trans*-hydrogens, and ϕ is of course zero for *cis*-hydrogens. For these dihedral angles assuming *sp*^{3} hybridization the *cis*-coupling constant is calculated to be 8.0 c.p.s. and the *trans*-, 6.4-7.0 c.p.s., from Conroy's curve, while Karplus' equations lead to calculated values of 8.2 c.p.s. for the *cis*- and 3.8-4.3 c.p.s. for the *trans.* Thus both theoretical treatments predict the *cis* vicinal coupling will be greater than the *trans* vicinal coupling in cyclopropanes, assuming *sp*^{3} hybridization of the C-H bonds. The latter assumption is probably a poor one

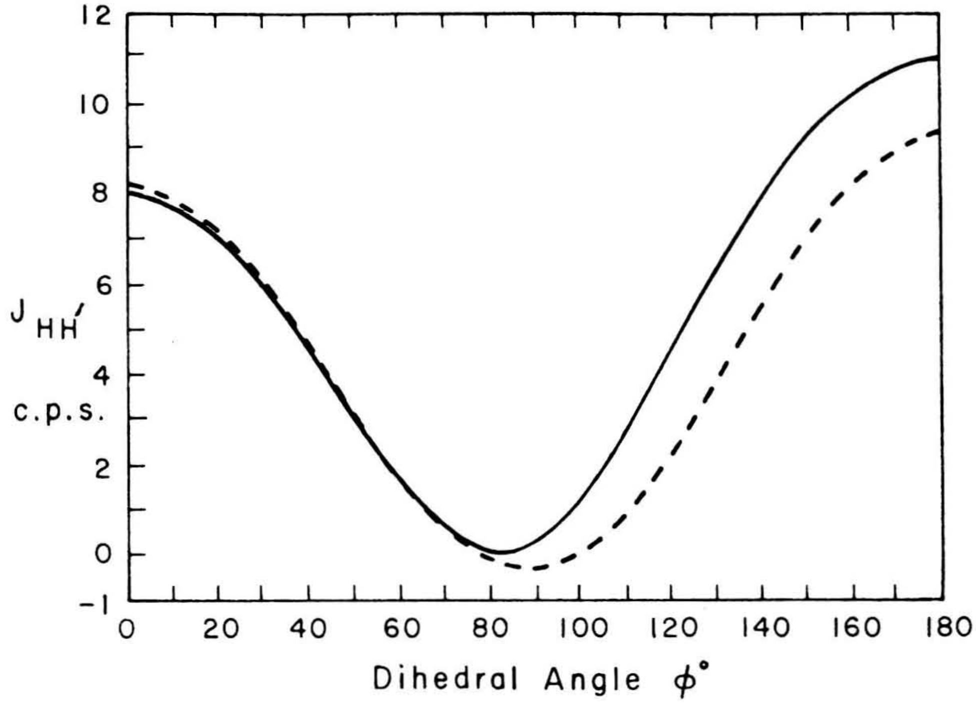


Fig. 10.— Theoretical curves showing the variation of the vicinal proton-proton spin coupling constant with the dihedral angle ϕ between the C-H bonds for carbon $\underline{sp}^3$ hybridization. The dashed line is calculated from Karplus' Equation 1 and the solid line is due to Conroy (74).

for cyclopropanes, as will be discussed later. Vicinal coupling constants were measured for some tetrasubstituted cyclopropanes in which the stereochemical disposition of the cyclopropyl hydrogens is unambiguously known. These are collected in Table XI. The analyses of the cyclopropyl resonances were straightforward for these compounds since they were either AB or AXY systems (Y side-chain hydrogen).

The *cis*-coupling constants were found to be greater than the *trans*- in agreement with theory. It would be desirable to have more examples of such cyclopropanes with *cis*-oriented hydrogens to establish the generality of this conclusion. Compound II and its *cis*-isomer are important since both have the same substituents α-to the cyclopropyl hydrogens. The only difference between them is the orientation of the groups and this leads to a much larger coupling constant for the *cis*-compound than for the *trans*. The observed coupling constants for *cis*- and *trans*-hydrogens in Table XI lie in quite narrow ranges which do not overlap. It would be preferable to obtain coupling constants for less highly-substituted cyclopropanes. However, in view of the rigid structure of the cyclopropyl ring it is unlikely that large distortions of the bond angles will occur.

It is appropriate at this point to draw attention to the work of Closs and Closs (75) who, without any experimental support, proposed contrary to the above results that *trans*-vicinal coupling constants were greater than *cis*- in cyclopropanes. They then used this assignment to

TABLE XI

Vicinal Coupling Constants in Cyclopropanes.

Compound	Stereochem.[a]	$J_{\underline{vic}}$, c.p.s.
trans-3-(*trans*-2'Carboxypropenyl) -2, 2-dimethylcyclopropane-1-carboxylic acid(I)	*trans*	5.7
Dimethyl ester of I	*trans*	5.4
Dimethyl *trans*-caronate(dimethyl 2, 2-dimethyl-cyclopropane-*trans*-1, 2-dicarboxylate)	*trans*	5.6[b]
2, 2-Dimethyl-*trans*-3-phenylcyclopropane-1-carboxylic acid (II)	*trans*	5.7
Carboxamide of II	*trans*	6.0
2, 2-Dimethyl-*cis*-3-phenylcyclopropane-1-carboxylic acid	*cis*	9.1
2-Oxa-7, 7-dichloronorcarane	*cis*	8.6

[a] Relation of cyclopropyl hydrogens.

[b] Obtained from the ^{13}C satellite spectrum.

distinguish between stereoisomers obtained in the reaction of chlorocarbene with olefins. The results agreed with their considerations of non-bonded intereactions in the two possible transition states III and IV for addition of chlorocarbene to an unsymmetrical olefin. They predicted that if the combined "steric requirements" of R_1 and R_2 were smaller than those of R_3 and R_4, transition state III would be much more stable than IV and the product resulting from it would predominate. In all of the olefins studied the substituents were alkyl groups or hydrogen atoms and it was assumed that the "steric requirements" of the former were greater than that of the latter. Since the coupling constant assignment of Closs and Closs should now be reversed, it is apparent that their argument regarding non-bonded interactions in III and IV must also be incorrect. One is therefore led to the interesting conclusion that an interaction exists between the chlorine and the alkyl groups in the transition state which tends to hold them together and to yield products in which the maximum number of alkyl groups are cis- to the chlorine atom.

The results of Table XI were applied to vicinal coupling constants obtained from an exact analysis of the proton ^{13}C-satellite spectra of sym-1, 1-disubstituted cyclopropanes. These are A_2B_2 systems and the cis- and trans-coupling constants cannot be identified from an analysis of the spectra. Assignments were made for these cases and for tri- and tetra-substituted cyclopropanes on the basis of Table XI. The results are summarized in Table XII.

Combining the results of Tables XI and XII, we see that the cis-coupling constants lie in the range 9.8 ±1.3 c.p.s. while the trans-coupling constants have the values 6.4 ±1.6 c.p.s., and these

TABLE XII

Assigned Vicinal Coupling Constants in Cyclopropanes.

Compound	J_{vic}(trans), c.p.s.	J_{vic}(cis), c.p.s.
1, 1-Dichlorocyclopropane	7.95	11.05
1, 1-Dimethylcyclopropane	5.9	9.7
Spirohexane	6.5	9.9
Spiropentane	4.9	8.6
Dimethyl 1-methylcyclopropane-cis-1, 2-dicarboxylate	6.3[a]	-
2-Benzoyl-1-cyano-1, 3-diphenylcyclopropane, isomer V, m.p. 168.5°	7.3	-
2-Benzoyl-1-cyano-1-(4-nitrophenyl)-3-phenylcyclopropane, VI isomer, m.p. 151°	7.2	-
VI, isomer, m.p. 170°	-	10.4
Carboxamide from V	7.5	-
1-Nitrocyclopropane-cis-1, 2-dicarboxylic anhydride[b]	6.3	9.0

[a] From numerical analysis of ABX spectrum, considered accurate to ±0.4 c.p.s.

[b] Reference 71, from ABX spectrum; coupling constants found to have the same sign.

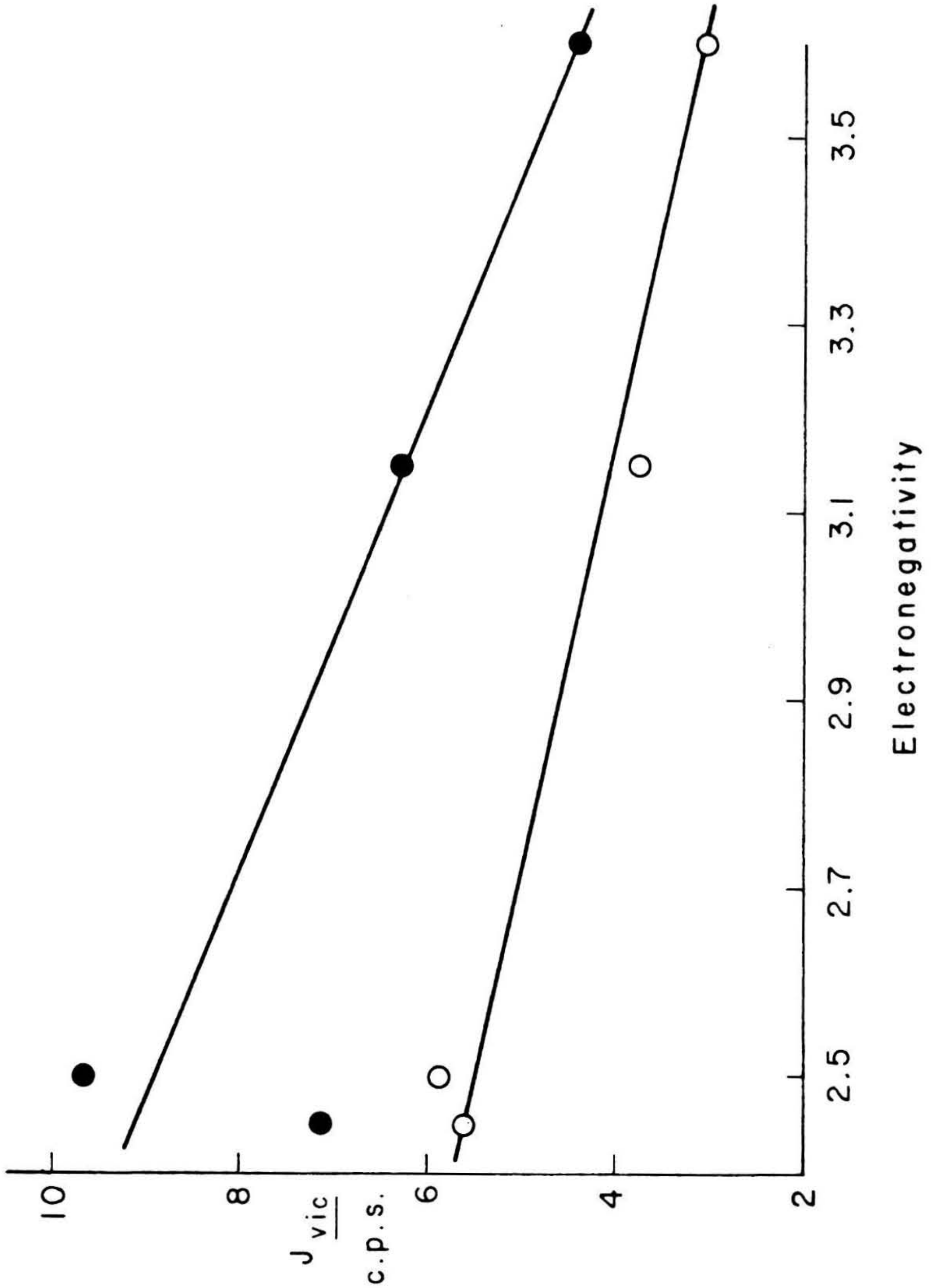
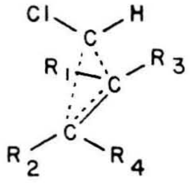


Fig. 11.— Dependence of the vicinal *cis*- (shaded circles) and *trans*- (open ciccles) proton-proton spin coupling constants in small-ring compounds on electronegativity. Points in order of increasing electronegativity of the hetero-atom are for ethylene sulfide, 1,1-dimethylcyclopropane, ethylene imine, and ethylene oxide.

ranges do not overlap. The smaller spread for the *cis*-values than for the *trans*- would be consistent with changes in the dihedral angle ∅ being the cause of variation in the *trans*-coupling constants, the *cis*-hydrogens remaining more-or-less eclipsed. However, this is unlikely to be the sole explanation for the variation. The observed *cis*-values are uniformly higher than those predicted by theory for sp^3 hybridization, while the range calculated for the *trans*-values by Conroy is more than covered by the experimental coupling constants. It is not reasonable to expect the observed constants to agree closely with values calculated on the assumption of sp^3 hybridization since the vicinal coupling constant probably also depends on the H-C-C angle (67), and in cyclopropanes this is likely to be larger than the tetrahedral angle. Both the *cis*- and *trans*- coupling constants for cyclopropanes are considerably larger than the constants $J_{\underline{cis}}$ = 4.6 ±0.5 c.p.s. and $J_{\underline{trans}}$ = 2.2 ±0.5 c.p.s. found by Reilly and Swalen (72) for substituted epoxides. Since the *cis*-hydrogens are eclipsed in cyclopropane and ethylene oxide and the H-C-H angle in ethylene oxide is only about 2° less than in cyclopropane (69), it seems improbable that these differences can be attributed to variations in dihedral angle.

A possible explanation may be found by consideration of Figure 11 in which *cis*- and *trans*- coupling constants measured for ethylene oxide, ethylene imine and ethylene sulfide by Mortimer (76), using the ^{13}C-satellite technique, are plotted against the electronegativity values for the hetero-atom given by Daudel, et al. (77). Included are the coupling constants for 1, 1-dimethylcyclopropane which was taken as the compound most closely resembling cyclopropane itself. A fairly good linear correlation with electronegativity holds for the trans-coupling constants, while an approximate dependence is discernible for the cis-coupling constants. This relation apparently does not extend to the geminal coupling constants, since these are generally larger for epoxides than for cyclopropanes, as noted earlier. A weak dependence of coupling constant on electronegativity has been reported by Glick and Bothner-By (78) for monosubstituted ethanes, who also found that J decreased with increasing electronegativity. The effect is more pronounced in vinyl compounds (68) where all coupling constants are found to decrease approximately linearly with increasing electronegativity.

Referring again to Table XII; some assignments were made for several tetra-substituted aryl-cyclopropanes on the basis of the magnitudes of the cyclopropyl coupling constants. These compounds were prepared some time ago by Allen, et al. (79) by treatment of stereoisomeric bromonitriles VII with base, but their stereochemistry was not known. Each compound may have four possible structural isomers,



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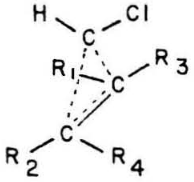
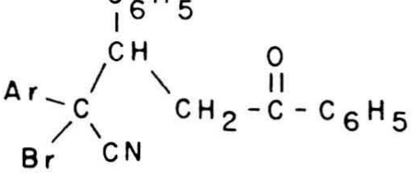
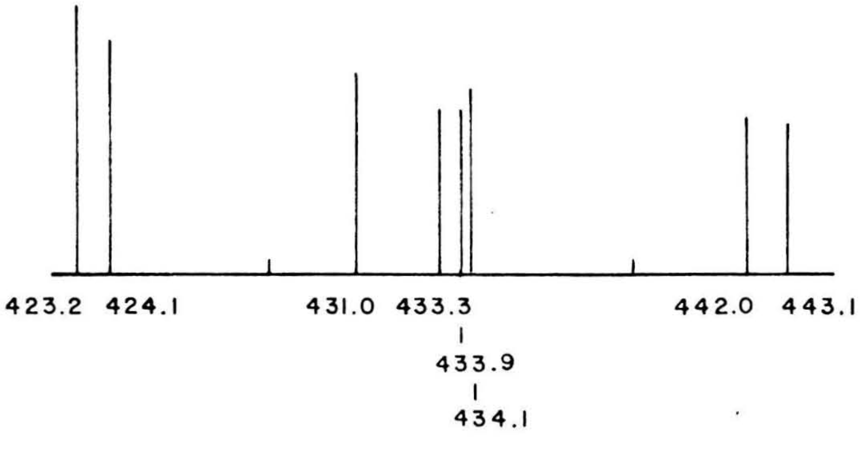


IV



VII



VIII

Computed upfield proton ^{13}C-satellite for 1,1-dichlorocyclopropane. Line frequencies are in c.p.s. relative to benzene (cf. Fig. 12, upper).

two for each orientation of the cyclopropyl hydrogens. The assignments in Table XII indicate that the isomers of VI are cis- trans-isomers, while in V and its amide the cyclopropyl hydrogens are trans-disposed. The foregoing is an illustration of the use of coupling constant data in structure elucidation of isomeric cyclopropanes.

The ^{13}C-satellite method using ^{13}C in natural abundance is very useful for obtaining coupling constants between nuclei that have the same chemical shift. It has been applied (80, 76) to systems giving A_2B_2 satellite spectra, for which the analysis was similar to that used for the cyclopropanes. The observed upfield ^{13}C-satellites for four sym-1, 1-disubstituted cyclopropanes are given in Figures 12 and 13. The satellite for 1, 1-dichlorocyclopropane shows more detail than the others and it will be discussed more fully. The computed satellite spectrum for 1, 1-dichlorocyclopropane is shown in VIII. The peak at lowest field was given approximately the same chemical shift as that in Figure 12 in order to compare the spectra. Good agreement between computed and observed spectra was found for this and all other similar ^{13}C-satellites. The peaks at 433.9 and 434.1 c.p.s. in the computed spectrum are superimposed to give a large single peak in the observed spectrum. The resonance may be analyzed as an A_2B_2 system approaching A_2X_2. It was found by computation that if the peaks in VIII are numbered 1 to 8 in order of increasing field,

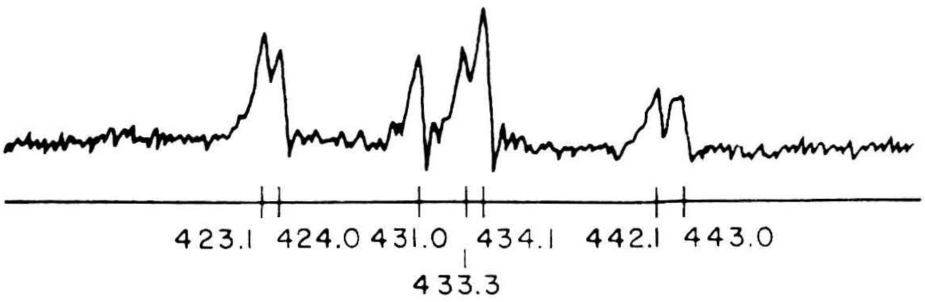


Fig. 12a.— Proton upfield ^{13}C-satellite n-m-r spectrum of 1,1-dichlorocyclopropane for ^{13}C in natural abundance. Peak frequencies are in c.p.s. relative to benzene as internal standard.

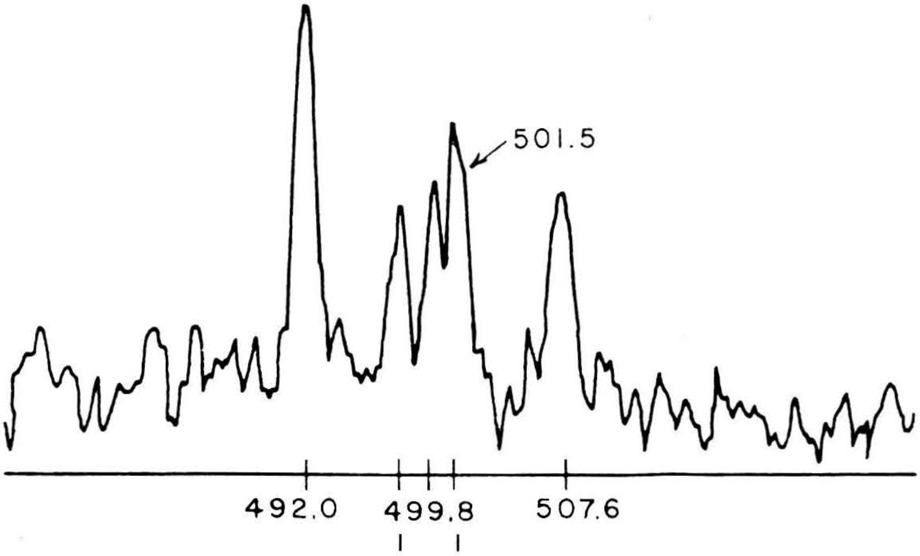


Fig. 12b.— Proton upfield ^{13}C-satellite n-m-r spectrum of 1,1-dimethylcyclopropane for ^{13}C in natural abundance. Peak frequencies are in c.p.s. relative to benzene as internal standard.

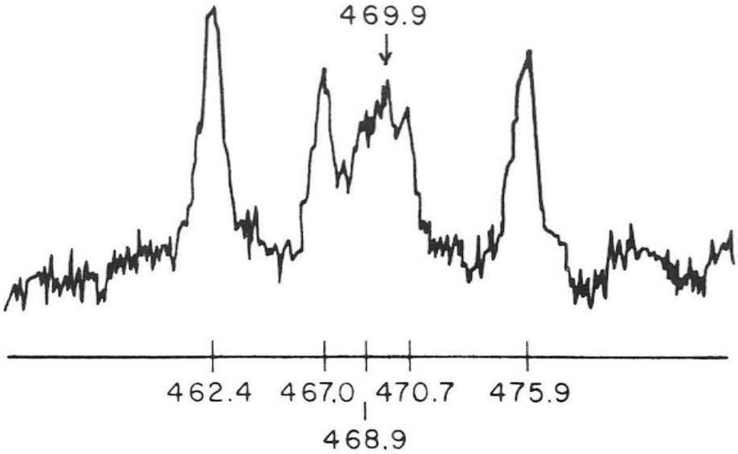


Fig. 13a.— Proton upfield ^{13}C-satellite n-m-r spectrum of spiropentane. Peak frequencies are in c.p.s. relative to benzene as internal reference.

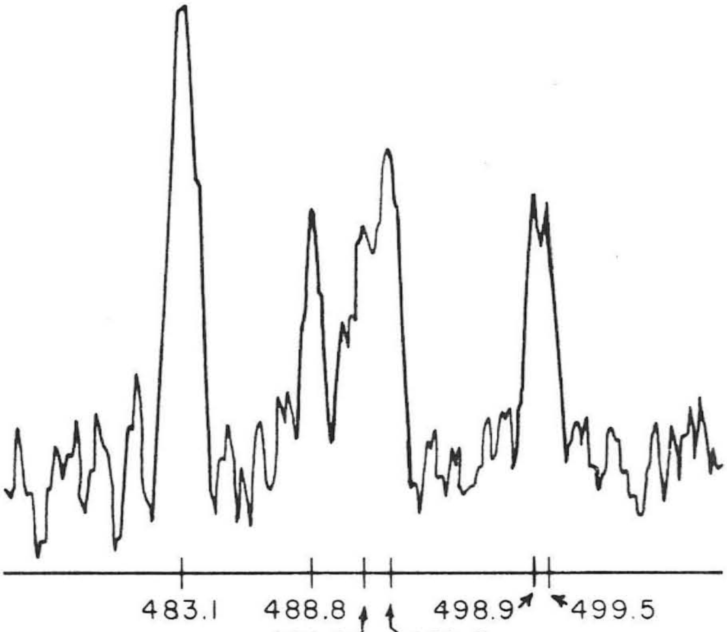


Fig. 13b.— Proton upfield ^{13}C-satellite n-m-r spectrum of spirohexane. Peak frequencies are in c.p.s. relative to benzene as internal standard.

then only peaks 4 and 5 are dependent on $J_{\underline{gem}}$; the separation between peak 2 and 8 is precisely equal to $J_{\underline{cis}} + J_{\underline{trans}}$; and the separation between peak 3 and 6 is exactly equal to $J_{\underline{cis}} - J_{\underline{trans}}$. $J_{\underline{gem}}$ was obtained by computation by finding the value which gave a separation between peak 3 and 4 in agreement with the observed. Arguments given by Mortimer (76) for small-ring systems with hetero-atoms indicate that one may deduce that $J_{\underline{cis}}$ and $J_{\underline{trans}}$ have the same sign from the satellite spectra. These arguments are equally applicable to the cyclopropanes and the same conclusion is reached, in agreement with theory. For smaller values of the vicinal coupling constants, each pair of outer lines in VIII become quite closely spaced and appear superimposed in most of the observed spectra.

Table XII shows that 1, 1-dichlorocyclopropane has the largest cis- and trans-coupling constants of any of the cyclopropanes investigated, while spiropentane has the smallest values. These results cannot be correlated with the external bond angle at the 1-position since the latter is 112° for 1, 1-dichlorocyclopropane and 61.5° for spiropentane (69), both less than the value of 118° for cyclopropane. The reasons for these large variations in coupling constants are not yet clear. Certainly the values for the highly distorted molecule, spiropentane, might be expected to be somewhat abnormal. Spirohexane is found to have coupling constants comparable with those of 1, 1-dimethylcyclopropane, and thus appears to be normal.

N-m-r ^{13}C-satellite spectra were also taken for cyclopropane and for hexafluorocyclopropane. The upfield satellites are shown in Figure 14. These are similar in that each consists of five main groups of peaks. The cyclopropane satellite is less symmetrical than that for the perfluoro-compound due in part in the smaller ^{13}C-H coupling constant. Muller and Pritchard (81) have studied the ^{13}C-satellite spectrum of cyclopropane and described it as a "normal" quintet with approximate intensity ratios 1:4:6:4:1. They concluded that the *cis*- and *trans*-coupling constants must be nearly identical and had the values 7.5 ±0.5 c.p.s. The validity of this conclusion is subject to considerable doubt since computed spectra for the A_2B_2 case of cyclopropane were unsymmetrical and extremely complicated, even for equal vicinal coupling constants. It did not prove possible to obtain individual coupling constants from the spectra of cyclopropane or hexafluorocyclopropane due to the complexity of the computed resonances. However, computation showed that the separation between the second and fourth resonances (numbered with increasing field) in the cyclopropane satellite was approximately equal to $J_{\underline{cis}} + J_{\underline{trans}}$. The value found for this quantity was 15.0 c.p.s. for cyclopropane, consistent with a possible *cis*-coupling constant of 9.5 c.p.s. and a *trans*-value of 5.5 c.p.s. For hexafluorocyclopropane this separation was 12.3 c.p.s., indicating sizeable fluorine-fluorine vicinal coupling constants. While on the subject of fluorine spin-coupling in cyclopropanes it is relevant to note that an example of angular dependence of hydrogen-fluorine coupling in cyclopropanes was found by Phillips (82) and has been quoted by Pople, et al. (38). In 1-methyl-2, 2-difluorocyclopropane IX the fluorine spectrum shown an AB pattern with J = 157 c.p.s. The signals from one of the fluorine nuclei are split into doublets, postulated to be by the single proton at the 1-position. The signals from the other fluorine nucleus are split into triplets, presumed by the above authors to be by the two hydrogens at the 3-position. A more reasonable assignment is that it is the 3-hydrogen *cis*- to the methyl group which splits one of the fluorine resonances, and the remaining two *cis*-cyclopropyl hydrogens at the 1- and 3-positions which couple with the other fluorine. Thus in hydrogen-fluorine coupling also, one of the vicinal coupling constants is much larger than the other.

The ^{13}C-H and ^{13}C-F coupling constants were measured from the satellite spectra of the cyclopropanes and are collected in Table XIII. The ^{13}C-H values lie in the fairly narrow range 162.1 ±4.4 c.p.s. Shoolery (83) and Muller and Pritchard (81) found an approximately linear relation between ^{13}C-H coupling constants and the *s*-character in the C-H bond in hydrocarbons. For *sp*^{3}, *sp*^{2} and *sp*

TABLE XIII

^{13}C-H and ^{13}C-F Coupling Constants in Cyclopropanes.

Compound	J, c.p.s.
1,1-Dichlorocyclopropane	166.5
1,1-Dimethylcyclopropane	158.7
Spiropentane	159.8[a]
Spirohexane	157.8
Cyclopropane	161.8[b]
Hexafluorocyclopropane	328.7

[a] Taken as twice the frequency difference between the parent peak and the center of the upfield satellite.

[b] In good agreement with the value 161 c.p.s. reported in Ref. 81.

C-H bond hybridization, $J_{^{13}C\text{-}H}$ was found to be near 125, 160 and 250 c.p.s. respectively. The fact that the observed value for cyclopropane is close to that for sp^2 hybridization may be taken as good support for theoretical models (84, 85) of cyclopropane which envisage a C-H bond hybridization approaching sp^2. In this connection it would be interesting to know the ^{13}C-H coupling constant for cyclopropene, since the vinyl hydrogens in this molecule exhibit acetylenic reactivity (86). A value close to that for acetylene is indicated. The

^{13}C-H coupling constant for spiropentane is close to that for cyclopropane and one may tentatively conclude that, despite the additional strain in spiropentane, its C-H bond hybridization is essentially the same as in cyclopropane. The coupling constant for 1, 1-dichlorocyclopropane is seen to be about 5 c.p.s. greater than that for cyclopropane. Shoolery (83) and Muller and Pritchard (87) found that electronegative substituents attached to the carbon atom bonded to hydrogen produced a sharp increase in the ^{13}C-H coupling constant, attributed to a lowering of the electron density about the carbon nucleus and a resultant decrease in the electron screening of the nucleus. A similar explanation may apply for 1, 1-dichlorocyclopropane. This case is of interest since the effect is transmitted through an additional C-C bond.

There are no published values for ^{13}C-F coupling constants, so comparisons with the J for hexafluorocyclopropane cannot be made. The latter is larger than the corresponding figure for cyclopropane by a factor of two, consistent with the generally larger coupling constants for fluorine compared with hydrogen (38). A ^{13}C-isotope effect on fluorine was found in the analysis of the satellite spectra of hexafluorocyclopropane. The center-point between the two satellites, corresponding to fluorines attached directly to ^{13}C, was found at 6.4 c.p.s. to higher field than the parent peak due to the normal compound. An effect of the same order of magnitude has been observed by Lauterbur (88) for other fluoro compounds.

The n-m-r spectrum of 1-phenyl-1-bromocyclopropane is shown in Figure 15. This is a good example of an A_2B_2 spectrum in which the coupling constants are of the order of the chemical shift. It did not prove possible to extract coupling constants for this case due to complications introduced by the presence of two different cis-coupling constants. However, the spectrum could be roughly analyzed by the method of moments (89) and gave δ = 16.3 c.p.s. for the neat liquid, and $J_{\underline{trans}}^2 + J_{\underline{gem}}^2 = 98.6$ c.p.s. The latter figure seems too high on the basis of representative gem- and trans-coupling constants given earlier. The moment method gave a respectable answer of $J_{\underline{cis}}^2 + J_{\underline{trans}}^2 = 182$ for the ^{13}C-satellite spectrum of 1,1-dichlorocyclopropane, compared with the actual value of 185 c.p.s.

Chemical Shifts in Cyclopropanes.

A study of chemical shifts in cyclopropanes was of interest for it offered the possibility of gaining new insight into the electronic structure of the cyclopropyl ring. Also unusual shielding effects for substituents might operate due to the unique geometry of the ring.

A large body of evidence has accumulated which supports the concept that the cyclopropane ring system possesses double bond character (90, 91). This evidence is based on measurements of

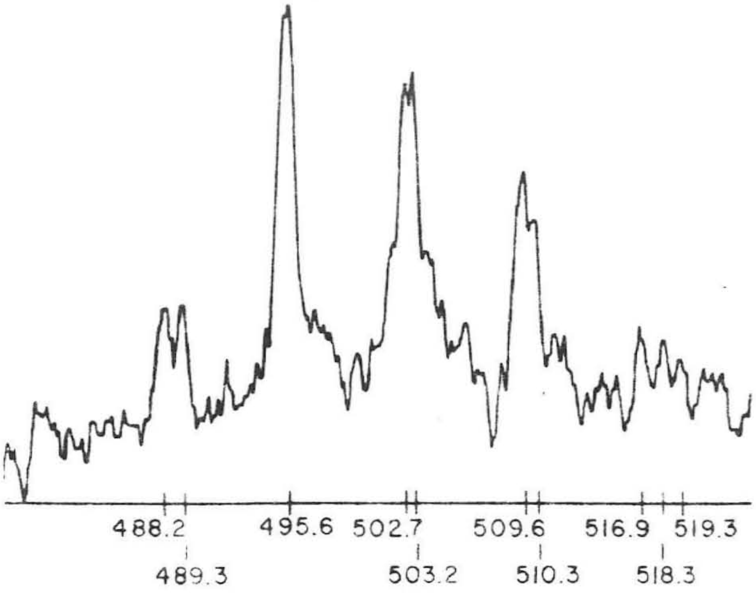


Fig. 14a.— Proton upfield ^{13}C-satellite *n-m-r* spectrum of cyclopropane. Peak frequencies are in c.p.s. relative to benzene as internal standard.

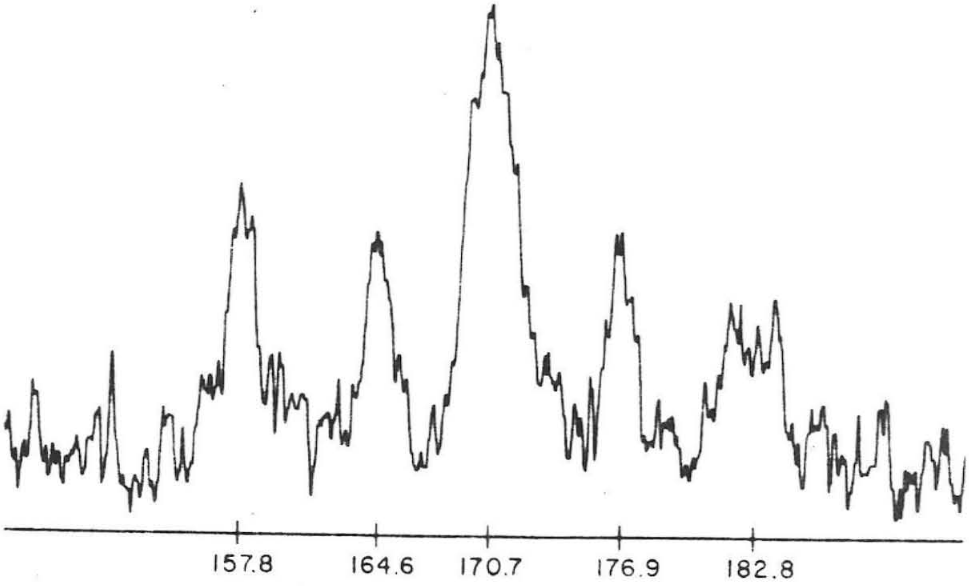


Fig. 14b.— Fluorine upfield ^{13}C-satellite *n-m-r* spectrum of hexafluorocyclopropane. Peak frequencies are in c.p.s. relative to the parent peak.

dipole moments, ultraviolet and infrared spectra and ionization potentials, as well as on criteria of chemical reactivity. Theoretical models for cyclopropane which accommodate the experimental results have been proposed by Walsh (84) and by Coulson and Moffitt (85). Walsh's model X considers the C-C in bonds in cyclopropane as being formed by overlap of <u>p</u>-orbitals on neighboring carbon atoms and by overlap of three $\underline{sp}^2$ orbitals on adjacent carbon atoms directed towards the center of the ring. The axes of the three <u>p</u>-orbitals are co-planar with the ring. This model assumes that four electrons occupy the molecular orbitals formed by overlap of the <u>p</u> atomic orbitals while two electrons occupy the central hybrid orbitals. Cyclopropane is thus considered as a "three-centered ethylene", although some localized bond character was envisaged by Walsh leading to a C-H bond hybridization between $\underline{sp}^3$ and $\underline{sp}^2$, but closer to $\underline{sp}^2$. Coulson and Moffitt's model involves formation of "bent" C-C bonds in cyclopropane by overlap of carbon hybrid orbitals which make an angle of 22° to the internuclear line. All six electrons are involved in the overlap of the hybrid orbitals, and Coulson and Moffitt predict a considerable degree of delocalization of these electrons. They also indicated on the basis of XI that the C-H bonds in cyclopropane would be more closely akin to those of ethylene than those of ethane.

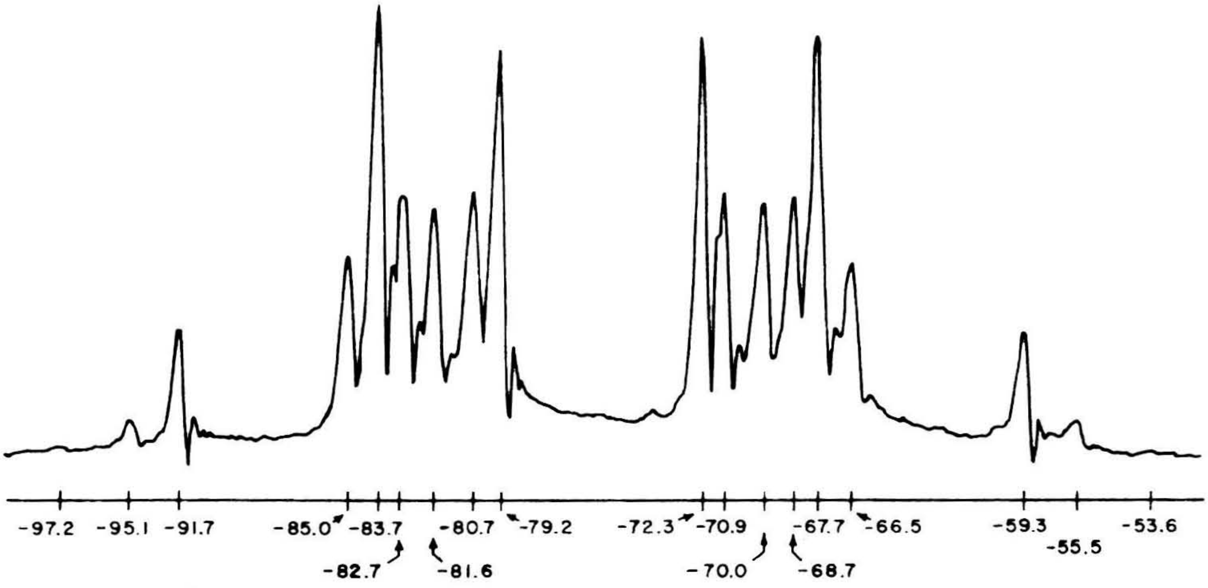


Fig. 15.— Proton *n-m-r* spectrum (cyclopropyl resonance) of 1-phenyl-1-bromocyclopropane. Peak frequencies are in c.p.s. relative to tetramethylsilane as internal standard.

In view of the fact that both theoretical treatments of cyclopropane predict a C-H bond hybridization approaching $\underline{sp}^2$, one might crudely expect that the chemical shift of the hydrogens in cyclopropane would be similar to that for ethylene. In contrast the cyclopropane resonance is found to occur at very high field (38) and there are generally large chemical shift differences between vinyl and cyclopropyl resonances. Factors other than carbon hybridization must therefore be sought to explain this apparent anomaly. The greater mobility predicted by the theoretical studies, of the ring electrons in cyclopropane compared with ordinary saturated compounds suggested that part of this anomalous diamagnetic shift might be due to a cyclopropane ring-current effect (92). In a magnetic field a ring current could be induced which would lead to an induced magnetic field opposing or reinforcing the applied field depending on the position of the attached hydrogen atom relative to the ring. The establishment of the reality of the ring-current effect in cyclopropane would have an important bearing on discussions of the electronic structure of the ring, and to this end the τ values (93) of a number of cyclopropane hydrocarbons were measured. These are collected in Table XIV. Comparison of the cyclopropyl chemical shifts for 1, 1-dimethylcyclopropane, spiropentane and spirohexane indicates that as the external C-C-C angle is decreased the cyclopropyl resonance is shifted to lower field. The reason for this behavior is not clear.

TABLE XIV

Chemical Shifts of Cyclopropane Hydrocarbons.

Compound	τ, side-chain	τ, cyclopropyl
Cyclopropane		9.78[a]
1, 1-Dimethylcyclopropane	8.95	9.80
Spiropentane		9.27
Spirohexane	7.94[b]	9.66
Dicyclopropylmethane	8.91[c]	
Nortricyclene[c]	CH 8.09 CH_2 8.82	9.04
Bicyclo[2. 2. 1] heptane	CH 7.79[d]	

[a] In agreement with Ref. 94.

[b] The cyclobutyl hydrogens gave a single line.

[c] Values are for infinite dilution in carbon tetrachloride. The *n-m-r* spectrum of nortricyclene is shown in Figure 16.

[d] Included for comparison; in agreement with 7.81 τ quoted in Ref. 95.

Waugh and Fessenden (96) and Johnson and Bovey (97) have calculated the chemical shift changes in aromatic systems due to ring-current effects by considering the circular precession of the π - electrons in two regions above and below the plane of the aromatic ring under the influence of the component of the applied field which is

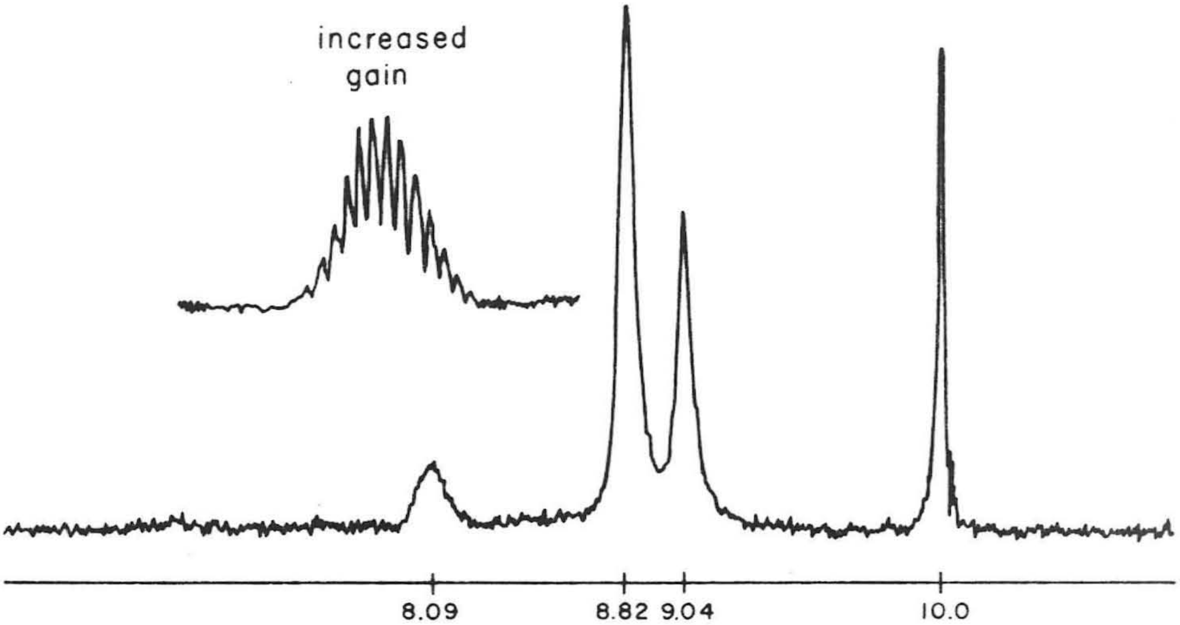


Fig. 16.— Proton n-m-r spectrum of nortricyclene. Chemical shifts are in τ units. An insert shows the methine resonance under higher resolution.

perpendicular to this plane. This method was applied to the calculation of expected chemical shifts in several cyclopropanes both for hydrogens attached to the cyclopropyl ring and for side-chain hydrogens. The results are summarized in Table XV and are compared with the observed shifts. The mobile electrons (four for the Walsh model and six for Coulson and Moffitt's model) were assumed to precess in the plane of the cyclopropane ring. Molecular parameters given by Goldish (69) were used. Calculations were carried out for (Case A) the radius of the ring-current equal to that of the circle circumscribing the ring (0.88 A for cyclopropane) and (Case B) of the circle passing through the center of maximum electron density (assumed to be 0.5 A from the carbon atom) of a p orbital oriented as in the Walsh model X (1.01 A for cyclopropane). The assumed ring-current for cyclopropane leads to two regions in the space surrounding the ring. The boundary between these regions takes the form of a toroidal shell. For a hydrogen nucleus in a region near the equatorial plane of the ring a paramagnetic effect on its resonance frequency is calculated, while in a region inside the ring, or somewhat above it and reasonably close to its three-fold axis, a diamagnetic effect is predicted.

The calculated values in Table XV are in approximate qualitative agreement with the observed chemical shift differences. Since some degree of localization of the C-C bond electrons in cyclopropane

TABLE XV

Summary of Calculations of Ring-Current Effects on Chemical Shifts in Cyclopropanes.

Compound	$\Delta\tau$, side-chain					$\Delta\tau$, cyclopropyl				
	obsvd.	Case A		Case B		obsvd.	Case A		Case B	
		4e	6e	4e	6e		4e	6e	4e	6e
Cyclopropane						1.22[a]	0.33	0.49	0.68	1.03
Nortricyclene (CH)	0.30[b]	0.39	0.57	0.49	0.73					
1, 1-Dimethylcyclopropane[f]	-0.15[c]	0.21	0.31							
Dicyclopropylmethane[g]	0.16[c]	0.42	0.63							
Spirohexane (in-plane)[d]	-0.10	-0.14	-0.21	-0.19	-0.29					
" (out-of-plane)[d]	-0.10	0.06	0.10	0.10	0.16					
Spiropentane[e]						-0.51	-0.06	-0.10	-0.06	-0.09
Bicyclo [1.1.0]butane[h] (exo)							-0.10	-0.16	-0.11	-0.16
(endo)							1.08	1.62	1.35	2.03
Cyclopropene[i] (vinyl)						-1.42				
(CH_2)						1.04				

Key to Table XV

4e and 6e refer to the number of electrons assumed to be involved in the ring-current.

[a] compared with cyclohexane (92).

[b] bicyclo [2.2.1] heptane was taken as a model compound in which the cyclopropyl ring was absent.

[c] obtained by comparison with shifts for aliphatic hydrocarbons given in Ref. 94.

[d] cyclobutyl hydrogens coplanar or out-of-plane with the cyclopropyl ring; observed $\Delta\tau$ are relative to cyclobutane (92).

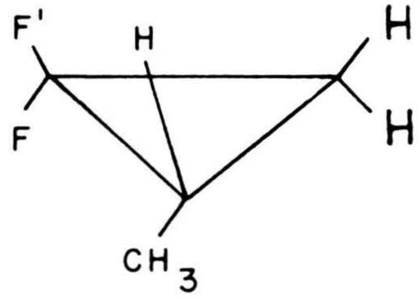
[e] calculated $\Delta\tau$ takes account of modification of ring-current due to a geometry different from cyclopropane.

[f] calculated as the average for four conformations of the C-H bond.

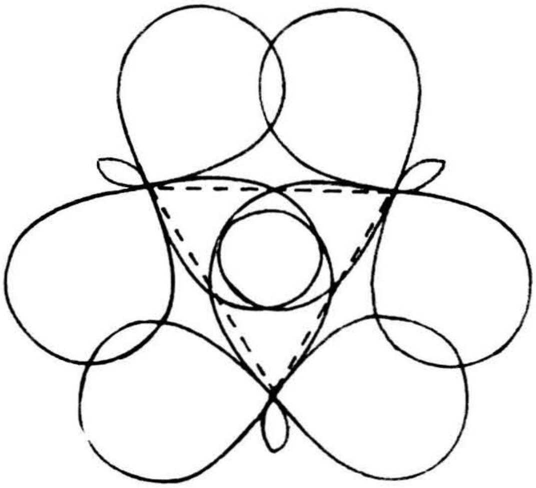
[g] assumed to be twice that for 1,1-dimethylcyclopropane.

[h] for CH_2 hydrogens relative to cyclopropane.

[i] observed values from Ref. 92 relative to cyclohexene.



IX



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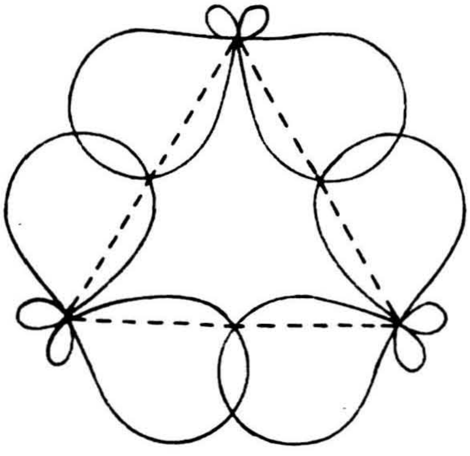
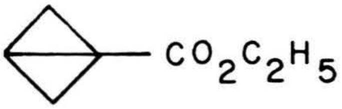


XI



XII

is likely, the calculated ring-current effects are probably upper-limits. The ring-current effect only provides a partial explanation for the high-field position of the resonance in cyclopropane. The magnetic anisotropy of the C-C bond is probably a factor in determining the shielding of the cyclopropane hydrogens. Wiberg and Nist (92) calculated that the shielding due to this factor is 0.25 τ in cyclopropane. C-C and C-H bond anistropy probably also make substantial contributions to the observed chemical shifts in Table XV.

The ring-current effect may in part be responsible for the anomalously low vinyl chemical shift, and for the high methylene shift, in cyclopropene. A large difference in chemical shift is calculated between the endo- and exo-methylene hydrogens in bicyclo-[1.1.0] butane. Wiberg and Ciula (98) observed a shift of 1.26 τ between these hydrogens in ethyl bicyclo [1.1.0]-butane -1- carboxylate XII. This may well be larger than can be accounted for on the paramagnetic effect of the carbethoxyl group. The calculations for the ring-current effect on the chemical shifts of the side-chain hydrogens in 1, 1-dimethylcyclopropane and dicyclopropylmethane is complicated by the possibility of rotation about C-C bonds.

In this connection it is interesting to note that the ring-current effect provides a possible explanation for the fact that in 3-cyclopropyl-1, 5-hexadiene and 1, 4-dicyclopropyl-1, 5-hexadiene (see Part I) the side-chain methine resonance occurs at higher field than does the side-chain methylene resonance. This is the reverse of the usual order (94) and could arise if the methine hydrogen experienced a diamagnetic effect resulting from the cyclopropane ring-current, due to high populations of conformations XIII in which the methine hydrogen is eclipsed with the cyclopropane ring. Diamagnetic shifts of 0.77 to 1.15 τ are calculated for this conformation.

The preceeding results cannot be taken as establishing the existence of a ring-current effect in cyclopropanes, but such an effect is consistent with several of the experimental results that are not readily explainable in other ways. It has also been invoked to rationalize the unusually large molar diamagnetic susceptibility of cyclopropane (99).

Chemical shifts were also measured for a number of cyclopropanes with electronegative substituents attached to the ring. These are collected in Table XVI. The de-shielding effects of substituents on the adjacent cyclopropyl hydrogens are unusually large, For systems in which free rotation about C-C bonds is possible the paramagnetic effect of β -substituents generally leads to a downfield shift of the α -hydrogen resonance of between 0 and 0.6 τ (94). The fact that the effect for cyclopropanes is much greater than this may be attributed to the unique stereochemical relation between groups

TABLE XVI

Chemical Shifts of Substituted Cyclopropanes.

Compound	τ Value
1, 1-Dichlorocyclopropane	8.53
Dimethyl 1, 2-dimethyl-<u>cis</u>-1, 2-dicarboxylate	8.10[a]
"	9.42[b]
Dimethyl methylenecyclopropane-<u>trans</u>-1, 2-dicarboxylate	7.23
" (vinyl)	4.40
Dimethyl 3, 3-dimethylcyclopropane-<u>trans</u>-1, 2-dicarboxylate	7.89
Hexafluorocyclopropane (ϕ value)	159 ±2.2[c]

[a] For the cyclopropyl hydrogen cis to the carbethoxyl groups.

[b] For the cyclopropyl hydrogen trans to the carbethoxyl groups.

[c] At 56.4 Mc. relative to fluorotrichloromethane.

attached to the cyclopropane ring. Analysis of the ABX-type n-m-r spectrum of dimethyl 1-methylcyclopropane-cis-1, 2-dicarboxylate using the coupling constant data of Table X and XI indicated that the paramagnetic effect of the carbomethoxyl group attached to the cyclopropane ring was much greater for the adjacent cis-β-cyclopropyl hydrogen than for the trans. On this basis, the τ value for the cyclopropyl hydrogen trans to the carbomethoxyl groups in dimethyl 1, 2-dimethyl-cis-1, 2-dicarboxylate indicates that it is only slightly de-shielded.

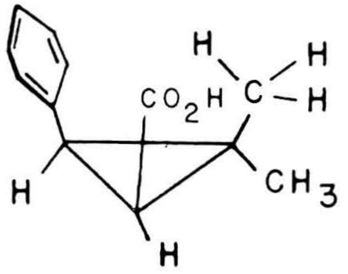
The fact that the vinyl resonance for dimethyl methylenecyclopropane-trans-1, 2-dicarboxylate occurs at 1.0 τ to lower field than for isobutene may in part be due to the effect of the carbomethoxyl groups. It is also interpretable in terms of the cyclopropane ring-current effect since the vinyl hydrogens lie in the plane of the cyclopropane ring.

Analysis of the n-m-r spectra of the cis-(XIV) and trans-(XV) isomers of 2, 2-dimethyl-3-phenylcyclopropane-1-carboxylic acids as solutions in chloroform showed that the chemical shift between the methyl groups was approximately 31 c.p.s. for the trans-acid and only 2 c.p.s. for the cis-acid. This result appears to indicate that the methyl group cis to the phenyl group in both cases experiences a diamagnetic shift due to the magnetic anisotropy of the benzene ring. The conformations XIV and XV show how one hydrogen of the cis-methyl group can be made to lie nearly over the center of the benzene ring, which should lead to a large diamagnetic effect (96). In XIV the diamagnetic effect of phenyl and paramagnetic effect of carboxyl on the cis-methyl group might almost cancel whereas in XV they magnify the shift between the gem-dimethyl groups. This explanation requires a

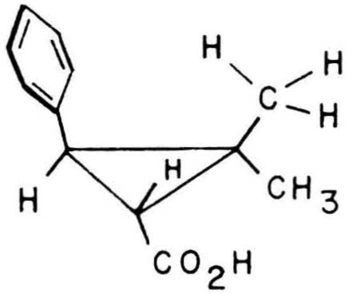
$R = -CH=CH_2$

$R = -CH_2-CH=CH_2$ or $-CH_2-CH=CH-$◁

XIII



XIV



XV

preferred orientation of the phenyl group with respect to the cyclopropane ring as shown. A similar orientation was postulated by Aleksanian, et al. (100) for phenylcyclopropanes on the basis of Raman spectral evidence.

The fluorine resonance of hexafluorocyclopropane occurs at very high field relative to fluorotrichloromethane. Filipovich and Tiers (101) found that 1-fluorohexane gives a resonance at 219 p.p.m. from this reference compound, so that the unique position of cyclopropane in proton spectra may not extend to fluorine n-m-r. However the hexafluorocyclopropane resonance has a higher chemical shift than that of any perfluorocarbon reported so far.

Configurational Stability of the Cyclopropyl Grignard Reagent.

Nordlander (3) observed changes in the n-m-r spectrum of cyclobutylmagnesium chloride in going from room temperature to -37° which he attributed to a possible slowing down of the inversion rate of the magnesium atom attached to the ring carbon atom. This observation stimulated a study of the n-m-r spectrum of cyclopropylmagnesium bromide as a function of temperature.

Walborsky and Impastato (102) obtained 60% retention of configuration when optically active 1-bromo-1-methyl-2, 2-diphenylcyclopropane was treated with butyllithium in 1:1 benzene-petroleum ether at 6°, and methanol was added to the resulting cyclopropane lithium

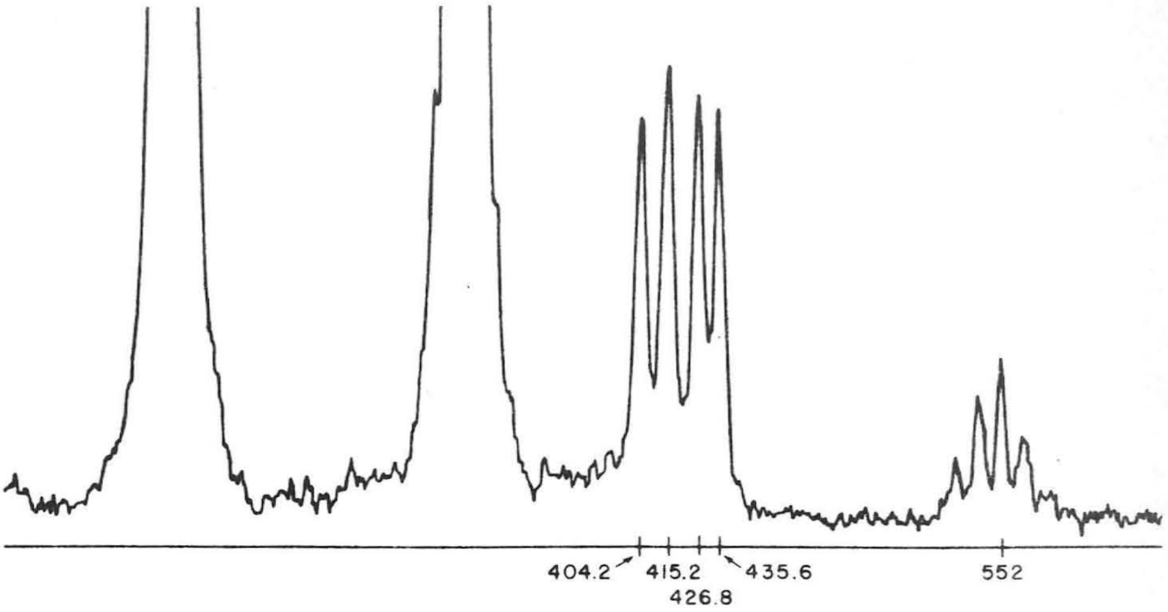


Fig. 17a.— Proton n-m-r spectrum of cyclopropylmagnesium bromide in tetrahydrofuran at 30°. Chemical shifts are in c.p.s. relative to benzene as internal reference (not shown). The off-scale peaks are due to tetrahydrofuran.

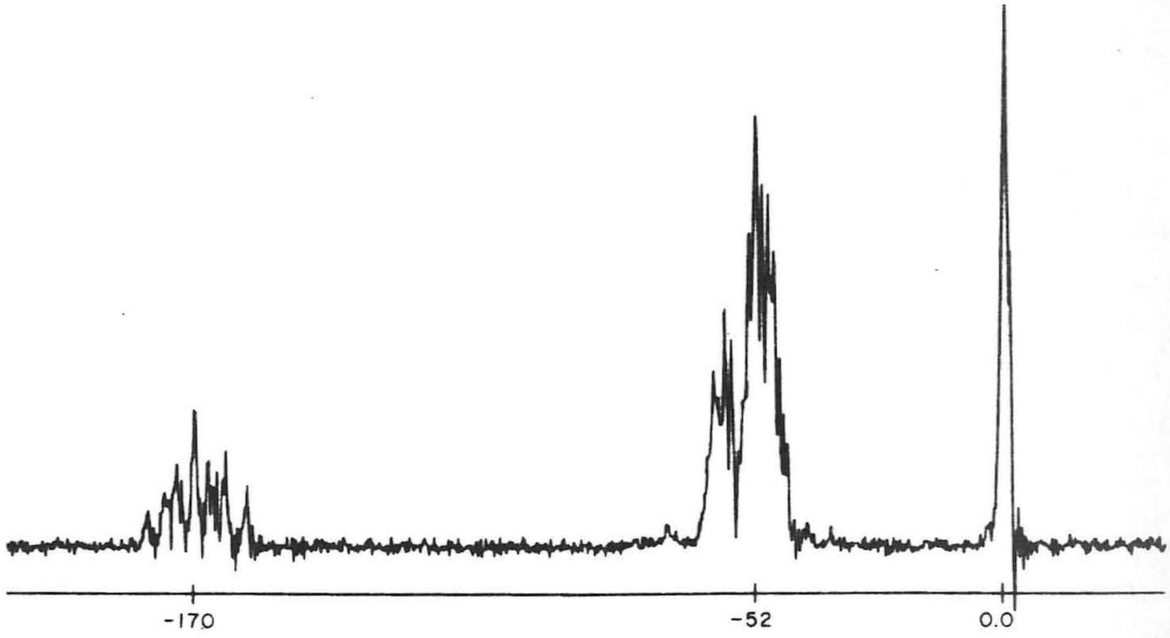


Fig. 17b.— Proton n-m-r spectrum of cyclopropyl bromide. Chemical shifts are in c.p.s. relative to tetramethylsilane as internal standard.

reagent. Stereospecific conversions of cis- and trans-2-methylcyclopropyllithium reagents in pentane-ether at 0° to carboxylic acids have been reported by Applequist and Peterson (103) and overall retention of configuration was observed. These results contrast with the reactions of Grignard reagents from optically-active halides which have always been observed to lead to complete racemisation at the position bearing the halogen atom in the starting material (104).

The n-m-r spectrum of cyclopropylmagnesium bromide in tetrahydrofuran at 30° is shown in Figure 17. The spectrum of the Grignard reagent was essentially unchanged in the temperature range -40 to +170°. If rapid inversion of the -MgX group at the carbon atom to which it is attached were to occur the β -hydrogen resonance would be expected to be a doublet. Since it is a quartet it is concluded that, on the n-m-r time scale, rapid effective inversion of the -MgX group does not take place. In confirmation of this result it was found that the methyl doublet in the n-m-r spectrum of 2, 2-dimethylcyclopropyl magnesium bromide in tetrahydrofuran did not collapse even at 175°. These observations indicate high configurational stability for the cyclopropyl Grignard reagent. In order to observe a possible slow inversion, the n-m-r spectrum of the Grignard reagent from cis-2-methylcyclopropyl bromide might be revealing.

EXPERIMENTAL

All boiling points and most of the melting points are uncorrected. Corrected melting points were taken with a Reichert Kofler Block apparatus. Elemental analyses were performed by Dr. A. Elek, Elek Microanalytical Laboratories, Los Angeles. Infrared spectra were determined using either a Perkin-Elmer double-beam recording infrared spectrophotometer, Model 21, or a Beckman infrared spectrometer, Model IR-7. Vapor chromatograms were obtained with a Perkin-Elmer Vapor Fractometer, Model 154-C, except where noted. The nuclear magnetic resonance spectra were recorded at 60 Mc, with the Varian Associates high-resolution spectrometer (V-4300B) with 12-in. magnet and equipped with flux stabilizer, constant-temperature magnet cooling, and field homogeneity control coils. Where *n-m-r* spectra were not calibrated, multiplets were assigned to various structural groups on the basis of chemical shift comparison with other calibrated spectra run at the same sweep-rate, and consideration of their relative intensities. Resonances are generally described in order of increasing field.

Part I

1,1-Diphenylbutane-1,4-diol was prepared by the method of Vozza (109) from 1 mole of phenylmagnesium bromide and 0.5 mole of γ-butyrolactone. Crystallization from benzene-ligroin yielded needles, 77.5 g., m.p. 104-106.5°; second crop, 8.1 g., m.p. 103.5-106° (total 70.8%), lit. (109) m.p. 108-109°.

2,2-Diphenyltetrahydrofuran.— 1,1-Diphenylbutane-1,4-diol was dehydrated by a procedure similar to that of Hudson and Schmerlaib (110). The diol, 5 g., was heated with 0.5 g. of anhydrous cupric sulfate in an open flask at 150° for 1.5 hr. After cooling, 20 ml. of ether and 30 ml. of water were added. The ether layer was washed with water and dried over sodium sulfate. Evaporation of the ether yielded an oil, which crystallized from benzene-pentane as prisms, 2.25 g. (48.5%), m.p. 67.5-69°, lit. (109) m.p. 66-68°. The product was identified as 2,2-diphenyltetrahydrofuran, rather than the desired (γ,γ-diphenylallyl)-carbinol, by a strong band at 1053 cm^{-1} in the infrared spectrum, characteristic of tetrahydrofurans (111), and by the lack of O-H absorption. This reaction has also been reported by Vozza (109).

(γ,γ-Diphenylallyl)-carbinyl p-Toluenesulfonate.— To a solution of 48.4 g. (0.2 mole) of 1,1-diphenylbutane-1,4-diol in 70 ml. of pyridine at 0° was added 50 g. (0.26 mole) of p-toluenesulfonyl chloride over

0.5 hr. The mixture was stirred at room temperature for 5 hr., then poured into 250 ml. of 2 N hydrochloric acid and extracted with 400 ml. of ether in four portions. The ether extracts were washed repeatedly with 2 N hydrochloric acid, then with 2 N sodium bicarbonate solution and water. The ether solution was dried over sodium sulfate and evaporated. Crystallization of the residue from dichloromethane-pentane yielded needles, 26.8 g., m.p. 80-83.5°; second crop, 3.1 g., m.p. 82-83.5° (total 39.6%). The product was identified by unsaturation tests, * bands at 1370, 1190 and 1178 cm^{-1} in the infrared spectrum due to the sulfonate group (111), and the lack of O-H absorption. Two crystallizations from methanol afforded an analytical sample, m.p. 84.5-85.5°.

Anal. Calcd. for $C_{23}H_{22}O_3S$: C, 72.97; H, 5.86; S, 8.47. Found: C, 72.83; H, 5.77; S, 8.46.

Infrared examination of the mother liquor indicated the presence of considerable 2,2-diphenyltetrahydrofuran.

(γ,γ-Diphenylallyl)-carbinyl Chloride from (γ,γ-Diphenylallyl)-carbinyl p-Toluenesulfonate.— A solution of 9.7 g. (0.026 mole) of (γ,γ-diphenylallyl)-carbinyl _p_-toluenesulfonate and 7 g. (0.165 mole) of anhydrous lithium chloride in 100 ml. absolute ethanol, was refluxed for 15 hr. Most of the ethanol was then evaporated, and the residue

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*Decolorization of 5% bromine in chloroform and of 2% potassium permanganate in acetone were used as tests for unsaturation throughout this work.

was poured into water and extracted three times with 50 ml. of ether. The ether extracts were dried over sodium sulfate and evaporated. The residue was distilled through a Claisen head and gave 6.05 g. (97.1%) of the chloride, b.p. 150° (1 mm.) $\underline{n}^{24}$D 1.5982. The chloride was unsaturated, and the n-m-r spectrum of a carbon tetrachloride solution showed phenyl peaks, vinyl triplet, α-methylene triplet and β-methylene quartet.

Anal. Calcd. for $C_{16}H_{15}Cl$: C, 79.20; H, 6.23; Cl, 14.61. Found: C, 79.31; H, 6.25; Cl, 14.49.

(γ, γ-Diphenylallyl)-carbinyl Bromide from (γ, γ-Diphenylallyl)-carbinyl p-Toluenesulfonate.— A solution of 15 g. (0.04 mole) of the tosylate and 14 g. (0.161 mole) of anhydrous lithium bromide in 200 ml. of acetone was refluxed for 15 hr. The mixture was worked up as for (γ, γ-diphenylallyl)-carbinyl chloride and gave 11.75 g. of an oil which was chromatographed on a column of 350 g. of pentane-washed Merck alumina. Elution with pentane (5 x 1 ℓ.) yielded an eluate which was distilled through a Claisen head to yield 10.24 g. (90.1%) of (γ, γ-diphenylallyl)-carbinyl bromide, b.p. 165-170° (2 mm.), $\underline{n}^{25}$D 1.6150. The product was unsaturated and its infrared spectrum was very similar to that of (γ, γ-diphenylallyl)-carbinyl chloride.

Anal. Calcd. for $C_{16}H_{15}Br$: C, 66.91; H, 5.26; Br, 27.83. Found: C, 66.92; H, 5.20; Br, 27.82.

Ethyl Cyclopropanecarboxylate.— The reaction conditions were chosen for convenience rather than for optimal yield. A solution of 100 g. (1.16 mole) of cyclopropanecarboxylic acid and 17.4 ml. of concentrated sulfuric acid in 160 g. (3.48 mole) of absolute ethanol was refluxed for 8 hr. Ethanol and the products were then distilled off through a Claisen head at 25 mm. The distillate was fractionated using a 12-in. Vigreux column. After an ethanol forerun, there were obtained two fractions, 7 g., b.p. 100-129°, and 76.9 g. (58%), b.p. 129-131.5°. The second fraction was shown by v-p-c to be pure ethyl cyclopropanecarboxylate, $\underline{n}^{25}D$ 1.4130, while the first fraction contained in addition an unidentified side-product. Roberts (112) gives b.p. 83-84° (150 mm.), $\underline{n}^{25}D$ 1.4183, for this ester.

Diphenylcyclopropylcarbinol.— The best procedure will be described. To a solution of phenylmagnesium bromide, prepared from 245 g. (1.56 mole) of bromobenzene and 37 g. (1.52 g. atom) of magnesium turnings in 618 ml. of ether, was added a solution of 78.2 g. (0.686 mole) of ethyl cyclopropane carboxylate in 100 ml. of ether over 1 hr. The mixture was stirred at room temperature for 40 hr., then acidified with 600 ml. of 3 N hydrochloric acid. The ether layer was separated, the aqueous layer was extracted with three 150-ml. portions of ether, and the combined ether extracts were washed with sodium bicarbonate solution and water, dried over sodium sulfate and evaporated.

The residue crystallized from hexane as prisms, 140 g. (91.1%), m.p. 84-84.5°, lit. (34) m.p. 83°. The product was saturated, and its infrared spectrum showed O-H bands at 3600 and 3450 cm^{-1}. The _n-m-r_ spectrum of a carbon tetrachloride solution of the product showed phenyl peaks, hydroxyl singlet, cyclopropyl methine quintet and perturbed cyclopropyl methylene doublet. Diphenylcyclopropylcarbinol has also been prepared by Lipp,et al. (34) from cyclopropyl cyanide and phenylmagnesium bromide via phenylcyclopropylketone.

(γ, γ-Diphenylallyl)-carbinyl Chloride from Diphenylcyclopropylcarbinol.— A solution of 5 g. (0.022 mole) of diphenylcyclopropylcarbinol and 2.1 g. (0.027 mole) of acetyl chloride in 15 ml. of benzene was refluxed for 6 hr. The excess acetyl chloride and solvent were then evaporated and the residue was distilled through a Claisen head and gave 4.94 g. (91%) of a liquid, b.p. 162° (2.5 mm.), $\underline{n}^{28}$D 1.5950. The product was unsaturated and its infrared spectrum was identical with that of the (γ, γ-diphenylallyl)-carbinyl chloride described earlier except for small peaks at 3590 and 980 cm^{-1}.

When this reaction was repeated in the presence of one molar equivalent of dimethylanaline in ether, half of the diphenylcyclopropylcarbinol was recovered and the infrared spectrum of the remainder of the product showed bands at 1747 and 1235 cm^{-1} probably due to acetates.

(γ,γ-Diphenylallyl)-carbinyl Bromide from Diphenylcyclopropylcarbinol.— A solution of 10 g. (0.045 mole) of diphenylcyclopropylcarbinol in 20 ml. of dichloromethane was added to 6 g. (0.022 mole) of phosphorus tribromide over 0.5 hr. with ice-cooling. The mixture was stirred for 1 hr. at room temperature, then the excess phosphorus tribromide was decomposed by addition of ice. The dichloromethane layer was separated, washed with water, dried over sodium sulfate and evaporated. The residue was distilled through a Claisen head and yielded 12.0 g. (93.8%) of bromide, b.p. 169° (2 mm.), $\underline{n}^{24}$D 1.6167. The product was unsaturated and its infrared spectrum was identical with that of (γ,γ-diphenylallyl)-carbinyl bromide prepared from the corresponding tosylate. Except for slight differences in chemical shift, the n-m-r spectrum of the product was identical with that of (γ,γ-diphenylallyl)-carbinyl chloride. No trace of cyclopropyl absorption was detected, indicating that diphenylcyclopropylcarbinyl bromide was not an isolable product of the reaction. This result is contrary to the work of Lipp, et al. (34) who have stated, without giving experimental details, that treatment of diphenylcyclopropylcarbinol with phosphorus tribromide yielded diphenylcyclopropylcarbinyl bromide, b.p. 138° (1.5 mm.).

(γ,γ-Diphenylallyl)-acetic Acid from (γ,γ-Diphenylallyl)-carbinyl Chloride.— A solution of 3 g. (0.0124 mole) of (γ,γ-diphenylallyl)-carbinyl chloride, in 25 ml. of ether, was added dropwise over

0.5 hr. to 0.32 g. (0.013 g. atom), previously etched with iodine in ether, of high-grade resublimed magnesium turnings, in 15 ml. of refluxing ether in a round-bottomed flask fitted with a reflux condenser and calcium chloride drying-tube. No attempt was made to exclude air from the system, other than the use of a drying-tube. The mixture was refluxed for 15 hr., then a large excess of solid carbon dioxide was added to it, followed by 10 ml. of concentrated hydrochloric acid in 30 ml. of ice water. The ether layer was separated, washed with water, and extracted with 150 ml. of 10% sodium carbonate solution in four fractions. The sodium carbonate extracts were acidified with 5 N hydrochloric acid, then extracted with four 30-ml. portions of ether. The ether extracts were washed twice with water, dried over sodium sulfate and when evaporated yielded a crystalline residue amounting to 0.99 g. (31.7%). The acid crystallized from hexane as prisms, m.p. 83-83.5°. Its infrared spectrum in chloroform showed bands at 3480 (weak), 2300-2700 (broad) and 1710 cm^{-1} (strong), typical of a carboxyl group. The _n-m-r_ spectrum showed carboxyl singlet, phenyl peaks, vinyl triplet and a broad peak due to overlapping α- and β-methylene resonances, indicating that diphenylcyclopropylacetic acid was not a product. The acid was unsaturated.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 79.55, 81.94; H, 6.06, 6.56.

(γ,γ-Diphenylallyl)-acetic acid was also obtained exclusively from a similar reaction using tetrahydrofuran as solvent.

<u>5,5-Diphenylpentanoic Acid.</u>— A solution of 0.665 g. (2.6 mmole) of (γ,γ-diphenylallyl)-acetic acid in 20 ml. of absolute ethanol was hydrogenated in the presence of 20 mg. of platinum oxide for 15 hr. After 2.5 hr., 50 ml. (80%) of the theoretical amount of hydrogen had been absorbed at atmospheric pressure. The solution was filtered, then evaporated to yield an oil which crystallized from hexane as needles, 0.414 g. (61.6%), m.p. 88-89.5°, lit. (113) m.p. 89-90°. The hydrogenation was also carried out on a larger scale using 26 g. (0.103 mole) of carboxylic acid and 0.1 g. of platinum oxide in 50 ml. of ether. After 37 hr., 2.8 ℓ. of hydrogen had been taken up (theor. 2.4 ℓ.). Crystallization of the product from hexane afforded 23.6 g. (90.1%) of 5,5-diphenylpentanoic acid, m.p. 90-92.5° (corr.). The <u>n</u>-<u>m</u>-<u>r</u> spectrum of a chloroform solution of the acid showed carboxyl singlet, phenyl singlet, methine triplet, and a broad multiplet due to overlapping methylene peaks.

<u>(γ,γ-Diphenylallyl)-carbinyl Formate.</u>— A solution of 3 g. (13.4 mmole) of diphenylcyclopropylcarbinol in 30 g. (0.652 mole) of 99% formic acid was refluxed for 4 hr., then allowed to stand at room temperature for 15 hr. The mixture was poured into water, extracted with ether, and the ether extract was washed repeatedly with saturated sodium bicarbonate solution, then with water, dried over sodium sulfate

and evaporated. The residue was microdistilled* at 5 mm. with a bath at 200° and gave 2.87 g. (86.2%) of substantially pure (γ, γ-diphenylallyl)-carbinyl formate, $\underline{n}^{26.5}D$ 1.5818. The product was unsaturated, and its infrared spectrum was similar to that of (γ, γ-diphenylallyl)-carbinyl chloride except for strong bands at 1730 and 1163 cm^{-1} due to the formate group. Evidence from lithium aluminum hydride reduction of the product (see below) indicates that it may be contaminated with the isomeric <u>diphenylcyclopropylcarbinyl formate.</u>

<u>Anal.</u> Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.84; H, 6.34.

<u>(γ, γ-Diphenylallyl)-carbinol.</u>— A solution of 2 g. (8 mmole) of (γ, γ-diphenylallyl)-carbinyl formate in 20 ml. of ether was added dropwise to a solution of 0.25 g. (6.6 mmole) of lithium aluminum hydride in 20 ml. of ether during 5 min. The mixture was refluxed for 4 hr., then stirred at room temperature for 15 hr. Water (10 ml.) was then added, the ether layer was decanted and combined with an ether extract of the residual paste. The ether solution was washed with water, dried over sodium sulfate and evaporated. The residue was microdistilled at 3 mm. pressure with a bath at 180° and gave 1.71 g. (95%) of crude (γ, γ-diphenylallyl)-carbinol as a viscous liquid, $\underline{n}^{27}D$ 1.5915, lit. (109)

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*The term "microdistilled" here and later refers to direct distillation from a 2-5 ml. round-bottomed flask connected by a standard-taper joint to a shallow U-tube, in which the distillate collects. This procedure does not allow one to determine the boiling point.

b.p. 135-137° (0.6 mm.), $\underline{n}^{25}$D 1.5948. Its infrared spectrum in carbon tetrachloride showed hydroxyl bands at 3600, 3330, 1044 and 1030 cm^{-1}. The n-m-r spectrum of the product in carbon tetrachloride showed phenyl peaks, vinyl triplet, hydroxyl singlet, methylene quartet and several other multiplets. Inspection of this spectrum indicates that diphenylcyclopropylcarbinol is a probable minor component.

Diethyl Benzylhydrylmalonate.— The procedure of Gupta and Sunthankar (114), involving the reaction of two moles of phenylmagnesium bromide with one mole of diethyl ethoxymethylenemalonate, was found to be superior to the reaction of benzhydryl bromide with sodiomalonic ester (115) for the preparation of this compound. The product from the reaction of 43.2 g. (0.2 mole) of diethyl ethoxymethylenemalonate with phenylmagnesium bromide prepared from 72 g. (0.45 mole) of bromobenzene, was distilled through a Claisen head and gave a forerun, 7.45 g., b.p. 100-180° (3 mm.), and a main fraction, 53.1 g., b.p. 180-240° (3 mm.). The main fraction crystallized from hexane as needles, 45.1 g. (69%), of diethyl benzhydrylmalonate, m.p. 50.5-52.5°, lit. (114) m.p. 53°.

2-Benzhydrylpropane-1,3-diol.— To a solution of 1.5 g. (39.5 mmole) of lithium aluminum hydride in 50 ml. of ether was added a solution of 10 g. (30.7 mmole) of diethyl benzhydrylmalonate in 30 ml. of ether, at such a rate as to keep the ether refluxing (0.5 hr.). The mixture was refluxed for a total of 6 hr. and allowed to stand for 15 hr.

Excess hydride was decomposed with 5 ml. of _t_-butanol, and 15 ml. of water and 150 ml. of 6 N sulphuric acid were then added. The ether layer was separated, washed with sodium bicarbonate solution and water, dried over sodium sulfate and on evaporation of the ether yielded 8 g. of crystals. These were recrystallized from benzene-ligroin to yield 2-benzhydrylpropane-1,3-diol as needles, first crop, 5.71 g., m.p. 79-81°, second crop, 0.71 g., same m.p., (total 86.5%). The infrared spectrum of the product in carbon tetrachloride showed strong hydroxyl bands at 3600, 3340 and 1030 cm^{-1}. An analytical sample was crystallized twice from benzene-ligroin and had m.p. 81-82°.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.46; H, 7.55.

When the reaction was conducted on four times the above scale a product melting near 60° was obtained, and it may have been contaminated with methyl ethers, which are often produced in hydride reductions of dicarbonyl compounds.

2-Benzhydryl-1,3-dibromopropane.— Treatment of 2-benzhydrylpropane-1,3-diol with phosphorus tribromide led to intractable products which were not investigated further. Reaction of the diol with hydrobromic acid-sulfuric acid mixture was more successful. A mixture of 10.32 g. (61.2 mmole) of 48% aqueous hydrobromic acid and 1.68 ml. of concentrated sulfuric acid was added dropwise to the 6 g. (24.8 mmole) of diol, over 10 min. with stirring. Concentrated sulfuric acid (2.7 ml.) was then added over 15 min. The mixture was heated at 120° for 6 hr., a brown upper layer being formed after 10 min. heating, then poured into water and extracted with three 50-ml. portions of ether. The ether extracts were washed with sodium bicarbonate solution and water, dried over sodium sulfate and when evaporated yielded 8.2 g. of crude product.

The residue was chromatographed on a column of 210 g. of pentane-washed Merck alumina. Elution with pentane (6 x 600 ml.) and 1:1 benzene-pentane (5 x 600 ml.) gave an eluate which was microdistilled at 1.5 mm. with a bath at 160° and yielded 0.77 g. of an oil which subsequently crystallized. The product was recrystallized from pentane and yielded flat needles, m.p. 78.5-80° (Fraction I). Fraction I was saturated and gave a positive Beilstein halogen test. Its infrared spectrum (carbon tetrachloride solution) showed no hydroxyl bands, but had sharp peaks at 1430 and 1260 cm^{-1}. Two further crystallizations from pentane afforded an analytical sample, m.p. 80-81°.

Anal. Calcd. for $C_{16}H_{16}Br_2$: C, 52.22; H, 4.38; Br, 43.42. Found: C, 52.12; H, 4.50; Br, 43.25.

Further elution of the material on the alumina column with ether (16 x 600 ml.) afforded a liquid eluate (Fraction II). Fraction II was microdistilled at 1.5 mm. with a bath at 190° and yielded 3.79 g. of a viscous oil. The infrared spectrum of the distillate was similar to that of Fraction I except for the presence of weak hydroxyl bands at 3620 and 3400 cm^{-1}. The latter may arise from a bromohydrin by-product. Fraction II could not be crystallized under any conditions tried, and it was used directly in the preparation of diphenylcyclopropylmethane.

<u>Diphenylcyclopropylmethane from 2-Benzhydryl-1,3-dibromopropane.</u>— To a solution of 2.32 g. (6.3 mmole) of 2-benzhydryl-1,3-dibromopropane in 3 ml. of 95% ethanol and 0.3 ml. of water was added 1.7 g. (26 mmole) of zinc dust, and the mixture was refluxed for 2 hr. The zinc was filtered off and washed with ethanol. The filtrate was poured into water and extracted with three 50-ml. portions of ether. The ether extracts were washed with water, dried over sodium sulfate and evaporated. The residue was microdistilled at 1.5 mm. with a bath at 160° and afforded 1.46 g. of a liquid giving a positive Beilstein test. Since the yield was greater than the expected theoretical yield, the debromination reaction was repeated using this distillate and refluxing for 3 hr. The same isolation procedure afforded 1.34 g. of saturated product, giving a negative Beilstein test. The product was chromatographed on a column of 40 g. of pentane-washed alumina. Elution with pentane (6 x 150 ml.) gave an eluate which was microdistilled at 1.5 mm. with a bath at 140°, and yielded 0.585 g. (44.7%) of diphenylcyclopropylmethane, $\underline{n}^{22.5}D$ 1.5747. The product was shown to be better than 99% pure by <u>v-p-c</u>. It was saturated, and its infrared spectrum

(carbon tetrachloride solution) showed a cyclopropyl band at 1019 cm^{-1} and a band at 727 cm^{-1}. The n-m-r spectrum showed phenyl peaks, methine doublet, cyclopropyl methine multiplet and complex upfield cyclopropyl methylene peaks.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.06; H, 7.74.

When the reaction was repeated on a larger scale using different batches of crude 2-benzhydryl-1,3-dibromopropane, an unidentified saturated impurity of shorter retention time than diphenylcyclopropylmethane was produced to the extent of up to 20%. Such mixtures were not used in reactions involving diphenylcyclopropylmethane.

Diphenylcyclopropylmethane from Diphenylcyclopropylcarbinol.— Several attempts were made to prepare diphenylcyclopropylmethane by reduction of diphenylcyclopropylcarbinol. Smooth reduction of the alcohol occurred in some cases, but isolation of pure diphenylcyclopropylmethane was precluded by formation of rearranged hydrocarbons. No detectable reaction of the carbinol took place with lithium aluminum hydride in refluxing ether over 15 hr. Diphenylcyclopropylcarbinol was not reduced by platinum and hydrogen in ethanol solution. Addition of acetic acid led to uptake of 80% of the theoretical hydrogen, but a complex mixture of products was formed and this was not examined further.

Raney nickel catalyst containing absorbed hydrogen was prepared by the method of Mozingo, et al. (116). A solution of 3 g. (13.4 mmole) of diphenylcyclopropylcarbinol in 100 ml. of absolute ethanol was refluxed for 1 hr. in the presence of 12 g. of the Raney nickel. Longer reaction times led to some saturation of the phenyl groups. The catalyst was filtered off through Celite and washed with ethanol. The solvent was distilled off through a 12-in. Vigreux column. The residue was microdistilled at 2 mm. with a bath at 135° and gave 2.63 g. of distillate, $\underline{n}^{23}D$ 1.5640. No hydroxyl bands were detected in the infrared spectrum of the product. Examination by v-p-c at 250° showed three peaks of retention time: 8.1 min. (5%), 10.2 min. (36%) and 11.8 min. (59%).* The predominant reaction product had the same retention time as diphenylcyclopropylmethane. Since the product was slightly unsaturated, the peak of retention time 8.1 min. was thought to be due to 1,1-diphenylbutene formed by rearrangement. However, the retention time for the latter, prepared as described later, was 10.5 min. The n-m-r spectrum of the product showed phenyl peaks, methine doublet (diphenylcyclopropylmethane), methine triplet, and a broad complex upfield region. The methine triplet probably arises from 1,1-diphenylbutane,

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*A Loenco Model 15 gas chromatograph fitted with a ft. by 3/8 in. i.d. stainless-steel column packed with Apiezon L grease on firebrick, with helium as carrier gas at an inlet pressure of 15 lbs./sq. in., was used in this and all subsequent analyses of mixtures containing diphenylcyclopropylmethane and/or 1,1-diphenylbutene.

since no appreciable vinyl resonance was detected.

Similar results were obtained in the hydrogenation of diphenylcyclopropylcarbinol in 50% ethanol-acetic acid with 10% palladium-on-carbon catalyst. V-p-c analysis of the resulting hydrocarbon product showed peaks at 10.1 min. (42%) and 11.7 min. (58%). These were assigned to 1,1-diphenylbutane and diphenylcyclopropylmethane on the same basis as above. No reduction of the alcohol occurred in neutral ethanol solution with palladium-on-carbon catalyst, nor with Raney nickel alloy and aqueous sodium hydroxide in ethanol-toluene (117).

Reactions of the Grignard Reagent from (γ, γ-Diphenylallyl)-carbinyl Bromide.—

(a) Ammonium Chloride Solution.— On warming a solution of 10 g. (34.8 mmole) of (γ, γ-diphenylallyl)-carbinyl bromide in 50 ml. of ether with 1 g. (41.2 mg. atom) of magnesium in a round-bottomed flask fitted with reflux condenser and calcium chloride drying-tube, the Grignard reagent rapidly formed. The mixture was refluxed for 3 hr., then 12 ml. of a solution of 7.6 g. of ammonium chloride in 23 ml. of water was added dropwise with stirring. The ether layer was decanted, the residual paste was extracted twice with ether, and the combined ether layers were washed with ammonium chloride solution and water, dried over sodium sulfate and evaporated. The product was distilled through a micro-Claisen head and gave 6.56 g. (90.5%) of almost pure

1,1-diphenylbutene, b.p. 117° (1.5 mm.), $\underline{n}^{22}D$ 1.5902, lit. (118) b.p. 109° (0.4 mm.), $\underline{n}^{20}D$ 1.5904, and 0.4 g. of residue. The hydrocarbon was strongly unsaturated and its n-m-r spectrum showed phenyl peak, vinyl triplet, methylene quintet and methyl quartet. However, v-p-c analysis at 250° indicated that the product consisted of diphenylcyclopropylmethane (4%) and 1,1-diphenylbutene (96%). The difference in retention time between the peaks was 3.5 min., so that they overlapped slightly. Satisfactory analysis of the v-p-c trace could be made by assuming the peaks to be symmetrical, which was found to be true for authentic samples of the individual components. Relative percentages of components were derived for this, and other cases to be described, by a single peak area measurement with a planimeter or by weighing cutout traces of the v-p-c peaks.

(b) Oxygen.— The Grignard reagent was prepared from 10.7 g. (37.8 mmole) of (γ,γ-diphenylallyl)-carbinyl bromide and 1 g. (41.2 mg. atom) of magnesium in 60 ml. of ether. The mixture was refluxed for 2 hr., then cooled to -20° and oxygen was passed over the solution for 4 hr. at -20° with stirring. A solution of 5 g. of ammonium chloride in 17 ml. of water was then added. The ether layer was decanted and the residual paste was extracted with two 40-ml. portions of ether. The combined ether layers were washed with water, dried over sodium sulfate and evaporated. Distillation of the resulting oil through a micro-Claisen head (1 mm.) gave four fractions: I, 1.46 g., b.p. 110-

147°; II, 2.23 g., b.p. 147-158°; III, 1.80 g., b.p. 158-164°; IV, 1.66 g., b.p. 164-165°; and 0.57 g. of residue. On standing for several days Fraction II partially crystallized. Recrystallization from ligroin yielded 0.24 g. of prisms, m.p. 82-84°, which m.p. was undepressed on admixture with authentic diphenylcyclopropylcarbinol. The other fractions could not be induced to crystallize. Infrared and n-m-r spectra of Fractions I and IV indicated the presence of 1,1-diphenylbutene and (γ, γ-diphenylallyl)-carbinol, respectively. Each fraction was chromatographed on a column of pentane-washed alumina (30 g. to 1 g. of mixture). The overall chromatographic results, corrected for losses prior to, and during, chromatography, will be given.

Elution with pentane afforded 1.48 g. (18.9%) of a hydrocarbon fraction. Elution with 2-10% ether-benzene gave diphenylcyclopropylcarbinol, 1.64 g. (19.3%), m.p. 84-85°, on crystallization from ligroin. Elution with ether yielded (γ, γ-diphenylallyl)-carbinol, 4.02 g. (47.5%). The (γ, γ-diphenylallyl)-carbinol was microdistilled at 1 mm. with a bath at 150°. A solution of the distillate in chloroform was treated with bromine until color persisted. Excess bromine and solvent were evaporated and the residue on crystallization from hexane gave 1,1-diphenyl-1,2-dibromobutan-4-ol as prisms, m.p. 95-96.5°, lit. (109) m.p. 96-97°. The n-m-r spectrum of (γ, γ-diphenylallyl)-carbinol showed a phenyl peak, vinyl triplet, hydroxyl singlet, α-methylene triplet and β-methylene quartet. The hydrocarbon fraction was microdistilled at

1 mm. with a bath at 120°. Analysis by *v-p-c* at 250° showed peaks due to diphenylcyclopropylmethane (23%), 1,1-diphenylbutene (77%), and a minor unidentified component of longer retention time. The *n-m-r* spectrum of this fraction showed peaks characteristic of both the hydrocarbons.

Lipp,et al. (34) have also described the formation of diphenylcyclopropylcarbinol on oxygenation of the Grignard reagent from what was erroneously considered to be diphenylcyclopropylcarbinyl bromide.

(c) *Carbon Dioxide*.– The Grignard reagent was prepared from 7.02 g. (27.8 mmole) of (γ, γ-diphenylallyl)-carbinyl bromide and 0.75 g. (30.9 mg. atom) of magnesium in 30 ml. of ether as before. The Grignard solution was refluxed for 1 hr., then an excess of solid carbon dioxide was added. The mixture was acidified with 2 N sulfuric acid, and after crystallization from hexane there was isolated (γ, γ-diphenylallyl)-acetic acid, 4.25 g. (69%), m.p. 81.5-83°, as in the previous reaction starting with (γ, γ-diphenylallyl)-carbinyl chloride. The ether layer remaining after extraction of the carboxylic acid by base was washed with water, dried over sodium sulfate and evaporated. The residue was microdistilled at 2 mm. with a bath at 150° and gave 0.83 g. (14.3%) of distillate and 0.58 g. of residue. Analysis of the distillate by *v-p-c* at 250° indicated the presence of diphenylcyclopropylmethane (21.5%), diphenylbutene (78.5%) and an unidentified component of longer retention time (23% of total). An attempt was made to characterize the latter by isolating a sample enriched in it by chromatography on alumina. This sample showed a strong band in the infrared at 1665 cm^{-1}, possibly due to benzophenone.

In another preparation, the Grignard reagent from 25.4 g. (88.5 mmole) of (γ, γ-diphenylallyl)-carbinyl bromide and 3 g. (0.123 g. atom) of magnesium in 100 ml. of ether, was carboxylated and 17.1 g. (76.8%) of (γ, γ-diphenylallyl)-acetic acid was isolated in the same way. The neutral fraction was microdistilled at 1.5 mm. with a bath at 150° and gave 1.85 g. (10.1%) of distillate and 2 g. of residue (tar). V-p-c analysis at 240° showed diphenylcyclopropylmethane (28.5%), 1,1-diphenylbutene (71.5%) and a small amount of the longer retention time component mentioned above. The highest yield of (γ, γ-diphenylallyl)-acetic acid isolated from this reaction was 81.8%.

(d) Phenylacetylene.— The Grignard reagent from 2.88 g. (0.01 mole) of (γ, γ-diphenylallyl)-carbinyl bromide and 0.3 g. (12.35 mg. atom) of magnesium in 15 ml. of ether was refluxed for 2 hr. To it was added a solution of 1.2 g. (11.75 mmole) of phenylacetylene in 5 ml. of ether over 5 min. The mixture was refluxed for 0.75 hr., then stirred for 15 hr. A solution of 3 g. of ammonium chloride in 10 ml. of water was added, and the ether layer was separated, dried over sodium sulfate and evaporated. The residue was microdistilled at 2.5 mm. with a bath at 145° and gave 1.88 g. (90.5%) of distillate and 0.33 g. of residue. Analysis by v-p-c at 250° indicated that the distillate consisted of diphenylcyclopropylmethane (10%) and 1,1-diphenylbutene (90%).

(e) Hydrogen Chloride.— The Grignard reagent prepared from 1.44 g. (5 mmole) of the bromide, and 0.2 g. (8.2 mg. atom) of magnesium in 8 ml. of ether was refluxed for 2 hr. Anhydrous hydrogen chloride gas was passed through a calcium chloride drying-tube and over the surface of the Grignard reagent with rapid stirring and ice-cooling. A fairly rapid gas flow was maintained for 15 min. When 10 ml. of water was added a rapid reaction involving the excess magnesium took place. The ether layer was separated, washed with 2 N sodium bicarbonate solution and water, dried over sodium sulfate and evaporated. The residue was microdistilled at 2.5 mm. with a bath at 140° and yielded 0.93 g. (89.5%) of distillate and 0.18 g. of residue. V-p-c analysis of the distillate at 240° showed diphenylcyclopropylmethane (9%) and 1,1-diphenylbutene (91%).

(f) Methanol.— The Grignard reagent prepared from 2.1 g. (7.29 mmole) of the bromide and 0.3 g. (12.3 mg. atom) of magnesium in 10 ml. of ether was refluxed for 2.5 hr. Anhydrous methanol, 0.24 g. (7.43 mmole), was added, the mixture was stirred for 15 min. then filtered through Celite. The filtrate was evaporated and the residue was microdistilled at 2 mm. with a bath at 150° and afforded 1.31 g. (86.6%) of distillate and 0.175 g. of residue. Analysis by v-p-c at 270° indicated that the distillate was composed of diphenylcyclopropylmethane (5%) and 1,1-diphenylbutene (95%).

(g) Carbon Dioxide, Absence of Oxygen.— The Grignard reagent was prepared and reacted using degassed materials in a helium atmosphere (119). The helium was purged of oxygen by passing it slowly through a 50 x 2.5-cm. glass tube filled with copper shavings and maintained at 250°. A solution of 2 g. (6.95 mmole) of (γ,γ-diphenylallyl)-carbinyl bromide and two drops of 1,2-dibromoethane in 15 ml. of anhydrous ether was placed in a flask fitted with a reflux condenser and helium inlet interchangeable with a vacuum line. The solution was degassed three times by the freezing and thawing technique, admitting helium during periods of warming. High-purity resublimed magnesium, 0.5 g. (20.3mg. atom), in a flask connected to the vacuum line was flamed for several minutes at 1 mm. The flask was quickly disconnected, the magnesium shavings were rapidly poured into the Grignard reaction flask with outflow of helium, and the system was resealed and held under positive helium pressure. The degassing cycle was repeated twice with the magnesium present. On warming, the Grignard reagent rapidly formed and was refluxed for 1 hr. Meanwhile, a flask containing an excess of powdered solid carbon dioxide was pumped out for 10 min. to ensure removal of oxygen. It was then connected directly to the Grignard flask while maintaining the helium atmosphere, and the carbon dioxide was poured into the Grignard solution with stirring. The mixture was stirred for 15 hr. under helium, then 2 N hydrochloric acid was added. The ether layer was separated, extracted twice with 10% sodium carbonate solution, washed with water, dried over sodium sulfate and evaporated. Microdistillation of the resulting neutral fraction at 2 mm. with a bath at 145-155° gave 0.318 g. (22%) of distillate and 0.43 g. of residue.

V-*p*-*c* analysis at 250° showed diphenylcyclopropylmethane, 1,1-diphenylbutene and a small amount of the longer retention time component. Six measurements were made, each from a different *v*-*p*-*c* run, of the relative percent composition of the hydrocarbon mixture. The average percentage was obtained and the standard deviation calculated. The composition was diphenylcyclopropylmethane (26.3±1.1%) and 1,1-diphenylbutene (74%). The standard deviation provides a good estimate of errors in the *v*-*p*-*c* analysis of similar mixtures of these hydrocarbons. The yield and composition of the neutral fraction was therefore essentially unaffected by exclusion of oxygen.

(h) *Cobaltous Chloride*.— The Grignard reagent from 5 g. (17.4 mmole) of (γ,γ-diphenylallyl)-carbinyl bromide and 0.5 g. (20.6 mg. atom) of magnesium in 25 ml. of ether was refluxed for 2 hr. Anhydrous cobaltous chloride, 0.1 g. (0.77 mmole), was added and the mixture was refluxed for a total of 16.5 hr. and stirred at room temperature for 38 hr. Excess solid carbon dioxide was then added to decompose the remaining Grignard reagent, followed by a solution of 3.8 g. of ammonium chloride, in 12 ml. of water. The same isolation procedure used for previous carboxylations afforded acidic and neutral fractions. The crude acid (2.2 g.) crystallized from hexane as prisms of (γ,γ-diphenylallyl)-acetic acid, 1.72 g. (39.2%), m.p. 80.5-82°. The neutral fraction was microdistilled at 2 mm. with a bath at 150° and gave 1.27 g. (35.1%) of distillate and 0.61 g. of residue. Analysis by v-p-c at 250° showed that the distillate consisted of diphenylcyclopropylmethane (35%) and 1,1-diphenylbutene (65%). An attempt was made to isolate some characterizable product from the distillation residue. However, the eluate resulting from chromatography of the residue on alumina and elution with pentane could not be induced to crystallize.

(i) Cadmium Chloride.– To 10 ml. (7.5 mmole) of a solution of the Grignard reagent prepared from the 75.8 g. (0.264 mole) of bromide and 10 g. (0.411 g. atom) of magnesium in 300 ml. of ether (2 hr. reflux), was added 1.3 g. (7.1 mmole) of anhydrous cadmium chloride over 3 min. A further 10 ml. of ether was added and the mixture was refluxed for 24 hr. The solution then gave a negative Gilman test (120), indicating that all the Grignard reagent had reacted. Organocadmium compounds give negative Gilman tests (32). After addition of 3 N hydrochloric acid a vigorous reaction occurred, probably due to hydrolysis of the cadmium reagent. The ether layer was separated, washed with potassium carbonate solution and water, dried over sodium sulfate and evaporated. The product was microdistilled at 3.5 mm. with a bath at 160° and yielded 1.43 g. (91.6%) of distillate and

0.2 g. of residue. Examination by v-p-c at 290° showed that the distillate was pure 1,1-diphenylbutene. No trace of diphenylcyclopropylmethane could be detected. This was confirmed by the n-m-r spectrum. A free radical dissociation of the cadmium reagent, of the type observed by Cason and Fessenden (32) for dibutenylcadmium, does not seem to have been the predominant mode of reaction since the hydrolysis results showed that a large proportion of the cadmium reagent was intact.

Metalation of Diphenylcyclopropylmethane (Attempted).— A 0.647 N solution of n-butyllithium, 14 ml. (9.05 mmole), prepared from n-butyl bromide and freshly cut lithium wire, in ether was added to a solution of 1.56 g. (7.5 mmole) of diphenylcyclopropylmethane in 5 ml. of ether over 5 min. in an apparatus fitted with a calcium chloride drying-tube. A yellow color immediately developed. The mixture was refluxed for 2 hr., then poured rapidly over a slurry of an excess solid carbon dioxide in ether. The product was separated into acidic and neutral fractions as in previous preparations of (γ, γ-diphenylallyl)-acetic acid. The small liquid acid fraction (0.38 g.) showed no phenyl absorption in the infrared, and from v-p-c and infrared evidence probably consists mainly of pentanoic acid. The neutral fraction was microdistilled at 2 mm. with a bath at 100-135° and yielded 1.97 g. of distillate. Analysis by v-p-c at 250° showed two unidentified peaks of short retention time and a large peak due to diphenylcyclopropylmethane. The former are likely to be products derived from side-reactions of the butyllithium. No 1,1-diphenylbutene was detected.

Gilman and Gray (121) have obtained enhanced yields in metalation of a variety of hydrocarbons in tetrahydrofuran and ether-tetrahydrofuran mixtures. To an ice-cooled solution of 1.2 g. (5.77 mmole) of diphenylcyclopropylmethane in 12 ml. of anhydrous tetrahydrofuran (redistilled from lithium aluminum hydride) was added dropwise 16 ml. (8.72 mmole) of a 0.545 N solution of n-butyllithium in ether over 0.5 hr. The mixture turned a deep cherry-red color (possibly due to the diphenylcyclopropylmethyl anion) which persisted during stirring for 5 hr. at room temperature. The color was immediately discharged on addition of excess solid carbon dioxide. Using the same isolation procedure as above there were obtained a small acidic fraction (98 mg.) as an oil, and a neutral fraction. The acidic fraction could not be induced to crystallize. It was unsaturated and its infrared spectrum was similar in many respects to that of (γ,γ-diphenylallyl)-acetic acid except for strong bands at 2900, 2840 and weak bands at 720, 672 cm^{-1}. The neutral fraction was microdistilled at 2 mm. with a bath at 130-170° and gave 1.34 g. of distillate and 0.14 g. of residue. V-p-c analysis at 250° indicated that the composition of the distillate was similar to that found in the first metalation above, consisting largely of diphenylcyclopropylmethane. No 1,1-diphenylbutene was observed. Bennett and Bunce (36) were also unsuccessful in metalating phenylcyclopropylmethane with butyllithium and amylsodium.

Reaction of (γ, γ-Diphenylallyl)-carbinyl Bromide with Lithium.— A solution of 6 g. (20.9 mmole) of (γ, γ-diphenylallyl)-carbinyl bromide in 10 ml. of ether was added dropwise to 0.4 g. (57.2 mg. atom) of freshly-cut lithium wire in 10 ml. of ether at room temperature over 1 hr. The system was maintained under dry nitrogen throughout the course of the reaction. After about half of the bromide had been added the solution became cloudy. The mixture was stirred for 3 hr. at room temperature, then poured over a slurry of excess solid carbon dioxide in ether. Prior to reaction with carbon dioxide, a 2 ml. aliquot of the pale-yellow reaction mixture was pipetted into dry tetrahydrofuran but no color change was observed. The product was separated into a small acidic fraction (35 mg.) and a neutral fraction by the procedure given for previous preparations of (γ, γ-diphenylallyl)-acetic acid. The acidic fraction was unsaturated, but could not be induced to crystallize and was not examined further. The neutral fraction was microdistilled at 2 mm. with a bath at 160° and gave 1.08 g. (26.9%) of distillate and 3.55 g. of residue. The large viscous residue, which appears to be polymeric in nature, could not be induced to crystallize. Except for strong phenyl absorption and weak bands at 1030 and 1070 cm^{-1}, its infrared spectrum was featureless. A possible explanation for some of the polymer is that the lithium reagent attacks the bromide yielding 1,1-diphenyl-1,3-butadiene by dehydrobromination. 1,1-Diphenyl-1,3-butadiene is known to resinify at least partially on distillation at 0.3 mm.

(122). V-p-c examination of the distillate at 250° showed that it consisted of diphenylcyclopropylmethane (41%) and 1, 1-diphenylbutene (59%). The n-m-r spectrum showed peaks characteristic of both compounds. As a check on the accuracy of the v-p-c analysis the composition of the mixture was measured from the n-m-r spectrum by comparing areas under multiplets due to each hydrocarbon. These areas were determined by weighing cutout traces of the peaks. The calculated relative proportion of diphenylcyclopropylmethane was found to be 39% by comparing the cyclopropyl methylene region due to it with the methyl triplet due to 1, 1-diphenylbutene. Comparison of the methine doublet of the former with the vinyl triplet of the latter leads to the figure 43%. The mean of these (41%) is in excellent agreement with the v-p-c value, and provides strong support for the accuracy of the v-p-c analysis of these mixtures.

Reaction of Ethylmagnesium Bromide and Cobaltous Chloride with (γ,γ-Diphenylallyl)-carbinyl Chloride.— To a solution of ethylmagnesium bromide, prepared from 1.8 g. (16.5 mmole) of ethyl bromide, and 0.47 g. (19.3 mg. atom) of magnesium in 10 ml. of ether was added 0.4 g. of anhydrous cobaltous chloride. A solution of 3 g. (12.4 mmole) of (γ,γ-diphenylallyl)-carbinyl chloride in 5 ml. of ether was added dropwise to the refluxing mixture over 5 hr. Additional cobaltous chloride (about 0.3 g.) was added every hour during the addition of organic halide (total cobaltous chloride used, 1.9 g., 14.6 mmole). This procedure is taken from that of Urry and Nicolaides (43). The mixture was refluxed for 3 hr. then stirred for 15 hr. at room temperature. Excess solid carbon dioxide was added, and the neutral fraction was isolated as described previously. It was microdistilled at 1 mm. with a bath at 150° and gave 1.67 g. (59.6%, based on reacted chloride), of distillate and 0.97 g. of tar. *V-p-c* analysis of the distillate at 250° showed 1,1-diphenylbutene (56%), diphenylcyclopropylmethane (7%), unreacted chloride (17%) and the same unidentified component (20%) observed in previous reactions of the Grignard reagent. The relative composition of the hydrocarbons was thus diphenylcyclopropylmethane (11.5%) and 1,1-diphenylbutene (88.5%).

2-Phenylbutane-1,4-diol.— A solution of 19.5 g. (0.1 mole) of phenylsuccinic acid (123) in 500 ml. of ether was added to a solution of

12.5 g. (0.329 mole) of lithium aluminum hydride in 400 ml. of ether in a flask fitted with reflux condenser, drying-tube and magnetic stirrer. The addition took 2 hr. and the mixture was refluxed for a further 20 hr. Ice water (50 ml.) was then added cautiously followed by 200 ml. of 6 N sulfuric acid. The ether layer was separated, and combined with two 100-ml. ether extracts of the aqueous layer. The ether solution was washed with sodium bicarbonate solution and water, dried over sodium sulfate and evaporated. The combined aqueous washings were continuously extracted with ether for 15 hr. and the resulting extract was added to the main product. Distillation of the product through a Claisen head afforded 12.2 g. (73%) of 2-phenylbutane-1,4-diol as a viscous oil, b.p. 170° (4 mm.), lit. (124) b.p. 165° (4 mm.). After several weeks the diol crystallized and had m.p. 63-67° without further purification, lit. (125) m.p. 70°. The infrared spectrum of a chloroform solution of the diol showed phenyl absorption and hydroxyl bands at 3600, 3390 and 1040 cm^{-1}. In other preparations of the diol yields up to 81.5% were obtained.

2-Phenylbutane-1,4-diol bis-phenylurethan was prepared in 58% yield from the diol by the procedure of Vogel (126) and crystallized from ethanol-hexane, m.p. 111-112°, lit. (124) m.p. 113°.

1,4-(2-Phenyl)-butyl bis-p-Toluenesulfonate.— p-Toluenesulfonyl chloride, 4.2 g. (22 mmole) , was added portionwise to a solution of 1.66 g. (10 mmole) of 2-phenylbutane-1,4-diol in 6.3 g. (80 mmole) of pyridine over 0.5 hr. at 10° with stirring. The mixture was stirred for 3 hr. at 15° then 5 ml. of water was added, followed by 12 ml. of concentrated hydrochloric acid in 40 ml. of water. The mixture was extracted with four 40-ml. portions of ether, and the ether layer was washed repeatedly with 2 N hydrochloric acid, then with sodium bicarbonate solution and water. The resulting ether solution was dried over sodium sulfate and when evaporated yielded 4.3 g. of oil. A portion, 0.6 g., of the product was chromatographed on a column of 18 g. of 50% benzene-pentane-washed alumina. Elution of the alumina column with this solvent and with 10% ether-benzene afforded 0.58 g. of oil, which crystallized on trituration with methanol at 0°. The bulk of the product crystallized from acetone-methanol as needles, 2.56 g., m.p. 70-73°, second crop, 1.09 g., m.p. 72-74° (total yield 77%). Its infrared spectrum in carbon tetrachloride showed phenyl absorption and strong tosylate bands at 1370, 1190 and 1178 cm^{-1}. Two further crystallizations from methanol afforded an analytical sample, m.p. 73-74°.

Anal. Calcd. for $C_{24}H_{26}O_6S_2$: C, 60.73; H, 5.52; S, 13.52. Found: C, 60.92; H, 5.56; S, 13.60.

4-Chloro-2-phenylbutyl p-Toluenesulfonate.— It was hoped that treatment of 1,4-(2-phenyl)-butyl bis-p-toluenesulfonate with strong base might effect selective elimination of the tosylate group at the 1-position.

However, reaction of the bis-tosylate with potassium hydroxide in ethanol and with potassium t-butylate in t-butanol led to mixtures of products and to recovery of much of the starting material. The chlorotosylate was therefore prepared in order to magnify the differences between the leaving-groups at the 1- and 4-positions. A solution of 2.1 g. (49.5 mmole) of anhydrous lithium chloride, in 125 ml. of dry acetone was added dropwise to a refluxing solution of 21.2 g. (44.7 mmole) of 1,4-(2-phenyl)-butyl bis-p-toluenesulfonate in 50 ml. of acetone over 0.5 hr. The mixture was refluxed for 17 hr., concentrated on the steam bath to about 40 ml., then poured into 250 ml. of water and extracted with three 50-ml. portions of ether. The ether extracts were washed with water, dried over sodium sulfate and evaporated. The residue crystallized from acetone-methanol as needles of 4-chloro-2-phenylbutyl p-toluenesulfonate, 11.5 g. (76%), m.p. 90-92°. The product gave a positive Beilstein halogen test and its infrared spectrum showed phenyl and tosylate absorption. Three further crystallizations from methanol afforded an analytical sample, m.p. 91-92°.

Anal. Calcd. for $C_{17}H_{19}O_3SCl$: C, 60.27; H, 5.64; S, 9.46; Cl, 10.47. Found: C, 59.80; H, 5.34; S, 9.92; Cl, 10.29.

(β-Phenylallyl)-carbinyl Chloride.— Treatment of 4-chloro-2-phenylbutyl p-toluenesulfonate with lithium diisopropylamide in refluxing ether led to recovery of about half of the starting material, while heating it at 100° with dimethylsulfoxide and sodium carbonate (127) gave mixtures which did not contain the desired (β-phenylallyl)-carbinyl chloride. However, smooth elimination of the tosylate group was effected with potassium hydroxide and potassium t-butylate. A solution of 1.1 g. (19.6 mmole) of potassium hydroxide in 20 ml. of absolute ethanol was added to a refluxing solution of 6 g. (17.7 mmole) of the chlorotosylate in 60 ml. of anhydrous t-butanol over 1 hr. The mixture was refluxed for 1 hr., concentrated to 25 ml. under reduced pressure, then poured into 200 ml. of water and extracted with three 75-ml. portions of ether. The ether extracts were washed with water, dried over sodium sulfate and evaporated. Pentane, 20 ml., was added to the resulting oil and 1.49 g. of unreacted chlorotosylate, m.p. 92-93°, crystallized out and was removed by filtration. The filtrate was chromatographed on a column of 90 g. of pentane-washed alumina. Elution of the alumina column with pentane (5 x 300 ml.) afforded a liquid eluate which was microdistilled at 3 mm. with a bath at 100° and gave 1.18 g. of distillate. Analysis by v-p-c at 175° showed that the distillate consisted of 20% of a short retention time component and 80% of the major product, subsequently shown to be (β-phenylallyl)-carbinyl chloride. Thus the yield of the latter based on reacted chlorotosylate was 42%. Distillation of the combined products from several similar reactions yielded the short retention time component, b.p. 60-62° (16 mm.) and pure (β-phenylallyl)-carbinyl chloride, b.p. 80-82° (7 mm.), $n^{25}D$ 1.5480. The latter was unsaturated and gave a positive Beilstein halogen test. Its infrared spectrum in carbon tetrachloride showed bands at 1633 and 904 cm^{-1} due to the $C=CH_2$ group, phenyl absorption, and a weak band at 1575 cm^{-1} due to phenyl conjugated with a double bond. The *n-m-r* spectrum showed phenyl peaks, vinyl doublet (considerable secondary splitting was apparent), α-methylene triplet and β-methylene triplet.

Anal. Calcd. for $C_{10}H_{11}Cl$: C, 72.07; H, 6.66; Cl, 21.28. Found: C, 72.03; H, 6.70; Cl, 20.75.

The low-boiling component isolated in this reaction was tentatively identified as 2-phenyl-1,3-butadiene, formed by double elimination, on the basis of the following evidence. After standing for several days in contact with air it partially resinified. The infrared spectrum of a freshly prepared solution in carbon tetrachloride showed phenyl absorption, and bands at 1590 (conjugated $C=$), 991 and 916 (strong, $-CH=CH_2$) and at 900 cm^{-1} (strong $C=CH_2$). The *n-m-r* spectrum showed phenyl peaks, complex vinyl peaks roughly divisible into $=CH-$ and $=CH_2$ regions, and a few low-intensity upfield peaks probably due to polymer.

Results very similar to those found using potassium hydroxide as base were obtained with potassium *t*-butylate in refluxing *t*-butanol. The yields and composition of the products were quite comparable.

(β-Phenylallyl)-acetic Acid.— The Grignard reagent from β-phenylallyl)-carbinyl chloride was prepared using the entrainment method of Pearson, et al. (128). A solution of 1.13 g. (6 mmole) of 1,2-di-

bromomethane in 15 ml. of ether was added dropwise to a refluxing solution of 1 g. (6 mmole) of (β-phenylallyl)-carbinyl chloride and 0.4 g. (16.5 mg. atom) of magnesium in 25 ml. of ether over 15 hr. Excess solid carbon dioxide was added, followed by 5 ml. of concentrated hydrochloric acid in 20 ml. of ice water. When the same isolation procedure used in previous carboxylations of the Grignard reagent from (γ, γ-diphenylallyl)-carbinyl bromide was carried out, a crystalline acid (0.83 g.) was obtained. Recrystallization from ligroin gave large plates of (β-phenylallyl)-acetic acid, 0.64 g. (60.6%), m.p. 96-97.5°. The acid was unsaturated and depressed the m.p. of authentic 1-phenylcyclobutanecarboxylic acid (m.p. 105-106.5°) to 72-90°. The infrared spectrum of the acid in chloroform showed phenyl absorption, carboxyl peaks at 3470, 3010, 2650, 1710, and 1290 cm^{-1}, a weak band at 1575 cm^{-1} due to phenyl conjugated with a double bond, and bands at 1633, 902 cm^{-1} due to $C=CH_2$. This spectrum was quite different from that of 1-phenylcyclobutanecarboxylic acid. The n-m-r spectrum of a chloroform solution of the product showed carboxyl singlet, phenyl peak, vinyl doublet, and overlapping triplets due to α- and β-methylene groups.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.85; H, 6.87.

Reaction of Cobaltous Chloride with the Grignard Reagent from (β-Phenylallyl)-carbinyl Chloride.— A solution of 0.932 g. (5.6 mmole) of (β-phenylallyl)-carbinyl chloride in 9 ml. of ether was added to 0.2 g.

(8.23 mg. atom) of magnesium and 0.8 g. (6.15 mmole) of anhydrous cobaltous chloride in 10 ml. of ether over 0.5 hr. After 3 hr. at reflux the appearance of the solution had not changed, so a further 0.2 g. of magnesium was added, followed by a solution of 1.05 g. (5.6 mmole) of 1,2-dibromoethane in 5 ml. of ether over 4 hr. After 1 hr. the solution had become very dark in color. The mixture was refluxed for 15 hr., then an excess of solid carbon dioxide was added. Use of the same isolation procedure described for previous carboxylations yielded a neutral fraction but no acidic fraction. The neutral fraction was microdistilled at 38 mm. with a bath at 110-130° and gave 0.389 g. (52.6%) of distillate and 0.323 g. of residue. Analysis by _v-p-c_ at 110° of the distillate showed peaks at 10.8 min. (4.6%), 12.6 min. (6.6%), 15.5 min. (80.6%) and 22.8 min. (8.1%). The last peak had the same retention time as authentic phenylcyclobutane. The infrared spectrum of the distillate in carbon tetrachloride showed phenyl absorption and bands at 1625 (C=C conjugated), 1572 (conjugated phenyl) and 895 cm^{-1} ($C=CH_2$). Its _n-m-r_ spectrum showed phenyl peaks, vinyl doublet (with secondary splitting), β-methylene quartet, α-methylene triplet and other small peaks. These spectra indicate that the major product of the reaction is _2-phenyl-1-butene_, which thus corresponds to the _v-p-c_ peak at 15 min.

The reaction was repeated by adding a solution of 1.25 g. (6.65 mmole) of 1,2-dibromoethane in 10 ml. of ether to a solution of 1.105 g.

(6.64 mmole) of (β-phenylallyl)-carbinyl chloride, 0.95 g. (7.3 mmole) of cobaltous chloride, and 0.5 g. (20.6 mg. atom) of magnesium in 20 ml. of ether at reflux over 2.5 hr. The mixture was refluxed for 20 hr. To the cooled mixture was added slowly 13 ml. of 2 N hydrochloric acid with stirring. The ether layer was separated, washed with sodium bicarbonate solution and water, dried over sodium sulfate and evaporated. The residue was microdistilled at 42 mm. with a bath at 105-130° and gave 0.548 g. (62.6%) of distillate and 0.37 g. of tar. *V-p-c* analysis of the distillate at 110° showed peaks at 8.0 min. (1.7%), 9.5 and 10.1 min. (8.1%), 12.0 min. (5.6%), 14.4 min. (70.6%) and 21.6 min. (14.0%). The peak at 12.0 min. had the same retention time as the by-product formed in the preparation of (β-phenylallyl)-carbinyl chloride and assigned the structure 2-phenyl-1,3-butadiene. It may be present both as a contaminant in the chloride and as a bona fide reaction product. Authentic phenylcyclobutane had the same retention time as the peak at 21.6 min.

The distillates from the two reactions were combined and redistilled through a micro-Vigreux head and gave four fractions, b.p. 90-98° (77 mm.), and the hold-up (Fraction V). Analysis by *v-p-c* at 108° showed that the first four fractions consisted largely of 2-phenyl-1-butene, lit. (190) b.p. 81-82° (20 mm.), together with other minor products, while Fraction V contained 32% of the component having the same retention time as phenylcyclobutane and 68% of 2-phenyl-1-butene.

The n-m-r spectrum of Fraction V decisively indicated that the unidentified component was not phenylcyclobutane, but was in fact 2-phenyl-2-butene. Apart from strong peaks due to 2-phenyl-1-butene there were observed a vinyl quartet of quartets, midfield methyl singlet and methyl doublet. Considerable secondary splitting of the methyl peaks was evident, and the areas under the peaks were in the ratio 1:3:3 respectively, consistent with the structure of 2-phenyl-2-butene. It is not known which stereoisomer was obtained. The n-m-r spectra of phenylcyclobutane and of phenylcyclobutene are quite different from this spectrum, the latter exhibiting a singlet for the vinyl hydrogens (92).

3,5-Hexadienoic Acid.— The procedure was a modification of that given by Paul and Tchelitcheff (130). A solution of 85 g. (0.755 mole) of chlorobenzene in 105 ml. of dry benzene was added to 32.8 g. (1.43 g. atom) of sodium chips in 250 ml. of benzene at 50° over 1 hr., in a 2-ℓ. round-bottomed flask fitted with mechanical stirrer, nitrogen inlet and drying-tube. Slight cooling was required when the reaction was well started. The mixture was stirred for 3.5 hr. at room temperature, then a solution of 50 g. (0.735 mole) of 1,4-pentadiene in 70 ml. of benzene was added over 10 min. Nitrogen flow was interrupted during the addition. After 40 hr. of stirring at room temperature, excess solid carbon dioxide was added to the mixture with stirring, keeping the temperature above 0°. Ice water, 700 ml., was added cautiously to decompose the considerable quantity of unreacted sodium. The mixture was transferred to a separatory funnel and the emulsion which formed was dispersed by addition of 300 ml. of ether. The dark aqueous layer was separated, the benzene-ether layer was extracted with water, and the combined aqueous layers were acidified to pH 2 with 3 N hydrochloric acid. The liberated carboxylic acid was extracted with four 200-ml. portions of ether, the ether extracts were washed with water, dried over sodium sulfate and evaporated under reduced pressure. The residue was distilled through a Claisen head, b.p. 85-105° (4.5 mm.), and gave 18.2 g. (22%) of carboxylic acid and 3.9 g. of tar. Analysis by v-p-c showed a single peak for the product, although spectral evidence indicated that more than one component was present. The distillate had $n^{22}D$ 1.4924, lit. (130) for 3,5-hexadienoic acid, $n^{20}D$ 1.4850. The n-m-r spectrum of the product exhibited carboxyl singlet, complex vinyl region, perturbed α-methylene doublet, and a small methyl doublet. The latter is probably due to sorbic acid, which is known to be formed from 3,5-hexadienoic acid by base-catalyzed rearrangement (130). No attempt was made to remove it since purification of 3,5-hexadienoic acid is less convenient than of some of its derivatives. The infrared spectrum of the acid showed bands at 2600, 1710, and 1280 cm^{-1} due to the carboxyl group; 1660 and 1610 cm^{-1} (conjugated C=C); 1000, 905 cm^{-1} ($CH=CH_2$); and 950 cm^{-1} (-CH=CH-).

In another preparation, the sodium derivative of 1,4-pentadiene derived from 64 g. (0.57 mole) of chlorobenzene, 26.3 g. (1.14 g. atom) of sodium and 40 g. (0.588 mole) of 1,4-pentadiene in a total of 340 ml. of benzene was poured onto a slurry of an excess of solid carbon dioxide in ether. The mode of addition of carbon dioxide was thus reversed relative to the above preparation. Examination of the crude acidic product by _v-p-c_ at 175° showed two main peaks at 5.2 min. (30%) and 10.0 min. (70%, 3,5-hexadienoic acid). The former could not have been sorbic acid since 3,5-hexadienoic acid contaminated by considerable amounts of sorbic acid gave only a single unsymmetrical peak in the _v-p-c_. Distillation of the product through a Claisen head gave a fraction, 8.67 g., b.p. 80-93° (4.5 mm.). A later fraction, b.p. 100-101° (4.5 mm.), was shown to be essentially pure 3,5-hexadienoic acid. Analysis of the first fraction by _v-p-c_ showed that it consisted of a 50% mixture of 3,5-hexadienoic acid and the lower-boiling component. Evidence that the latter was divinylacetic acid was obtained by comparison of the infrared spectrum of this fraction with that of 3,5-hexadienoic acid. The conjugated C= bands at 1660, 1610, 1000 and 905 cm^{-1} due to 3,5-hexadienoic acid were much less intense and new strong bands at 1640, 990 and 925 cm^{-1} due to an unconjugated $-CH=CH_2$ group appeared.

Use of n-butyllithium instead of phenylsodium as metalating agent gave very low yields of impure 3,5-hexadienoic acid. Some improvement of yield (to 26.4%) is obtained with a fine dispersion of sodium in isooctane (131) instead of sodium chips.

3,5-Hexadien-1-ol.— A solution of 17.7 g. (0.158 mole) of crude 3,5-hexadienoic acid in 70 ml. of ether was added to a solution of 6.1 g. (0.16 mole) of lithium aluminum hydride in 100 ml. of ether over 0.5 hr. The mixture was refluxed for 3 hr., then stirred at room temperature for 15 hr. Water was added, followed by sufficient 2 N sulfuric acid to dissolve the resulting paste. The ether layer was separated, the aqueous layer was extracted twice with ether, and the combined ether layers were washed with sodium bicarbonate solution and water. The ether solution was dried over sodium sulfate and evaporated under reduced pressure. Distillation of the residue through a Vigreux head at 30 mm. yielded the following fractions: I, 1.23 g., b.p. 30-79°; II, 3.25 g., b.p. 79-82°; III, 4.84 g., b.p. 82°; IV, 0.68 g., b.p. 82°, $n^{22.5}_D$ 1.4890. The holdup was microdistilled at 30 mm. with a bath at 100° and gave 1.18 g. of distillate (Fraction V) and 1.9 g. of residue. The total yield of crude 3,5-hexadien-1-ol was thus 11.2 g. (72%). Analysis by v-p-c at 120° showed that Fraction I contained about 25% of 3,5-hexadien-1-ol as well as water and two unidentified components of shorter retention time than the dienol. Fractions II and III consisted predominantly of the dienol plus small amounts of the latter components, while Fraction IV was essentially pure 3,5-hexadien-1-ol. Fraction V contained a trace of higher-boiling material. Fraction IV was used for analysis and spectral characterization.

Anal. Calcd. for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 72.96; H, 10.40.

The n-m-r spectrum showed complex vinyl region, hydroxyl singlet, α-methylene triplet, β-methylene quintet and small upfield doublet. The latter is attributed to the methyl group in 2,4-hexadien-1-ol derived from sorbic acid. The multiplicity of the β-methylene resonance is anomalous since a quartet would be expected from first-order considerations. The ratios of the intensities of the components of the quintet were approximately binomially related (1:3.6:6.0 observed), and the form of the quintet was unchanged in the spectrum of a dilute solution of the dienol in pyridine (132). The infrared spectrum of the dienol showed bands at 3620, 3330 and 1043 due to hydroxyl; 3070 and 3000 due to vinyl CH; 1657 and 1608 from conjugated C=C, 1002 and 902 for $-CH=CH_2$; and 950 cm^{-1} due to -CH=CH-. Evidence for the conjugated diene system in the product was gained by its ultraviolet spectrum in cyclohexane ($c = 0.102$ mmole/ℓ.) which showed an intense maximum at 2260 A, $\log \epsilon = 4.3$, characteristic of conjugated dienes (133). No attempt was made to purify Fractions II-V further, but they were combined and used directly in the preparation of the tosylate. Attempts to prepare the dienol by reaction of 1, 3-butadienylmagnesium bromide with ethylene oxide were thwarted by the fact that 1-bromo-1, 3-butadiene did not react with magnesium under even the most favorable conditions.

<u>1-Hexa-3, 5-dienyl p-Toluenesulfonate.</u>— p-Toluenesulfonyl chloride, 7 g. (36.8 mmole) was added to a solution of 3.26 g. (33.3 mmole) of crude 3, 5-hexadien-1-ol in 10.5 g. (0.133 mole) of pyridine at 5° over 15 min. The mixture was stirred for 3.5 hr. at room temperature, then poured into water and extracted with three 50-ml. portions of ether. The ether extracts were washed repeatedly with water, dried over sodium sulfate and when evaporated under reduced pressure yielded 6.95 g. (83%) of the crude tosylate as a colorless liquid. This was not purified further, but was used directly in the subsequent reaction.

<u>1-Bromo-3, 5-hexadiene.</u>— A solution of 18.6 g. (74 mmole) of crude 1-hexa-3, 5-dienyl p-toluenesulfonate and 30 g. (0.345 mole) of anhydrous lithium bromide in 90 ml. of dry acetone was refluxed for 1.5 hr. Most of the acetone was distilled off through a 12-in. Vigreux column, and the residue was poured into water and extracted with three 70-ml. portions of pentane. The pentane extracts were washed with water, dried over sodium sulfate, and the solvent was distilled off

through a 12-in. Vigreux column. The residue was fractionated through a Vigreux head at 40 mm. and gave the following fractions: I, 2.51 g., b.p. 55-68°; II, 1.57 g., b.p. 68-72°; III, 2.13 g., b.p. 72-75°; IV, 1.03 g., b.p. 75°, $\underline{n}^{22.5}D$ 1.5170. The holdup was microdistilled at 41 mm. with a bath at 90° and gave 1.63 g. of distillate (Fraction V) and 0.66 g. of residue. Analysis by v-p-c at 103° showed that Fractions IV, V were pure 1-bromo-3,5-hexadiene, while Fractions II, III also contained small amounts, and Fraction I large amounts, of two unidentified components of shorter retention time. The infrared spectrum of the pure bromodiene in carbon tetrachloride showed bands at 1607, 1652 due to conjugated C=C; 1002 and 905 (both strong) due to $-CH=CH_2$; and 950 cm^{-1} from -CH=CH-. Evidence for a conjugated diene system in the product was obtained by its ultraviolet spectrum in cyclohexane which displayed an intense maximum at 2265 A, log $\epsilon = 4.41$. The n-m-r spectrum of the bromodiene is shown on the following page, and is consistent with the required structure except that the β-methylene resonance is a quintent. First-order analysis would predict a quartet, considering only the hydrogens on C_1 and C_3, and assuming approximately equal spin-coupling constants between these and the β-methylene hydrogens. This anomaly was also observed in the n-m-r of the corresponding alcohol. Computations for the related, but simpler, system $-\overset{4}{C}H=\overset{3}{C}H-\overset{2}{C}H_2-$ showed that such anomalies are probably due to nearly identical chemical shifts for the C_3 and C_4 hydrogens. Such a situation

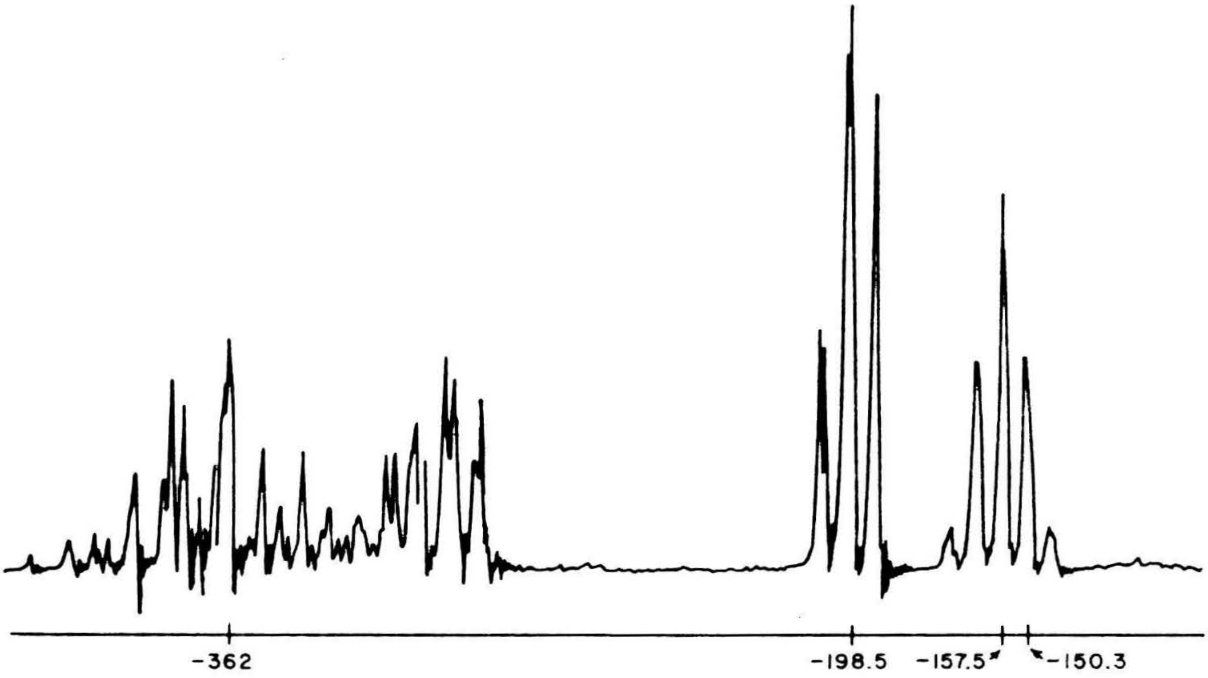

Fig. 18.— Proton n-m-r spectrum of 1-bromo-3, 5-hexadiene. Chemical shifts are in c.p.s. relative to tetramethylsilane as internal standard (not shown).

leads to unusual patterns for the C_2 methylene resonance which bear little resemblance to the expected asymmetric doublet. The fact that allylcarbinyl chloride shows a slightly perturbed β-methylene quartet in the *n-m-r* (17), rather than a more complicated pattern, is because in this case there is *ca.* 50 c.p.s. difference in chemical shift between the C_3 and C_4 hydrogens.

Anal. Calcd. for C_6H_9Br: C, 44.76; H, 5.63; Br, 49.64. Found: C, 44.80; H, 5.61; Br, 49.54.

A solution of 0.805 g. (5 mmole) of the bromodiene in 6 ml. of ether was hydrogenated in the presence of 50 mg. of platinum oxide at atmospheric pressure. After 2 hr. the theoretical volume of hydrogen had been absorbed. The solution was decanted from the catalyst and the ether was evaporated. The residue was microdistilled at 88 mm. with a bath at 100° and gave 0.49 g. (59.8%) of 1-bromohexane, $n^{23.5}D$ 1.4472, lit. (190) $n^{23.5}D$ 1.4478. The infrared and *n-m-r* spectra of this product were identical with those of 1-bromohexane.

In another preparation of 1-bromo-3,5-hexadiene, the yield of pure bromodiene was 60% based on crude 1-hexa-3,5-dienyl *p*-toluenesulfate. The bromodiene gave preliminary indications of enhanced reactivity in S_N1-type reactions in that it reacted notably faster with 2% ethanolic silver nitrate solution than did 1-bromohexane.

4,6-Heptadienoic Acid.— When a solution of 2.13 g. (13.2 mmole) of 1-bromo-3,5-hexadiene in 12 ml. of ether was stirred with 0.4 g. (16.4 mg. atom) of high-purity resublimed magnesium turnings in a round-bottomed flask fitted with reflux condenser and drying-tube, the Grignard reagent rapidly formed. A strong fish-like odor was immediately noted in the environs of the Grignard reaction flask, which was later associated with hydrocarbon coupling products isolated from reactions of the Grignard reagent. Since neither the bromide nor products of reactions of water or oxygen with the Grignard reagent have this odor, one may tentatively conclude that the coupling products are produced during formation of the Grignard reagent. After 15 min., most of the magnesium had reacted and the solution was refluxed for 24 hr., then poured onto an excess of solid carbon dioxide with stirring. A solution of 1 g. of ammonium chloride in 10 ml. of water was added, followed by 15 ml. of water. The aqueous layer was brought to pH 8 by addition of a few ml. of dilute ammonium hydroxide. The aqueous layer was separated and combined with an aqueous extract of the ether layer. The combined aqueous layers were acidified with dilute hydrochloric acid and extracted with 350 ml. of ether and three 50-ml. portions of pentane. The combined pentane-ether extracts were washed with water, dried over sodium sulfate and evaporated under reduced pressure. Similar treatment of the original ether layer gave a neutral fraction.

Microdistillation of the acid fraction at 2 mm. with a bath at 105° afforded 0.701 g. (42.4%) of 4,6-heptadienoic acid, $\underline{n}^{24}$D 1.4840. The n-m-r spectrum of the acid showed carboxyl singlet, complex vinyl region very similar in detail to that of 1-bromo-3,5-hexadiene, and a large unsymmetrical methylene peak due to overlapping α- and β-methylene resonances. No cyclopropyl absorption was detected. Evidence for a conjugated diene system in the acid was secured by the ultraviolet spectrum, which exhibited a maximum at 2254 A, log ϵ = 4.40 (cyclohexane solution). The infrared spectrum of the product was similar to that of the bromodiene except for the presence of carboxyl bands.

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 65.88; H, 7.94.

Since the acid gave only a single peak in the v-p-c at 160° immediately after isolation, the discrepancy in the carbon value is attributed to slight decomposition of the acid prior to analysis. The neutral fraction was microdistilled at 13 mm. with a bath at 100° and gave 0.355 g. (33.1%) of hydrocarbon distillate. The components of this neutral fraction are discussed in the next section. The reaction was repeated with Grignard reagent from 3.4 g. (21.1 mmole) of 1-bromo-3,5-hexadiene and 0.8 g. (32.9 mg. atom) of resublimed magnesium in 20 ml. of ether. The Grignard reagent was heated under reflux for 72 hr., and the excess solid carbon dioxide was added to the mixture followed by a solution of 1 g. of ammonium sulfate in 16 ml. of water. Use of the same isolation procedure described above afforded acidic and neutral fractions. The acidic fraction was microdistilled at 3 mm. with a bath at 110° and gave 0.69 g. (25.9%) of 4,6-heptadienoic acid. The yield is somewhat lower than in the previous reaction but this may have resulted from reversal of the mode of reaction with carbon dioxide. Microdistillation of the neutral fraction at 50 mm. with a bath at 140° afforded 0.769 g. (45.0%) of distillate and 0.35 g. of residue. Uncondensed low-boiling materials from this distillation were collected by a Dry Ice trap. The yield of hydrocarbon fraction is seen to be somewhat greater than in the first reaction in which a shorter reflux period was employed. The components of the neutral fraction are discussed in the next section.

1,6-Dicyclopropyl-1,5-hexadiene and 1,4-Dicyclopropyl-1,5-hexadiene.— The neutral fraction from the first reaction in the preceding section was examined by v-p-c at 145° and found to give peaks at 4.1, 4.8, 7.8 (total 3%), 12.9 (35%) and 23.5 min. (62%). The last two peaks were later shown to be due to 1,4-dicyclopropyl-1,5-hexadiene and 1,6-dicyclopropyl-1,5-hexadiene respectively. The ultraviolet spectrum of this mixture in cyclohexane did not reveal any maximum above 2100 A, but only exhibited a steady decrease in end-absorption out to 2480 A where ϵ was zero. This indicates absence of appreciable amounts of conjugated dienes in the neutral fraction.

Analysis by *v-p-c* at 143° of the neutral fraction from the second reaction prior to distillation indicated peaks at 0.4 (7%), 0.7 (1.5%), 2.5 (1%), 3.5 (2.5%), 4.0 (2.5%), 6.2 (3.5%); 10.3, 1,4-dicyclopropyl-1,5-hexadiene (31%); and 18.4 min., 1,6-dicyclopropyl-1,5-hexadiene (51%). The two neutral fractions were combined with the product of reaction of the Grignard reagent with cobaltous chloride, which is described in the next section, and which was shown by *v-p-c* to yield essentially the same products as above, plus some additional ones of intermediate retention time which were easily distinguishable from the dicyclopropyldienes. The resulting mixture (*ca.* 1.5 g.) was analyzed (134) by preparative *v-p-c* on a Beckman Megachrom instrument equipped with eight 6-ft. x 5/8-in. i.d. columns in parallel, packed with siliconized firebrick. The column temperature was 123° and the helium flow-rate was 13.1 ℓ. per min. Peaks were observed at 21.5 (small), 29.5 (small), 33.7 (Fraction I), 41.2 (small), 48.0 (Fraction II), and 56 min. (Fraction III). The total yield of fractions I, II and III was approximately 60% of the injection sample, and the yields of Fractions I and III were in the ratio of *ca.* 3:5 respectively, as in the original sample. Fractions I and III were shown by *v-p-c* comparison to be the two main pure components in the above neutral fractions, while Fraction II was derived from the cobaltous chloride reaction discussed in the next section. Fraction I had $n^{22.5}$D 1.4754 while Fraction III had $n^{22.5}$D 1.4897.

The infrared spectrum of Fraction I in carbon tetrachloride showed bands at 3075, 3000 due to vinyl CH; 1662, 960 for -CH=CH-; 1635, 992, 911 from $-CH=CH_2$; 1042 and 1017 cm^{-1} due to cyclopropyl. In contrast, the spectrum of Fraction III showed bands at 3075, 3000 due to vinyl CH; 1662, 959 for -CH=CH- (much stronger than in Fraction I); 1042 and 1018 cm^{-1} due to cyclopropyl. The n-m-r spectrum of Fraction I (see next page) showed complex vinyl absorption including $=CH_2$ resonances, methylene triplet, strongly split methine multiplet lying partly upfield of the triplet, cyclopropyl methine multiplet, and complex cyclopropyl methylene peaks situated in the 9.5 to 10 τ region (93). The n-m-r spectrum of Fraction III (see page 171)displayed complex vinyl absorptions, a methylene multiplet consisting of three peaks of unequal intensity, cyclopropyl methine multiplet and complex cyclopropyl methylene peaks in the 9.5 to 10 τ range. All the above peaks bear the expected intensity relations to one another. The above spectral evidence leaves little doubt that Fraction I is 1, 4-dicyclopropyl-1, 5-hexadiene and Fraction III is 1, 6-dicyclopropyl-1, 5-hexadiene.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found for 1, 4-cyclopropyl-1, 5-hexadiene: C, 88.78 ; H, 11.19. Found for 1, 6-dicyclopropyl-1, 5-hexadiene: C, 88.72; H, 11.05.

Reactions of the Grignard Reagent from 1-Bromo-3, 5-Hexadiene.—

(a) Cobaltous Chloride.— To a refluxing suspension of 1.77 g.

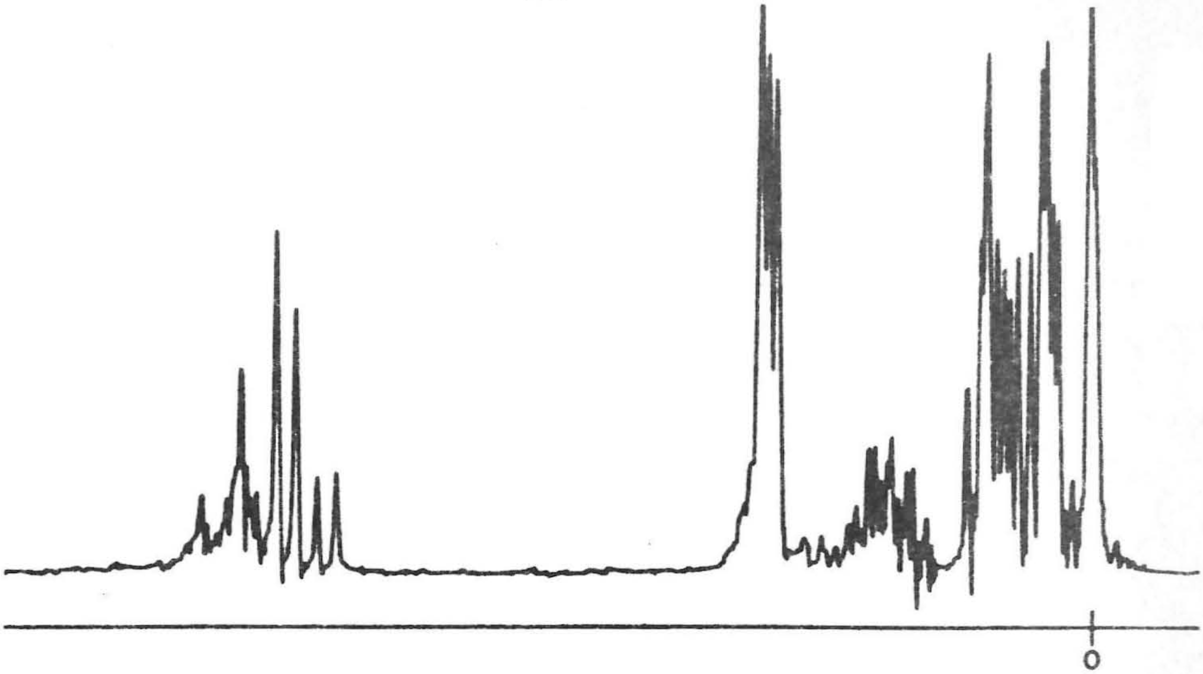

Fig. 19a.— Proton n-m-r spectrum of 1,6-dicyclopropyl-1,5-hexadiene. Tetramethylsilane is the internal standard.

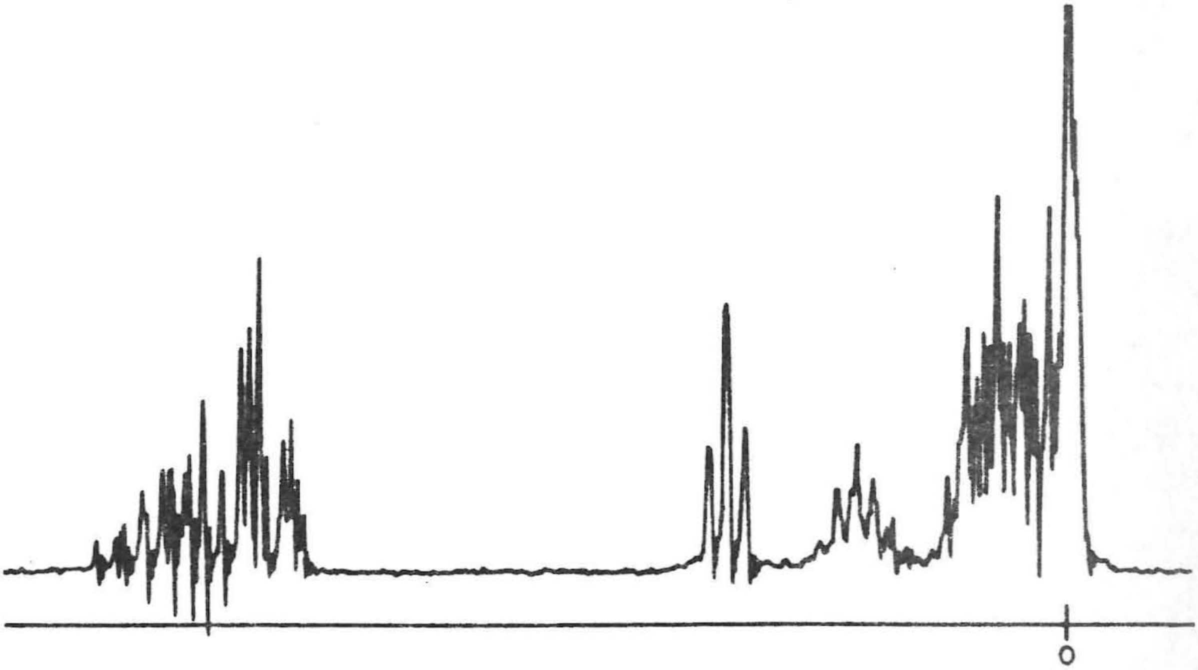

Fig. 19b.— Proton n-m-r spectrum of 1,4-dicyclopropyl-1,5-hexadiene. Tetramethylsilane is the internal standard.

(13.6 mmole) of anhydrous cobaltous chloride and 0.332 g. (13.6 mg. atom) of resublimed magnesium in 25 ml. of ether in a round-bottomed flask fitted with reflux condenser and drying-tube, was added a solution of 1.99 g. (12.3 mmole) of 1-bromo-3,5-hexadiene in 20 ml. of ether over 0.5 hr. The dark mixture was refluxed for 8 hr., then stirred for 15 hr. at room temperature. Excess solid carbon dioxide was added, but no carboxylic acid was obtained. The neutral fraction was isolated as described in the preparation of 4,6-heptadienoic acid and examined by v-p-c at 142° prior to distillation. It showed peaks at 0.3 (15%), six peaks from 0.6 to 7.9 (8%), 9.8 (29%, 1,4-dicyclopropyl-1,5-hexadiene), 12.3 (7.5%), and 17.7 min. (40%, 1,6-dicyclopropyl-1,5-hexadiene). The peak of shortest retention time may be an artifact from the solvent. The product was microdistilled at 40 mm. with a bath at 140-160° and gave 0.408 g. (40.8%) of distillate and 0.31 g. of tar. The peak at 12.3 min. was broad and probably was a composite peak due to at least two substances. This peak was not present in the neutral fraction from the carboxylation of the Grignard reagent. Its main component was isolated in very small yield by preparative v-p-c (Fraction II) as described in the preceding section. The infrared spectrum of Fraction II showed bands at 3075, 3000 due to vinyl CH; 1662, 959 for -CH=CH- adjacent to cyclpropyl; 1650, 1600 from conjugated C=C; 1000 and 897 due to $-CH=CH_2$; 950 for -CH=CH- conjugated; and 1042, 1018 cm^{-1} from cyclopropyl. It is thus almost a superposition of typical cyclopropylallyl- and 3,5-hexadienyl- group bands observed previously. The n-m-r spectrum of Fraction II (see next page) exhibited complex vinyl region, unsymmetrical methylene quintet, broad strongly split multiplet due to overlapping methylene and cyclopropyl methine resonances, and complex cyclopropyl methylene peaks in the 9.5 to 10 τ region. The spectral evidence is best accommodated by the structure of 1-cyclopropyl-1,6,8-nonatriene, composed formally of coupled γ-cyclopropylallyl- and 3,5-hexadien-1-yl units. The perturned methylene quintet in its n-m-r spectrum probably arises from overlap of the C_3 and C_5 methylene resonances, while the C_4 methylene resonance superposes the cyclopropyl methine multiplet. Inspection of the spectrum showed that the intensities of the peaks were in approximately the correct ratio.

(b) Allyl Bromide.— A solution of 3.21 g. (19.9 mmole) of 1-bromo-3,5-hexadiene, in 15 ml. of ether was added dropwise to 2.9 g. (0.12 mg. atom) of magnesium turnings in 10 ml. of ether over 5 hr. The formation and reaction of the Grignard reagent were conducted in an atmosphere of prepurified nitrogen at all times. The Grignard solution was stirred for a further hour, then filtered through a sintered-glass disk to remove unreacted magnesium. To the filtrate was added 2.42 g. (20 mmole) of allyl bromide over 10 min. The mixture became warm and turned cloudy due to formation of magnesium bromide. It was stirred at room temperature for 15 hr., then water was added, the ether layer was separated, washed with water, dried over sodium sulfate and

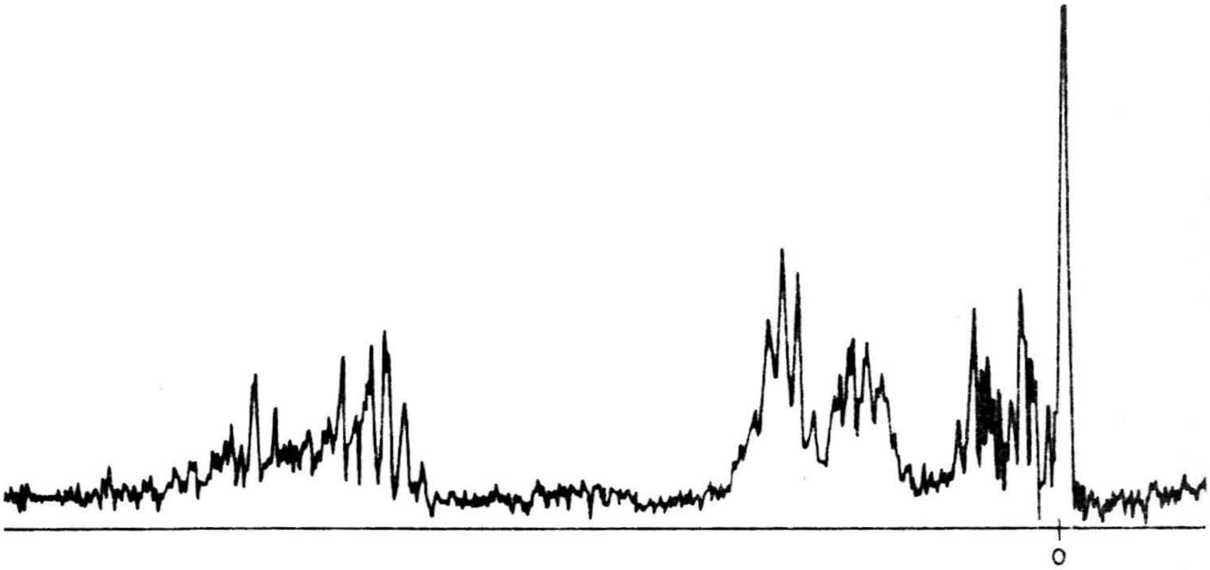

Fig. 20.— Proton n-m-r spectrum of Fraction II from reaction of cobaltous chloride with the Grignard reagent from 1-bromo-3,5-hexadiene. Probable structure: 1-cyclopropyl-1,6,8-nonatriene.

evaporated. The residue was examined by v-p-c at 140° and showed several small peaks of short retention time, three larger peaks due to the main products of the coupling reaction and smaller peaks due to 1,4-dicyclopropyl-1,5-hexadiene and 1,6-dicyclopropyl-1,5-hexadiene. The relative amounts of the latter were not determined, but they were formed to a significant extent.

The product was analyzed (134) by preparative v-p-c on the Megachrom at 60° under conditions similar to those described for the separation of the dicyclopropyldienes. There were obtained three fractions: Fraction I, at 30.2 min. (6%); Fraction II at 59 min. (87%); and Fraction III at 67.5 min. (7%). The relative percentages of the components were determined on a Beckman GC-2 vapor fractometer prior to separation. Unfortunately, the yields of Fractions I and III were too small to obtain elemental analyses. However, their spectra provided convincing evidence for their structures. The infrared spectrum of Fraction I in carbon tetrachloride showed bands at 1636, 992 and 912 due to $-CH=CH_2$ and at 1015 and 1042 cm^{-1} for cyclopropyl. Fraction II displayed bands at 1649, 1600 due to C=C conjugated; 1637 for lone C=C; 1000, 898 (lone), 908 (conjugated) due to $-CH=CH_2$, and 947 cm^{-1} from $-CH=CH-$. Fraction III showed bands at 1662, 959 for $-CH=CH-$; 1636, 1000 910 due to $-CH=CH_2$; and 1018, 1042 cm^{-1} for cyclopropyl. The n-m-r spectrum of Fraction I (see next page) exhibited complex vinyl resonances

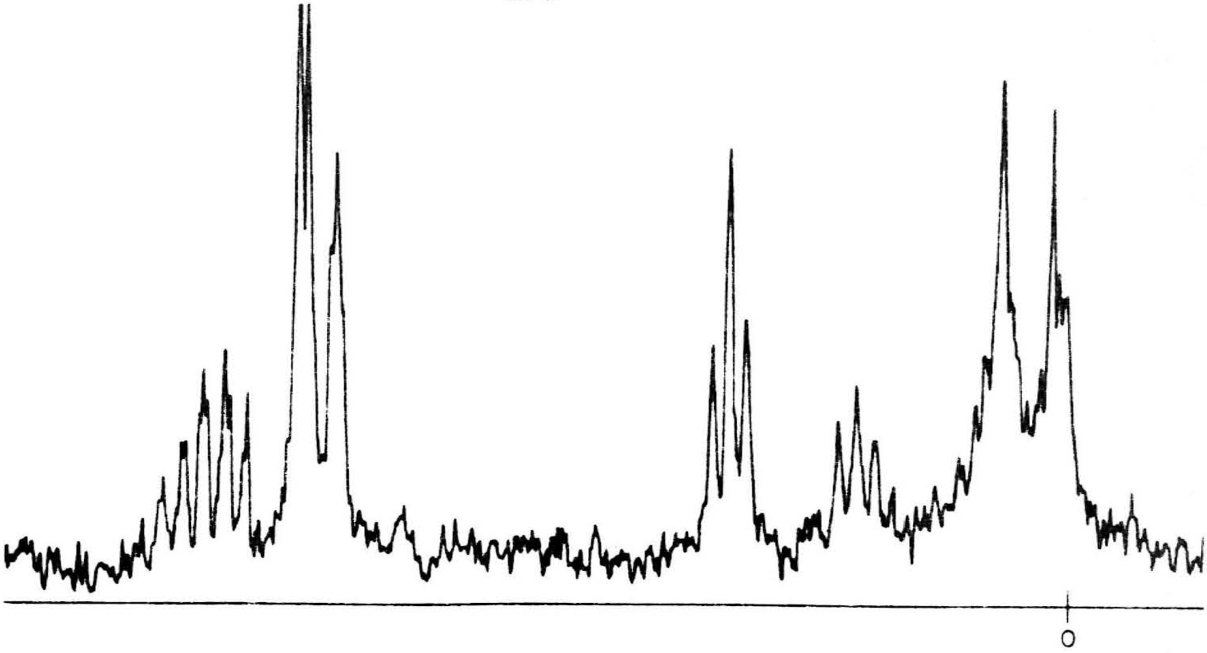

Fig. 21a.— Proton n-m-r spectrum of 3-cyclopropyl-1,5-hexadiene. Tetramethylsilane is internal standard (not shown).

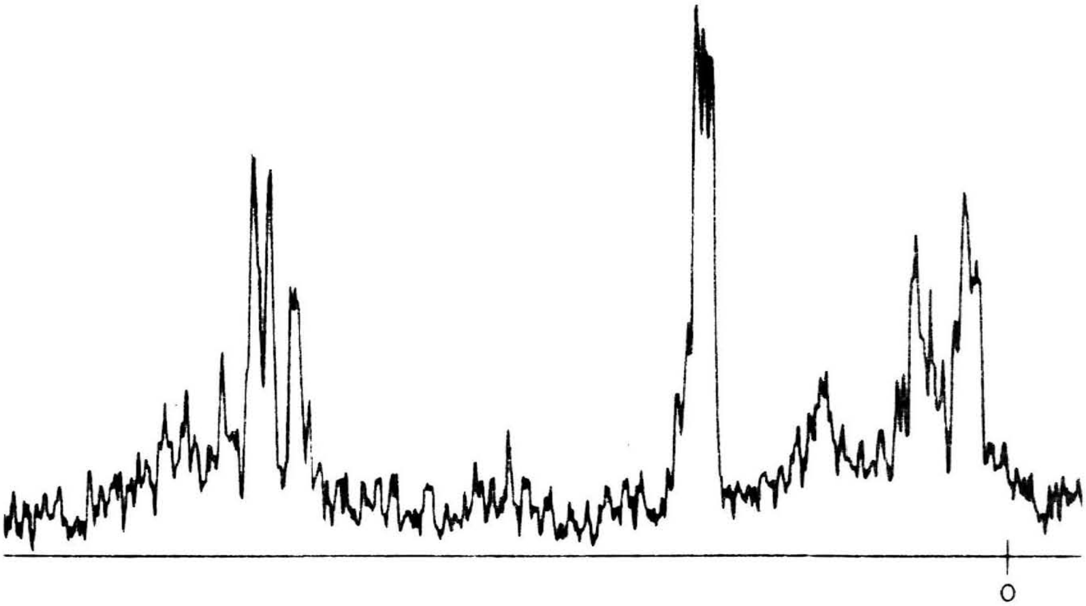

Fig. 21b.— Proton n-m-r spectrum of 1-cyclopropyl-1,5-hexadiene. Tetramethylsilane is internal standard (not shown).

including $=CH_2$, methylene triplet, perturbed methine quintet, cyclopropyl methine multiplet and cyclopropyl methylene peaks near 9.5 to 10 τ. It is interesting to note that the side-chain methine hydrogen is more shielded than the methylene hydrogens. This is the reverse of the usual order and can be explained on the basis of high population of conformations in which the methine hydrogen is eclipsed with the cyclopropyl ring and experiences a diamagnetic cyclopropane ring-current effect (see Part II of this thesis). A similar anomaly was noted in the case of 1,4-dicyclopropyl-1,5-hexadiene. Fraction II showed complex vinyl peaks, methylene quartet, and perturbed methylene quintet. Fraction III (see page 176) exhibited vinyl $=CH-$ and $=CH_2$ peaks, large methylene multiplet consisting of three closely-spaced peaks and cyclopropyl methylene and methine region. The appearance of the methylene peaks was very similar to that found for 1,6-dicyclopropyl-1,5-hexadiene.

These spectra demonstrate conclusively that Fraction I is *3-cyclopropyl-1,5-hexadiene*, that Fraction II is *nona-1,3,8-triene*, and that Fraction III is *1-cyclopropyl-1,5-hexadiene*. Nona-1,3,8-triene had $n^{22}D$ 1.4668.

Anal. Calcd. for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.39; H, 11.50.

(c) *Ethanol*.— The Grignard reagent was prepared from 3 g. (18.6 mmole) of 1-bromo-3,5-hexadiene in 15 ml. of ether and 2.8 g.

(0.115 g. atom) of magnesium turnings in 10 ml. of ether under prepurified nitrogen exactly as in section (b). After 0.5 hr. of stirring, 2 ml. of absolute ethanol in 5 ml. of ether was added dropwise over 15 min. Use of the isolation procedure described in (b) gave a hydrocarbon product which on analysis by v-p-c at 160° showed several low-retention time products and a small amount of the two cyclopropylallyl coupling products. Re-examination by v-p-c at 38° showed peaks at 5.2, 5.5, 5.8 (small); 7.0, allylcyclopropane (10%); 9.3, 1,3-hexadiene (77%); 11.9 and 12.7 (13%). The percentages given are for the four main components relative to their total, and are not precise due to difficulties of resolution in the v-p-c. They may be somewhat high for the minor components. Comparison with the v-p-c of the volatile products previously trapped during distillation of the neutral fraction from reaction of the Grignard reagent with carbon dioxide, showed that 1,3-hexadiene and allylcyclopropane were major components of the latter. Several other unidentified peaks were also present.

The ethanol product was analyzed (134) by preparative v-p-c on the Megachrom at 25° and gave Fraction I at 29.0 min., Fraction II at 34.0 min., and Fraction III corresponding to peaks at 45.0 and 48.3 min. No peak corresponding to cyclohexene was detected in this, or any of the previous v-p-c analyses of the ethanol product, indicating that formation of cyclohexenyl Grignard reagent by cyclization of the hexadienyl Grignard reagent does not occur to a detectable extent. The infrared spectrum of Fraction I was identical with that of allylcylopropane (2) except for bands at 1118 and 1378 cm^{-1} due to an impurity which overlapped the allylcyclopropane peak slightly in the _v-p-c_. Fraction II generated bands at 1598, 1648 due to C=C conjugated; 897 and 1000 for $-CH=CH_2$; and 947 cm^{-1} due to -CH=CH- . Fraction III showed bands at 1651, 1665, due to _cis_ and _trans_-HC=CH-; 712 for _cis_ -CH=CH-(?); 958 for _trans_ -CH=CH- ; 1018 and 1042 due to cyclopropyl; and an unidentified band at 972 cm^{-1}. The relative proportion of the constituents of Fraction III as measured from the Megachrom curve was 64.5% for the 45 min. peak and 35.5% for the 48.3 min. peak. The _n-m-r_ spectrum of Fraction I was identical with that of authentic allylcyclopropane (2) except for a small midfield triplet and moderate-sized peaks, due to the impurity, between the methylene and cyclopropyl peaks of allylcyclopropane. Fraction II exhibited complex vinyl peaks, perturbed methylene quintet and methyl triplet. Thus in 1,3-hexadiene the multiplicity of the β-methylene resonance agrees with that predicted by first-order analysis, although the observed quintet is not binomial, the central component being relatively less intense than usual. Fraction III showed strongly split vinyl =CH-, unsymmetrical methyl triplet and complex cyclopropyl peaks in the 9.5 to 10 τ region. The methyl resonance could arise from a superposition of two methyl doublets of unequal intensity.

The spectral data indicate that Fraction I is predominantly allylcyclopropane, Fraction II is 1,3-hexadiene and Fraction III is probably a mixture of *cis*- and *trans*-*propenylcyclopropane*. The evidence for the last assignment is not rigorous, however, since the yield of Fraction III was very low and spectra were taken with rather dilute solutions. It is not known which isomer predominates in the mixture.

(d) *Oxygen.*— The Grignard reagent was prepared using the same quantities and procedure as in Section (c), except that the bromide was dissolved in 20 ml. of ether and the addition period was 7 hr. Dry oxygen was then passed over the surface of the Grignard solution for 3 hr. with stirring. Saturated aqueous ammonium sulfate solution, 4 ml., in 30 ml. of water was added and the products isolated as described in section (b). *V*-*p*-*c* analysis at 140° showed peaks of short retention time due to allylcyclopropane, 1,3-hexadiene and two other unidentified components; a peak due to 3,5-hexadien-1-ol and at least three other alcohols; and sizeable peaks for 1,4-dicyclopropyl-1,5-hexadiene and 1,6-dicyclopropyl-1,5-hexadiene. The proportion of the low-boiling hydrocarbons and cyclopropylallyl coupling products relative to the main products (the alcohols) was considerably greater than in reactions (b) and (c). The *v*-*p*-*c* resolution of the alcohol peaks was not sufficiently good to obtain relative percentages for all the alcohols, but the alcohol having the lowest retention time was well separated from the others, and was formed to the relative extent of 34% while 3,5-hexadien-1-ol and the other alcohols of longer retention time made up 66%.

The product was analyzed (134) by preparative v-p-c on the Megachrom at 90° and gave Fraction I at 10.1 min., Fraction II, 3,5-hexadien-1-ol at 17.0 min., Fraction III at 21.7 min. and a very small fourth fraction at 25.0 min. for which no definite structural assignment was made. The infrared and n-m-r spectra of Fraction II, $n^{22}D$ 1.4830, were identical with those of authentic 3,5-hexadien-1-ol. The infrared spectrum of Fraction I in carbon tetrachloride showed hydroxyl bands at 3600, 3390, 1023 (conjugated C-O); and bands at 1641, 920 and 990 cm^{-1} due to $-CH=CH_2$. Cyclopropyl bands in the 1000-1040 region were obscured by the large C-O stretching peak at 1023 cm^{-1}. Fraction III showed bands at 3605, 3360, 1005 for hydroxyl; 1662, 1632 due to C=C; 960 for -CH=CH- ; 1018 and 1042 cm^{-1} due to cyclopropyl. The n-m-r spectrum of Fraction I (see next page) exhibited vinyl =CH- and $=CH_2$ peaks, hydroxyl singlet partly overlapping methine triplet, and cyclopropyl peaks in the 9.5 to 10 τ region. Fraction III (see page 183) showed vinyl -CH= peaks, a small methylene doublet and a large methylene doublet at slightly higher field, hydroxyl singlet and cyclopropyl peaks. The spectral evidence demonstrates that Fraction I is vinylcyclopropylcarbinol and that Fraction III is a mixture of cis- and trans-γ-cyclopropylallyl alcohol. It is not known which isomer predominates in

Fig. 22a.— Proton n-m-r spectrum of vinylcyclopropylcarbinol. Tetramethylsilane is internal standard.

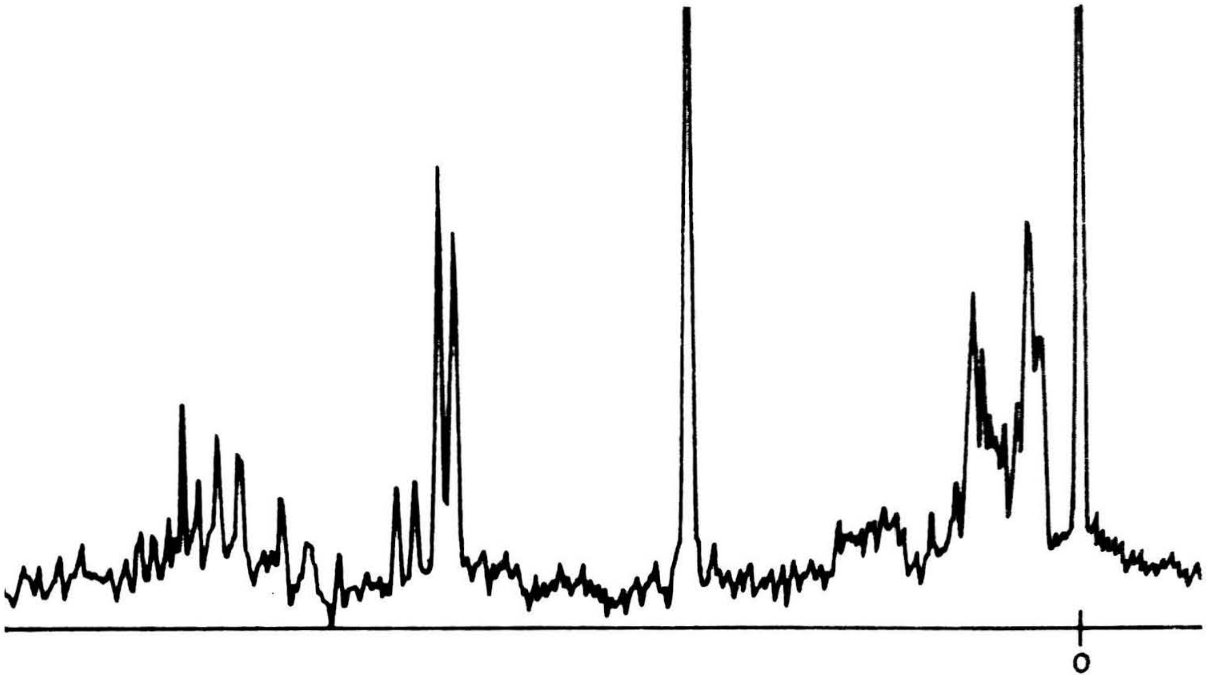

Fig. 22b.— Proton n-m-r spectrum of a mixture of cis- and trans-γ-cyclopropylallyl alcohol. Tetramethylsilane is internal standard.

Fraction III, but the relative intensity of the methylene doublets in the n-m-r indicates that one isomer predominates by a ratio of about 3:1 over the other. The v-p-c retention times of the products from each reaction (a), (b), (c) and (d), follow a general rule in that the retention times decrease for the order of radicals, γ-cyclopropylallyl > hexa-3,5-dienyl > α-cyclopropylallyl.

β-Carbomethoxy-γ,γ-diphenylvinylacetic acid was prepared by Stobbe condensation of 29.2 g. (0.16 mole) of benzophenone and 35.2 g. (0.241 mole) of dimethyl succinate with potassium t-butylate using the procedure of Johnson and Daub (135). The only modifications were the addition of 16 ml. of benzene to the reaction mixture to prevent crystallization of the t-butyl alcohol in the condenser, and the use of dimethyl instead of diethyl succinate. The wet crystalline product was not purified further, but was used directly in the ensuing decarboxylation reaction. A dried sample had m.p. 128-129°.

γ,γ-Diphenylvinylacetic acid was prepared from the above approximately 40 g. (0.136 mole) of β-carbomethoxy-γ,γ-diphenylvinylacetic acid by hydrolysis and decarboxylation in a refluxing mixture of 635 ml. of glacial acetic acid, 423 ml. of 48% aqueous hydrobromic acid and 212 ml. of water, using the method of Johnson, et al. (136). The diacid product was recrystallized from aqueous ethanol and gave first crop, 28.6 g., m.p. 117.5-119°; second crop, 4.9 g., m.p. 117-119° (total 87.7% based on benzophenone), lit. (136) m.p. 117.5-118.5°.

4,4-Diphenyl-3-buten-1-ol-1,1-$\underline{d}_2$.— A solution of 14 g. (58.9 mmole) of γ,γ-diphenylvinylacetic acid in 80 ml. of ether was added dropwise to a solution of 2.02 g. (48.1 mmole) of lithium aluminum deuteride in 75 ml. of ether over 0.5 hr. The mixture was refluxed for 4 hr. then stirred for 40 hr. at room temperature. A solution of 5 g. of ammonium sulfate in 50 ml. of water was added and the resulting precipitate was removed by filtration through Celite. The ether layer of the two-phase filtrate was separated and the aqueous layer was extracted with two 30-ml. portions of ether. The combined ether extracts were washed with water, dried over sodium sulfate, and evaporated. The residue was distilled through a Claisen head and gave 9.82 g. (74%) of 4,4-diphenyl-3-buten-1-ol-1,1-$\underline{d}_2$, b.p. 164-165° (2 mm.), $\underline{n}^{24}$D 1.6069. The n-m-r spectrum of a carbon tetrachloride solution of the product showed phenyl singlet, vinyl triplet, hydroxyl singlet and β-methylene doublet in agreement with the required structure. No α-methylene resonance was observed.

4, 4-Diphenyl-1,1-$\underline{d}_2$-but-3-en-1-yl p-Toluenesulfonate.— 10 g. (52.5 mmole) of p toluenesulfonyl chloride was added to a solution of 9.5 g. (42 mmole) of 4,4-diphenyl-3-buten-1-ol-1,1-$\underline{d}_2$ in 14 g. (0.177 mole) of pyridine over 15 min. with ice-cooling and stirring. After a further 15 min. the ice-bath was removed, the mixture was stirred for a further 6 hr. at room temperature, then poured into water and extracted with four 100-ml. portions of ether. The ether layer was washed repeatedly with water, dried over calcium sulfate and evaporated. The residue was 12.9 g. (80.5%) of 4,4-diphenyl-1,1-$\underline{d}_2$-but-3-en-1-yl p-toluenesulfonate, m.p. 82-84°.

4,4-Diphenyl-1-bromo-3-butene-1,1-$\underline{d}_2$. - A solution of 12.9 g. (33.9 mmole) of 4,4-diphenyl-1,1-$\underline{d}_2$-but-3-en-1-yl p-toluenesulfonate and 15 g. (0.143 mole) of lithium bromide in 150 ml. of acetone was refluxed for 3 hr. Most of the acetone was distilled off and the residue was treated with 50 ml. of water and extracted with four 75-ml. portions of pentane. The pentane extracts were washed with water, dried over sodium sulfate and evaporated. The residue was chromatographed on 100 g. of pentane-washed alumina. Elution of the alumina column with pentane (8 x 300 ml.) gave an eluate which was distilled through a micro-Claisen head and yielded 8.71 g. (89%) of 4,4-diphenyl-1-bromo-3-butene-1,1-$\underline{d}_2$, b.p. 157-160°(2 mm.), $\underline{n}^{23}$D 1.6157. The n-m-r spectrum of the product in carbon tetrachloride showed phenyl singlet, vinyl triplet, β-methylene doublet and several very small peaks including three peaks close to phenyl due to an unidentified impurity. The latter did not interfere in any way with the preparation, or interpretation of the n-m-r spectrum, of the derived Grignard reagent. No α-methylene peaks were detected. The infrared spectrum of the product was identical with that of (γ,γ- diphenylallyl)-carbinyl bromide except for the absence of a band at 1270 cm^{-1} and the appearance of bands at 1135, 1000 cm^{-1}.

Grignard Reagent from 4,4-Diphenyl-1-bromo-3-butene-1,1-$\underline{d}_2$.— The apparatus and techniques used for preparing the Grignard reagent in the form of an n-m-r sample have been described by Nordlander (3). The Grignard reagent was maintained in an atmosphere of prepurified nitrogen throughout its preparation and transfer to an n-m-r tube. High-purity resublimed magnesium (0.15 g., 6.16 mg.atom) in 5 ml. of ether was activated by addition of several drops of 1,2-dibromoethane. A solution of 0.65 g. (2.25 mmole) of 4,4-diphenyl-1-bromo-3-butene-1,1-$\underline{d}_2$ in 7 ml. of ether was added dropwise with magnetic stirring at 20° over 1.75 hr. The mixture was stirred for 3 hr. at 20° and magnesium was noticeably consumed. It was filtered through a fritted-glass disk and most of the ether was evaporated at 20° by passage of a current of nitrogen over the surface of the solution. This stage took 1 hr. The residual Grignard solution was poured into n-m-r tubes attached to the evaporation flask, and these were sealed under nitrogen and cooled in Dry-Ice until examined by n-m-r. The n-m-r spectrum of the Grignard reagent was taken 6.25 hr. after the start of its preparation and was found to be invariant with time. This fact and the presence of a sizeable α-methylene singlet at high-field indicated that rearrangement of deuterium to the β-position in the Grignard reagent was already complete by the time the first spectrum was taken. In another preparation this time was 5 hr., so that equilibration of the α- and β-positions was complete in less than 5 hr. at 20°. The spectrum also indicated the presence of substantial amounts of 1,1-diphenylbutene, with deuterium in the 3- and 4-positions, which gave rise to midfield methylene peaks, and a vinyl singlet superimposed on a vinyl triplet, both appearing near a similar pattern for the Grignard reagent. Since the Grignard reagent was prepared under conditions which were rigorously anhydrous and which were very unlikely to leave any bromide unreacted, the presence of 1,1-diphenylbutene is the only tenable explanation for the second vinyl multiplet. Thus it is very probable that the latter is formed during reaction of the bromide with magnesium. The phenyl resonance consisted of two main peaks showing secondary splitting, which are probably due to the phenyl group in the Grignard reagent and in 1,1-diphenylbutene, which are chemically shifted. A broad peak was also evident between the methyl resonance of the ether and its upfield ^{13}C-satellite which, in view of its high-field position, was attributed to cyclopropyl hydrogens. The cyclopropyl multiplet could arise either from deuterated diphenylcyclopropylmethane formed during reaction of the bromide with magnesium or from the diphenylcyclopropylcarbinyl form of the Grignard reagent, or both. The ratio of the area of this peak to that of the α-methylene singlet of the Grignard reagent was 1:1.87. Thus the molar ratio of diphenylcyclopropylcarbinyl compounds to total Grignard reagent was 1:3.74, assuming that the cyclopropyl peak arises from two hydrogens per molecule.

When 71.3 g. (2.23 mmole) of anhydrous methanol was added to the _n-m-r_ sample of the Grignard reagent a dense white precipitate was formed, most of which on centrifugation went to the top of the tube. The _n-m-r_ spectrum of the liquid product was drastically simplified relative to that of the Grignard reagent. Superimposed vinyl triplet and singlet due to the α- and β-deuterated forms of 1,1-diphenylbutene respectively, a methylene triplet for the α-deuterated hydrocarbon and a small broad peak in the cyclopropyl region were observed. The ratio of the intensity of the cyclopropyl peaks to the vinyl peaks was 1: 6.96. Thus the relative proportion of deuterated diphenylcyclopropylmethane formed is calculated to be 7%, in reasonable agreement with the value 5% found in an earlier preparative reaction. A second preparation of the Grignard reagent was carried out as before by adding a solution of 1.3 g. of the deuterated bromide in 14 ml. of ether to 0.3 g. of magnesium in 10 ml. of ether at 29° over 0.75 hr. The mixture was stirred for 2.25 hr. at 29°, then filtered and evaporated at 20° for 0.75 hr. Half of the residue was transferred to an _n-m-r_ tube and its spectrum examined. The spectrum differed somewhat from that of the first preparation, particularly in the detail of the cyclopropyl region, which consisted of several distinct lines rather than a single broad peak. The other half of the residue was evaporated to dryness and 5 ml. of dry benzene was added, then evaporated. A further 5 ml. of benzene was added, followed by a solution of 0.73 g. (4.56 mmole) of bromine in 3.2 ml. of benzene. This corresponds to about the two equivalents necessary to react with the Grignard reagent and saturate the double-bonded compounds. The product was filtered and evaporated. The n-m-r spectrum of the residue in carbon tetrachloride was very complicated in the methylene and methyl regions. However, several small peaks were detected in the cyclopropyl region which were very similar in appearance and chemical shift to those, relative to tetramethylsilane as internal reference, present in the spectrum of the parent Grignard reagent. These are attributed to deuterated diphenylcyclopropylmethane, and at least part of the cyclopropyl resonance in the spectrum of the Grignard reagent probably arises from the latter. Any diphenylcyclopropylcarbinyl bromide formed from the Grignard reagent is expected to isomerize rapidly to (γ,γ-diphenylallyl)-carbinyl bromide on the basis of earlier failures to isolate the former bromide under mild conditions.

The n-m-r spectrum of unlabelled Grignard reagent from (γ,γ-diphenylallyl)-carbinyl bromide and chloride were taken by Nordlander (39). The resolution was not as good as obtained with the deuterated Grignard reagent so that detection of the cyclopropyl peaks was more difficult, although twice as many hydrogens would be giving rise to these peaks. Only small broad peaks were observed in the cyclopropyl region. A significant feature of these spectra was the appearance of part of the methyl triplet of 1,1-diphenylbutene just to the high-field side of the ether methyl peaks.

4-Methylpentane-1, 4-diol-1, 1-$\underline{d}_2$.— To a solution of 4.2 g. (0.095 mole) of lithium aluminum deuteride in 70 ml. of ether was added a solution of 19.3 g. (0.169 mole) of 4, 4-dimethyl-4-butyrolactone in 50 ml. of ether over 0.5 hr. The mixture was refluxed for 17 hr., then 5 ml. of methanol and 6.1 ml. of saturated aqueous ammonium sulfate were added. The resulting mixture was refluxed for 1 hr. and filtered. The filter cake was extracted with ether and the combined ether solutions were evaporated. Distillation of the residue through a Claisen head afforded a forerun, 2.78 g., b.p. 70-85° (1.5 mm.) and 4-methylpentane-1, 4-diol-1, 1-$\underline{d}_2$, 14.4 g., b.p. 85-86° (1.5 mm.), lit. (137) for unlabelled compound, b.p. 99-101° (2.4 mm.). The forerun was redistilled through a micro-Claisen head and gave a fraction b.p. 37-87° (2 mm.) which was discarded, and 4-methylpentane-1, 4-diol-1, 1-$\underline{d}_2$, 2.04 g., b.p. 87-90° (2 mm.), (total 81.2%). The n-m-r spectrum of a chloroform solution of the product showed two separate hydroxyl singlets, a methylene singlet and a large methyl singlet. The C_2 and C_3 methylene hydrogens presumably have the same chemical shift. When one drop of hydrochloric acid was added to the n-m-r sample the two hydroxyl singlets collapsed to a single peak of double the intensity of each, because of rapid proton exchange.

1, 4-Dibromo-4-methylpentane-1, 1-$\underline{d}_2$ was prepared by the method of Willimann and Schinz (137). A solution of 16.5 g. (0.137 mole) of 4-methylpentane-1, 4-diol-1, 1-$\underline{d}_2$ in 5 g. of pyridine was added dropwise to 30.3 g. (0.112 mole) of phosphorous tribromide at 0° over 1 hr. The mixture was stirred for 2 hr. at room temperature and most of the product was distilled from the reaction flask through a Claisen head, b.p. 85-123° (80 mm.). The residue was poured into water, extracted with ether, and the ether extract was washed with sodium bicarbonate solution and water, dried over sodium sulfate and evaporated. The resulting oil was microdistilled at 83 mm. with a bath at 125° and gave 1.58 g. of distillate. Redistillation of the main fraction through a Claisen head yielded 25.1 g. (total 79.3%) of crude product, b.p. 80-128° (65 mm.), lit. (137) b.p. 105-111° (85 mm.). The n-m-r spectrum of the main fraction showed small vinyl triplet and singlet, a small methylene doublet, broad methylene singlet and large methyl singlet due to 1,4-dibromo-4-methylpentane-1,1-$\underline{d}_2$; and medium methyl singlet just upfield of the latter. The extraneous peaks not due to the required dibromide are attributed to 1-bromo-4,4-dimethyl-3-butene-1,1-$\underline{d}_2$ and 1-bromo-4-methyl-4-pentene-1,1-$\underline{d}_2$ formed by elimination of the elements of hydrogen bromide in two ways from the dibromide.

1-Bromo-4,4-dimethyl-3-butene-1,1-$\underline{d}_2$ (Attempted).— The procedure was similar to that of Willimann and Schinz (137). A solution of 26.6 g. (0.108 mole) of the crude 1,4-dibromo-4-methylpentane-1,1-$\underline{d}_2$ (from the reaction described in the previous section) in 9.5 g. (0.12 mole) of pyridine, was slowly warmed with an oil-bath.

When the temperature of the bath reached about 80° pyridine hydrobromide began to precipitate out. The temperature of the bath was raised slowly to 100°, then held there for 15 min. The product was distilled directly through a Claisen head and gave 12.6 g. (71%) of a mixture of unsaturated bromides, b.p. 85-90° (90 mm.), lit. (137) for 1-bromo-4,4-dimethyl-3-butene, b.p. 84-85° (84 mm.). In the v-p-c, the distillate showed a single peak with a shoulder on the low retention time side, indicating that it consists of at least two structurally different bromides of similar boiling point. The infrared spectrum of the product in carbon tetrachloride showed bands at 1648, 892 due to $C=CH_2$ and at 1668 cm^{-1} due to $C=CH-$, among others. Its n-m-r spectrum exhibited vinyl triplet, broad methylene doublet and methyl doublet due to 1-bromo-4,4-dimethyl-3-butene-1,1-d_2; and broad vinyl singlet, broad mid-field singlet and an upfield quartet attributed to 1-bromo-4-methyl-4-pentene-1,1-d_2. The n-m-r spectrum indicated that comparable amounts of the two bromides were formed in the elimination reaction. No evidence was found for rearrangement of the deuterium in 1-bromo-4,4-dimethyl-3-butene-1,1-d_2 in the product.

The product was dissolved in ether, washed with 10% potassium carbonate solution and water, dried over sodium sulfate and evaporated. The two bromides postulated to compose the bulk of the product could not be separated by distillation through a center-rod vacuum-jacketed column. In order to remove any possible allylic-type bromides present

10.4 g. (63 mmole) of the bromide mixture was dissolved in 75 ml. of acetone and 4.7 g. (31.3 mmole) of sodium iodide was added. The solution was stirred at room temperature for 0.5 hr., after which time a considerable precipitate of sodium bromide had formed. It was then poured into 750 ml. of water and extracted with four 150-ml. portions of pentane. The pentane extracts were washed with sodium bisulfite solution, sodium bicarbonate solution and water, dried over sodium sulfate and evaporated. The residue was distilled through a micro-Vigreux head and gave two fractions, b.p. 83-85° (90 mm.) and 85-87° (90 mm.). The *n-m-r* spectra of these fractions were essentially identical with that of the original bromide mixture indicating that no fractionation of the isomers had occurred, and therefore that one of them is unlikely to be allylic-type.

Reduction of (γ,γ-Diphenylallyl)-carbinyl Bromide with Triphenyltin Hydride.— Analysis of the products of a preliminary reduction of (γ,γ-diphenylallyl)-carbinyl bromide with tributyltin hydride was complicated by closely similar *v-p-c* retention times for tributyltin bromide, 1,1-diphenylbutene, **diphenylcyclopropylmethane**.The more reactive and higher-boiling triphenyltin hydride was therefore chosen as reducing agent. A mixture of 1.33 g. (3.79 mmole) of triphenyltin hydride and 1 g. (3.48 mmole) of (γ,γ-diphenylallyl)-carbinyl bromide was stirred for 48 hr. at room temperature while maintaining it in an atmosphere of prepurified nitrogen. Crystals of triphenyltin bromide, m.p. 112-

117°, lit. (171) m.p. 120.5°, settled out. The mixture was extracted with ether, the ether solution was evaporated, and the residue was microdistilled at 1.5 mm. with a bath at 160°, yielding 0.71 g. (98%) of distillate and 1.55 g. of residue. Examination of the distillate by the Loenco *v-p-c* at 250° showed peaks due to 1,1-diphenylbutene (86%) and diphenylcyclopropylmethane (14%), as well as small unidentified peaks of longer retention time.

The reaction was repeated by adding a solution of the hydride slowly to a solution of the bromide in inert solvent in order to observe any change in the proportions of the hydrocarbon products. A solution of 1.33 g. (3.79 mmole) of triphenyltin hydride in 10 ml. of hexane was added dropwise to a vigorously stirred solution of 1 g. (3.48 mmole) of (γ,γ-diphenylallyl)-carbinyl bromide in 10 ml. of hexane over 3.5 hr., while maintaining the system under nitrogen. The mixture was stirred for 18 hr. at room temperature, then the solvent was evaporated and the residue microdistilled at 2 mm. with a bath at 150-185°, yielding 0.86 g. of distillate and 1.44 g. of triphenyltin bromide, m.p. 117-120°, on crystallization from hexane. Analysis of the distillate by *v-p-c* at 240° showed peaks due to 1,1-diphenylbutene (88%, 87%, mean 87.5%) and diphenylcyclopropylmethane (12%, 13%, mean 12.5%). The relative proportion of the hydrocarbons was thus comparable to that obtained in the first reaction.

Reaction of N-Bromosuccinimide with Diphenylcyclopropylmethane.— N-Bromosuccinimide (1.5 g., 8.4 mmole), 1.56 g. (7.5 mmole) of diphenylcyclopropylmethane, and 17 mg. (0.104 mmole) of α,α'-azoisobutyronitrile in 6.5 ml. of carbon tetrachloride were refluxed for 2.5 hr. The cooled mixture was filtered to remove the upper layer of crystalline succinimide, 0.767 g. (92%). The filtrate was evaporated and the residue was microdistilled at 1.5 mm. with a bath at 160°, yielding 1.76 g. of distillate and 0.28 g. of tar. The product was unsaturated and gave a positive Beilstein halogen test. Its n-m-r spectrum showed peaks due to considerable unreacted diphenylcyclopropylmethane, to (γ,γ-diphenylallyl)-carbinyl bromide, which was the major bromide product, and to a host of polybrominated products derived from it.

Autoxidation of Diphenylcyclopropylmethane.— A stream of oxygen was passed through a refluxing solution of 2.78 g. (13.4 mmole) of diphenylcyclopropylmethane and 0.2 g. (1.22 mmole) of α,α'azoisobutyronitrile in 10 ml. of dry benzene for 8 hrs. The solution then gave a weak positive hydroperoxide test with acetic acid and potassium iodide. A further 0.3 g. of α,α'-azoisobutyronitrile was added and oxygen was passed through the refluxing mixture for 10 more hours. It then gave a somewhat stronger hydroperoxide test. However, no alcohols were isolated after hydrogenation of the mixture in the presence of platinum oxide and chromatography of the product on alumina. A total of 2.46 g.

(88.5%) of hydrocarbon was recovered which showed one peak in the v-p-c due to diphenylcyclopropylmethane. No 1,1-diphenylbutene was detected. The reaction was repeated under basic conditions to prevent inhibition (33) by acidic materials such as phenol. The reaction flask was washed with concentrated ammonium hydroxide, then oven-dried. A stream of oxygen was bubbled through a refluxing solution of 2.3 g. (11.1 mmole) of diphenylcyclopropylmethane and 0.3 g. of α,α'-azoisobutyronitrile in 5 ml. of chlorobenzene and 8 ml. of benzene in the presence of 0.5 g. of anhydrous sodium carbonate for 8 hr. The solution then gave a weakly positive test for hydroperoxide. Again no alcohols were obtained on hydrogenation and chromatography of the product on alumina, although tetramethylsuccinonitrile, m.p. 169-170°, was isolated and 2.15 g. (93%) of the diphenylcyclopropylmethane was recovered.

The rate of autoxidation of diphenylcyclopropylmethane was determined (51) using the apparatus and procedure described by Hammond et al. (50). The mixture to be oxidized consisted of a solution of 0.994 g. (4.77 mmole) of diphenylcyclopropylmethane and 2 ml. of a solution of 0.399 g. of α,α'-azoisobutyronitrile in 9.75 ml. of chlorobenzene, in 3 ml. of chlorobenzene. The kinetic measurements were carried out at a solution temperature of 70° and oxygen pressure of 745 mm. A plot of oxygen uptake versus time was linear up to 18 minutes, but thereafter fell off steadily indicating the operation of some sort of inhibition process. The rate was followed only to 3.2% uptake of the theoretical volume of oxygen. The initial rate of oxygen absorption was calculated to be 0.0765 ml. per minute by least squares.

<u>(γ, γ-Diphenylallyl)-carbinylmercuric Bromide</u>.— The Grignard reagent prepared from 5.76 g. (20 mmole) of (γ, γ-diphenylallyl)-carbinyl bromide and 0.6 g. of magnesium in 25 ml. of ether, as described previously for its reaction with phenylacetylene, was added dropwise to a vigorously stirred suspension of 8.22 g. (22.4 mmole) of mercuric bromide in 15 ml. of ether over 15 min. The mixture was refluxed for 2 hr., then stirred at room temperature for 24 hr. Water and 5% acetic acid were added, the ether layer was separated, washed with water and evaporated. The resulting solid was washed with hot 2% acetic acid on a Buchner funnel, then dried and crystallized from ethanol, and yielded 2.37 g. of (γ, γ-diphenylallyl)-carbinylmercuric bromide as needles, m.p. 117.5-120°. Two further crystallizations from ethanol and one from acetone gave an analytical sample, m.p. 123-124°. The mother liquors from the various crystallizations and washings were combined and evaporated and gave 2.24 g. of residue, which was chromatographed on 67 g. of pentane-washed alumina. Elution with pentane (8 x 250 ml.) and microdistillation of the eluate at 2.5 mm. with a bath at 140° afforded 0.743 (17.9%) of distillate. Examination of the distillate by <u>v</u>-<u>p</u>-<u>c</u> at

240° showed peaks due to 1,1-diphenylbutene (74%) and diphenylcyclopropylmethane (26%). Elution with ether (5 x 250 ml.) afforded 0.524 g. of (γ, γ-diphenylallyl)-carbinylmercuric bromide, m.p. 119.5-120.5°, after crystallization from ethanol. Thus the total yield of the mercurial was 29.5%. The infrared spectrum of a chloroform solution of the product showed aromatic absorption and bands at 1215, 1137, 1070 and 1030 cm^{-1}. The n-m-r spectrum of the mercurial in pyridine showed vinyl triplet, β-methylene quartet, and α-methylene triplet due to the presence of 16.9% of ^{199}Hg of spin 1/2 (138).

Anal. Calcd. for $C_{16}H_{15}HgBr$: C, 39.41; H, 3.10; Br, 16.39. Found: C, 39.32; H, 3.21; Br, 16.37.

1,1-Diphenylethylene from (γ, γ-Diphenylallyl)-carbinylmercuric Bromide.— A solution of 1.35 g. (2.78 mmole) of (γ, γ-diphenylallyl)-carbinylmercuric bromide and 1.14 g. (14.1 mmole) of hydrogen bromide in 12 ml. of glacial acetic acid was stirred at 85° for 6.5 hr., then for 38 hr. at room temperature. The mixture was poured into water and the acid was neutralized with sodium carbonate. The mixture was extracted with three 30-ml. portions of pentane, and the pentane extracts were washed with water, dried over sodium sulfate and evaporated. The residue was microdistilled at 2 mm. with a bath at 170° and gave 0.305 g. of distillate and 0.25 g. of tar. Examination of the distillate by v-p-c at 240° showed the main peak at 10.5 min. (82%), a peak at 15.5 min. (14%) due to 1,1-diphenylbutene, and an unidentified peak at 24 min. (4%). No peak corresponding to diphenylcyclopropylmethane was observed. The infrared spectrum of a carbon tetrachloride solution of the product showed phenyl absorption and bands at 1617 due to conjugated C=C, 1580 for conjugated phenyl, and 900 cm^{-1} (strong) due to $C=CH_2$. The n-m-r spectrum of the distillate showed large strongly-split phenyl peak, large vinyl singlet and other smaller peaks due to 1,1-diphenylbutene and the remaining products. This evidence indicated that the major product of the reaction was 1,1-diphenylethylene. The areas under the phenyl and vinyl n-m-r peaks were in the ratio 5.23:1, consistent with a mixture consisting mainly of 1,1-diphenylethylene plus small amounts of other phenyl-substituted compounds.

(γ,γ-Diphenylallyl)-acetonitrile.— A solution of 4.64 g. (16.2 mmole) of (γ,γ-diphenylallyl)-carbinyl bromide and 1.2 g. (18.2 mmole) of finely powdered potassium cyanide in 10 ml. of 95% ethanol was refluxed for 20 hr. A further 1.2 g. of potassium cyanide was added, and refluxing was continued for 8 more hours. Most of the ethanol was distilled off, the residue was poured into water and extracted with three 25-ml. portions of ether. The ether extracts were washed with water, dried over calcium sulfate and evaporated. The residue crystallized from methanol and gave (γ,γ-diphenylallyl)-acetonitrile, 2.38 g., m.p. 66-67.5°. Two further crystallizations from cyclohexane gave an analytical sample, m.p. 67.5-68.5°. The infrared spectrum of the product showed a sharp band at 2240 cm^{-1} due to $-C\equiv N$. A further 1.23 g. of the nitrile was isolated by chromatographing the mother liquors on alumina and eluting with benzene. Thus the total yield of crude nitrile was 95.8%. A satisfactory carbon analysis was not obtained. The nitrile was unsaturated.

Anal. Calcd. for $C_{17}H_{15}N$: C, 87.51; H, 6.48; N, 6.00. Found: C, 86.94; H, 6.31; N, 6.24.

5,5-Diphenyl-4-penten-1-ol.— A solution of 6.15 g. (24.4 mmole) of (γ,γ-diphenylallyl)-acetic acid in 50 ml. of ether was added to a solution of 1 g. (26.3 mmole) of lithium aluminum hydride in 25 ml. of ether over 15 min. The mixture was refluxed for 3 hr., stirred for 40 hr. at room temperature, then acidified with 2 N sulfuric acid. The ether layer was separated, the aqueous layer was extracted twice with ether, and the combined ether layers were washed with sodium bicarbonate solution and water, dried over sodium sulfate and evaporated. The residue was distilled through a Claisen head and gave 5.31 g. (91.5%) of 5,5-diphenyl-4-penten-1-ol as a viscous liquid, b.p. 174-177° (1.5 mm.), $n^{22.5}D$ 1.5959. The infrared spectrum of the product in carbon tetrachloride showed hydroxyl bands at 3600, 3330 and 1050 cm^{-1}, and aromatic absorption. Its n-m-r spectrum exhibited phenyl singlet, vinyl triplet, hydroxyl singlet, α-methylene triplet, β-methylene quintet and γ-methylene quartet, as expected.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.97; H, 7.65.

(γ, γ-Diphenylallyl)-acetyl chloride was prepared using the oxalyl chloride method of Wilds and Shunk (139), which gave a much cleaner product than did thionyl chloride. Water was added dropwise to a solution of 13.4 g. (53 mmole) of (γ, γ-diphenylallyl)-acetic acid in 15 ml. of methanol until the solution became cloudy. The mixture was then titrated with aqueous sodium hydroxide solution to phenolphthalein end-point. The solution was evaporated under reduced pressure on the rotary evaporator, then at 2 mm. for 2 hr., and finally at 2 mm. with a bath at 70° for 15 hr. in the presence of phosphorus pentoxide. The resulting sodium salt was finely powdered and suspended in 100 ml. of anhydrous ether. Pyridine (1 ml.) was added, followed by a solution of 11.9 g. (93.8 mmole) of freshly distilled oxalyl chloride, b.p. 60-61°, in 15 ml. of ether at -10°, as rapidly as the vigorous evolution of gas would permit. The mixture was stirred for 15 min. at -5° after the addition was complete, then allowed to warm to room temperature over 0.5 hr. The ether was evaporated under reduced pressure, 10 ml. of dry benzene was added, then evaporated, and the residue taken up in 30 ml. of benzene and filtered to remove sodium chloride. The filtrate was evaporated under reduced pressure and sufficient carbon tetrachloride was added to make a concentrated solution. The n-m-r spectrum of this solution showed phenyl peak, vinyl triplet and overlapping α-methylene triplet and β-methylene quartet, consistent with (γ, γ-diphenylallyl)-acetyl chloride.

N-Methyl-(γ, γ-diphenylallyl)-acetanilide.— A solution of 21.8 g. (0.203 mole) of N-methylaniline and 15.9 g. (0.202 mole) of pyridine in 80 ml. of dry benzene was added to a solution of (γ, γ-diphenyl allyl)-acetyl chloride, prepared from 50 g. (0.198 mole) of (γ, γ-diphenylallyl)-acetic acid, in 200 ml. of benzene over 0.5 hr. The reaction mixture became hot and pyridine hydrochloride precipitated out. Stirring was continued for 13 hr. at room temperature, then the mixture was poured into 2 N hydrochloric acid, the benzene layer was separated, and washed twice with 2 N hydrochloric acid, sodium bicarbonate solution and water. The benzene was distilled off and the product crystallized from cyclohexane and yielded 58 g. (85.7%) of N-methyl-(γ, γ-diphenylallyl)-acetanilide as prisms, m.p. 76-77.5°. An analytical sample was recrystallized from cyclohexane and had m.p. 77-78°. The n-m-r spectrum of the product in carbon tetrachloride showed phenyl peaks, vinyl triplet, N-methyl singlet and overlapping α- and β-methylene multiplets. Its infrared spectrum exhibited a strong band at 1662 cm^{-1} due to the anilide CO), and bands at 1125 and 1384 cm^{-1}.

Anal. Calcd. for $C_{24}H_{23}NO$: C, 84.42; H, 6.79; N, 4.10. Found: C, 84.04; H, 6.99; N, 4.07.

(γ, γ-Diphenylallyl)-acetaldehyde.— Attempts were made to prepare this aldehyde by reaction of the Grignard reagent from (γ, γ-diphenylallyl)-carbinyl bromide with ethyl orthoformate and hydrolysis of the resulting acetal, by lithium aluminum hydride reduction of (γ, γ-diphenylallyl)-acetonitrile, by oxidation of the tosylate from 5, 5-diphenyl-4-penten-1-ol with dimethyl sulfoxide and sodium bicarbonate at 150° (140), and by oxidation of 5, 5-diphenyl-4-penten-1-ol with chromic oxide in pyridine (141). None of these methods was feasible, although the infrared spectrum of the product of dimethyl sulfoxide oxidation of 5, 5-diphenyl-4-penten-1-yl p-toluenesulfonate indicated the presence of a considerable amount of the desired aldehyde. However, the latter could not be separated efficiently from side-products. The most successful preparation was based on the method of Weygand, et al. (142) and involved reduction of N-methyl-(γ, γ-diphenylallyl)-acetanilide with a deficiency of lithium aluminum hydride.

Lithium aluminum hydride, 1.12 g. (29.3 mmole), was added portionwise over 1 hr. to a solution of 25 g. (73.3 mmole) of N-methyl-(γ, γ-diphenylallyl)-acetanilide in 250 ml. of ether at 0° with stirring. The mixture was stirred for 7 hr. at 0°, then 2 N hydrochloric acid was added. The ether layer was separated, extracted three times with dilute hydrochloric acid, then washed with sodium bicarbonate solution and water, dried over sodium sulfate and evaporated. The infrared spectrum of the residue in carbon tetrachloride showed C=O bands at 1728 cm^{-1}

due to (γ, γ-diphenylallyl)-acetaldehyde and at 1662 cm^{-1} due to unreacted anilide. The latter was removed by dissolution of the product (19.4 g.) in benzene and filtration through a pad of 290 g. of alumina. The filtrate (1100 ml.) was evaporated and the residue was distilled through a Claisen head and gave 8.0 g. (46.3%) of (γ, γ-diphenylallyl)-acetaldehyde, b.p. 162-165° (2 mm.), $n^{26.5}$D 1.5940. The infrared spectrum of the product showed bands due to aldehyde C=O at 1728 cm^{-1} and C-H at 2720 and 2815 cm^{-1}. Its n-m-r spectrum in carbon tetrachloride showed broadened aldehyde singlet, phenyl peak, perturbed vinyl triplet and a group of three closely-spaced methylene peaks due to the α- and β-methylene groups. The spin-coupling constant between the formyl hydrogen and the α-methylene hydrogens was apparently very small.

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 85.98; H, 6.88.

The 2,4-dinitrophenylhydrazone was prepared and crystallized from ethanol-ethyl acetate as a mixture of two polymorphic forms which were separated by hand-picking; one, yellow needles, m.p. 140-141°, the other, orange prisms, m.p. 139-141°. The yellow form underwent a transition at 102°, turning orange and changing in crystalline shape but not melting.

(γ, γ-Diphenylallyl)-acetic Acid from (γ, γ-Diphenylallyl)-acetaldehyde.— To a solution of 1.5 g. (6.35 mmole) of (γ, γ-diphenylallyl)-acetaldehyde in 8 ml. of ethanol was added a solution of 3.65 g. (21.5 mmole) of silver nitrate in 7.5 ml. of water. Then a solution of 1.2 g. (30 mmole) of sodium hydroxide in 10 ml. of water was added over 3 hr. with stirring. The mixture was stirred for 18 hr. at room temperature and a silver mirror gradually formed. The solution was filtered and the filtrate was acidified with 3 N hydrochloric acid, then extracted with three 15-ml. portions of ether. The ether solution was extracted with a solution of 3 g. of sodium hydroxide in 50 ml. of water. The sodium hydroxide extracts were acidified with concentrated hydrochloric acid and extracted with three 20-ml. portions of ether. The combined ether extracts were washed with water, dried over sodium sulfate and evaporated. The residue crystallized from hexane and gave 0.779 g. (48.6%) of (γ, γ-diphenylallyl)-acetic acid. Recrystallization from cyclohexane afforded prisms, m.p. 81.5-82.5°, undepressed by admixture with authentic (γ, γ-diphenylallyl)-acetic acid. More of the acid crystallized out from the mother liquors of the first crystallization indicating that the actual yield of acid was somewhat greater than 48.6%.

Attempted Decarbonylation of (γ, γ-Diphenylallyl)-acetaldehyde.— The procedure and apparatus for carrying out preparative decarbonylations of aldehydes have been discussed in detail by Schuster (2), and were used in the present work. (γ, γ-Diphenylallyl)-acetaldehyde, 2.43 g. (10.3 mmole), was placed in a 25-ml. three-necked flask fitted with nitrogen inlet, reflux condenser and dropping funnel containing 0.226 g. (1.55 mmole) of di-t-butyl peroxide. The top of the condenser was connected to a calibrated separatory funnel filled with water and inverted in a trough of water. The system was flushed with prepurified nitrogen for 15 min., then the reaction flask was immersed in an oil-bath maintained at 140°. The nitrogen flow was continued for a short time, then the inlet was closed off. The di-t-butyl peroxide, b.p. 53-54° (106 mm.), was then added with stirring. After 1.5 hr. only 5 ml. of gas had been collected, so a further 0.225 g. of peroxide was added, followed by the same quantity 3 hr. later. After 7.5 hr. at 140°, only 25 ml. of gas had been evolved. The product was microdistilled at 2 mm. with a bath at 175-190° and gave 1.09 g. of distillate and 1.4 g. of tar. Examination of the distillate by the Loenco v-p-c at 280° showed four small peaks of retention time close to that of authentic 1,1-diphenylbutene as well as others of longer retention time, so that no definite assignment could be made. The size of the peaks in the region of interest indicated that the desired hydrocarbons could only constitute a very small fraction of the total product.

A second run was made with a solution of 2 g. (8.47 mmole) of aldehyde in 10 ml. of o-dichlorobenzene at 140°. A total of 45 mole %

of peroxide was added over 8.5 hr. and 65 ml. of gas was collected. The solvent was distilled off and the residue after microdistillation at 1.5 mm. with a bath at 175-190° gave 0.696 g. of distillate and 1.37 g. of tar. Analysis of the distillate by v-p-c at 275° showed small broad peaks at 30.5, 34.6 and 38.3 min. as well as large unidentified peaks at 47.5, 69.5 and 82.0 mins. Authentic 1,1-diphenylbutene and diphenylcyclopropylmethane gave peaks at 33.4 and 37.7 min., and could thus be only minor components of the product. Similar results were obtained in decarbonylations carried out at 150° with pure aldehyde, with solutions of the aldehyde in o-dichlorobenzene and decalin at 160°, and using pure aldehyde at 140° with steam passing through the condenser jacket to remove t-butyl alcohol and acetone (143).

In the v-p-c analyses of the products from all these reactions, the three unidentified peaks of long retention time were prominent. In some cases the infrared spectrum of the products showed a carbonyl band due to unreacted aldehyde. The three main components of the product are likely to be relatively non-polar compounds, such as hydrocarbons or ethers, since they were eluted from a column of alumina by pentane. The infrared spectrum of their mixtures were almost featureless, showing only phenyl absorption. Clearly, decarbonylation of the aldehyde was being inhibited by side-reactions.

t-Butyl (γ, γ-Diphenylallyl)-peracetate.– To a solution of (γ, γ-diphenylallyl)-acetyl chloride, prepared from 10.96 g. (0.04 mole) of sodium (γ, γ-diphenylallyl)-acetate, and 3.84 g. (42.4 mmole) of dry t-butyl hydroperoxide, b.p. 40-42° (25-30 mm.), in 80 ml. of ether at -5° was added a solution of 3.36 g. (42.4 mmole) of dry pyridine in 15 ml. of ether over 1 hr. Pyridine hydrochloride precipitated out; the solution was allowed to warm to room temperature, then was stirred for 1 hr. The reaction mixture was poured into 10% sulphuric acid, the ether layer was separated, washed with 10% sulphuric acid, twice with 10% sodium carbonate solution and with water, dried over sodium sulfate and evaporated under reduced pressure. The residue was chromatographed on a column of 50 g. of pentane-washed Florosil, and eluted with pentane (3 x 1 ℓ.). Crystallization of the eluate from pentane at 0° gave 8.17 g. (63%) of t-butyl (γ, γ-diphenylallyl)-peracetate as needles, m.p. 42-42.5° (corr.). The infrared spectrum of the product showed a characteristic perester C=O band at 1777 cm^{-1} and bands at 1387, 1365 and 2980 cm^{-1} due to the t-butyl group. Its n-m-r spectrum exhibited phenyl peaks, perturbed vinyl triplet, a group of closely-spaced peaks due to the α- and β-methylene hydrogens and a large t-butyl singlet. A satisfactory carbon analysis for the perester was not obtained, probably owing to slight deterioration of the sample prior to analysis, since the pure perester melted sharply.

Anal. Calcd. for $C_{21}H_{24}O_3$: C, 77.75; H, 7.46. Found: C, 76.68, 76.85, 77.26; H, 7.49, 7.30, 7.11.

t-Butyl 5,5-diphenylperpentanoate was prepared from 5,5-diphenylpentanoic acid by the same method as for t-butyl (γ,γ-diphenylallyl)-peracetate. Sodium 5,5-diphenylpentanoate, prepared from 23.6 g. (92.9 mmole) of acid, was suspended in 175 ml. of ether and 1.75 ml. of pyridine at -5° and a solution of 14 ml. of oxalylchloride in 24 ml. of ether was added over 0.5 hr. The solution was allowed to warm to room temperature, then stirred for 1 hr. The ether was evaporated and 30 ml. of dry benzene was added, then evaporated. A further 100 ml. of benzene was added, the mixture was filtered and the filtrate was evaporated to dryness. To a solution of the resulting acid chloride and 10.1 ml. of t-butyl hydroperoxide in 175 ml. of ether at -5° was added a solution of 8.3 ml. of pyridine in 30 ml. of ether over 0.5 hr. After allowing the mixture to stand for 40 hr. at 0° the product was isolated in the manner described previously for (γ,γ-diphenylallyl)-peracetate. The product was chromatographed on a column of 175 g. of pentane-washed Florosil, and elution with pentane (3 x 800 ml.) gave an oil, which on crystallization from pentane at 0° furnished 16.3 g. (53.8%) of t-butyl 5,5-diphenylperpentanoate. Recrystallization from pentane at 0° afforded 15.3 g. of flat needles, m.p. 50-50.5° (corr.). The infrared spectrum of the product in carbon tetrachloride showed strong perester CO) band at 1777 cm^{-1} and *t*-butyl bands at 1387, 1362 and 2980 cm^{-1}. Its *n-m-r* spectrum exhibited phenyl peak, methine triplet, overlapping methylene peaks due to the α-, β- and γ-methylene groups, and *t*-butyl singlet. No vinyl peaks were detected.

Anal. Calcd. for $C_{21}H_{26}O_3$: C, 77.27; H, 8.03. Found: C, 77.30; H, 8.01.

Thermal Decomposition of *t*-Butyl (γ, γ-Diphenylallyl)-peracetate in the Presence of Hydrogen Donors.—

(a) *Cumene*.— The apparatus and procedure for all runs were essentially the same as for the decarbonylation of (γ, γ-diphenylallyl)-acetaldehyde described earlier, except that, of course, no initiator was needed. The reactions were conducted in an atmosphere of nitrogen, the system having been swept with nitrogen for 15 min. prior to the start of the reaction. Only the temperature of the heating-bath was measured, but this probably approximated the temperature of the reaction mixture quite closely for the dilute solutions of the perester used. The perester, 2 g. (6.17 mmole), in 7 ml. of cumene, b.p. 150-151°, was heated in a bath at 110° for 16 hr. and 55 ml. of gas was collected. The theoretical volume of carbon dioxide was 138 ml. The solvent was distilled and the infrared spectrum of the residue showed a medium band at 1782 cm^{-1} possibly due to unreacted perester and weak C=O bands at 1710 and 1731 cm^{-1}. The residue was chromatographed on alumina, and elution with pentane (5 x 200 ml.) and microdistillation of the eluate at 3 mm. with a bath at 150-180° furnished 0.3 g. of distillate and 0.2 g. of tar. The distillate showed no carbonyl bands in the infrared, but analysis by Loenco v-p-c at 270° showed broad peaks at 2-25 min. due to dicumene, small peaks at 33.4 min. (92%) for 1,1-diphenylbutene and at 37.8 min. (8%) for diphenylcyclopropylmethane, a small peak at 60.5 min. and very large peaks at 68.9 and 81.2 min. The reaction was repeated with 2 g. of perester in 10 ml. of cumene at 140° and, after 2.5 hr., 105 ml. of gas was collected, most of it in the first half-hour. The infrared spectrum of the crude product showed a medium carbonyl band at 1782 cm^{-1}. After chromatography of the product and microdistillation of the eluate as described above there was obtained 0.358 g. of distillate and 0.2 g. of tar. Analysis of the distillate by v-p-c at 275° showed a large peak due to dicumene, a medium peak for 1,1-diphenylbutene (89%) at 33.6 min. and for diphenylcyclopropylmethane (11%) at 38.8 min., a small peak at 60.5 min and very large peaks at 68.4 and 80.3 min. The last three peaks had essentially the same retention time as three similar peaks at 60.2, 67.6 and 80.1 min. for the product of the decarbonylation of (γ,γ-diphenylallyl)-acetaldehyde, determined on the same v-p-c run, which may indicate common products for the two reactions. A third reaction with 2 g. of perester in 50 ml. of cumene at 140° yielded 125 ml. of gas after 5.5 hr., and, after chromatography and microdistillation of the eluate, furnished 0.489 g. of distillate and

0.32 g. of tar. Analysis of the distillate by v-p-c showed peaks due to dicumene, 1,1-diphenylbutene (86%) and diphenylcyclopropylmethane (14%), and the three large peaks of long retention time observed previously. Crystallization of the distillate from methanol afforded 0.125 g. of dicumene as needles, m.p. 117.5-118.5 (corr.), lit. (144) m.p. 118-119°.

(b) Benzhydrol.— When 2 g. of the perester was heated with 10 g. of benzhydrol at 140° for 14.5 hr., 15 ml. of gas was collected. After chromatography of the product on alumina, elution with pentane and microdistillation of the eluate there was obtained 0.23 g. of product. Analysis by v-p-c showed small peaks due to 1,1-diphenylbutene (95%) and diphenylcyclopropylmethane (5%) in addition to the three large peaks of longer retention time observed previously. A second reaction in which 2 g. of perester was heated with 5.68 g. (30.9 mmole) of benzhydrol in 100 ml. of chlorobenzene for 12.5 hr. afforded 145 ml. of gas. The solvent was distilled and the same isolation procedure used above gave 0.146 g. of product. Analysis by v-p-c showed a small peak due to 1,1-diphenylbutene (but no detectable diphenylcyclopropylmethane), as well as the usual long retention time peaks. Benzophenone, 0.74 g., m.p. 40-48°, identified by its infrared carbonyl band at 1660 cm^{-1}, was isolated from the chromatogram of the product on alumina, and was probably formed by disproportionation of hydroxybenzhydryl radicals.

(c) Benzyl Mercaptan.— The perester, 2 g., was heated with 7.64 g. (61.6 mmole) of benzylmercaptan in 20 ml. of o-dichlorobenzene at 130° for 15 hr. Only 25 ml. of gas was collected. The solvent was distilled and the residue was chromatographed on alumina. Elution of the column with pentane afforded 1.35 g. of dibenzyl disulfide, m.p. 69.5-70.5°, lit.(171) m.p. 71°, while elution with ether yielded 0.93 g. of an oil which exhibited a strong carbonyl band at 1708 cm^{-1} in the infrared. The latter is probably the product of induced-decomposition of the perester.

(d) Tetralin.— A solution of 2 g. of the perester in 50 ml. of tetralin was heated at 130° for 6 hr. and 85 ml. of gas was collected. The solvent was distilled and the product was chromatographed on alumina. Elution of the alumina column with pentane and microdistillation of the eluate afforded 0.304 g. of distillate and 0.38 g. of tar, while elution with ether gave 1.6 g. of an oil which showed carbonyl bands at 1780 and 1683 cm^{-1} in the infrared. Analysis by v-p-c at 265° of the pentane-eluted material showed a large peak due to 1,1-diphenylbutene and peaks due to the three long-retention time components observed previously. No diphenylcyclopropylmethane was detected.

(e) Tributyltin Hydride.— An unsatisfactory feature of the above decompositions was the very low yields of the desired hydrocarbons, 1,1-diphenylbutene and diphenylcyclopropylmethane, obtained due to poor competition of hydrogen-abstraction processes with important side-reactions. To avoid this the powerful hydrogen donor, tributyltin hydride (57), b.p. 68-70° (1.5 mm.),was used. The reactions were carried out by heating 1 g. (3.08 mmole) of the perester with varying amounts of tributyltin hydride in an inert solvent, chlorobenzene, o-dichlorobenzene or t-butylbenzene. The total volume of the solution was maintained constant at about 54.5 ml., so that the initial concentration of perester was constant at 0.0565 M. The hydrocarbon fraction was isolated in each case by distilling the solvents and repeatedly chromatographing the residue on pentane-washed alumina, followed by microdistillation of the pentane-eluate. The chromatography served to remove tributyltin oxides which were formed on contact of residual tributyltin hydride with air. This isolation procedure did not effect any fractionation of the isomeric hydrocarbons since they exhibited the same chromatographic and distillation behavior. The hydrocarbon fractions were analyzed with the Loenco v-p-c at 250-275° using the Apiezon L column described earlier. The procedure for isolation of the hydrocarbon fractions incurred some mechanical losses and the actual yields of the desired hydrocarbons were estimated to be as high as 50% in most cases, somewhat higher than the isolated yields. In most of the v-p-c analyses a small peak was observed due to tributyltin chloride, which was a minor contaminant of the hydride used. Its presence did not affect the course of the reactions nor the analysis of

TABLE XVII

Thermal Decomposition of t-Butyl (γ, γ-Diphenylallyl)-peracetate in the Presence of Tributyltin Hydride

Run	Bath Temp., °C	Time, Hr.	Conc. of Bu_3SnH, M	Solvent	Yield of Hydrocarbon, g.	Gas, ml.	% of Diphenylcyclopropylmethane*
1	110	24	0.056	C_6H_5Cl	0.095	35	4.5%
2	110	24	0.28	C_6H_5Cl	0.098	30	5
3	110	24	0.56	C_6H_5Cl	0.21	50	6
4	150	16	0.112	o-$C_6H_4Cl_2$	0.34	50	-
5	110	38	0.28	$C_6H_5C(CH_3)_3$	0.32	25	6
6	130	22	0.28	$C_6H_5C(CH_3)_3$	0.23	40	5.5
7	150	24	0.28	$C_6H_5C(CH_3)_3$	0.26	55	5

*The percentages given refer to diphenylcyclopropylmethane relative to diphenylcyclopropylmethane plus 1,1-diphenylbutene and are accurate to approximately ± 0.5%.

the products. The theoretical yield of carbon dioxide was approximately 69 ml. The results obtained are summarized in Table XVII.

Except for runs no. 1 and 4, where the concentration of tributyltin hydride was rather low, the yields of the three long-retention-time products mentioned **previously** were negligible, as determined by v-p-c. The infrared spectrum of the product of the fourth reaction prior to chromatographic treatment showed a medium intensity carbonyl band at 1647 cm^{-1} possibly due to tributyltin (γ,γ-diphenylallyl)-acetate, the expected product of induced decomposition of the perester. The crude products of Reactions 6 and 7 were extracted with aqueous potassium carbonate solution. The combined extracts were acidified and yielded 0.126 g. of an oil acidic fraction which could not be induced to crystallize. Its infrared spectrum showed weak bands at 1786 and 1758 cm^{-1}, and a strong carbonyl band at 1710 cm^{-1} at the same frequency found earlier for (γ,γ-diphenylallyl)-acetic acid. The latter could be formed by reaction of (γ,γ-diphenylallyl)-acetoxy radicals with tributyltin hydride, by rapid hydrolysis of tributyltin (γ,γ-diphenylallyl)-acetate (145), or by direct reduction of the perester by tributyltin hydride at the -O-O- bond. In Reactions 5, 6 and 7 , the yield of gas increased markedly with the temperature of the reaction, indicating that the activation energy for decomposition of the perester exceeded those of major side-reactions. No attempt was made to analyze the gas, but it presumably consisted mainly of carbon dioxide and methane (56). Evidence that diphenylcyclopropylmethane was indeed a product of the above decompositions was secured by isolating a sample of the hydrocarbon mixture enriched in the component giving rise to the peak assigned to diphenylcyclopropylmethane. This was achieved by preparative v-p-c analysis of the combined products of several of the above reactions on the Loenco vapor fractometer at 250° with a helium inlet pressure of 10 lbs./sq. in. The n-m-r spectrum of the resulting enriched sample showed strong peaks due to 1,1-diphenylbutene in addition to a midfield methine doublet and complex cyclopropyl methylene peaks characteristic of diphenylcyclopropylmethane. The relative proportion of diphenylcyclopropylmethane to diphenylcyclopropylmethane plus 1,1-diphenylbutene in this sample was calculated, by comparison of the intensities of the vinyl triplet of the latter with the methine doublet of the former, to be 34%, in favorable agreement with the value (36%) measured from the v-p-c curve.

An attempt was made to separate the three unidentified long-retention-time products, obtained in earlier decompositions of the perester, by preparative v-p-c analysis of the combined products of several reactions. The best that could be achieved with the limited resolution of the Loenco v-p-c at 275° was the isolation of three fractions (I, II and III) enriched in each of the three products in order of increasing retention time. The molecular weight of Fraction II was found (148) to be 216, indicating that it could not consist of (γ , γ -diphenylallyl)—carbinyl-diphenylcyclopropylmethyl dimers (calcd. 414). Elemental analysis of Fractions I and II showed that their major components were not hydrocarbons and probably contain two or three oxygen atoms per molecule.

Anal. Found for Fraction I: C, 68.09; H, 5.14. Found for Fraction II: C, 72.70; H, 5.04.

The infrared spectrum of Fraction I showed phenyl absorption, weak bands at 1712, 1668 and 1640 cm^{-1}, and complex peaks of medium intensity in the 1400-1500 and 1000-1100 cm^{-1} region. There were no prominent bands due to *t*-butyl groups in the 1300-1400 cm^{-1} range. Fraction II was similar to Fraction I, while Fraction III also showed a strong band at 1455 cm^{-1} and medium intensity bands at 1372, 1393 (*t*-butyl ?) and 1131 cm^{-1} (C-O stretch ?), indicating that it may contain a *t*-butyl ether. The *n-m-r* spectrum of Fraction I showed broad strongly-split phenyl peak, small vinyl doublet and several methylene and methyl multiplets. Fraction II was similar except for the presence of a small vinyl triplet and two methylene doublets. Fraction III showed a strongly split phenyl peak and a small methyl singlet, possibly due to a *t*-butyl group. The phenyl peaks were much broader and showed much more fine-structure than those in the parent perester and the formation of these products is probably associated with structural changes on, or in the immediate environs of, the phenyl groups.

Kinetics of Thermal Decomposition of t-Butyl (γ, γ-Diphenylallyl)-peracetate. — The procedure for following the kinetics of decomposition of t-butyl peresters has been described in detail by Hiatt (61), and was employed in the present work (149). Chlorobenzene, the solvent for the kinetic runs, was purified by shaking it with small amounts of concentrated sulfuric acid until the acid was no longer colored. The chlorobenzene was then washed with water, 10% sodium bicarbonate solution and again with water. After 15 hr. over calcium chloride, it was distilled from phosphorus pentoxide through an 18-in. Vigreux column and a center cut, b.p. 120.0°, was collected. Perester for the kinetic runs had m.p. 42-42.5°. The frequency of the infrared transmission minimum for the carbonyl group of the perester was found for a 0.1 M solution of the perester in chlorobenzene, by taking infrared transmission readings at 9.5 cm^{-1} intervals over the range 1765-1780 cm^{-1}. The minimum percent transmission was observed at 1773.5 cm^{-1}. A Beer's Law plot was made by measuring in turn the percent transmission, at the frequency of the carbonyl minimum, of chlorobenzene solutions approximately 0.01, 0.02, 0.03..., 0.14, and 0.15 M in perester, each of which was prepared by dissolving an accurately weighted amount of the perester in 1ml. of chlorobenzene. Solutions of the perester in chlorobenzene were thus found to obey Beer's Law over the concentration range 0.01-0.15 M. Since solutions of *t*-butyl 5,5-diphenylperpentanoate in chlorobenzene did not obey Beer's Law for concentrations exceeding 0.1 M, both peresters were run at approximately the same initial concentration of 0.1 M. A 0.5 M solution of *t*-butyl (γ, γ-diphenylallyl)-peracetate was prepared by dissolving 1.622 g. in 10 ml. of chlorobenzene. To this solution was added 40 ml. of a saturated solution (*ca.* 0.31 M, see reference 149) of iodine (to prevent induced decomposition of the perester) in chlorobenzene. An aliquot, 0.5 ml., of the resulting mixture was placed in each of forty necked-down 15 x 125-mm. Pyrex culture-tubes. The tubes were frozen and sealed under vacuum.

Two runs were made, taking about 20 points for each, in a mineral oil-bath (150) at 109.7° (corr.). The maximum variation in the temperature of the bath was ± 0.03°. After all the tubes had been placed in the bath a 2-min. warm-up period was allowed, during which reaction was assumed to be negligible, then the first tube was withdrawn and rapidly quenched in Dry Ice. The infinity point was withdrawn after about 48 hr. The percent infrared transmission (T) was then measured for the contents of each tube with chlorobenzene in the solvent cell, and the instrument previously set on 100% transmission for pure chlorobenzene in both cells. If T_o is the initial T and T_∞ is the T for the infinity point, then, since Beer's Law is obeyed,

$$\frac{C}{C_o} = \frac{\log T_\infty - \log T}{\log T_\infty - \log T_o}$$

where C_o is the initial concentration of perester and C is the concentration at a later time. The results obtained are recorded in Tables XVIII and XIX.

For the last two points in each run (excluding the infinity point) T was greater than T_∞. This implies that small amounts of products are being formed which absorb in the region of the perester carbonyl band. These points have been omitted. However, T_∞ should still be used as a basis for plotting the other points, since it is being specifically employed (rather than T_o) to correct for extraneous absorptions (61). The plot obtained for Run 2 is shown on the following page. A first-order law is followed up to almost 3.5 hr. Thereafter the points deviate markedly from the initial straight line and a wide scatter is obtained, apparently due to the sudden onset of secondary reaction (s) which proceed at a faster rate. The fairly good initial straight lines (see expanded plot of initial points for Run 2, page 224) obtained in both runs probably represent solely the simple first-order decomposition of the perester, and this has been assumed in the subsequent treatment.

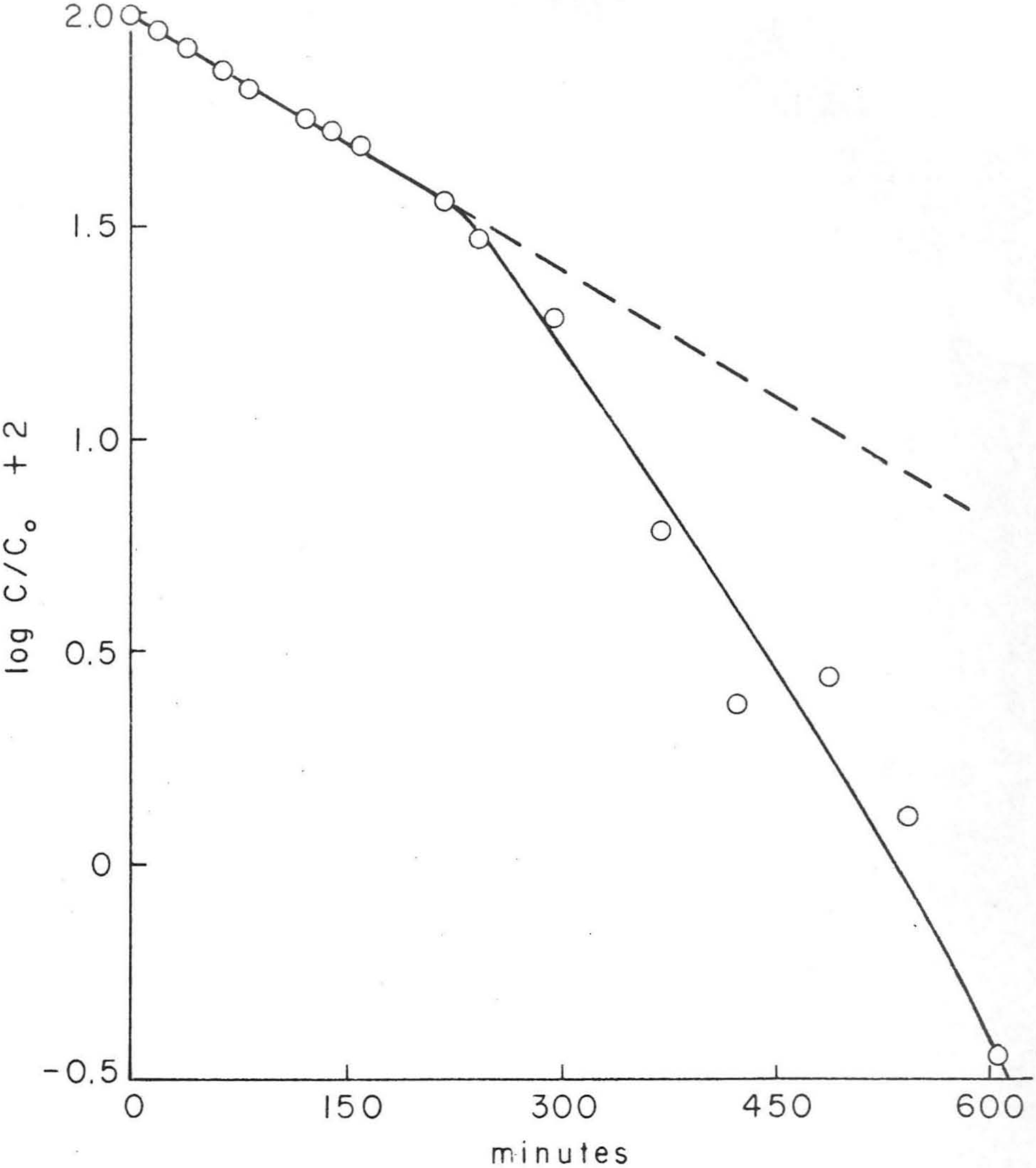

Fig. 23.— Thermal decomposition of t-butyl (γ,γ-diphenylallyl)-peracetate in chlorobenzene at 109.7° in the presence of iodine, showing the variation of log of the concentration of the perester with time; Run 2.

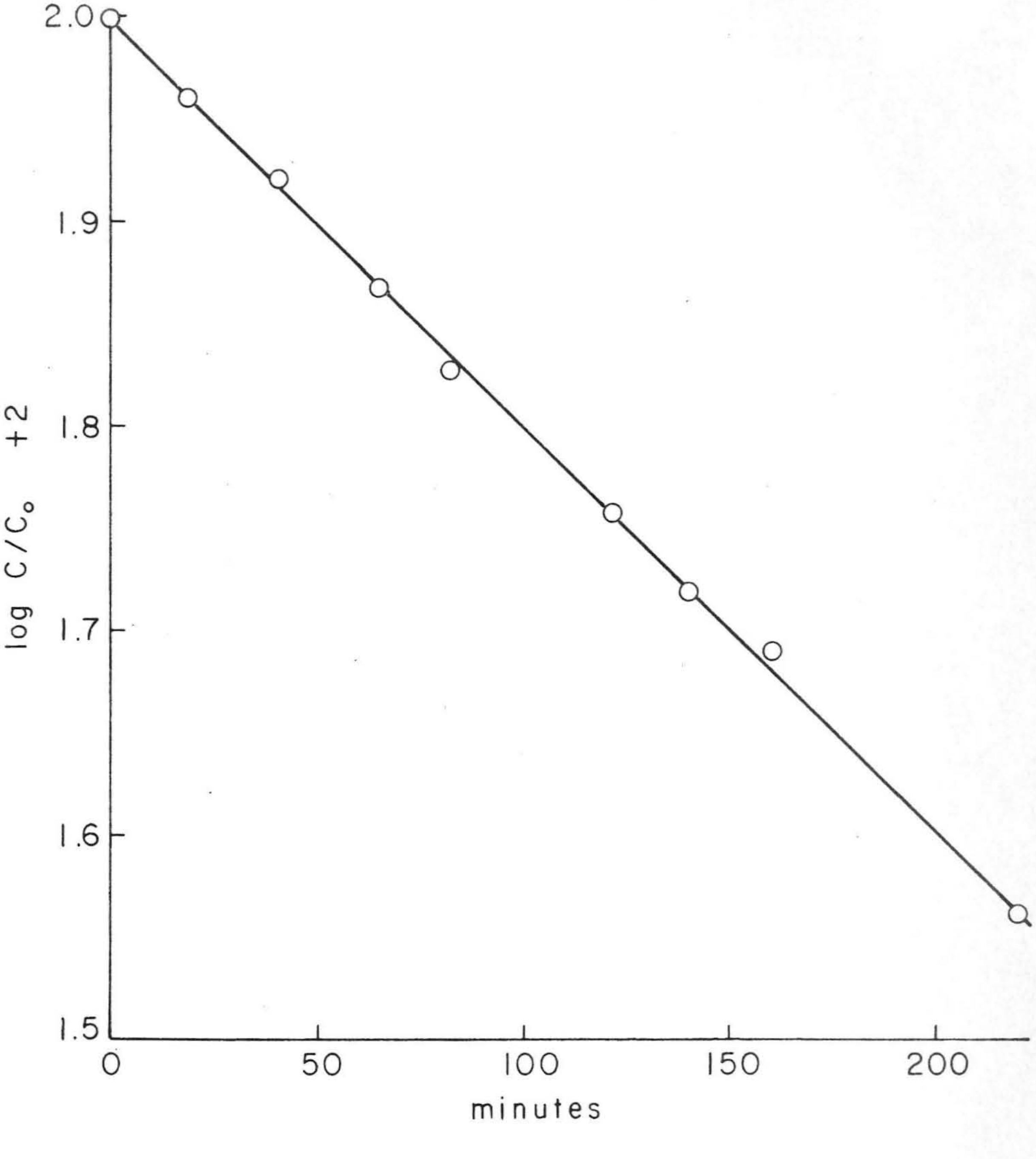

Fig. 24.— Thermal decomposition of t-butyl (γ,γ-diphenylallyl)-peracetate in chlorobenzene at 109.7° in the presence of iodine. Expanded plot of early points for Run 2.

TABLE XVIII

Thermal Decomposition of t-Butyl (γ , γ -Diphenylallyl)-peracetate at 109.7°C. Run 1.

Time, min.	T, 1773.5 cm^{-1}	log T_{∞}-log T	log(C/C_o x 100)
0	38.6	0.3729	2.000
19	39.1	0.3673	1.994
40.5	42.5	0.3311	1.948
87.5	49.8	0.2623	1.847
113	52.2	0.2418	1.812
135	56.2	0.2098	1.750
155.5	58.0	0.1961	1.721
176.5	61.2	0.1727	1.666
195	63.7	0.1554	1.620
214.5	66.5	0.1367	1.564
272	76.2	0.0775	1.318
331.5	84.3	0.0337	0.956
393.5	90.1	0.0048	0.110
468.5	86.5	0.0225	0.781
500.5	86.3	0.0235	0.800
537	87.4	0.0180	0.684
571.5	90.7	0.0019	-0.293
609.5	92.0	-0.0043	
658.5	92.1	-0.0048	
2971.5	91.1		

TABLE XIX

Thermal Decomposition of t-Butyl (γ , γ -Diphenylallyl)-peracetate at 109.7°C. Run 2.

Time, min.	T, 1773.5 cm^{-1}	$\log T_{\infty} - \log T$	$\log(C/C_o \times 100)$
0	36.2	0.4003	2.000
19	39.1	0.3668	1.962
40.5	42.2	0.3337	1.921
65.5	45.9	0.2962	1.869
82.5	49.0	0.2688	1.827
121.5	53.6	0.2298	1.759
140.5	56.1	0.2100	1.720
160.5	57.9	0.1963	1.691
220	65.0	0.1461	1.562
242	69.4	0.1176	1.468
296	76.1	0.0776	1.288
370.75	86.0	0.0245	0.787
422	89.0	0.0096	0.380
487	88.7	0.0111	0.443
540.5	89.9	0.0052	0.114
604.5	90.7	0.0014	-0.456
655	91.2	-0.0010	
746.5	91.7	-0.0034	
2871	91.0		

The irregular behavior observed in the latter part of each run may explain the complexity of products obtained from decompositions of the perester (see preceding section). A fast acid-catalyzed decomposition of the perester is conceivable, but this would be expected to follow a rather smooth concentration variation with time. The rate constants were obtained from the slopes of the expanded plots of the early points.

Run 1: $\underline{k} = 7.78 \times 10^{-5}$ sec^{-1}

Run 2: $\underline{k} = 7.63 \times 10^{-5}$ sec^{-1}

Mean $\underline{k} = 7.71 \times 10^{-5}$ sec^{-1}

$\underline{t}_{1/2} = 2.5$ hr.

The maximum deviation of the observed rate constants from the mean is only 1%. In order to ensure that the only effect of iodine on the rate was to eliminate induced decomposition, a run was made in which the concentration of perester was held constant at 0.1 M and the concentration of iodine was varied from zero to approximately 0.25 M. All tubes were heated at 109.7° for 3 hr., and the infrared transmission of the contents of each tube was measured. All of the tubes except that represented by the first column still contained some iodine at the end of the run. Strangely, the rate increased significantly when iodine was first added, but further addition of iodine increased the rate, only slightly for an eight-fold increase in iodine concentration. Actually,

TABLE XX

Thermal Decomposition of *t*-Butyl (γ , γ -Diphenyallyl)-peracetate at 109.7° in the Presence of Iodine.

Initial Conc. I_2, M:	0	0.031	0.062	0.093	0.124	0.155	0.186	0.217	0.248
Transmissions (1773.5 cm^{-1}):	53.8	63.7	62.3	63.4	63.7	64.3	64.5	65.0	65.8

the first addition of iodine would be expected to decrease the rate by preventing induced decomposition. Unfortunately, a duplicate of the first tube was not made, so that this result is unconfirmed. The remaining figures indicate that varying amounts of excess iodine do not affect the rate markedly.

Kinetics of Thermal Decomposition of t-Butyl 5,5-Diphenylperpentanoate.— The perester used for the kinetic runs had m.p. 50-50.5°. The frequency of the carbonyl minimum for the perester in chlorobenzene was found by the same method used in the preceding section to be at 1773.5 cm^{-1}. This value is identical with that for *t*-butyl (γ , γ -diphenylallyl)-peracetate and illustrates the negligible effect of a β - double bond on the frequency of the carbonyl band. Solutions of *t*-butyl 5,5-diphenylperpentanoate in chlorobenzene were found to obey Beer's Law for concentrations up to 0.1 M, but to deviate from it at higher concentrations. An initial concentration of 0.1 M was therefore used in the kinetic runs. A 0.5 M solution of the perester was made up by dissolving 1.632 g. in 10 ml. of chlorobenzene, and 40 ml. of a saturated solution of iodine in chlorobenzene was added. The rate measurements were carried out under precisely the same conditions as for t-butyl (γ, γ-diphenylallyl)-peracetate. Two runs were made at 109.7°. The results are summarized in Tables XXI and XXII. By inspection of the plot for Run 1, page 230, the decomposition is seen to follow the first-order law closely. Rate constants were obtained from the slope of this, and a similar plot for Run 2.

Run 1: $k = 5.61 \times 10^{-5}\,\mathrm{sec}^{-1}$

Run 2: $k = 5.37 \times 10^{-5}\,\mathrm{sec}^{-1}$

Mean $k = 5.49 \times 10^{-5}\,\mathrm{sec}^{-1}$

$t_{1/2} = 3.5$ hr.

The maximum deviation of the observed rate constants from the average is only 2.2%. An iodine check run was made exactly as described for t-butyl (γ, γ-diphenylallyl)-peracetate. The solutions containing varying initial concentrations of iodine were heated at 109.7° for 3 hr. and the following results were obtained.

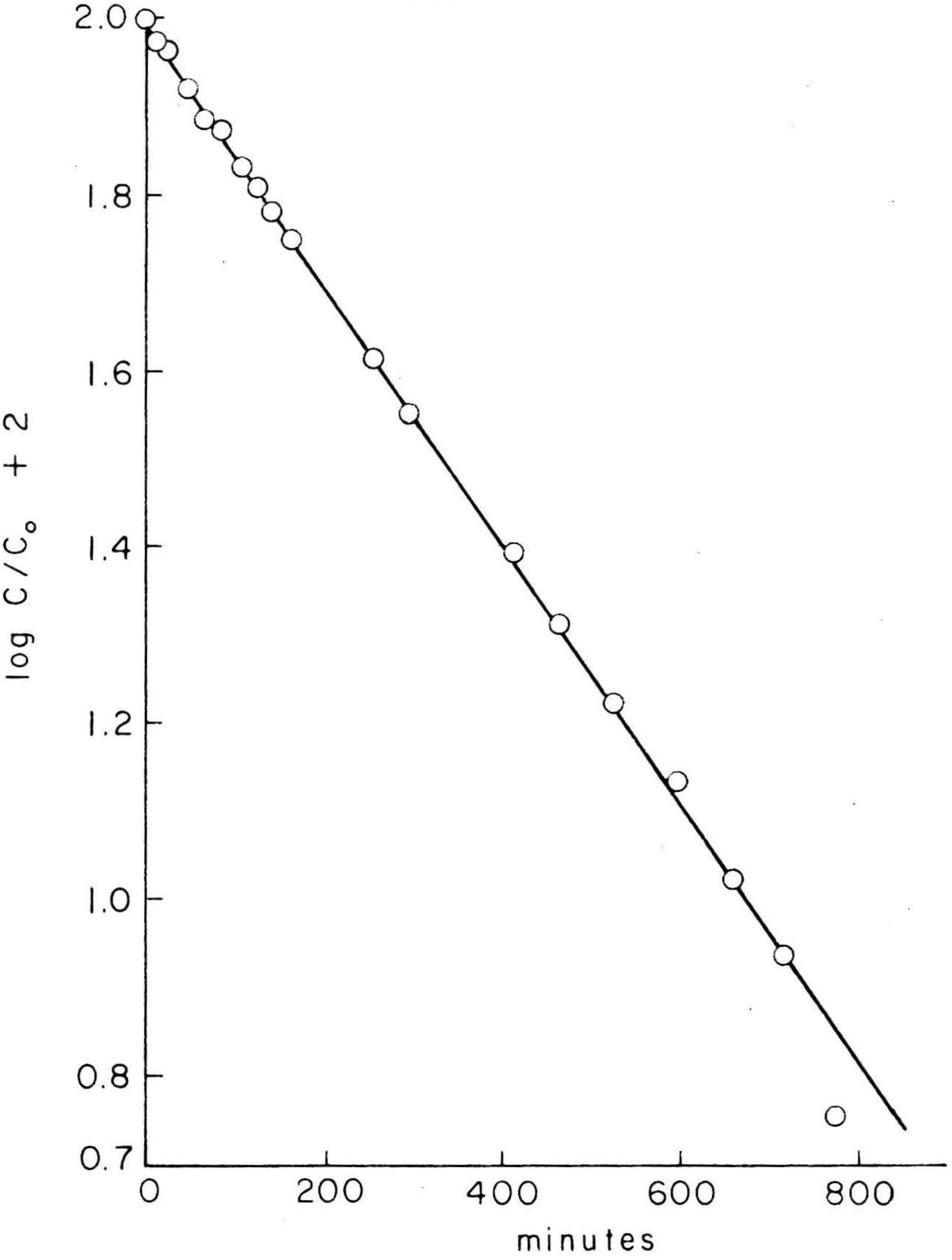

Fig. 25.— Thermal decomposition of t-butyl 5,5-diphenylperpentanoate in chlorobenzene at 109.7° in the presence of iodine, showing the variation of the log of perester concentration with time; Run 1.

TABLE XXI

Thermal Decomposition of t-Butyl 5,5-Diphenylperpentanoate at 109.7°C. Run 1.

Time, min.	T, 1173.5 cm^{-1}	$\log T_{\infty} - \log T$	$\log(C/C_o \times 100)$
0	36.4	0.4350	2.000
9.5	38.8	0.4073	1.971
20.5	39.7	0.3973	1.961
41.5	43.2	0.3606	1.919
62	46.0	0.3333	1.884
81	47.0	0.3240	1.872
102.5	50.2	0.2954	1.832
121.5	52.1	0.2793	1.808
139.5	54.1	0.2629	1.781
160.25	56.4	0.2448	1.750
252.5	65.5	0.1799	1.617
292.25	69.4	0.1547	1.551
411	77.3	0.1079	1.395
462.25	80.5	0.0903	1.317
524.25	83.7	0.0734	1.227
595	86.4	0.0596	1.137
659	89.1	0.0462	1.026
713.5	90.8	0.0380	0.941
772.5	93.6	0.0248	0.756
3069	99.1		

TABLE XXII

Thermal Decomposition of *t*-Butyl 5,5-Diphenylperpentanoate at 109.7°C. Run 2.

Time, min.	T, 1173.5 cm^{-1}	$\log T_{\infty} - \log T$	$\log(C/C_o \times 100)$
0	37.5	0.4216	2.000
21	40.2	0.3914	1.968
45	42.4	0.3682	1.941
65.5	46.8	0.3254	1.888
83	48.0	0.3144	1.873
105	50.8	0.2897	1.837
127	52.3	0.2771	1.818
142.5	55.2	0.2537	1.779
169	56.4	0.2443	1.763
189.5	58.6	0.2277	1.733
245	64.2	0.1881	1.650
307.75	69.2	0.1555	1.567
367	73.1	0.1317	1.495
420	75.8	0.1159	1.439
526.5	81.7	0.0834	1.296
622	85.2	0.0652	1.189
658	86.3	0.0596	1.150
732.5	89.7	0.0428	1.007
786.5	91.7	0.0332	0.896
1618	99.0		

TABLE XXIII

Thermal Decomposition of _t_-Butyl 5,5-Diphenyl-perpentanoate at 109.7° in the Presence of Iodine.

Initial Conc. I_2, M:	0	0.031	0.062	0.093	0.124	0.155	0.186	0.217	0.248
Transmission (1773.5 cm^{-1}):	70.5	57.7	58.0	58.4	60.3	59.3	60.5	61.1	61.4

The rate showed the expected decrease on addition of iodine, attributed to prevention of induced decomposition of the perester. For an eight-fold increase in iodine concentration there was only a relatively small increase in rate.

PART II

N-m-r Spectra.— Chemical shifts were measured by means of a Hewlett-Packard Model 200AB audio oscillator and Model 521C frequency counter. For low-temperature spectra, the samples were cooled by nitrogen which was generated by controlled boiling of liquid nitrogen and passed via insulated pipes through a quartz vacuum-jacketed probe insert (151). For high-temperature spectra, the samples were heated by nitrogen passed over a resistance-wire heating element connect to a Variac. Temperatures were measured using a calibrated copper-constantan thermocouple with a Leeds and Northrup precision potentiometer.

Cyclopropyl Bromide was prepared by the method of Roberts, et al. (17), and on distillation through a center-rod fractionating column had b.p. 67.5-68°. No impurities were detected by v-p-c.

2, 2-Dimethylcyclopropanecarboxylic acid was prepared from 2, 2-dimethyl-1,3-propanediol via the *bis*-tosylate and 2, 2-dimethylcyclopropylnitrile by the procedures of Nelson, et al. (152). It was distilled through a Claisen head and had b.p. 96-100° (17 mm.), lit. (152) b.p. 83-84° (5 mm.). Its n-m-r spectrum showed carboxyl singlet, a quartet for the cyclopropyl hydrogen α - to the carboxyl group, large methyl doublet and several cyclopropyl methylene peaks which were part of the cyclopropyl ABX-type pattern.

2,2-Dimethylcyclopropanecarbonyl Chloride.— To 33.1 g. (0.29 mole) of 2,2-dimethylcyclopropanecarboxylic acid was added 38.1 g. (0.32 mole) of thionyl chloride over 20 min. The mixture was stirred at room temperature for 20 min., then heated under reflux for 45 min. The product was distilled through an 8-in. vacuum-jacketed Vigreux column and gave 33.9 g. (88.2%) of acid chloride, b.p. 138-142° (mostly at 142°).

2,2-Dimethylcyclopropanecarbonyl Peroxide.— The procedure was similar to that given by De Tar and Carpino (153) for the preparation of cyclopropanecarbonyl peroxide. To a solution of 33.9 g. (0.256 mole) of 2,2-dimethylcyclopropanecarbonyl chloride and 12.6 g. (0.134 mole) of 1:1 urea-hydrogen peroxide complex in 250 ml. of dry ether at 0° was added 20.8 g. (0.264 mole) of pyridine dropwise over 0.5 hr. with stirring. The mixture was allowed slowly to warm to room temperature over 15 hr. with stirring. The precipate was filtered off and the filtrate was washed five times with water, dried over sodium sulfate and after evaporation under reduced pressure gave 23.6 g. of an oil, which was presumed to be crude peroxide. Crystallization at -70° from pentane furnished 5.3 g. of a solid. All attempts to obtain a second crop yielded only low-melting solids, which melted at room temperature. The peroxide was not purified further but was used directly in the preparation of 2,2-dimethylcyclopropyl bromide.

2, 2-Dimethylcyclopropyl bromide was prepared by a method similar to that for cyclopropyl bromide (17). A solution of 23.6 g. (0.104 mole) of the crude 2, 2-dimethylcyclopropanecarbonyl peroxide in 39 ml. of m-dichlorbenzene (Eastman, white-label) was added over 1.5 hr. to a stirred solution of 75 g. (0.226 mole) of carbon tetrabromide in 24 ml. of m-dichlorobenzene heated with a bath at 135°. Smooth evolution of gas occurred during the addition. Distillation of the product through a center-rod fractionating column gave 3.37 g. of a fraction b.p. 95-130°. Large quantities of an acidic gas, probably hydrogen bromide, were evolved during the distillation, for reasons which are not clear, and a considerable amount of the desired 2, 2-dimethylcyclopropyl bromide was probably lost in the gas stream. The distillate was washed with 10% sodium carbonate solution and water, dried over sodium sulfate, and fractionated through a micro-Vigreux head. Boiling-points were inaccurate since very slow distillation was employed. Four fractions (total 1.17 g.) and a fifth fraction, 0.37 g., were collected. The n-m-r spectra of the first four fractions were similar to that shown on the following page (for the second fraction) and indicated that they consisted predominantly of 2, 2-dimethylcyclopropyl bromide, as well as some minor impurities. The cyclopropyl hydrogens exhibit a typical ABX pattern as expected. The spectrum for the fifth fraction showed that it was seriously

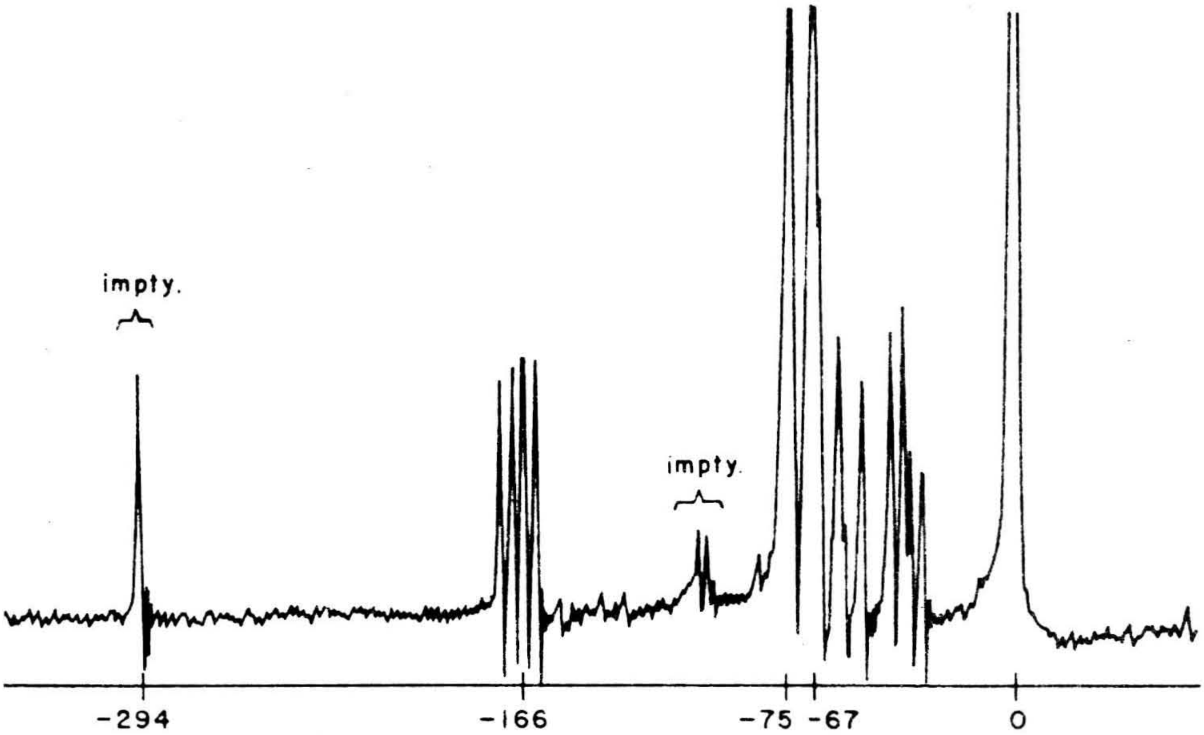

Fig. 26.— Proton n-m-r spectrum of 2,2-dimethylcyclopropyl bromide. Chemical shifts are in c.p.s. relative to tetramethylsilane as internal standard. Peaks due to impurities are marked.

impure and it was not used in the preparation of the Grignard reagent. The infrared spectrum of the second fraction in carbon tetrachloride showed a medium-intensity band at 1031 cm^{-1} due to the cyclopropyl group, which is characteristic of 1-substituted-2, 2-dimethylcyclopropanes (152). In view of the very low yield, the above is clearly not the method of choice for the preparation of 2, 2-dimethylcyclopropyl bromide, and the modified Hunsdiecker procedure of Cristol and Firth (168), might be preferable.

Cyclopropylmagnesium Bromide.— A general procedure for preparation of Grignard reagents for n-m-r analysis has been described in Part I of the Experimental for 4, 4-diphenyl-1-bromo-3-butene-1, 1-d_2. An atmosphere of prepurified nitrogen was maintained throughout the preparation of the Grignard reagent and its transfer to an n-m-r tube. Tetrahydrofuran was used as solvent, and after two distallations from lithium aluminum hydride, had b.p. 65-65.5°. High-purity resublimed magnesium, 0.4 g. (16.4 g. atom), in 2 ml. of tetrahydrofuran was activated by addition of several drops of 1, 2-dibromoethane. A solution of 1 g. (8.26 mole) of cyclopropyl bromide in 10 ml. of tetrahydrofuran was then added over 2.5 hr. with stirring at room temperature. The mixture was stirred at room temperature for 3.5 hr., then heated at 50° for 0.5 hr., and finally filtered. Upon concentration of the filtrate in a stream of nitrogen, a considerable amount of crystalline material separated out which is probably a complex of magnesium bromide and tetrahydrofuran. The supernatant solution of Grignard reagent was sealed into n-m-r tubes after addition of benzene as internal reference.

The n-m-r spectra of cyclopropyl bromide and of the derived Grignard reagent at 30° are shown on page 118. The α-hydrogen resonance in the Grignard reagent lies at very high field and corresponds to a chemical shift of about 12 τ. The n-m-r spectrum of the Grignard reagent was also taken at -40°, 61°, 90°, 140° and 170°, and was essentially unchanged in this range.

2, 2-Dimethylcyclopropylmagnesium bromide was prepared under the same conditions used for cyclopropylmagnesium bromide. A solution of 1.1 g. (7.4 mmole) of 2, 2-dimethylcyclopropyl bromide in 13 ml. of tetrahydrofuran was added to 0.35 g. (14.4 mmole) of activated magnesium in 2 ml. of tetrahydrofuran. When the reaction was complete, the solution was filtered and, upon concentration, a considerable amount of what appeared to be Grignard salt complex separated. A sample of the supernatant liquid was sealed into n-m-r tubes with some benzene added as internal reference. The n-m-r spectrum of the resulting solution showed methyl peaks of approximately equal intensity at 364.3, 367.1 and 375.6 c.p.s., complex cyclopropyl peaks upfield of these including a prominent broadened singlet at 424.8 c.p.s., and a weak α-hydrogen resonance at 538 c.p.s. in the approximate form of a quartet as expected for the X part of an ABX system. Two of the methyl peaks were probably due to the Grignard reagent and the chemical shift between them was therefore either 8.5 or 11.3 c.p.s. The other methyl peak must arise from an impurity, probably 1,1-dimethylcyclopropane. The n-m-r spectrum of this solution was essentially unchanged at -41°, 104° and 175°, and the methyl doublets did not collapse at high temperatures.

Computation of n-m-r spectra (154) was carried out with IBM 704 and 7090 high-speed digital computers using a program developed by Dr. A. A. Bothner-By of the Mellon Institute. Input data consisted of sets of chemical shifts and coupling constants, and the output listed line frequencies and intensities, corresponding to the allowed transitions, arranged in a somewhat arbitrary order.

N-m-r Spectra, Physical Properties and Sources of Selected Cyclopropanes.— Most of the cyclopropanes studied were generously donated by authors of recent papers on cyclopropane chemistry, to whom grateful acknowledgement is made. In such cases, the physical properties are those given by the respective authors for the compounds at the time of their preparation. Some changes may have occurred since that time. Chloroform was frequently used as a solvent for substituted cyclopropanes. The small amount of ethanol which the spectro-grade material contains may be quantitatively removed by extracting the solvent three times with water, drying over calcium chloride for 24 hr., and filtering. Chemical shifts and spin-coupling constants were (except where noted) determined for well-separated peaks by side-band superposition from a solvent or internal reference peak and were accurate to ±0.1 and ±0.2 c.p.s. respectively. For closely-spaced or broad peaks they were measured by interpolation from two side-bands placed on either side of the resonance and are considered accurate to ±0.2 c.p.s. In the latter cases, the values given are the average of three or four separate measurements. τ values (93) were obtained with 5% w/v solutions in carbon tetrachloride (except where noted) using tetramethylsilane as internal reference. Proton or fluorine ^{13}C-satellite spectra were taken for ^{13}C in natural abundance. Hydrogen-^{13}C coupling constants were obtained as the difference between the chemical shifts of the centers of the low- and high-field satellites. The centers of the satellites were identified by the method of moments (89, 38).

(1) Cyclopropane was obtained from the Matheson Chemical Company.

(2) Hexafluorocyclopropane was a sample from Dr. D. C. England of the du Pont Company. The chemical shifts of the ^{13}C-satellite

peaks were determined at 56.4 Mc., using side-bands from the parent difluoromethylene peak. The ϕ^* value (101) of the latter peak was measured by interpolation with a 50% solution of hexafluorocyclopropane in fluorotrichloromethane, by generating an approximately 600 c.p.s. side-band and sweeping rapidly through to the fluorotrichloromethane peak. The value found was the average of five measurements.

(3) 1,1-Dichlorocyclopropane was isolated (172) as a product of the photochlorination of cyclopropane. It was distilled through a center-rod fractionating column and the fraction b.p. 74.5° (744.5 mm.), $\underline{n}^{25}$D 1.4373, lit. (167) b.p. 74-75°, n^{20}D 1.4400, was used.

(4) 1,1-Dimethylcyclopropane was a sample prepared by Cox (155) and was used without further purification.

(5) Spiropentane was obtained from Professor D. E. Applequist and was reported to have b.p. 36-38°. It had been distilled after treatment with bromine and dried over calcium hydride. Minor impurities obscured the low-field ^{13}C-satellite so that the ^{13}C-hydrogen coupling constant had to be taken as twice the frequency difference between the parent methylene peak and the center of the high-field satellite. This procedure introduced only a small error (ca. 1 c.p.s. too large) since ^{13}C-isotope effects on hydrogen are known to be small (156). Spiropentane was reported (70) to give a sharp signal at 4.04 p.p.m. from water (60 Mc.).

(6) Spirohexane was a pure sample from Professor D. E. McGreer (157), who noted that at 40 Mc. it showed two n-m-r peaks at 2.89 and 4.59 p.p.m. from water due to the cyclobutyl and cyclopropyl hydrogens respectively.

(7) 1-Phenyl-1-bromocyclopropane was prepared in these laboratories by Dr. D. I. Schuster. Its n-m-r spectrum showed that it was pure.

(8) 1,3,4,5-Tetramethyl-2-methylenebicyclo [3.1.0] hex-3-ene was obtained from Dr. L. de Vries (158), who reported its cyclopropyl methylene resonance as a "peak" at -2.07 c.p.s. from tetramethylsilane (40 Mc.). Under high-resolution the cyclopropyl resonance appeared as an AB quartet, which was analyzed (as were all other AB systems) using the equations,

$$J = \frac{1}{2}(b-a)$$

$$= (ab)^{1/2}$$

where a equals the frequency separation of the inner doublet and b of the outer doublet. In this way, δ , the chemical shift between the cyclopropyl hydrogens, was found to be 3.9 c.p.s. for the neat liquid. The average τ -value for the cyclopropyl hydrogens was 9.48 τ .

(9) Nortricyclene was a pure sample obtained from Professor H. Hart. Since the τ values were critical, they were obtained by

measuring the chemical shifts of the maxima or geometric center of each resonance for volume fractions of nortricyclene in carbon tetrachloride of approximately 1, 0.25, 0.06, 0.016 and extrapolating to infinite dilution.

(10) Dimethyl 1-Methylcyclopropane-*cis*-1,2-dicarboxylate.— The parent diacid, m.p. 139-141°, was provided by Professor L. L. McCoy (160), and was esterified with an excess of diazomethane in benzene. The product was microdistilled at 3 mm. with a bath at 80°. The neat liquid dimethyl ester showed cyclopropyl peaks of varying intensities at 93.6, 99.7, 101.7, 108.1, 113.1, 117.8, 119.8, 123.9, 142.2, 146.5, 150.2 and 154.7 c.p.s. from the low-field methoxyl peak. The spectrum was analyzed as an approximate ABX system (38) in which the quartet at high-field was assigned to the cyclopropyl methylene hydrogen *trans* to the two carbomethoxy groups.

(11) Dimethyl 1-Methylcyclopropane-*trans*-1,2-dicarboxylate.— The parent diacid, m.p. *ca.* 170°, was obtained from Professor L. L. McCoy (160), and was esterified with excess diazomethane. The resulting dimethyl ester was microdistilled at 2 mm. with a bath at 65-70°. The *n-m-r* spectrum of the neat liquid ester showed cyclopropyl peaks of varying intensities at 76.2, 82.9, 84.6, 91.3, 122.4, 126.5, 130.5, 135.2, 144.4, 147.0, and 150.9 c.p.s. relative to the methoxyl peak at lowest field. The

spectrum was analyzed as an approximate ABX system in which the quartet at low-field was assigned to the cyclopropyl hydrogen α-to one of the carbomethoxyl groups.

(12) Dimethyl 1,2-Dimethylcyclopropane-*cis*-1,2-dicarboxylate. was provided by Professor L. L. McCoy (160) and contained 7% of the *trans*-isomer, which did not interfere with the analysis of the spectrum for the *cis*-compound. For a 5% w/v solution of the diester in carbon tetrachloride, analysis of the cyclopropyl methylene quartet indicated that the chemical shift between the cyclopropyl hydrogens was 79.0 c.p.s.

(13) *trans*-3-(*trans*-2'-Carboxypropenyl)-2,2-dimethylcyclopropane-1-carboxylic acid was the dextrorotatory enantiomer, m.p. 164-165°, obtained from Professor Y. Inouye (161). Its *n-m-r* spectrum was taken on a chloroform solution of the acid and all of the cyclopropyl lines were visible.

(14) Methyl *trans*-3-(*trans*-2'-Carbomethoxypropenyl)-2,2-dimethylcyclopropane-1-carboxylate, m.p. 80°, was provided by Professor Y. Inouye. The *n-m-r* spectrum of a solution of the ester in chloroform showed that none of the cyclopropyl lines were obscured by methyl peaks.

(15) Dimethyl Ester of Feist's Acid.— Feist's acid was obtained from Professor A. T. Blomquist and Dr. E. F. Ullman. It was

esterified with excess diazomethane, and the product was microdistilled at 2.5 mm. with a bath at 95-100° and gave the diester, $\underline{n}^{24}D$ 1.4648. Ullman's observation (162) of splitting of the vinyl and cyclopropyl peaks of Feist's acid into a triplet (apparent J ≐ 2.5 c.p.s.) was confirmed for the case of the dimethyl ester (J was not determined). The high-field cyclopropyl ^{13}C-satellite was too complex to interpret.

(16) Dimethyl Methylenecyclopropane-1, 1-Dicarboxylate was obtained from Dr. E. F. Ullman, who reported (162) that the diethyl ester exhibited "weakly split" vinyl and cyclopropyl peaks at 49 and 180 c.p.s., respectively, from benzene as external standard at 40 Mc. The parent diacid reportedly gave similar peaks at 35 and 163 c.p.s., respectively. The n-m-r spectrum of the dimethyl ester showed a complex vinyl multiplet and a cyclopropyl triplet (apparent J = 2.1 c.p.s.). The vinyl and cyclopropyl resonances were quite different in appearance.

(17) Dicyclopropylmethane was provided by Professor H. Hart (163). The acyclic methylene resonance appeared as a broadened doublet (apparent J = 6.4 c.p.s.) near the cyclopropyl methine peaks. The τ value for the center of this doublet was obtained by extrapolation to infinite dilution as described for nortricyclene above.

(18) Dimethyl trans-Caronate (Dimethyl 2,2-Dimethylcyclopropane-trans-1,2-dicarboxylate).— trans-Caronic acid was obtained from Professors Y. Inouye and M. Matsui, who reported m.p. 210-212° and 212-213° respectively. The combined samples were esterified with excess diazomethane, and the product was microdistilled at 14 mm. with a bath at 125-130° and gave diester, $n^{24}D$ 1.4434. The high-field cyclopropyl ^{13}C-satellite consisted of a slightly unsymmetrical doublet. The ^{13}C-hydrogen coupling constant could not be measured since the low-field satellite was obscured by the methoxyl peak. Samples of crude cis-caronic acid were also obtained from the above authors, but the n-m-r spectrum of the dimethyl ester showed that it was seriously impure (probably contaminated by the trans-ester) and the cyclopropyl ^{13}C-satellites could not be observed. The diacid had been prepared (164) by basic hydrolysis of diester of established stereochemistry, and it was apparent that extensive isomerization of the cis- to the trans-compounds had occurred. N-m-r provides an easy way of detecting such isomerization.

(19) 2,2-Dimethyl-trans-3-phenylcyclopropane-1-carboxylic acid was provided by Professor F. Sorm (169), and had m.p. 102°. The n-m-r spectrum was taken on a saturated solution of the acid in chloroform. Approximate chemical shifts (accurate to ±1 c.p.s.) were obtained for the methyl and cyclopropyl hydrogens by interpolation from a tetramethylsilane peak (internal reference) and the

low-field cyclopropyl doublet, which had been accurately calibrated. The chemical shift between the cyclopropyl hydrogens was thus found to be 48 c.p.s., and 31 c.p.s. between the gem-dimethyl groups.

(20) 2,2-Dimethyl-cis-3-phenylcyclopropane-1-carboxylic acid was supplied by Professor F. Sorm (169), and had m.p. 134°. The n-m-r spectrum was taken on a saturated solution of the acid in chloroform. Approximate chemical shifts were obtained for the methyl and cyclopropyl hydrogens as described for the trans-acid in the preceding section. The chemical shift between the cyclopropyl hydrogens was 39 c.p.s., and between the gem-dimethyl groups was only 2 c.p.s.

(21) 2,2-Dimethyl-trans-3-phenylcyclopropane-1-carboxamide was obtained from Professor G. W. Perold (165), and had m.p. 140°. Its n-m-r spectrum was taken on a saturated solution of the amide in chloroform. Approximate chemical shifts were 55 c.p.s. between the cyclopropyl hydrogens and 27 c.p.s. between the gem-dimethyl groups, obtained as described in section (19).

(22) 2-Oxa-7,7-dichloronorcarane was provided by Professor W. E. Parham (166), who gave b.p. 50-52° (1.6 - 1.9 mm.), $n^{25.7}D$ 1.4981, for this compound. Its n-m-r spectrum showed two main groups of peaks, the larger group at high-field being assigned to the methylene hydrogens at C_4, C_5 and the cyclopropyl methine hydrogen at C_6; and the smaller group at low-field to the methylene hydrogens at C_3 and the

cyclopropyl methine hydrogen at C_1. The latter gave a prominent unsymmetrical doublet on the low-field side of the lower group of peaks, due to cis-vicinal spin coupling with the cyclopropyl methine hydrogen at C_7.

(23) Stereoisomer of 2-Benzoyl-1-cyano-1,3-diphenylcyclopropane was obtained from Professor C. F. H. Allen (170) and had m.p. 168.5°. The isomer as a saturated solution in chloroform showed a chemical shift between the cyclopropyl hydrogens of 3.7 c.p.s. The stereochemical disposition of the two cyclopropyl hydrogens was not known prior to the present n-m-r study.

(24) Stereoisomers of 2-Benzoyl-1-cyano-1-(4-nitrophenyl)-3-phenylcyclopropane were provided by Professor C. F. H. Allen, and had m.p. 151° and 170°. The sterochemical relationship of the two cyclopropyl hydrogens was unknown at the time of the n-m-r work with these isomers.

(25) 2-Benzoyl-1,3-diphenylcyclopropane-1-carboxamide was a stereoisomer supplied by Professor C. F. H. Allen, and corresponded in stereochemistry to the nitrile stereoisomer, m.p. 168.5°, mentioned in section 23 above. The n-m-r spectrum was taken on a saturated solution of the amide in chloroform.

Methine Chemical Shifts in Bicyclic Hydrocarbons.—

(1) Bicyclo[2.2.1]heptane was a sample, m.p. 88-88.4°, prepared by W. G. Woods in these laboratories. The methine resonance appeared as a broad symmetrical peak at low field, while the methylene resonances were rather complex.

(2) Bicyclo[2.2.2]octane was obtained from Professor C. A. Grob, and it had been purified by gas chromatography. The n-m-r spectrum of a 5% w/v solution of the hydrocarbon in carbon tetrachloride surprisingly showed only a single sharp peak at 8.49 τ. Careful scanning of the spectrum over a wide range did not reveal any separate methine resonance. The chemical shifts of the methylene and methine hydrogens were apparently identical under these conditions.

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PROPOSITIONS

1. In recent years considerable experimental evidence has been obtained which demonstrates the importance of "homoallylic" interaction involving a double bond situated in the β,γ-position relative to the reactive center (1, 2, 3). Carbonium ion-type reactions involving such homoallylic participation are often characterized by an abnormally rapid rate of solvolysis relative to the corresponding dihydro-compound, by the isolation of products containing a cyclopropane ring, and by stereochemical criteria.

In contrast, interactions across two intervening methylene groups between a γ,δ-double bond and a reactive center have received scant attention. Indications that such phenomena may be important are found in the fact that cyclobutylcarbinyl chloride solvolyzes about 320 times faster than n-propyl chloride, and in cyclobutylcarbinyl-cyclopentyl interconversions in carbonium ion-type reactions (4). The following simple L.C.A.O. molecular orbital calculations on the β-(allyl)-ethyl system I are proposed in illustration of such 2, 5 interactions. The calculations were modeled on those of Simonetta and Winstein (5) and Woods, Carboni and Roberts (6) for the homoallyl and dehydronorbornyl systems respectively. The p-orbital axes at C_2 and C_5 were assumed to be perpendicular to the adjacent carbon-carbon internuclear line, and 1, 5-overlap was neglected. Inclusion of the latter would be expected to stabilize the β-(allyl)-ethyl cation just as 1, 4-overlap does for bicyclobutonium ions relative to the homoallyl cation.

Strain energies (SE) in I due to angle bending were calculated using Equation 1.

$$\text{SE per angle in kcal./mole} = 165.2\left[0.996 - \frac{(0.5+1.5\cos\alpha/2)(0.577+2^{1/2}\cos\alpha/2)}{4}\right] \quad (1)$$

In I the axes of the vacant p-orbital at C_5 and the p-orbital of C_2 were made to lie in the C_2-C_3-C_4-C_5 plane, and at various values of the 2, 5-interatomic distance $R_{2,5}$, the calculated delocalization energy, DE, was corrected for the SE due to compression of the C_2-C_3-C_4 and C_3-C_4-C_5 angle, to yield a total energy, TE. Overlap of the 2- and 5-p-orbitals was increased by symmetrical compression of the C_2-C_3-C_4 and C_3-C_4-C_5 angles. The results are collected in Table I.

The maximum value of the net stabilization energy, 14. 4 kcal. / mole, calculated for the β-(allyl)-ethyl cation I is much greater than the value 2. 8 kcal. / mole calculated (7) for the most favorable orientation of the homoallyl cation. Similarly the unperturbed stabilization energy, 4. 4 kcal. / mole, for I exceeds that calculated for the homoallyl cation (1. 8 kcal. / mole). The reasons for this are that the 2, 5-distance in unperturbed I is almost the same as the 2, 4-distance (2. 51 A) in the

Table I

Summary of Calculations for the β-(Allyl)-ethyl System I[a]

$R_{2,5}$, A	β_{25}/β[b]	-DE	SE	-TE
2.57	0.4769	4.4	0	4.4
2.31	0.7037	8.9	0.6	8.3
2.05	0.9051	14.0	2.1	11.9
1.78	1.070	18.6	4.2	14.4
1.54	1.140	20.7	7.0	13.6

[a] All energies are in kcal./mole.

[b] β_{25}/β is the exchange integral for 2,5-overlap in terms of the exchange integral for ethylene.

unperturbed homoallyl system, while the relative orientation of the p-orbitals in I is more conducive to effective 2pσ overlap. However, I probably suffers more from cyclobutane-like non-bonded carbon-carbon repulsions (8) than does the homoallyl cation.

In order to gauge the importance of 2,5-interactions it is proposed that the solvolysis rates of tosylate II and its dihydro-derivative III be compared and the possibility of formation of bicyclo[2.2.1]hexane products IV via the non-classical cation V investigated.

2. Considerable uncertainty still surrounds the nature of the species in ether solutions of Grignard reagents, despite recent work by Dessy and coworkers (9). One of the earliest proposals was made by Schlenk (10) who suggested that Grignard reagents may be represented by the equilibrium

$$2\,RMgX \rightleftharpoons R_2Mg + MgX_2 \qquad (2)$$

where X = halogen. Discussions of all but the most recent evidence bearing on the constitution of Grignard reagents and the role played by the Schlenk equilibrium in rationalizing this evidence have been published elsewhere (11).

Dessy, et al. (9) reported that when diethylmagnesium (or diphenylmagnesium) and magnesium bromide labelled with radioactive ^{28}Mg were dissolved together in ether, precipitation of the magnesium bromide with dioxane after 36 hours left almost no radioactivity in the supernatant solution of diethylmagnesium (or diphenylmagnesium). Only 4.5% of exchange occurred for the ethyl case and 7.0% for the phenyl system. Dessy, et al. concluded that, since equimolar mixtures of dialkyl- (or diaryl) magnesium and magnesium bromide exhibit reactivity similar to that of Grignard reagents prepared from organic bromides and magnesium, the Schlenk equilibrium cannot be operative in Grignard reagents. They suggested that Grignard reagents are best represented as a complex between dialkyl- (or diaryl) magnesium and magnesium halide, the two types of magnesium never becoming interconverted.

As pointed out by Nordlander (12) there is no certainty that a solution prepared by mixing together a dialkyl- (or diaryl-) magnesium and magnesium halide in ether has the same constitution as a Grignard reagent prepared in the normal manner. The results of Dessy are surprising in view of the facile cleavage of the analogous dialkyl- or diaryl-mercury compounds by mercuric halides to alkyl- or aryl-mercuric halides (13).

It is likely that the question of the constitution of Grignard reagents will best be resolved by use of a non-destructive physical method. Accordingly nuclear magnetic resonance (n-m-r) spectroscopy might prove to be useful in this regard and the following experiments are proposed to attempt to elucidate the nature of the species containing the organic radicals in Grignard reagents.

(i) a comparison of the chemical shifts of the α-methylene resonances in diethylmercury and ethylmercuric bromide as solutions in ether relative to a given internal reference may indicate whether a chemical shift difference is to be expected between the α-methylene resonances in the species $(C_2H_5)_2Mg$ and C_2H_5 MgBr. If a considerable difference is expected on this basis and yet a negligible shift is observed (with respect to an internal reference) between the α-methylene resonances in ethyl Grignard reagent and diethyl magnesium, one might conclude that the ethyl groups in the Grignard reagent are bound to magnesium in the same fashion as in diethylmagnesium. This conclusion would be conditioned by the fact that the chemical shift measurements are made for species in somewhat different media.

(ii) If the n-m-r spectrum of the Grignard solution prepared from methyl bromide, bromobenzene and magnesium in ether showed two chemically-shifted methyl resonances this could be interpreted as evidence for diorganomagnesium derivatives as the predominant Grignard structures, since the two methyl resonances could arise from $CH_3MgC_6H_5$ and CH_3MgCH_3 moieties.

(iii) An examination of the fine-structure in the fluorine and proton α-methylene resonances of the Grignard solution prepared from 1,1-difluoroethyl iodide, ethyl iodide and magnesium in ether might provide evidence for the presence of diorganomagnesium compounds if spin-spin coupling across the magnesium in $CH_3CF_2MgCH_2CH_3$ occurs.

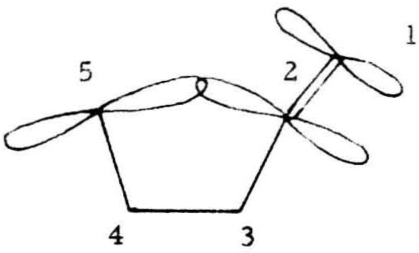
Allred and McCoy (14) recently observed rapid intermolecular exchange of methyl groups in concentrated solutions of dimethylzinc and dimethylcadmium in various solvents by n-m-r. The effects proposed in (i), (ii) and (iii) above may not be observed where rapid exchange of alkyl groups attached to magnesium occurs. However, Allred and McCoy found that the exchange rate decreased markedly with dilution of the $(CH_3)_2Zn$-$(CH_3)_2Cd$ system, so that reasonably dilute solutions of Grignard reagents may be preferable in (i), (ii) and (iii). Rapid intermolecular exchange of alkyl groups between Grignard and (say) cadmium reagents could be tested for using methyl Grignard reagent and dimethyl cadmium.

3. Although the thermal cycloaddition of alkene to alkene has become widely used as a method for preparation of cyclobutanes (15), very little is known concerning the mechanism of this intriguing reaction. Diradicals have frequently been proposed as intermediates but no unequivocal evidence has been found which supports them (15). The products are found to conform to a general rule that, of the possible isomeric adducts, that adduct will be produced which is formally derived from the most stable possible diradical formed by combination of the addends (15). The fact that this rule holds might be construed to imply that the transition state for the cycloaddition reaction closely resembles the most stable diradical formed from the addends. This in turn may indicate that at least one single bond between the addends is almost fully formed in the transition state. It is therefore of some consequence in understanding the mechanism of the cyclo-addition reaction to know how far the formation of single bonds between the addends has proceeded in the transition state. There will of course be two transition states if a diradical intermediate is involved, but the present discussion is confined to the first one encountered in proceeding in the forward direction along the reaction co-ordinate.

Szwarc and Matsuoka (16) compared the rates of addition of methyl radicals to styrene and trideuterostyrene (vinyl deuterated) in order to elucidate the structure of the transition state for the addition. Using the method developed by Streitwieser (17) they calculated that a change of configuration at the reaction center from trigonal to tetrahedral should lead to a ratio $k_D/k_H = 1.82$ for this reaction at 50°. Since only a small isotope effect $k_D/k_H = 1.09$ was observed they concluded that the transition state configuration deviated only slightly from that of the initial state and that the incipient C-CH_3 bond, formed in the transition state is comparatively long.

It is proposed that the relative rates of addition of 1,1-difluoro-2,2-dichloroethylene to styrene and the deuterated styrenes C_6H_5-$CD{=}CH_2$ and C_6H_5-$CH{=}CD_2$ be measured and compared. The product of cyclo-addition of styrene and 1,1-difluoro-2,2-dichloroethylene, formed in 58% yield after 3 hours at 130°, is known (18) to be the cyclobutane VI. It would of course be advisable to run the kinetics at a lower temperature if possible in order to magnify any observed isotope effects (19).

4. Although non-classical intermediates appear to be well established in certain carbonium ion-type reactions no unequivocal evidence for carbon participation in the formation of a free radical has been forthcoming. The most forceful claim to discovery of anchimeric



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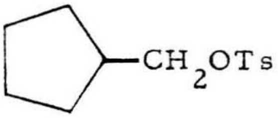

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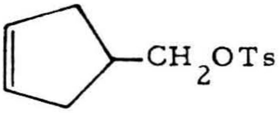

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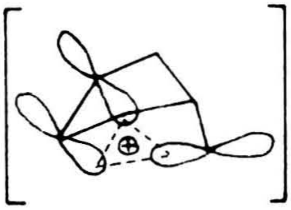

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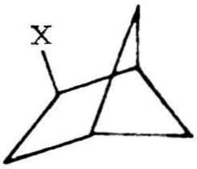

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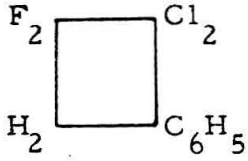

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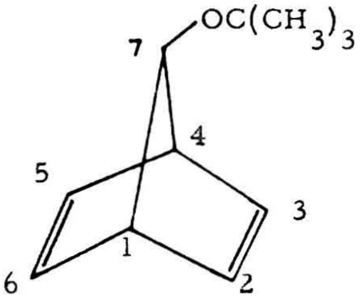

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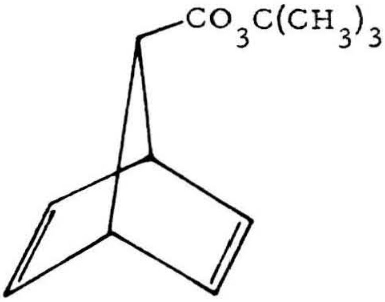

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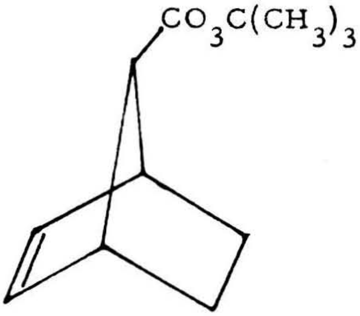

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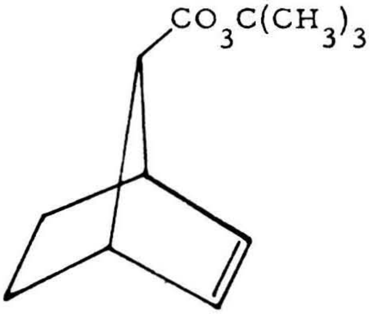

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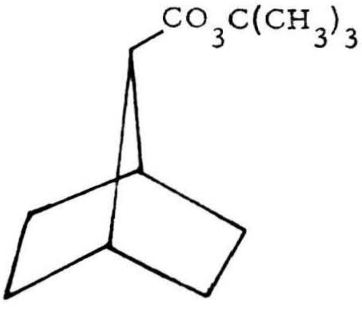

XI

assistance in the formation of a free radical has recently been made by Story (20). He obtained the t-butyl ether VII by reaction of norbornadiene with t-butyl perbenzoate in the presence of cuprous bromide, and suggested that formation of VII proceeded via anchimerically assisted hydrogen abstraction producing a free radical center at C_7. Since benzoate esters, rather than t-butyl esters, are the normal products of the reactions of t-butyl perbenzoate with olefins in the presence of cuprous bromide (21), a carbonium ion mechanism for the formation of VII was not ruled out.

The ultimate criterion for the formation of a non-classical intermediate in the rate-determining step of a reaction is generally an acceleration in rate relative to a reaction involving an analogously constituted starting material in which participation is not possible. Such an acceleration in rate indicates a driving-force for the reaction due to formation of the resonance-stabilized intermediate. Bartlett and Hiatt (22) have found evidence for concerted decomposition of a series of t-butyl peresters, in that they undergo thermal decomposition at rates parallel to the stability of the radical R· in the formula $RCO_3C(CH_3)_3$. Rate studies on perester decompositions would therefore appear to be an extremely useful means of investigating participation in the formation of free radicals.

The 7-norbornadienyl and 7-norbornenyl systems are worthwhile candidates for investigating non-classical character in the corresponding free radicals since simple molecular orbital calculations indicate delocalization energies of 8.7 and 3.9 kcal./mole respectively (23, 7) for these intermediates. It is proposed that the rates of thermal decomposition of the 7-norbornadienyl-VIII, anti-7-norbornenyl-IX, syn-7-norbornenyl-X and 7-norbornyl-XI t-butyl peresters be studied and compared to determine whether participation of the 2,3- and 5,6-double bonds occurs in the rate-determining step. It would also be of interest to know whether the product of decomposition of the anti-7-norbornenyl perester IX in carbon tetrachloride consists exclusively of anti-7-chloronorbornene or is a mixture of the syn- and anti- chlorides.

5. N-m-r spin-spin coupling constants are finding increasing use in obtaining information about the electronic and molecular structure of organic molecules. Although this field is still in its infancy, correlations have already been observed between vicinal proton-proton coupling constants and the dihedral angle between C-H bonds in alkanes (24, 25) and alkenes (24, 26), between geminal coupling constants and H-C-H angles (27, 28), between vicinal coupling constants and the electronegativity of substituents in alkanes (29) and alkenes (30), and finally a linear relation between the ^{13}C-H coupling constant and s character in the C-H bond has been found for hydrocarbons (31). The latter relation is particularly interesting since it offers a means of obtaining hybridization parameters that are not conveniently measured in any other way.

In view of the potential importance of spin-spin coupling constants in throwing new light on the structure of organic molecules it is interesting to note that no measurements of carbon-carbon coupling constants have been reported. The only carbon isotope that can be conveniently investigated by n-m-r spectroscopy is the ^{13}C nucleus, which has a spin of $\frac{1}{2}$. A large number of ^{13}C n-m-r spectra have been taken by Lauterbur (32) and Holm (33), and ^{13}C-H coupling constants could be measured to better than ± 5 c.p.s. from these spectra.

A general investigation of ^{13}C-^{13}C spin coupling constants in a variety of organic molecules is proposed. Since the natural abundance of ^{13}C nuclei is low (only 1.1%) it would be necessary to enrich the compounds to be studied with this isotope. Of particular interest in this study would be a comparison between the carbon-carbon coupling constants in the systems $^{13}C-^{13}C$, $^{13}C=^{13}C$, $^{13}C\equiv^{13}C$ and similarly in aromatic molecules. The effect of substituents on these 1, 2-couplings should be examined, particularly for the aromatic compounds, where the results might be correlated with a great deal of other quantitative data available. Also the effect of various types of complex formation on the 1, 2-coupling constants in unsaturated molecules may be revealing. Finally a comparison between the coupling constants for ^{13}C-nuclei separated by one, two, three, and perhaps more, carbon-carbon bonds should be made for both saturated and unsaturated systems.

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6. Considerable differences in reactivity, selectivity and sensitivity to stereoelectronic factors have recently been observed for substituted carbenes in solution, which appear to depend on the nature of the substituents and on the conditions under which the carbenes are produced. Thus unsubstituted CH_2 itself, generated photochemically from diazomethane in solution, adds readily to isolated double bonds and to aromatic systems and undergoes insertion reaction with C-H bonds forming $C-CH_3$ compounds in a more or less indiscriminate manner (34). On the other hand no evidence was found for C-H insertion with CH_2 generated from methyl chloride and phenylsodium (35). Carbomethoxycarbene, prepared by photolysis of methyl diazoacetate, adds readily to double bonds (36) and benzene, and undergoes C-H insertion although with somewhat more discrimination than CH_2 (37). Biscarbethoxycarbene from photolysis of diethyl diazomalonate adds to double bonds, and in insertion reactions with C-H bonds discriminates even more highly in the sense $3^\circ > 2^\circ > 1^\circ$ than carbomethoxycarbene (37). Doering and Knox (37) attribute this increasing discrimination in C-H insertions in the series CH_2, $CHCO_2CH_3$, $C(CO_2C_2H_5)_2$ to increasing stabilisation of the carbene center by resonance interactions with carboalkoxyl groups.

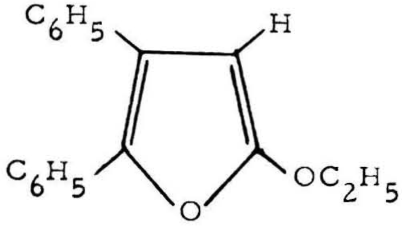
In contrast the carbene species produced by copper powder- or cupric sulfate-catalysed decomposition of ethyl diazoacetate does not add to aromatic systems nor undergo insertion reactions into C-H linkages (38). This and other behaviour led Skell and Etter (38) to postulate that the reactive intermediate in the copper-catalysed decompositions was a copper complex of carbethoxycarbene.

A further difference was noted by Breslow and Chipman (39), who found that thermal decomposition of ethyl diazoacetate catalysed by copper powder in the presence of diphenylacetylene gave the normal product of addition of carbethoxycarbene to the acetylene, while cupric sulfate-catalysed decomposition at a lower temperature also formed the furan XII. XII was presumed to be formed by 1,3-addition of the carbene as a copper complex.

Dibromocarbene (40), dichlorocarbene (41) and monochlorocarbene (42) generated by reaction of polyhalomethanes with strong bases, add readily to olefins but do not give C-H insertion products. Of this group, only chlorocarbene reacts by addition to benzene (43, 44). Considerable differences in selectivity have also been found for addition of these carbenes and carbethoxycarbene to various olefin pairs. For example, with cupric sulfate and ethyl diazoacetate, tetramethylethylene is only 1.6 times as reactive as 1-hexene, whereas this same olefin pair has a relative rate constant of 50 for additions of CBr_2 (45). Dibromocarbene (40) and dichlorocarbene (41) show parallel reactivity, although CBr_2 reacts relatively slower than CCl_2 the greater the degree of substitution of the olefin. Monochlorocarbene, for which the relative rates of addition to tetramethylethylene and 1-hexene is 12, was found to be generally less selective than dichloro- or dibromocarbene (46).

Skell and Etter (45) originally attributed the marked difference in selectivity between carbethoxycarbene (from cupric sulfate-catalysed decomposition of ethyl diazoacetate) and dibromocarbene to variations in resonance stabilisation of the ground state of the carbene. They considered the carbenes to be in the ground singlet state with sp^2 hybridisation at the carbene carbon atom, and a vacant p orbital at this center conferring electrophilic character on the intermediates. Dibromocarbene XIII was presumed to be stabilised by overlap of the vacant carbene p-orbital with p-orbitals of the bromine atoms, while the results for carbethoxycarbene XIV were explained away by assuming overlap of the carbonyl p-orbital only with the filled carbene sp^2 orbital, leaving the vacant carbene p-orbital free to be as indiscriminate as it pleased. On the basis of results obtained in the hydrolysis of various haloforms, Hine and Ehrenson (47) found that the ability to stabilise the electron deficiency of methylenic carbon atoms appears to vary in the order F > Cl > Br, and suggested that the relative electrophilic character of dihalocarbenes would vary in the order $CBr_2 > CCl_2 > CF_2$.

Skell, et al. (48) postulated that diphenylcarbene, generated by photolysis of diphenyldiazomethane, is a diradical species having the structure XV, with sp hybridisation at the carbene carbon atom and orthogonal aromatic nuclei. In reactions of diphenylcarbene with 2-butenes, addition to the double bond was observed and olefins were produced, possibly due to C-H insertion. Diphenylcarbene was found to react with 1,3-butadiene and 1,1-diphenylethylene more than 100 times as fast as with isobutene, 1-hexene or cyclohexene. Phenylcarbene, prepared by reaction of benzylchloride with butyllithium (49), adds to the double bond of cyclohexene and also yields 3-benzylcyclohexene possibly by selective insertion of the carbene into the allylic C-H bonds (49).



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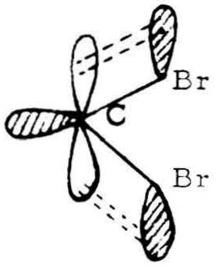

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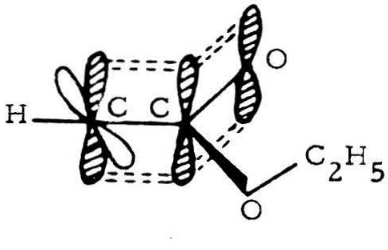

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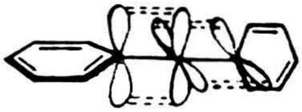

XV

From the above synopsis it is apparent that carbenes exhibit a wide range of reactivities depending on the substituents attached to the carbenoid carbon atom and on the mode of formation of the carbene. However in any particular case it is not clear to what extent resonance, inductive or steric effects of substituents are important in controlling the reactivity of the carbene. In order to attempt to disentangle these factors and determine the relative contributions of each, it is proposed that a series of olefins be allowed to compete in pairs for phenylcarbenes, diphenylcarbenes and phenylchlorocarbenes in which the aromatic rings are substituted with meta- and para- electron-withdrawing or electron-donating groups or with bulky ortho-substituents such as t-butyl. The olefin competition method has been used previously by Skell, Doering, Closs and their respective coworkers for comparison of carbene selectivity. The substituted aryl carbenes should also be prepared from different sources and their reactivity compared for individual substrates. Thus phenylcarbene might be generated by photolysis or copper-catalysed decomposition of phenyldiazomethane or by reaction of butyllithium with benzylchloride.

Phenylchlorocarbene has been added to the double bond of phenylketene dimethylacetal by Breslow, et al. (50), and was prepared by reaction of benzal chloride with potassium t-butoxide. It might also be produced by reaction of phenylbromodichloromethane with butyllithium (51) or by thermal decomposition of sodium dichlorophenylacetate in diglyme (52).

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