

I. THE FORMOLYSIS OF ALLYLCARBINYL TOSYLATES

II. STUDIES OF FLUOROALKADIENES BY
NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

III. THE DISSOCIATION CONSTANTS OF
METHYL ALKYL KETONE CYANOHYDRINS

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ABSTRACT

Allylcarbiny l tosylate was found to solvolyze in 98% formic acid 3.7 times faster than n-butyl tosylate. Changes in the rate ratio with nucleophilicity of the solvent suggest different mechanisms for these solvolyses. The formolysis products of allylcarbiny l tosylate, when corrected for secondary rearrangements, were found to be virtually identical with those from cyclobutyl tosylate. Deuterium-labeling experiments indicated complete scrambling of the methylene groups in the ring-closed products. These results are interpreted in terms of formation of bicyclobutonium ion intermediates. The rate acceleration for formolysis obtained upon methyl substitution in the 3- and 4-positions and phenyl substitution in the 4-position have been measured and found to be as large as 4500 for the 4,4-dimethyl substituted allylcarbiny l tosylate. The nature of the initial solvolytic transition state is discussed; the results are shown to be inconsistent with formation of classical carbonium ion intermediates.

1,1,4,4-Tetrafluoro-1,3-butadiene has been shown by dipole moment studies to exist in the s-trans conformation. The F^{19} - F^{19} spin-spin coupling constants for this compound were found to be very similar to those of bis-4,5-(difluoromethylene)-cyclohexene and perfluoro-1,2-dimethylenecyclobutane. These results are discussed in terms of the mechanism of fluorine-fluorine spin-spin coupling.

The dissociation constants of a series of methyl alkyl ketone cyanohydrins have been measured by nuclear magnetic resonance

spectroscopy. The heats of solution of the ketones and the cyanohydrins in methanol have been measured. The effect of alkyl groups on the heats of solution have been shown to be unimportant in determining the observed dissociation constants of the cyanohydrins of these ketones.

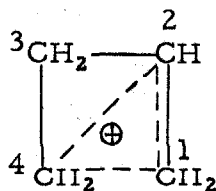
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I. THE FORMOLYSIS OF ALLYLCARBINYL TOSYLATES

Introduction

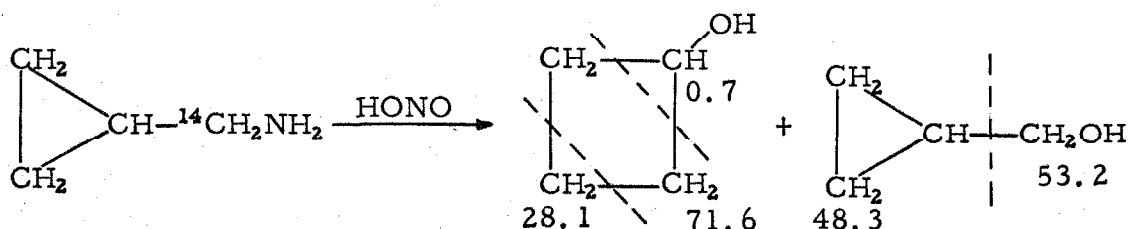
Numerous interconversion reactions of cyclopropylcarbinyll, cyclobutyl and allylcarbinyll derivatives have been reported in the last two decades (1a). In reactions where carbonium-ion intermediates can quite reasonably be assumed, cyclopropylcarbinyll and cyclobutyl derivatives are highly reactive and yield very similar products. Thus, the rate of solvolysis of cyclopropylcarbinyll chloride is 40 times and cyclobutyl chloride 1.5 times that of β -methylallyll chloride in 50% ethanol -50% water at 50° (1b); the reaction of cyclopropylcarbinol with thionyl chloride gives 69% cyclopropylcarbinyll chloride, 27% cyclobutyl chloride and 4% allylcarbinyll chloride, while cyclobutanol gives 69% cyclopropylcarbinyll chloride, 25% cyclobutyl chloride and 6% allylcarbinyll chloride (2). The striking facility with which cyclopropylcarbinyll, cyclobutyl and allylcarbinyll derivatives become interconverted in carbonium ion reactions combined with the high solvolytic reactivity of cyclopropylcarbinyll and cyclobutyl derivatives has led to the proposal that unsymmetrical bicyclic cations, termed bicylobutonium ions, I, are the reaction intermediates (3).

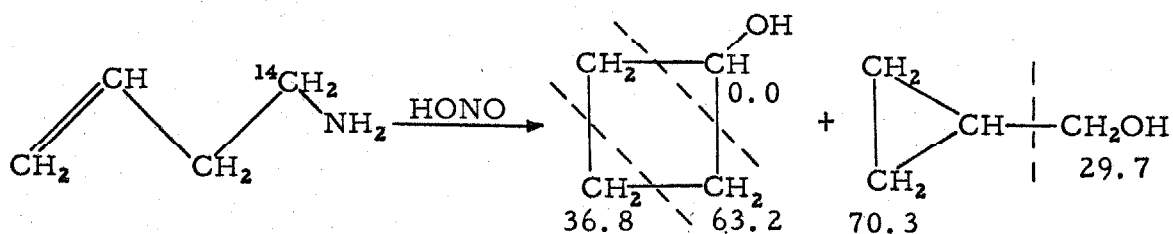


I

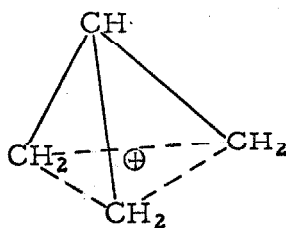
In another investigation the reaction of cyclopropylcarbinol- α - ^{14}C with Lucas reagent was found to yield allylcarbinyl chloride with the label statistically distributed among the three methylene groups (1b). Studies of the deamination of cyclopropylcarbinyl- (3) and allylcarbinyl- amines (4), the reactions of cyclopropylcarbinol and cyclobutanol with thionyl chloride (2), and the water-induced isomerization of cyclopropylcarbinyl chloride (2) using isotopic labeling techniques have shown that a high degree of equivalence of carbon atoms C_1 , C_3 , and C_4 is obtained in these reactions.

For example, the cyclobutanol and cyclopropylcarbinol resulting from the deamination of both cyclopropylcarbinyl-amine- α - ^{14}C (3) and allylcarbinylamine- α - ^{14}C (4) in aqueous nitrous acid were degraded and found to have the following ^{14}C distributions:



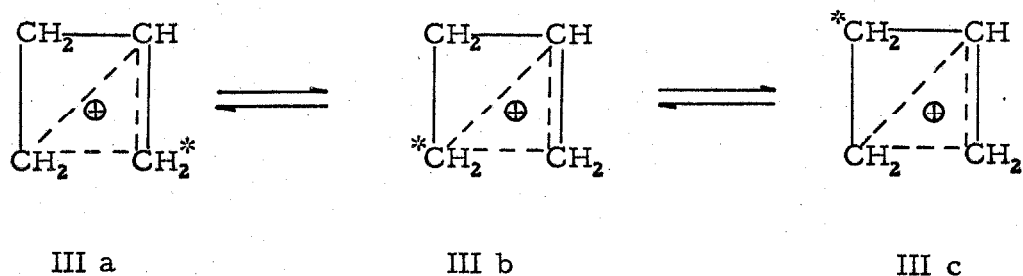


The single unsymmetrical non-classical ion, I, cannot account for the results since it would not be expected to give rise to the ^{14}C in the 3-position of cyclobutanol and the ring positions of cyclopropylcarbinol from cyclopropylcarbinylamine- α - ^{14}C deamination nor to the ^{14}C in the 2-position of cyclobutanol and the α -position of cyclopropylcarbinol from allylcarbinylamine- α - ^{14}C deamination. Similarly a completely symmetrical intermediate such as II, the tricyclobutonium ion (11, 12), cannot account for the observed results unless



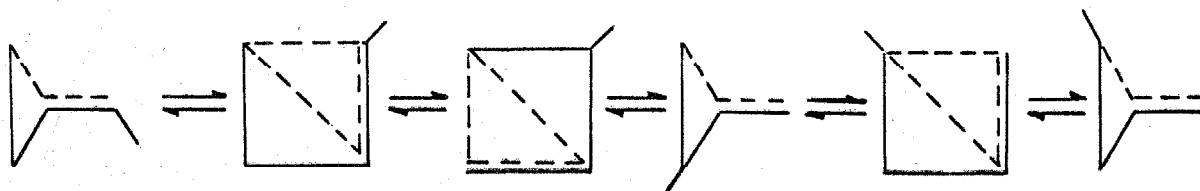
II

a competing reaction also occurs which gives only a small degree of rearrangement. The results in conjunction with the other findings have led to the suggestion that the carbonium ion-type interconversion of cyclopropylcarbinyl, cyclobutyl and allylcarbinyl derivatives involve three rapidly equilibrating non-classical "bicyclobutonium" ion intermediates, III a-c, (4).



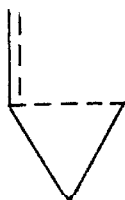
The three possible methylene-labeled bicyclobutonium ions, III a-c, are considered to interconvert readily, thereby shuffling ¹⁴C- or deuterium-labeled methylene groups between the 1-, 3-, and 4-positions. Each would react with nucleophilic reagents to give the same proportions of cyclopropylcarbinyl, cyclobutyl, or allylcarbinyl derivatives with, of course, the possibility of the label winding up in different positions depending on whether or not the product arises from IIIa, IIIb, or IIIc. To explain the ¹⁴C results it is necessary to assume that equilibration between III a-c is rapid, but not instantaneous, compared to rate of reaction with solvent.

More recently, Kover has concluded from studies of the label distribution in the products from the nitrous acid deamination of di-deutero-(α -methylallyl)-carbinylamine and dideutero-(2-methylcyclopropyl)-carbinylamine that homoallylic carbonium ions are also involved in the equilibrium (5).



However, such schemes yield little but undue complexity for the unsubstituted compounds and will not be considered further here.

Studies of participation of β -olefinic groups in solvolysis reactions have led to the formulation of the cationic intermediate either explicitly or from the resonance structures envisioned, as an unsymmetrical homoallylic ion, IV, (6,7) symmetrical homoallylic ion, V, (9,10,11) or unsymmetrical bicyclobutonium ion, III (3).

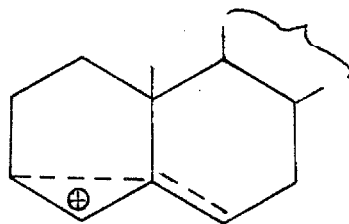


IV



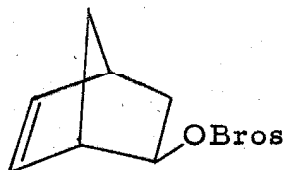
V

The stereochemistry and the kinetics of the solvolysis of cholesteryl derivatives indicate an important interaction between a carbonium ion and a β -vinyl substituent. The unsymmetrical homoallylic cation, VI, was proposed almost simultaneously by Winstein and Adams (6) and Dodson and Riegel (7).



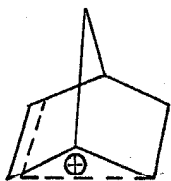
VI

The norbornenyl system is one for which both unsymmetrical (13,14) and symmetrical (15,8b) homoallylic cations have been visualized. The highly accelerated rate of solvolysis (16) of exo-norbornenyl brosylate, VII, and the results of Roberts and coworkers (15)

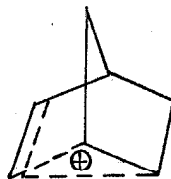


VII

on ^{14}C -scrambling in products of solvolysis of ^{14}C -labeled norbornenyl brosylate indicate that an unsymmetrical homoallylic ion, VIII, is first formed--but at least one additional cation is required. Winstein and Kosower have suggested that all three symmetrical, IX, and



VIII



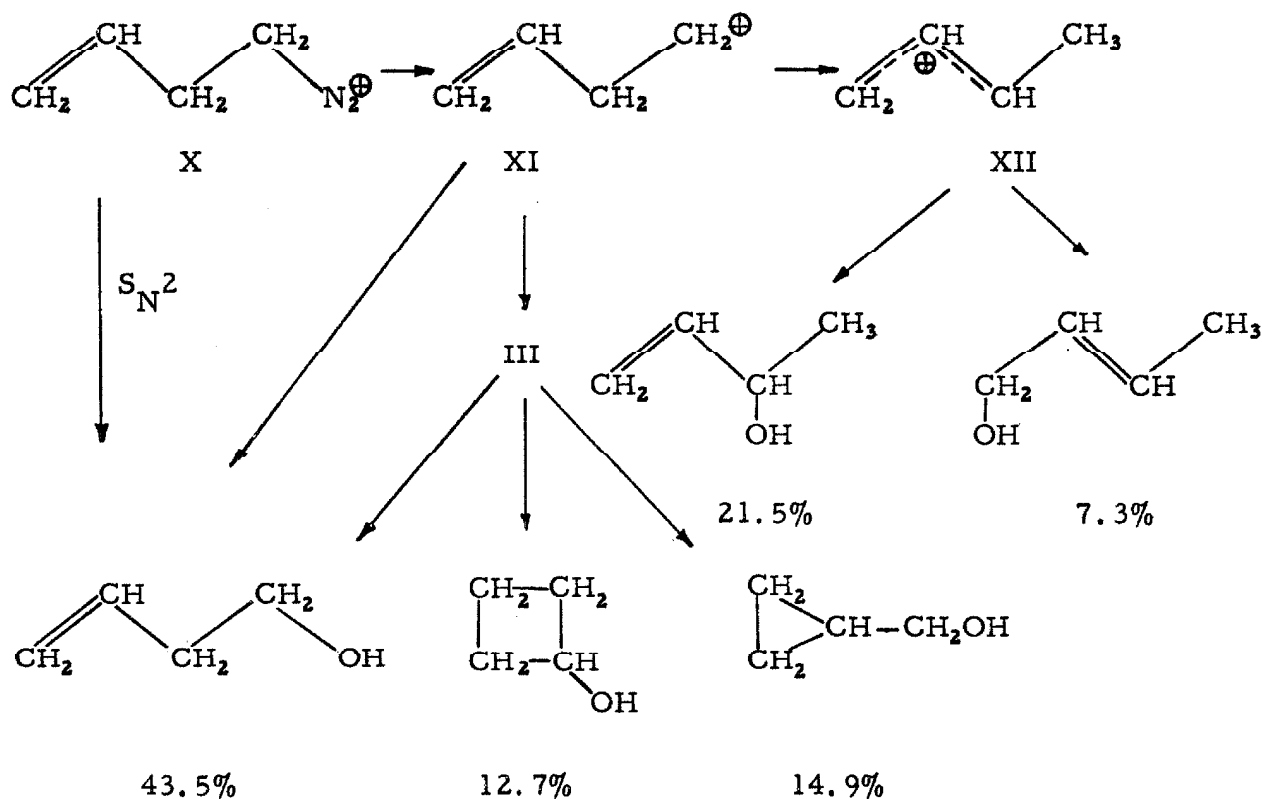
IX

unsymmetrical homoallylic cations, VIII, are involved (17). In both the norbornenyl and cholesteryl systems, bicyclobutonium ion-type intermediates are presumably precluded by the steric restrictions imposed by the carbon skeleton, since significant 1,4-interactions would require severe distortions of the carbon rings.

Theoretically, cations of structure III could also arise from solvolytic reactions of allylcarbinyl compounds. Previous investigations of the solvolyses of allylcarbinyl chloride (1), benzenesulfonate (11) and β -naphthalene sulfonate (18) afforded no evidence for bicyclobutonium ion intermediates (or even for ionic intermediates) even though such intermediates can very reasonably be invoked to account

for the products from the nitrous-acid deamination of allylcarbinyll-amine (4). However, deamination of amines has the disadvantage that comparative kinetic data cannot be obtained and "hot" (not fully solvated) carbonium ions may be produced (19). The products (Chart I) from the deamination of allylcarbinyllamine are not those expected if all of the reaction is occurring through the bicyclobutonium species--the

Chart I



methylallyl alcohols presumably arise from hydride shifts occurring in competition with bicyclobutonium ion formation in the decay of the

initial "hot" allylcarbinyll cation, XI. Further complication is provided by the fact that at least part of the allylcarbinyll derivatives formed may arise from an S_N2 -like substitution on the diazonium ion. X.

If previous formulations of the energetics of the reactions of allylcarbinyll derivatives are correct, S_N1 -type solvolysis of an allylcarbinyll compound would be expected to exhibit a small but measurable rate enhancement and give product ratios characteristic of bicyclobutonium ion intermediates. To check on these predictions, the products and the kinetics of the solvolysis of allylcarbinyll tosylate have been investigated.

Results and Discussion

The rate of solvolysis of allylcarbiny l tosylate, XIII, was determined using nuclear magnetic resonance (n.m.r.) spectroscopy (by Procedure A, see Experimental). The proton resonance of the p-methyl of the tosylate ester was found to overlap the resonance of the β -protons of the allylcarbiny l ester. For XIII, the rate of disappearance of the resonance of the α -protons of the tosylate ester was measured using diglyme as an internal standard. The diglyme concentration was approximately 0.1 that of the tosylate ester. At time t the fraction solvolyzed C was calculated from $\underline{C} = 1 - (\underline{x}s_0 / \underline{x}_0 \underline{s})$ where \underline{x}_0 = intensity of the central peak of the resonance of the α -protons of the tosylate ester at time t₀; s₀ = intensity of the methylene resonance of the internal standard at time t₀; x = intensity of the central peak of the resonance of the α -protons of the tosylate ester at time t, and s = intensity of the methylene resonance of the internal standard at time t. The rate of solvolysis was then calculated from a plot of log (1-C) versus time. The results are summarized in Table I. Each rate constant is the average of three separate determinations.

The rate of solvolysis of n-butyl tosylate, XIV, was also determined using n.m.r. spectroscopy by following the rate of disappearance of p-methyl resonance of the tosylate ester and the rate of appearance of the p-methyl resonance of the free toluenesulfonic acid. At time t, the fraction solvolyzed C was calculated from $\underline{C} = \underline{y} / (\underline{x} + \underline{y})$

Table I

Rates of Formolysis of AllylcarbinyI Tosylate and n-Butyl Tosylate

Compound	% Formic Acid in Solvent	Temp., °C	$k_1 \times 10^6 \text{ sec}^{-1}$
<u>n</u> -Butyl tosylate	80%	79.1	37.5
	80%	51.6	2.15
	98%	50.3	0.844
AllylcarbinyI tosylate	80%	79.1	60.8
	80%	51.6	2.76
	98%	50.3	3.11

where \underline{x} = intensity of the methyl resonance of tosylate ester at time \underline{t} and \underline{y} = intensity of the methyl resonance of *p*-toluenesulfonic acid at time \underline{t} . The rate of solvolysis was then calculated from the plot of $\log (1-\underline{C})$ versus time.

In these rate determinations, peak intensities rather than peak areas were determined. This method was chosen in order to permit the use of lower concentrations of the tosylate ester than that which would have been necessary for accurate integral determinations. The assumption that the peak intensities are proportional to the peak areas is undoubtedly very good for the methyl resonances of the tosylate ester and toluenesulfonic acid. The methyl groups in these two compounds are in virtually identical environments and their resonance peaks have identical shapes. The assumption that the peak intensities for the α -methylene resonance of allylcarbiny l tosylate and the methylene resonance of diglyme have the same proportionality to their integrated areas may not be entirely justified. However, these proportionality constants would cancel since the ratios of the peak intensities were used ($\underline{x}_o/\underline{x}_o$). In addition, the rate constants were determined under conditions of constant resolution. A typical rate curve is given in Figure 1.

A detailed analysis of the n.m.r. spectra of the samples used in the rate studies showed that in 98% formic acid, the products after many half-lives were allylcarbiny l and cyclobutyl formates, while the product after several months was a single component assigned the structure of 1,3-diformylbutane on the basis of its n.m.r. spectrum in

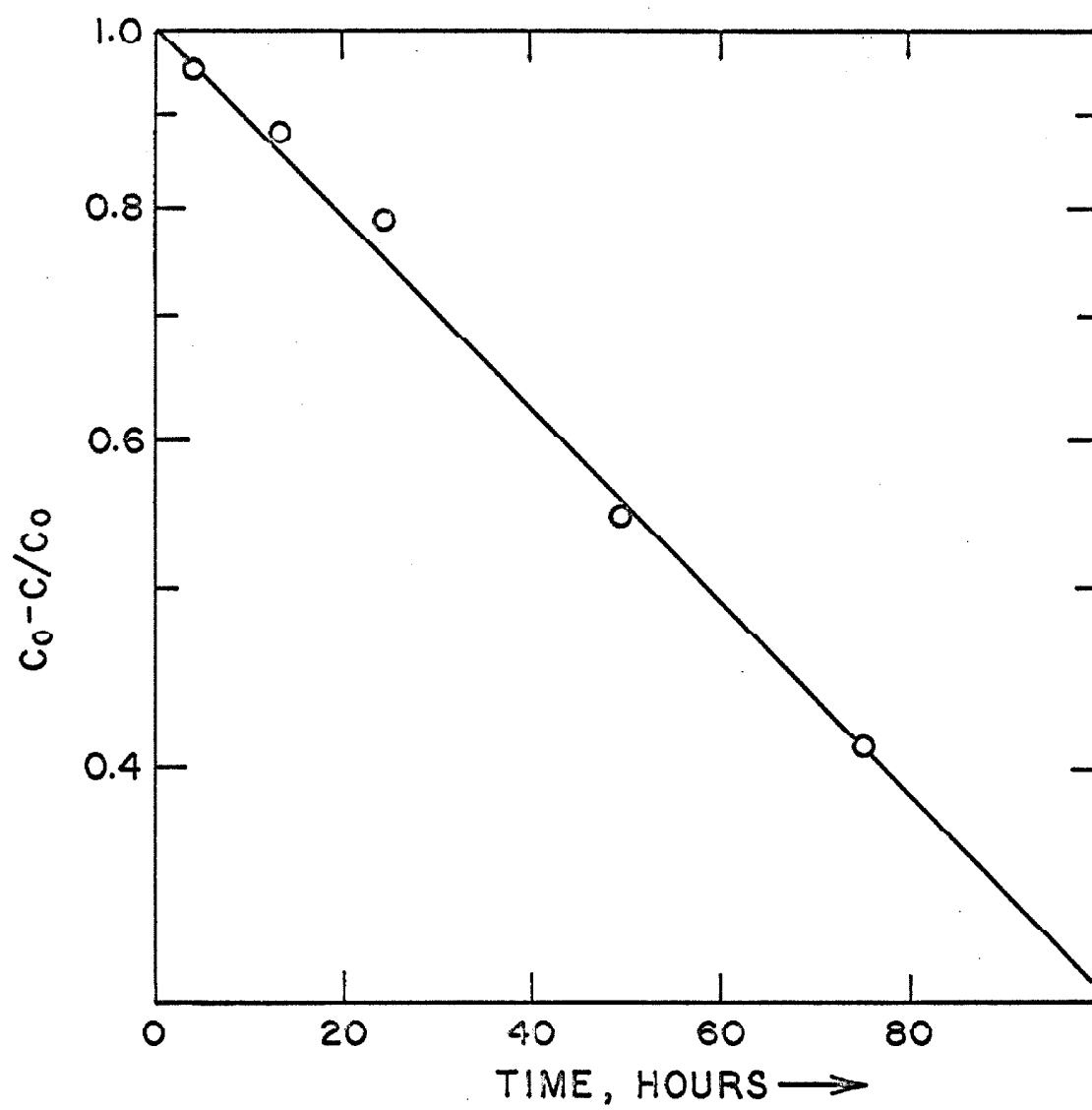


Figure 1. Rate of solvolysis of allylcarbiny tosylate



formic acid (sextet at 4.8 ppm; triplet at 3.9 ppm; quartet at 1.7 ppm and a doublet at 1.0 ppm, with areas of 1:2:2:3 respectively). This compound undoubtedly arises from the acid-catalyzed addition of formic acid to allylcarbinyl formate.

The stabilities of cyclopropylcarbinol, cyclobutanol, and allylcarbinol were determined in 98% formic acid containing added p-toluenesulfonic acid. Cyclopropylcarbinyl formate was found to rearrange to cyclobutyl formate (with added p-toluenesulfonic acid, the rate of rearrangement is estimated to be about the same as the rate of solvolysis of allylcarbinyl tosylate). Cyclobutyl formate is stable in formic acid (with added p-toluenesulfonic acid, the rate of rearrangement is less than 0.1 the rate of solvolysis of allylcarbinyl tosylate). Allylcarbinyl formate is also stable in formic acid. In formic acid containing 10% sodium formate, cyclopropylcarbinyl formate rearranges to cyclobutyl formate at about 0.1 the rate of solvolysis of XIII.

Allylcarbinyl tosylate was also solvolyzed in various mixtures of formic acid and sodium formate on a preparative scale. The formate esters were hydrolyzed in dilute sodium hydroxide. The resultant aqueous solutions were continuously extracted with ether. The concentrated ether extracts were analyzed by vapor-phase chromatography on a 1, 2, 3-tris-(2-cyanoethoxy)-propane (T.C.E.P.) column. The results are summarized in Table II. To provide a comparison for the product ratio expected from the bicyclobutonium ion intermediate in formic acid, the products from the solvolysis of cyclobutyl tosylate, XV, in various formic acid-sodium formate mixtures were determined by the method described above. These results are included in Table II.

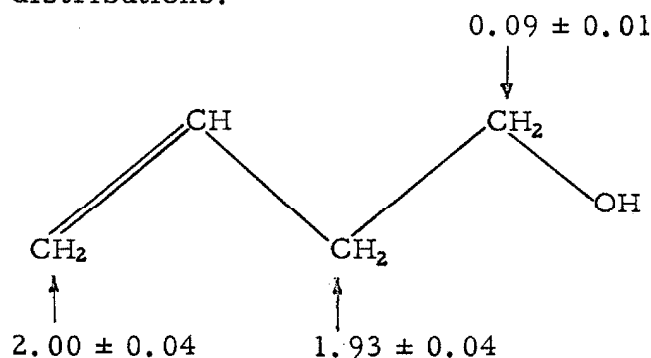
Table II

Formolysis Products of AllylcarbinyI Tosylate and Cyclobutyl Tosylate^a

Compound	% NaCHO ₂ ^b	Time, days	Cyclopropyl- carbinol, %	Products ^c		Ratio,  -CH OH 
				Cyclobutanol, %	Allyl- carbinol, %	
AllylcarbinyI tosylate	20	18	12.3	13.4	74.3	0.92
	15 ^d	21	14.4	32.0	53.6	0.45
	10	18	23.1	37.2	39.7	0.62
	5 ^d	21	3.3	70.2	26.5	0.05
Cyclobutyl tosylate	20 ^d	21	41.7	52.1	6.2	0.80
	15 ^d	21	29.8	60.8	9.4	0.48
	10	10	42.5	52.5	5.2	0.81
	5 ^d	21	3.7	90.2	6.1	0.04

^a Analyzed by v.p.c. using a 20-ft. T.C.E.P. column. ^b Weight per cent in 98% formic acid. ^c All analyses \pm 1%. ^d These experiments were run concurrently under identical conditions.

The labeled compound, 1,1-dideutero-3-buten-1-yl tosylate XVI, was prepared from 1,1-dideutero-3-buten-1-ol obtained by reduction of methyl 3-butenolate with lithium aluminum deuteride. Analysis of the tosylate by n.m.r. indicated greater than 99% isotopic purity. The labeled tosylate was solvolyzed (to ~ 95% completion) in formic acid containing 10% sodium formate. The formate esters were hydrolyzed with dilute sodium hydroxide. The alcohols were isolated by continuous ether extraction and separated by preparative v.p.c. The material recovery was estimated to be greater than 80%. The 60 Mcps. n.m.r. spectrum of the resulting allylcarbinol is shown in Fig. 2. The integrated areas of the proton resonances were determined by averaging thirty separate integrations using a H.P.405CR digital voltmeter for integral measurements. These gave, after normalizations the following proton distributions.

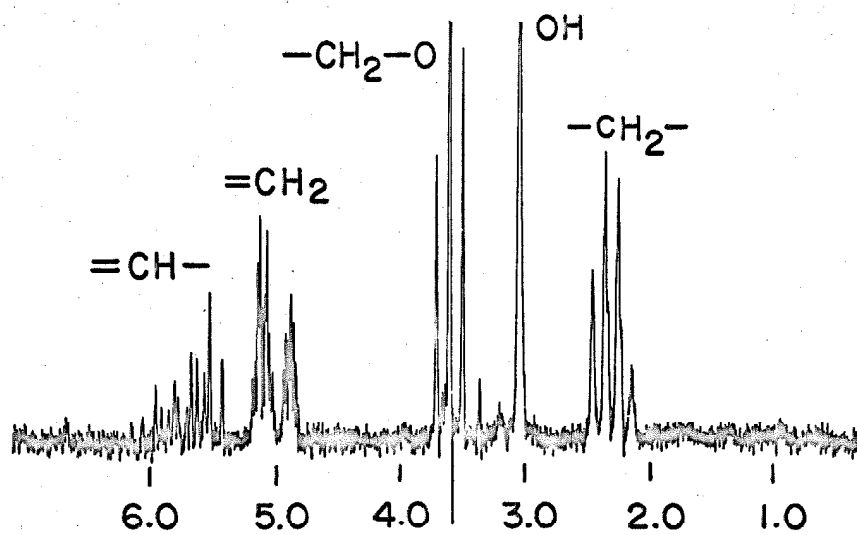


The 60 Mcps. n.m.r. spectrum of the recovered mixture of cyclopropylcarbinol and cyclobutanol from the formolysis of XVI is shown in Fig. 3. The integrated areas of the proton resonances were determined by averaging ten separate integrations using the digital voltmeter. For the cyclopropylcarbinol, the ratio of the methylene

Figure 2. A, The 60-Mcps nuclear magnetic resonance spectrum of allylcarbinol; B, the 60-Mcps nuclear magnetic resonance spectrum of allylcarbinol-D₂ from the formolysis of 1,1-dideutero-3-buten-1-yl tosylate.

-16a-

2A



2B

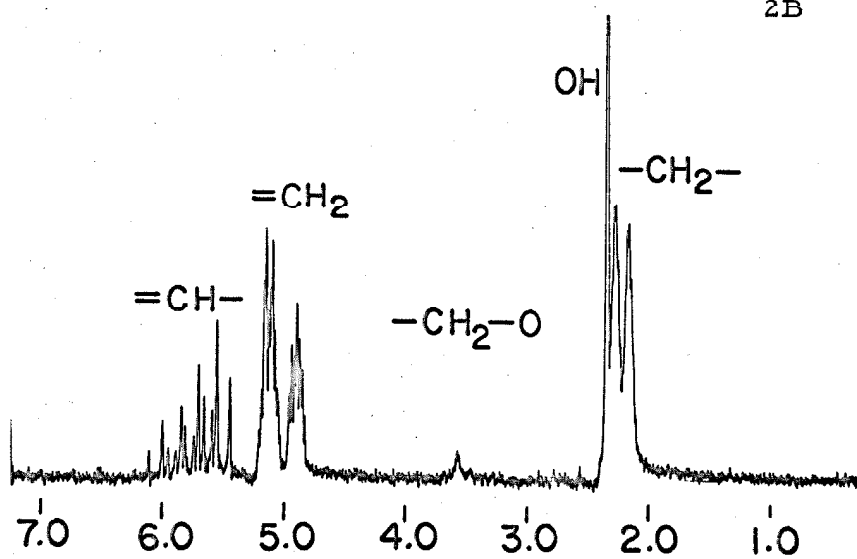
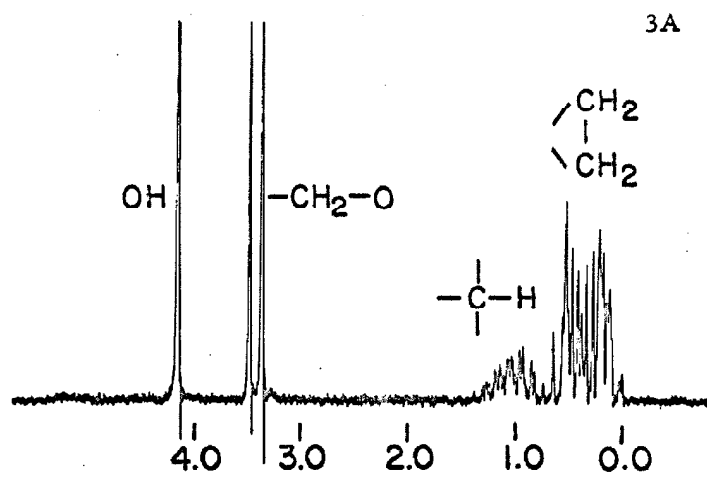
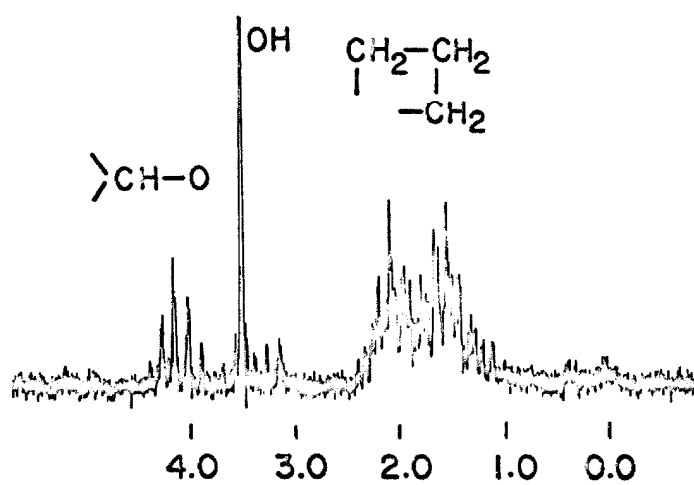


Figure 3. A, The 60-Mcps nuclear magnetic resonance spectrum of cyclopropylcarbinol; B, the 60-Mcps nuclear magnetic resonance spectrum of cyclobutanol; C, the 60-Mcps nuclear magnetic resonance spectrum of the mixture of cyclopropylcarbinol-D₂ and cyclobutanol-D₂ from the formolysis of 1,1-dideutero-3-buten-1-yl tosylate.

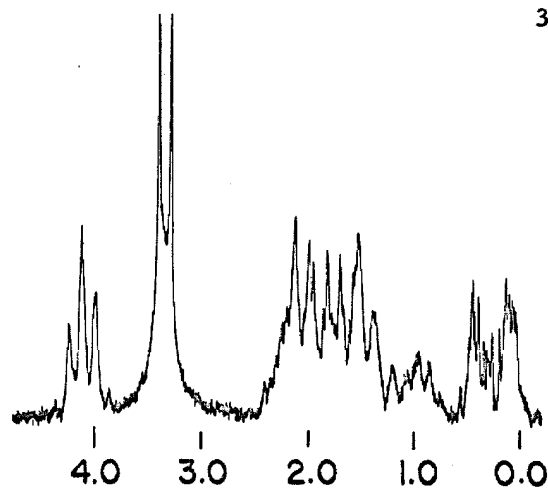
-17a-



3B



3C



protons to the β -ring protons was found to be 1.00 to 2.00. For the cyclobutanol, one cannot clearly distinguish the resonances for the 2- and 3-positions of the ring, but the general appearance of the spectrum suggests that the deuterium label is statistically distributed between the methylene groups.

If the double bond does not participate anchimerically in the ionization of allylcarbinyl tosylate, one would predict from a comparison of the acidities of 3-butenic acid ($K_A = 4.45 \times 10^{-5}$) and butanoic acid ($K_A = 1.56 \times 10^{-5}$) (23) that the allylcarbinyl compound would solvolyze slower than the saturated analog by a factor of 2. This is, in fact, confirmed by the reported rates of solvolysis of these types of compounds under conditions where anchimeric assistance to the ionization is not expected (Table III).

In 98% formic acid, allylcarbinyl tosylate solvolyses faster than n-butyl tosylate by a factor of 3.7. This rate enhancement, when compared to the results for the ethanolic solvents, suggests that a change in the solvolytic mechanism for allylcarbinyl tosylate has occurred in going from ethanol to formic acid solvent. This supposition is verified by the relative sensitivities of the rates of solvolysis of allylcarbinyl tosylate and n-butyl tosylate to changes in solvent nucleophilicity. If both reactions actually correspond to bimolecular displacement of the tosylate group by a solvent molecule, the rates should show the same sensitivity to an increase in the nucleophilicity of the solvent. For example, the relative solvolysis rate of methyl bromide to ethyl bromide in absolute ethanol is 2.60 and in 80% ethanol is 2.51 (22).

Table III

Rate of Solvolysis of Allylcarbiny and n-Butyl Derivatives in Ethanolic Solvents

Compound	Temp., °C	Solvent	Rate, sec ⁻¹	Ref.
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{OSO}_2\text{C}_{10}\text{H}_7$	60	100% EtOH	4.7×10^{-6}	18
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-\text{OSO}_2\text{C}_{10}\text{H}_7$	60	100% EtOH	8.7×10^{-6}	18
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{Cl}$	100	50% EtOH	1.66×10^{-6}	16
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	100	50% EtOH	7.95×10^{-6}	20
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{OSO}_2\text{C}_6\text{H}_5$	55	100% EtOH	2.3×10^{-6}	11
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-\text{OSO}_2\text{C}_6\text{H}_5$	55	100% EtOH	4.3×10^{-6}	21

However, if the two compounds do not solvolyze by the same mechanism, their solvolysis rates should not respond identically to an increase in the nucleophilicity of the solvent. The argument here is the one used by Bartlett and Bank with respect to anchimeric assistance in the formolysis of β -cyclopentenylethyl tosylate and its saturated analog (24).

The rate ratio for allylcarbiny l tosylate to n-butyl tosylate decreases from 3.7 in 98% formic acid to 1.3 in 80% formic acid. The relative insensitivity of the rate of solvolysis of allylcarbiny l tosylate to the change in the nucleophilicity of the solvent implies that XIII is solvolyzing by an S_N1 mechanism. Both the corrected rate ratio $k^{XIII}/k^{XIV} = 7.5$ and the difference in sensitivity of the rates to solvent changes must be a result of a change in solvolysis mechanism on going from allylcarbiny l tosylate to the saturated analog.

The products from the solvolysis of allylcarbiny l tosylate are not all stable in 98% formic acid. In the presence of sodium formate, the products are more stable but then a competitive S_N2 reaction of the tosylate with formate occurs, as evidenced by the increasing percentage of allylcarbiny l products with increasing formate concentration. By extrapolation to zero concentrations of sodium formate, it is predicted that approximately 10% of the products would have the allylcarbiny l structure under these conditions if the products were completely stable. The ratios of cyclopropylcarbiny l to cyclobutyl formate produced are essentially the same for the solvolysis of allylcarbiny l tosylate and cyclobutyl tosylate under comparable conditions. The cyclopropyl-

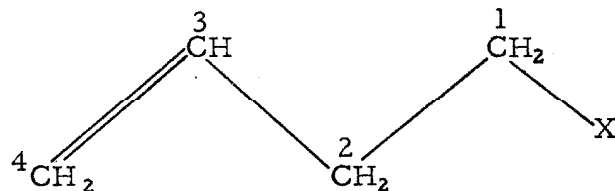
carbinyll to cyclobutyl product ratio is estimated to be about 1.0 under conditions where both products are stable. With the aid of these two extrapolations, the predicted initial product composition in 98% formic acid is $45 \pm 5\%$ cyclopropylcarbinyll, $45 \pm 5\%$ cyclobutyl and $10 \pm 5\%$ allylcarbinyll formates. This is in good agreement with the product mixtures usually obtained in carbonium-ion reactions of cyclopropylcarbinyll and cyclobutyl compounds. Thus, the reactions of cyclopropylcarbinyllamine and cyclobutylamine with nitrous acid, the solvolysis of cyclopropylcarbinyll, cyclobutyl and allylcarbinyll derivatives (1, 25), the reactions of cyclopropylcarbinol and cyclobutanol with thionyl chloride, and cyclopropylcarbinol with hydrogen bromide or phosphorous tribromide (26) all give mixtures having closely similar relative amounts of products with the cyclopropylcarbinyll, cyclobutyl and allylcarbinyll structures.

In contrast to allylcarbinyllamine deaminations (4), no methylallyl alcohols are obtained in the solvolysis of allylcarbinyll tosylate. The occurrence of these allyl alcohols in deamination implies that the initial carbonium ions from these two different reactions are not identical. The initial carbonium ion from the amine deamination is probably a highly energetic classical allylcarbinyll cation, XI. This carbonium ion can be deactivated by collisions to yield the bicyclobutonium ion, III; or it can undergo a hydride shift to produce a methylallyl cation, XII. In solvolysis, double-bond participation produces the bicyclobutonium ion without competing hydride shifts. The methylallyl alcohols from the amine deamination are thus abnormal products

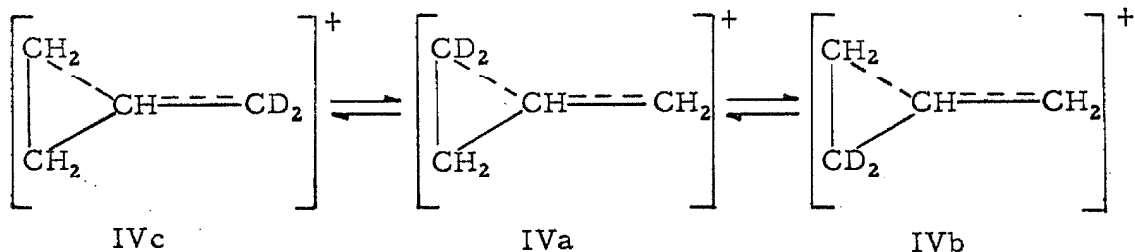
arising from a "cascade effect" for the hot carbonium ion produced in the decomposition of the diazonium ion, X.

The studies of the products from the solvolysis of labeled allylcarbinyl tosylate provide additional support for entrance into the equilibrating bicyclobutonium ion system from the allylcarbinyl side. As predicted from other results, the isotopic label is essentially statistically distributed between the methylene groups for both the cyclopropylcarbinyl and cyclobutyl products. The large percentage of allylcarbinyl products from S_N2 displacement under the conditions of the study makes determination of the label distribution in the allylcarbinyl products from the S_N1 reaction difficult. The difference observed for the distribution of the label in the 2- and 4-positions of the allylcarbinyl product are on the edge of the experimental error.

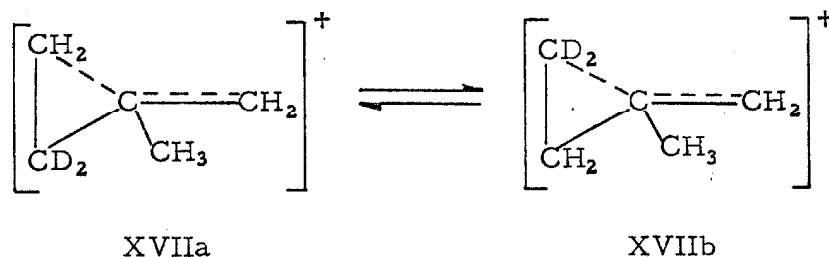
These differences, if real, suggest that equilibration of the methylene groups in positions 1 and 2 may be more rapid than equilibration of the methylene groups in positions 1 and 4. This could be



rationalized if the initial solvolytic intermediate were of the homoallylic



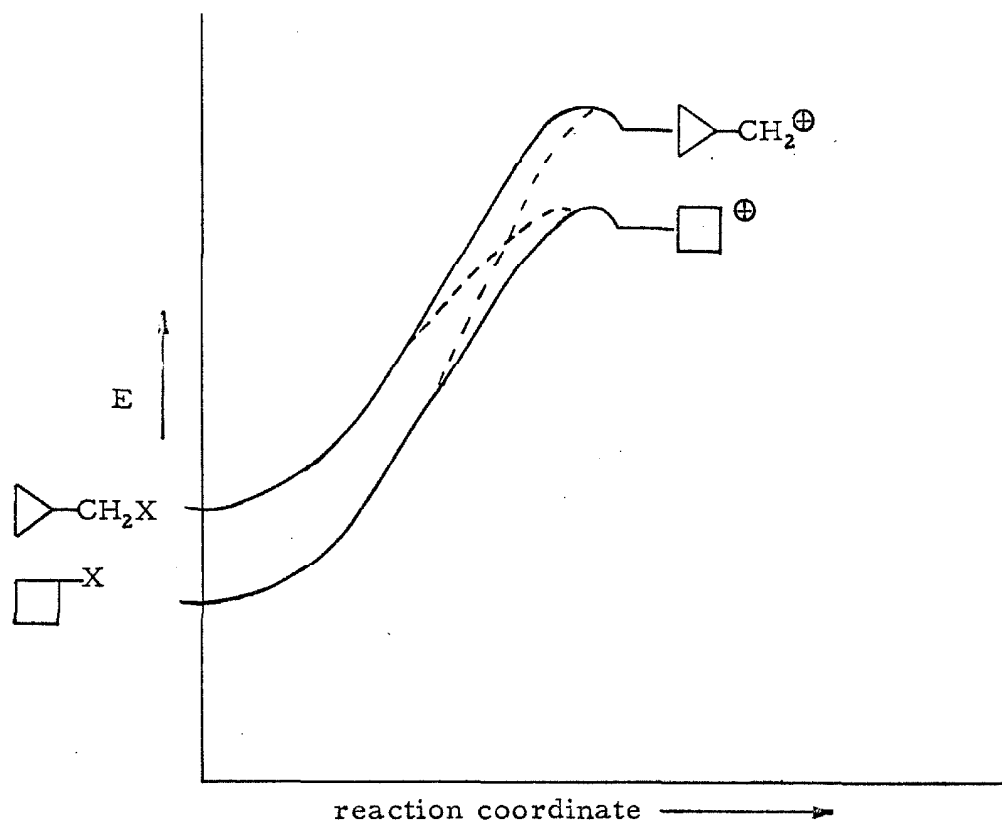
type IVa. A more rapid interconversion of IVa and IVb than IVa and IVc would then predict more redistribution into the 2- than into the



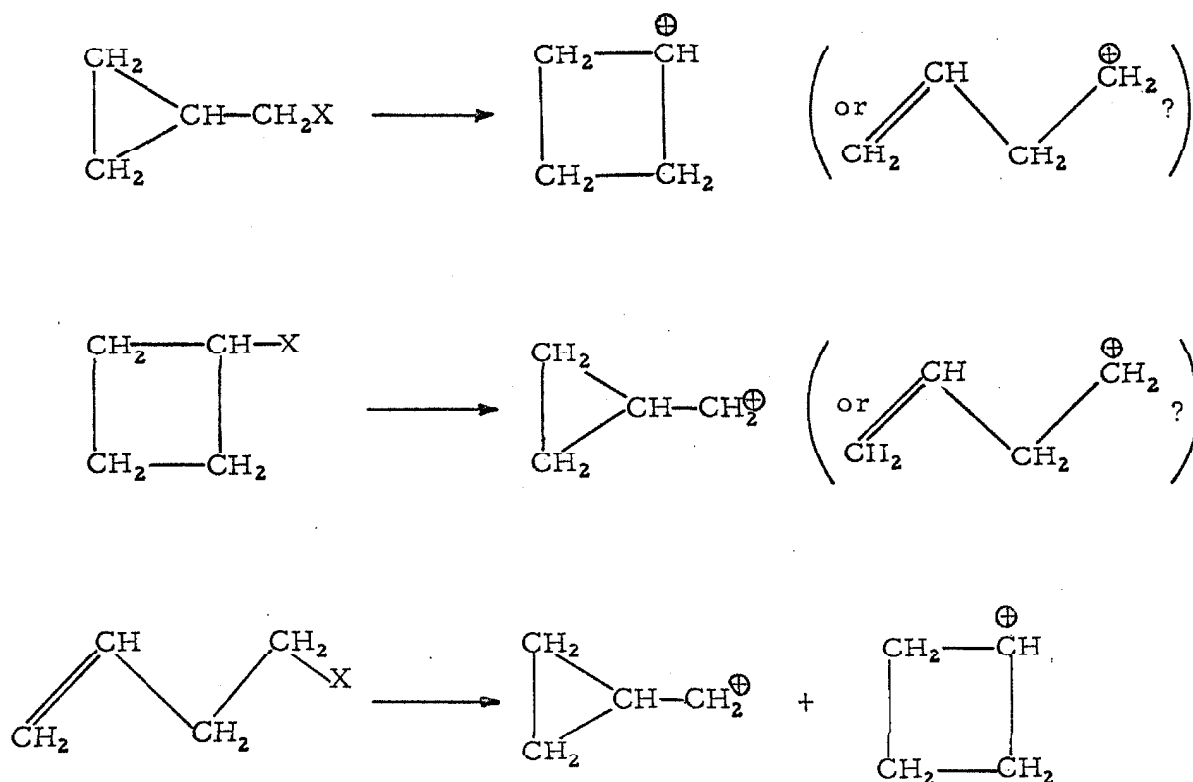
4-position. However, Kover has concluded from studies of the label distribution in the products from the deamination of dideutero-(β -methylallyl)-carbinylamine that equilibration of ions XVIIa and XVIIb is not easy (5). The inaccuracy of the present data prevents a firm decision on this point.

Alternative explanations for the rate enhancements and label redistribution in the solvolytic reactions of cyclopropylcarbinyl and cyclobutyl compounds have been offered by Brown (27). Arguments for non-classical intermediates based on solvolytic rate enhancements for cyclopropylcarbinyl halides and *p*-toluenesulfonates were originally dismissed by him on the grounds that solvolysis of some cyclopropylcarbinyl derivatives give no rearranged products but still show enhanced rates. This argument implies that any rate enhancement due to non-classical electron delocalization must result from the formation of an intermediate which will react with a nucleophile to give rearranged products. A logical extension of this argument would deny electron delocalization in a benzylic cation since no rearranged products are observed. Formation of rearranged products is not a necessary consequence of the intervention of non-classical cations as intermediates.

The enhanced rates have also been ascribed to relief of strain in the transition states for formation of intermediates with unspecified but "classical" structures (28). There can be no relief of strain in any classical sense in the ionization of a cyclopropylcarbinyl derivative to a cyclopropylcarbinyl cation. Relief of strain could occur if a cyclopropylcarbinyl derivative were to ionize to form a cyclobutyl cation or an allylcarbinyl cation. However this does not explain the rate enhancements observed in the solvolysis of cyclobutyl or allylcarbinyl derivatives. If the solvolyses of cyclopropylcarbinyl derivatives are accelerated because of formation of a cyclobutyl cation then the solvolyses of cyclobutyl derivatives cannot be accelerated because of formation of a cyclopropylcarbinyl cation. This is most clearly seen in the following reaction coordinate diagram.

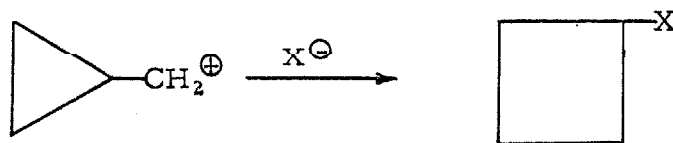


Rate enhancements in all three systems cannot be explained by the formation of rearranged classical ions on solvolysis. Furthermore, attempts to explain the observed product distribution are difficult to incorporate into this scheme.



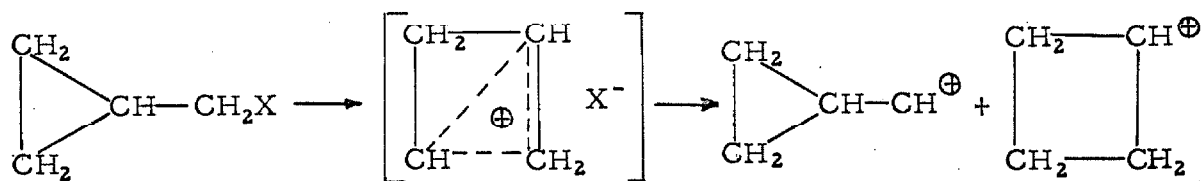
For example, the cyclobutyl derivatives would be highly reactive because they form cyclopropylcarbinyl cations directly. However this does not explain the very large fraction of cyclobutyl products observed. The equilibrium $\square^+ \rightleftharpoons \triangle\text{---CH}_2^+$ could be invoked for this but such an explanation cannot account for the rate enhancement unless $\square\text{---X}$ does not give \square^+ but only $\triangle\text{---CH}_2^+$. If so, formation of cyclobutyl product from \square^+ would violate the law of

microscopic reversibility. To avoid this difficulty, one could have



Such a reaction obviates all need for envisioning equilibrium between classical cations and furthermore requires a high percentage of the positive charge on the methinyl carbon of the ring. In conjunction with the other two systems, this type of explanation leads to insuperable difficulties.

In Brown's latest effort to escape the necessity of invoking non-classical intermediates in these systems, he has proposed that "ionization proceeds directly into a rapidly equilibrating set of classical cyclopropylcarbinyl and cyclobutyl cations, with the bicyclobutonium species representing the transitions state between the classical ions" (29). This would presumably also require the bicyclobutonium species as the transition state leading from the starting material to the solvolytic intermediates in order to explain the rate enhancements. It is difficult to see why one should have a non-classical transition state in the solvolysis of a cyclopropylcarbinyl compound to a cyclopropylcarbinyl cation. Any factors which lower the energy of the initial



Transition State

cationic transition state should also lower the energy of a similar cationic intermediate with respect to the classical intermediate. Cyclopropylcarbinyl chloride is about 1/15 as reactive as t-butyl chloride in S_N¹ reactions and can therefore be estimated to be about 10¹⁰/15 ≈ 10⁸ times more reactive in forming a carbonium ion than a primary chloride (30). Such a rate difference corresponds to a difference in activation energy on the order of 11 kcal. It does not seem feasible that such a large energy gain by formation of the initial non-classical transition state would be unimportant in the cationic intermediate. An explanation of the rate enhancement based on a non-classical transition state in the initial ionization was proposed some years ago by Roberts and coworkers.

Brown has recently argued in the 1- and 2-phenylnorbornyl systems that in an endothermic process, such as solvolysis, the transition state will resemble product (31). Since the first product in these solvolyses is presumed to be the non-classical ion, he concludes (by an overextension of the Hammond postulate) (32) that the transition states leading to this ion are virtually identical. Invoking of equivalence between transition state and the first product in solvolysis of cyclopropylcarbinyl, cyclobutyl and allylcarbinyl derivatives would require, by Brown's present explanation of the rate enhancements, non-classical bicyclobutonium intermediates. Brown has apparently recognized the fallacy of the argument he used in the norbornyl system and avoids using it for this system.

The observed product ratio requires that the relative concentrations and therefore the relative stabilities of cyclopropylcarbinyl,

cyclobutyl, and allylcarbinyl cations be on the order of 10:10:1. This requires that the cyclopropylcarbinyl cation be about 1.5 kcal more stable than the allylcarbinyl cation. In the absence of any interaction of the carbinyl cationic center with either substituent, the cyclopropylcarbinyl cation would be expected to be 5-7 kcal less stable than the allylcarbinyl cation (33). Brown suggests that "the cyclopropylcarbinyl cation is highly stabilized by some sort of electron release, but that this stabilization has nothing to do with any bonding between the carbonium carbon and either the two carbons of the ring, or with one of the three carbon-carbon bonds in the ring" (29). It is difficult to visualize electron release by the ring that does not involve in some way the C-C electrons. Apparently an inductive effect is required. The necessary σ^* constant to explain the proposed stability of the cyclopropylcarbinyl cation can be estimated by the following procedure. The largest known ρ^* value is for the acid-catalyzed hydrolysis of formals where $\rho^* = -4.173$ (34). As a conservative estimate assume $\rho^* = -10$ for the stability of carbonium ions. Since σ^* for an allyl group is 0.26**, the allylcarbinyl cation would be inductively destabilized by 1.5 kcal. This requires then that the cyclopropylcarbinyl cation be inductively stabilized by 5-7 kcal and implies (using $\rho^* = -10$) that the cyclopropylcarbinyl group has a σ^* value of at least -0.9. This is three times greater than the largest σ^* value previously reported ($\sigma^*_{\text{t-C}_4\text{H}_9} = -0.3$) (35). Such a large inductive stabilization of a cationic center by a cyclopropyl group does

**Calculated from the ionization constant of 3-butenic acid ($K_A = 1.56 \times 10^{-5}$) for which $\rho^* = 1.721$.

not seem reasonable and is not in accord with the fact that cyclopropylcarboxylic acid is a stronger acid than acetic acid.

In order to provide further support for the occurrence of bicyclobutonium ion intermediates in the solvolysis of allylcarbinyl derivatives and to gain more detailed information on the structure and charge distributions in these species, the rates and products of solvolysis of several substituted allylcarbinyl tosylates have been investigated.

In 98% formic acid, (β -methylallyl)-carbinyl tosylate appears to add solvent to the double bond at a rate comparable to the rate of solvolysis. After 30 minutes at 40°, no olefinic absorption could be detected in the n.m.r. spectrum of a sample of (β -methylallyl)-carbinyl tosylate in 98% formic acid. After several hours at 50° in 80% formic acid, the (β -methylallyl)-carbinyl tosylate was only 30% solvolyzed but the absorption of the olefinic protons in the n.m.r. spectrum had decreased by more than 70%. Similar difficulties were encountered in the use of 10% sodium formate in formic acid as a solvent.

At the suggestion of Dr. S. Borcic, a mixture of 10% pyridine in formic acid was investigated as a possible solvent. Using this solvent, no evidence could be found for the undesirable side reactions which had occurred in the other solvents; the solvolysis showed clean first-order kinetics. No really satisfactory explanation of the peculiarity of this unusual solvent can be offered, however, ion-pair phenomena may well be responsible.

The rate of solvolysis of (β -methylallyl)-carbinyl tosylate was determined by the previously described n.m.r. technique.

In order to obtain the rate acceleration provided by a methyl substituent on the methinyl center, the rate of solvolysis of allylcarbinyl tosylate was also determined in 10% pyridine in formic acid. The results are given in Table IV.

cis- and trans-3-Penten-1-ol were separated by preparative v.p.c. and found to be 98% pure by analytical v.p.c. The structural assignment is based on infrared studies of the 650 to 1000 cm^{-1} region (36). The material assigned the trans structure had the characteristic infrared absorption band at 955 cm^{-1} (Fig. 4). The material assigned the cis structure had the characteristic infrared absorption band at 690 cm^{-1} (Fig. 4).

The rates of solvolysis of cis- and trans-3-penten-1-yl tosylates were too fast to measure by the usual n.m.r. technique at 50°. For these two compounds, the n.m.r. tubes of the solutions of the tosylates in 10% pyridine in formic acid were placed in the variable temperature probe of the Varian V-4300B n.m.r. spectrometer. The probe temperature was controlled at $50.5 \pm 0.5^\circ$ * with a heated nitrogen stream. Spectra were taken continuously. The rates of solvolysis were then calculated in the usual fashion. The results are included in Table IV.

4-Phenyl-3-buten-1-ol was prepared by the addition of the Grignard reagent from β -styryl bromide to ethylene oxide. The cis- and trans-isomers were separated by preparative v.p.c. The

*The error indicates variation of temperature during the experiment; the absolute temperature in the sample tube is accurate only to $\pm 2^\circ$.

Table IV

Solvolysis Rates of Substituted Allylcarbinyl Tosylates

Compound	T., °C	Method ^d	$k_1 \times 10^4$	k_{rel}	k_{rel}
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OTs}$	50.3	A	0.00844 ^b		1
$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{OTs}$	50	A	0.0136 ^a	1	
	50.3	A	0.0311 ^b		3.7
$\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_2\text{OTs}$	50	C	2.89 ^a	210	770 ^e
	50.1	B	4.6 ^b		
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}=\text{CHCH}_2\text{CH}_2\text{OTs}$	50.1	C	0.614 ^a	45	165 ^e
$\text{CH}_3\text{C}(\text{CH}_3)=\text{CHCH}_2\text{CH}_2\text{OTs}$	50	A	0.0431 ^a	3.3	12 ^e
$\phi\text{CH}=\text{CHCH}_2\text{CH}_2\text{OTs}$	50.1	B	2.1 ^b	96 ^c	350 ^e
$\text{CH}_3\text{C}(\text{CH}_3)=\text{CHCH}_2\text{CH}_2\text{OTs}$	49.9	B	100 ^b	4500 ^c	16500 ^e

a) 10% pyridine in 98% formic acid

b) 98% formic acid

c) Based on trans-3-penten-1-yl tosylate as 210

d) See experimental section for procedures

e) Based on 3-buten-1-yl tosylate as 3.7

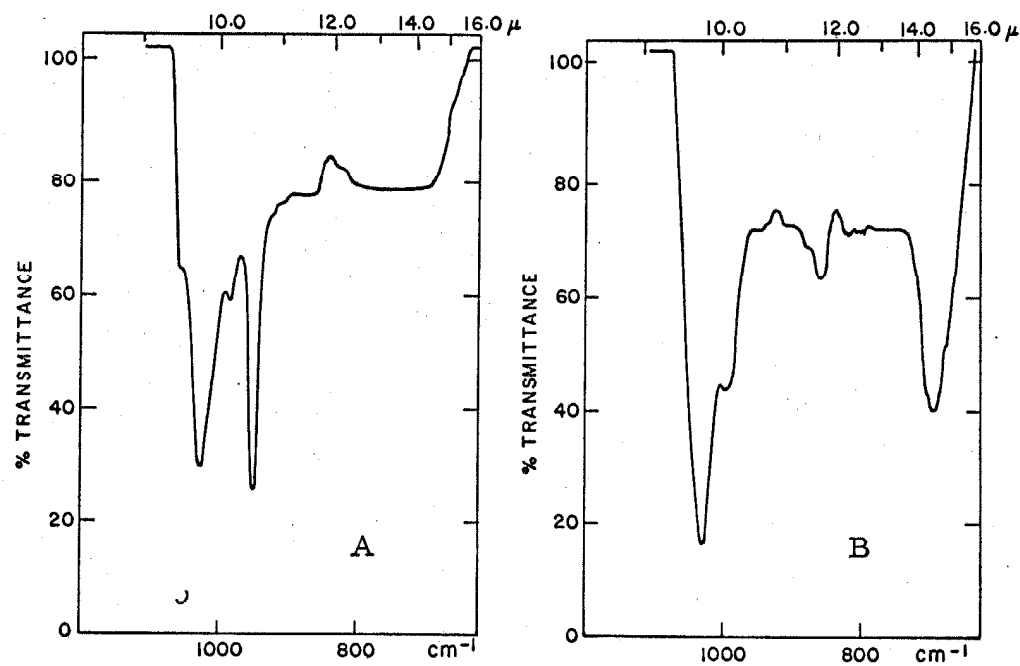


Figure 4. A, The infrared spectrum of trans-3-pentenol;
B, the infrared spectrum of cis-3-pentenol.

structural assignment was based on infrared spectra of the 650 to 1000 cm^{-1} region (37). The strong band at 735 cm^{-1} for the trans-compound splits into three bands at 735, 760 and 790 cm^{-1} in the cis-compound. As expected, the trans-compound was the major product (Fig. 5).

The rate of solvolysis of trans-4-phenyl-3-buten-1-yl tosylate was measured on an International Instrument Co. Difunctional Recording Titrater. A special Teflon cell cover (described in the experimental section) was constructed to provide a completely sealed reaction vessel. The amount of base added to maintain a constant pH was plotted against time. The rates were determined from the usual plot of $\log \frac{a_{\infty} + x}{a_{\infty}}$ versus time: a_{∞} = infinity titer, x = titer at time, t . It should be noted that the rate constants determined in this fashion are larger than the actual solvolytic rate constant if an internal rearrangement to a much less reactive material is occurring. The observed rate constant is the sum of the solvolytic rate constant, k_s , and the rearrangement rate constant, k_r (17). Estimates based on the infinity titers indicate that $k_r \ll 0.2 k_s$. An error as large as 20% in the observed rate constants would not effect the conclusions to be reached from these studies.

The rates of solvolysis of trans-3-penten-1-yl tosylate, 4-methyl-3-penten-1-yl tosylate and trans-4-phenyl-3-buten-1-yl tosylate were determined by the automatic titration procedure. These results are summarized in Table IV.

The products of formolysis of cis- and trans-3-penten-1-yl tosylate and (β -methylallyl)-carbinyl tosylate in 10% pyridine-formic

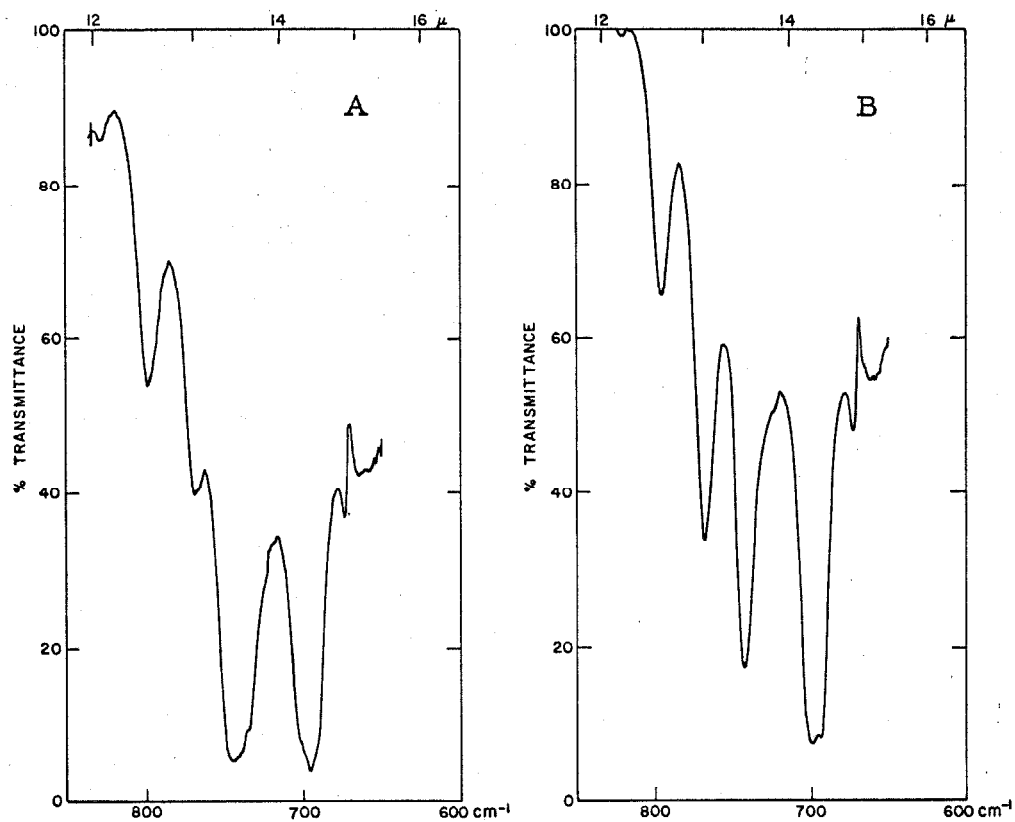


Figure 5. A, The infrared spectrum of trans-4-phenyl-3-butenol; B, the infrared spectrum of cis-4-phenyl-3-butenol.

acid were determined. The initial formolysis products were hydrolyzed with dilute sodium hydroxide and continuously extracted into ether. The resultant alcohols in the concentrated ether extracts were analyzed by v.p.c. on a 20-ft. T.C.E.P. column at 120°. The stability of α -cyclopropylethanol, the product expected from the 3-penten-1-yl tosylates, was determined by subjecting it to the formolysis conditions. The results are given in Table V. The products from the reaction of the corresponding amines with nitrous acid are given in Table VI (5, 38).

The ratio of 2-methylcyclobutanol to allylmethylcarbinol from the solvolysis of both trans-3-penten-1-yl tosylate and cis-3-penten-1-yl tosylate is about 0.7; the ratio obtained by subjecting α -cyclopropylethanol to the solvolysis conditions is 0.8. The ratios of 3-penten-1-ol to allylmethylcarbinol from solvolyses of both 3-penten-1-yl tosylates are about 2.4; the same ratio obtained by subjecting α -cyclopropylethanol to the solvolysis conditions is also 2.4. This implies that the initial product from the solvolysis of both cis- and trans-3-penten-1-yl tosylates has the cyclopropylmethylcarbiny structure.

The products from the deamination of 3-penten-1-yl amines differ in two respects: 1) a high percentage of structurally unrearranged material is obtained; 2) a high percentage of hydride shift product is formed. The unrearranged product in the amine deamination probably arises from a direct displacement reaction on the diazonium ion as was previously suggested (26). The substituted allyl alcohols result from hydride shifts in the initial "hot" carbonium ion produced by decomposition of the diazonium ion.

Table VI

Products from the Amine-Nitrous

Acid Reaction of Substituted Allylcarbinylamines

	$\begin{array}{c} \text{H}-\text{C}=\text{CH}-\text{CH}_2-\text{NH}_2^a \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_2\text{C}=\text{C}-\text{CH}_2-\text{NH}_2^b \end{array}$	
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2-\text{CH}-\text{CH}_2-\text{OH} \\ \\ \text{CH}_2 \end{array}$	0	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2-\text{C}-\text{OH} \\ \quad \\ \text{CH}_2-\text{CH}_2 \end{array}$	59
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2-\text{CH}-\text{CH}-\text{OH} \\ \quad \\ \text{CH}_2 \end{array}$	74	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2-\text{C}-\text{CH}_2-\text{CH}_2-\text{OH} \\ \\ \text{CH}_2 \end{array}$	29
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2-\text{CH} \\ \quad \\ \text{CH}_2-\text{CH}-\text{OH} \end{array}$	0	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2-\text{C}-\text{CH}-\text{CH}_3 \\ \quad \\ \text{CH}_2 \quad \text{OH} \end{array}$	6
$\begin{array}{c} \text{H}-\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{OH} \\ \\ \text{CH}_3 \end{array}$	10	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}=\text{C}-\text{CH}_2-\text{OH} \\ \\ \text{H} \end{array}$	6
$\begin{array}{c} \text{CH}_2 \\ \\ \text{CH}_3-\text{CH}-\text{CH}-\text{CH}_2-\text{OH} \end{array}$	0		
$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3-\text{CH}=\text{CH}-\text{CH}-\text{CH}_3 \end{array}$	16		

a) Ref. 38

b) Ref. 5

1-Methylcyclobutanol was essentially the only product obtained from the solvolysis of (β -methylallyl)-carbinyl tosylate. The very small amount of (β -methylallyl)-carbinol very probably is a secondary rearrangement product. Again, the rather different product mixture obtained upon deamination of (β -methylallyl)-carbinyl amine seems best explained by intervention of a direct displacement reaction on the diazonium ion accompanied by hydride shifts involving an initial hot carbonium ion.

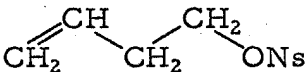
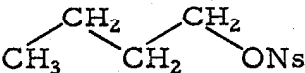
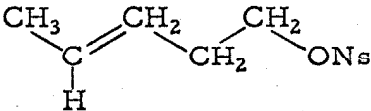
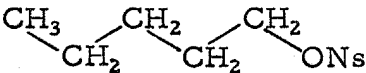
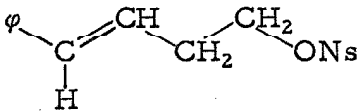
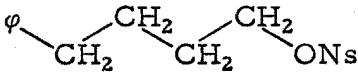
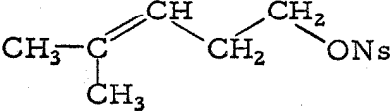
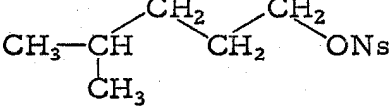
The observed rate accelerations require participation of the double bond in the transition state of the rate-determining step in formolysis. In ethanolysis of 3-penten-1-yl and 4-phenyl-3-buten-1-yl β -naphthalenesulfonate (39) the substituent has essentially no effect on the rate of solvolysis. Clearly the substituent produces no significant rate increase through either steric or inductive effects. A rate enhancement of 4500 by dimethyl substitution on a position 3 carbons removed from the reaction center cannot be due to either inductive or steric acceleration. The near additivity of the substituent effects supports the conclusion that the origin of the rate enhancement is electronic in nature.

The rates of ethanolysis of several of these same compounds have recently been determined (Table VII). Allylcarbinyl, trans-3-penten-1-yl and trans-4-phenyl-3-buten-1-yl β -naphthalenesulfonates all solvolyze slower than their saturated analogs in absolute ethanol at 60° (39). 4-Methyl-3-penten-1-yl β -naphthalenesulfonate shows a rate enhancement of only 47.5 under the same conditions (18). It is clear that the mechanism of these solvolyses has changed from S_N2 -like in

Table VII

Ethanolysis of Substituted Allylcarbinyl

β -Naphthalenesulfonates in Absolute Ethanol at 60°^a

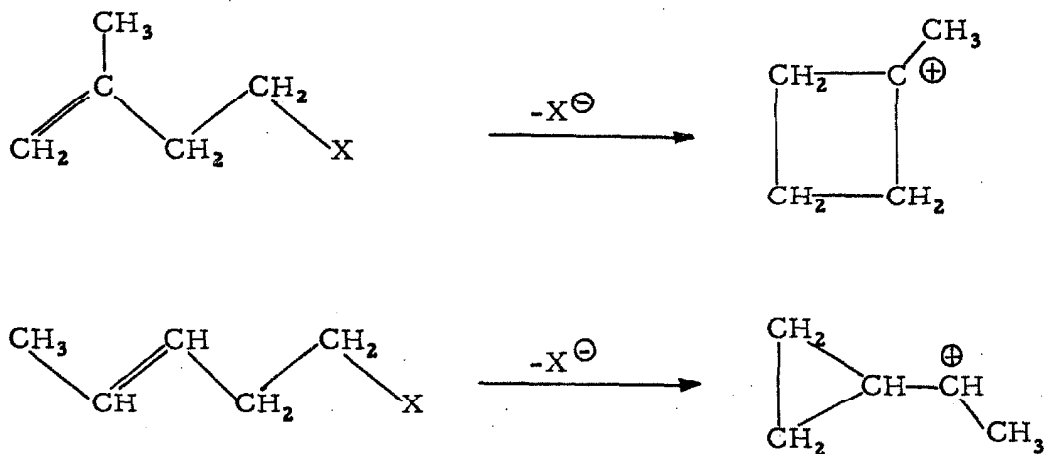
Compound	$k \times 10^6 \text{ sec}^{-1}$	k_{rel}
	4.8	0.55
	8.7	1
	6.3	0.77
	8.2	1
	6.7	0.90
	7.5	1
	57.0 ^b	47.5
	1.2 ^b	1

a) Ref. 39

b) Ref. 18

absolute ethanol to S_N1 -like in formic acid. The large relative rate changes on going to a less nucleophilic but a better ionizing solvent require involvement of the olefinic bond in the rate-determining transition state.

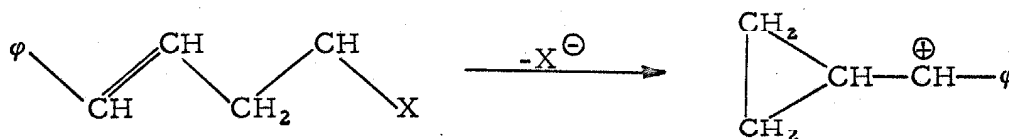
Attempts to rationalize these results on the basis of ionization of these allylcarbinyl derivatives to rearranged classical ions seems fruitless. As part of such an explanation, it would be required that the effect of γ -methyl substitution on the rate is the result of ionization to form a methylcyclobutyl cation, while the effect of δ -methyl substitution would be the result of ionization to a cyclopropylmethylcarbinyl cation.



If this were true, then since γ -methyl substitution produces a tertiary cyclobutyl cation and δ -methyl substitution produces a more highly strained secondary cyclopropyl cation, the rate enhancement of the γ -methyl substituent would be expected to be much larger than that for

a δ -methyl substituent. The observed results are exactly opposite to this prediction: a γ -methyl group produces only a 3-fold rate increase while a δ -methyl group produces more than a 200-fold increase.

Similarly, δ -phenyl substitution would produce a benzylic cation if ionization were occurring to produce the rearranged cation.



The cations derived from the δ -phenyl- and δ -methyl-substituted allylcarbinyl compounds would differ only in the nature of the substituent on the carbonium ion center. Since a phenyl substituent on a developing cationic center is known to produce much larger rate increases than a methyl substituent, the rate of solvolysis of trans-4-phenyl-3-buten-1-yl tosylate would be predicted, on this basis, to be much faster than the rate of solvolysis of trans-3-penten-1-yl tosylate. Again this prediction is not borne out; the phenyl substituted compound solvolyzes slower by a factor of 2. This argument should be valid even if "some sort" of inductive electron release from the cyclopropyl ring were occurring. No plausible explanation of the observed substituent effects in terms of classical carbonium ions appears possible.

Foote has shown that the acetolysis rates of many arenesulfonates are quantitatively correlated with the infrared carbonyl stretching frequencies of the corresponding ketones or aldehydes by the equation

$\log k$ (relative to cyclohexyl, 25°) = -0.132 ($\nu_{C=O}$ -1720) (40). The difference between the $\log k_{rel}$ (observed) and the $\log k_{rel}$ (calculated) is equated with the rate enhancements from anchimeric acceleration. The log of the rate enhancement for 4-methyl-3-penten-1-yl tosylate (41) is 4.2*. Schleyer states that these correlations are compelling evidence "for existence of bridged carbonium ions" (42).

In attempting a detailed explanation of the effect of substituents on the rates of solvolyses of allylcarbinyl derivatives, the effect of substituents on the rates of solvolyses of cyclopropylcarbinyl and cyclobutyl derivatives must also be considered.

The rates of solvolysis of several substituted cyclopropylcarbinyl derivatives have been reported and are summarized in Table VIII. The deuterium isotope effects which have been determined for these compounds are given in Table IX.

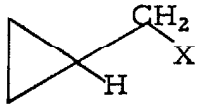
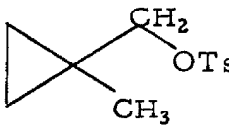
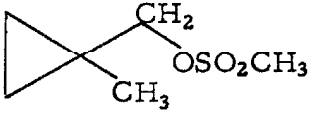
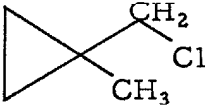
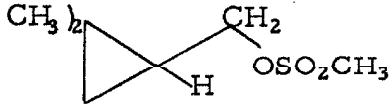
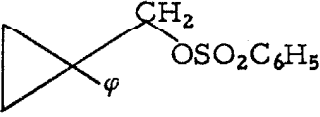
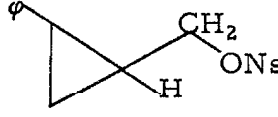
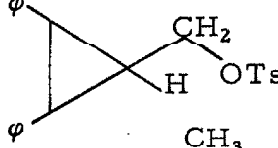
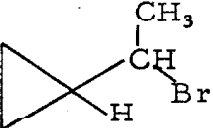
Less data are available on the effect of substituents on the rate of solvolyses of cyclobutyl compounds (Table X). The reported values for 2-methylcyclobutyl and 3-methylcyclobutyl are highly inaccurate; both starting materials were impure and failed to give first-order kinetics (38). The reported rate constants are probably lower limits.

If one admits the intermediacy of bicyclobutonium ions in these solvolyses, it may seem at first glance surprising that methyl and phenyl substitution produce relatively small increases in the rate of solvolyses of cyclopropylcarbinyl, cyclobutyl and allylcarbinyl derivatives. This marked insensitivity of the rate to phenyl substitution on any other but the α -carbon has also been observed in solvolyses

*Using ethyl arenesulfonate as a model compound.

-43-
Table VIII



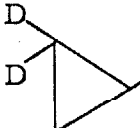
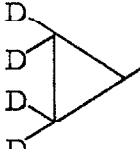
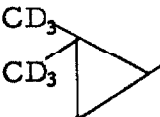

Solvolysis Rates of Substituted Cyclopropylcarbinyl
Compounds

Compound	T, °C	Solvent	k_{rel}	Ref.
			1.0	a
	20	HOAc	4.5	g
	20.0	96% EtOH	4.72	b
	30.0	50% EtOH	12.5	b
	20.0	96% EtOH	96	b
	20	HOAc	1.2	c
	25.0	90% aq. Dioxanne	<u>cis</u> 0.62	d
	25.0		<u>trans</u> 2.19	d
	30	abs. EtOH	0.34	e
	25	50% EtOH	1.8	f

a) Ref. 1; b) Ref. 43; c) Ref. 44; d) Ref. 45; e) Ref. 46;
f) Ref. 38; g) Ref. 47

Table IX

Deuterium Isotope Effects on the Solvolysis Rates
of Cyclopropylcarbinyl Compounds

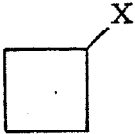
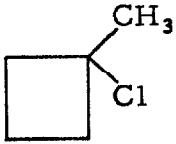
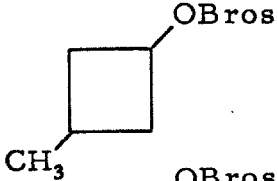
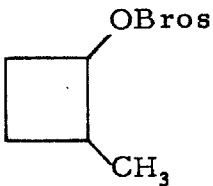
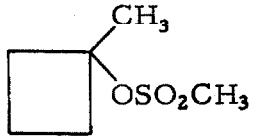
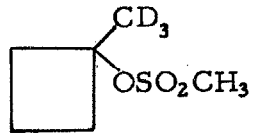
Compound	T°, C	Solvent	k_H/k_D	Ref.
 <chem>CD2OBs</chem>	20	96% EtOH	1.29	a
 <chem>CH2OBs</chem>	20	HOAc	1.15	a
 <chem>CH2OBs</chem>	20	96% EtOH	0.97	a
 <chem>CH2OBs</chem>	20	96% EtOH	0.99	a
 <chem>CH2OMs</chem>	20	96% EtOH	1.00	b
 <chem>CH2OMs</chem>	20	96% EtOH	1.00	b

a) Ref. 48

b) Ref. 43

Table X

Solvolysis Rates of Substituted Cyclobutyl Compounds

Compound	T, °C	Solvent	k _{rel}	Ref.
			1	a
	50	50% Ethanol	130	b
	25	50% Ethanol	0.6	c
	25	50% Ethanol	2.0	c
	20	96% Ethanol	180 ^d	e
	20	96% Ethanol	167 ^d	e

a) Ref. 1a

b) Ref. 26

c) Ref. 38

d) Calculated from data of S. Borcic et al. (43) assuming a rate ratio of 25 for cyclopropylcarbinyl to cyclobutyl

e) S. Borcic, Personal Communication, and Ref. 43

of other compounds where formation of non-classical ions has been postulated (31, 49-51).

The observed effects are not those expected if non-classical substituent effects were the same as classical substituent effects, differing only by a proportionality factor corresponding to the amount of charge on the substituted carbon atom.

One possible explanation for these small substituent effects is that these reactions have much smaller ρ^* values than the corresponding classical systems. Admittedly an accelerated reaction should show less sensitivity to substituent effects than an unaccelerated system. Thus the ρ for benzhydryl chloride solvolysis is -4.06 but the ρ for trityl chloride is only -2.68 (35). An accelerated classical system might therefore be expected to be less sensitive to substituent changes than a classical system.

Two objections can be raised against this explanation: 1) it fails to provide an explanation for the observed deuterium isotope effects; 2) it fails to explain the relative effects of methyl and phenyl substituents. For all analogous compounds, the methyl-substituted compound solvolyzes faster than the phenyl-substituted compound. Normally a phenyl group provides a much larger rate acceleration than a methyl group. (Trityl chloride solvolyzes 4.6×10^6 faster than t-butyl chloride at 25° in 85% aqueous acetone) (52).

The other explanation hinges more critically on the mechanism of the non-classical electron delocalization. Howden and Roberts have recently presented calculations of the delocalization energy of the

bicyclobutonium ion as a function of the geometry of the system (53). The orbitals involved in the cationic portion of the bicyclobutonium ion are not parallel and are probably not even pure p-orbitals. Therefore the resulting overlap and bonding will contain both σ - and π -type contributions.

In order to understand what effect a methyl or phenyl substituent at the different positions of the bicyclobutonium ions will have, one must first establish 1) how much of the carbonium ion stability is derived from σ -bonding and how much from π -bonding and 2) the relative effectiveness with which the substituent stabilizes the ion via π -bonding and σ -bonding in this system.

Using the model of the bicyclobutonium ion proposed by Howden and Roberts, Fig. 6, one can calculate approximate overlap integrals, $S_{\sigma\sigma}$ and $S_{\pi\pi}$, using the method of Woods, Carboni, and Roberts (54).

The S^0 in Table XI were taken from the figure on p. 30 of ref. 55.

These values and the equation

$$\begin{aligned} S'_{AB} &= S_{\sigma\sigma}' + S_{\pi\pi}' \\ &= S_{\sigma\sigma} \cos \theta_A \cos \theta_B + S_{\pi\pi} \sin \theta_A \sin \theta_B \cos \gamma \end{aligned}$$

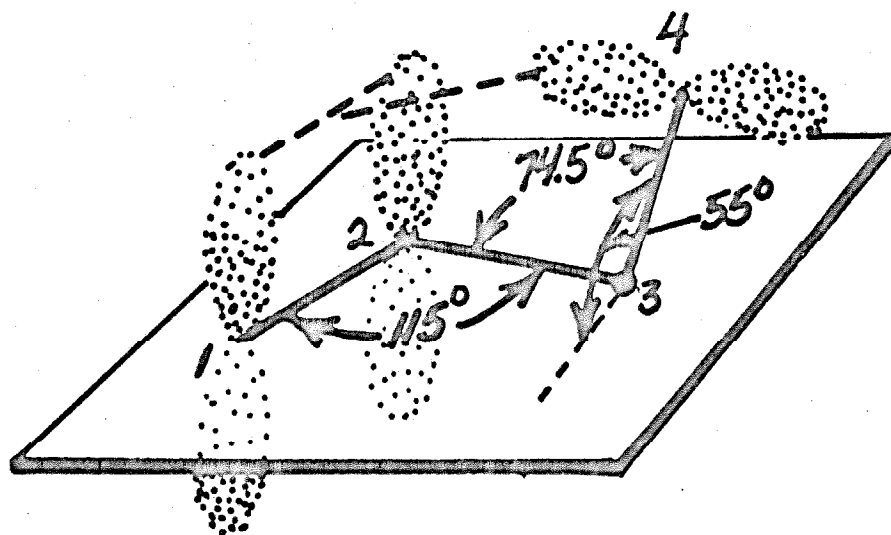
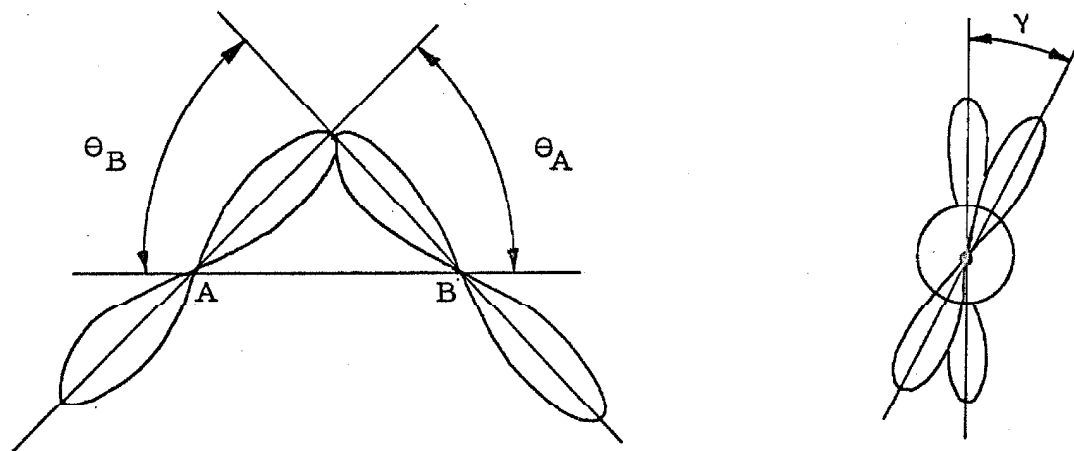


Figure 6. Howden and Roberts model for the bicyclobutonium ion (ref. 53).

where



were used to calculate the values in Table XII.

These values are certainly not exact but nonetheless indicate that about 50% of the stabilization of the bicyclobutonium ion results from sigma type bonding.

A methyl group is normally considered to stabilize a cationic center by inductive electron release through the σ -framework and by hyperconjugation through the π -framework. In the above system, any stabilization from a resonance or hyperconjugative effect should be greatly reduced. Consequently a methyl substituent on the above systems should produce only a small rate acceleration as is observed.

It is well established that a phenyl group withdraws electrons from σ bonds inductively and donates electrons to π bonds by electron delocalization. Therefore a phenyl group will destabilize the cation inductively but stabilize it by π -interaction. Since the maximum stabilization by π -overlap, which requires the phenyl group be in the nodal plane of the bonding molecular orbital, may not be possible,

Table XI

Overlap Integrals for Bicyclobutonium Ion

$r_{AB}(\text{\AA})$	$S_{2p\pi}^o$	$S_{2p\sigma}^o$
2.100	0.082	0.24
1.845	0.14	0.30
1.34	0.28	0.32

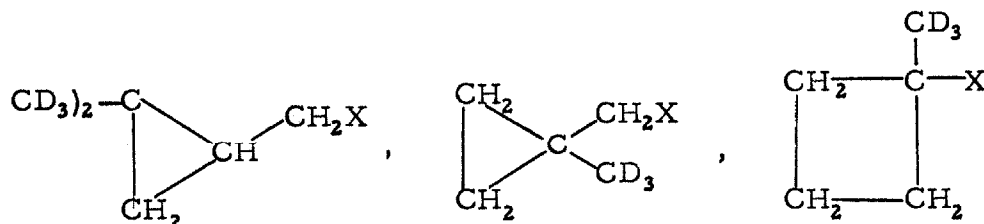
Table XII

Overlap Integrals for Bicyclobutonium Ion

S'_{AB}	$S'_{\sigma\sigma}$	$S'_{\pi\pi}$
S_{14}	0.12	0.025
S_{24}	0.16	0.040
S_{12}	0.0	0.28
S_{Total}	0.28	0.34

the π -interaction of a phenyl group with the bicyclobutonium ion electrons may be much reduced; it appears as if the two effects nearly cancel in these systems.

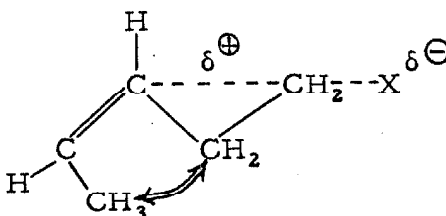
Secondary β -deuteriums isotope effects are commonly ascribed to hyperconjugative electron release in the transition state of solvolysis reactions. The isotope effect is very small where hyperconjugation cannot occur. The failure to observe isotope effects in the solvolysis of



is consistent with the strikingly small methyl and phenyl substituent rate effects. If the phenyl ring cannot conjugate with the developing cation in the transition state of the solvolysis reactions, one would not expect any rate effect from a hyperconjugative electron release from a CH_3 - relative to a CD_3 -group (43). A γ -methyl substituent on allylcarbinyl tosylate produces a rate acceleration of only 3.3 while a δ -methyl substituent produces a rate acceleration of 210. This implies that the charge developed at the γ -position is less than that developed at the δ -position (in the solvolytic transition state). This situation is most easily understood if the solvolytic transition state is presumed to resemble a homoallylic ion with a structure such as IV. Formation of a bicyclobutonium ion from an allylcarbinyl compound requires considerable structural reorganization to permit significant 1,4 and 2,4

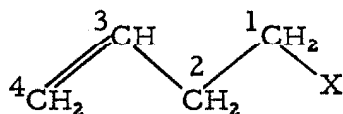
interactions. It is reasonable to expect 2,4 interactions to be established before 1,4 interactions since less structural reorganization is necessary. The relative amount of positive charge on the 1 and 2 carbon atoms is dependent on the amount of 1,4 interactions; increasing 1,4 interaction increases the amount of charge on positions 2 with respect to position 1. The rate of solvolysis of (β -methylallyl)-carbiny1 tosylate indicates that the 1,4 interaction is relatively unimportant in the transition state even though this interaction must be large in the intermediate since only 1-methylcyclobutyl products are formed.

The relative rates of solvolysis of cis- and trans-3-penten-1-yl tosylates can also be explained on this basis. The electronic effects of the cis- and trans-methyl group should be the same and produce the same rate enhancement. The cis compound solvolyzes slower because of steric interactions that develop as the homoallylic-like transition state is approached.

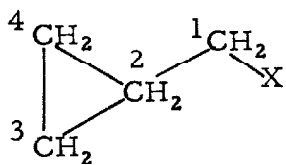


No solvolysis rates of α -substituted allylcarbinyl tosylates have been determined. However, α -substitution is expected to produce the largest rate enhancements in these systems. In general, one can therefore expect the rate enhancement by a given substituent on the

different positions to decrease in the order $1 \gg 4 > 3$.



Consideration of methyl group effects on the rate of solvolysis of the cyclopropylcarbinyl compounds suggests that similar arguments may apply here. Thus a 2-methyl substituent produces a solvolytic



rate increase of a factor 4.5 while a 4-methyl substituent is expected to produce a factor of greater than 10.* The difference is much less dramatic than in the allylcarbinyl system but again suggests that the amount of charge displaced to the 2-position may be less than to the 4-position in the solvolytic transition state. This would occur if delocalization of the 2,4-bonding electrons occurred before 1,4-overlap became fully developed. In view of the structural reorganization required on going from a cyclopropylcarbinyl compound to a bicyclobutonium ion, it seems plausible that delocalization of the bonding electron pair is established earlier on the reaction coordinate than 1,4-interaction. The latter interaction must be important in the intermediate since again 1-methylcyclobutyl products are formed

* Estimated from the effect of 4,4-dimethyl substitution.

exclusively.

Studies of the substituent effects on the 2- and 3-position of cyclobutyl compounds provide the only opportunity to investigate the relative rate enhancement on substitution of the two cationic methylene groups of the bicyclobutonium ion. In both the allylcarbinyl and cyclopropylcarbinyl systems one of these methylene groups carries the leaving group and should display a much more pronounced rate effect upon substitution than the other methylene group. If the model of Howden and Roberts at all reflects the relative charge densities on the carbon atoms of the bicyclobutonium ion (53), 2-methyl substitution should produce a larger rate enhancement than 3-methyl substitution. Silver reported that the rate of solvolysis of 2-methylcyclobutyl brosylate is three times that of 3-methylcyclobutyl brosylate (38); this is as expected. In addition, Silver reported that the rate of solvolysis of cyclobutyl brosylate is 1.5 times that of 3-methylcyclobutyl brosylate. However, as Silver points out, the reported rates of solvolysis of 2-methylcyclobutyl brosylate and 3-methylcyclobutyl brosylate probably represent lower limits. Further studies in this area are desirable.

Solvolyses of substituted allylcarbinyl, cyclopropylcarbinyl or cyclobutyl compounds yield predominantly α -substituted products. Substituent control of the product structure can result from two effects. The substituent can produce a substantial perturbation of the charge distribution in the non-classical intermediate. Although some charge perturbation is likely, no reasonable estimates of the magnitude of this effect are available. The effect of the substituent on the product

distribution could also result from electrical effects in the transition state leading to products. Reasonable arguments in favor of the latter proposal can be presented. It is well established that α -substitution produces a larger rate acceleration than remote substitution in small-ring compounds. By the law of microscopic reversibility, nucleophilic attack to produce the α -substituted product should also be faster than nucleophilic attack to produce a remotely substituted product. This can be illustrated by the following reaction coordinate

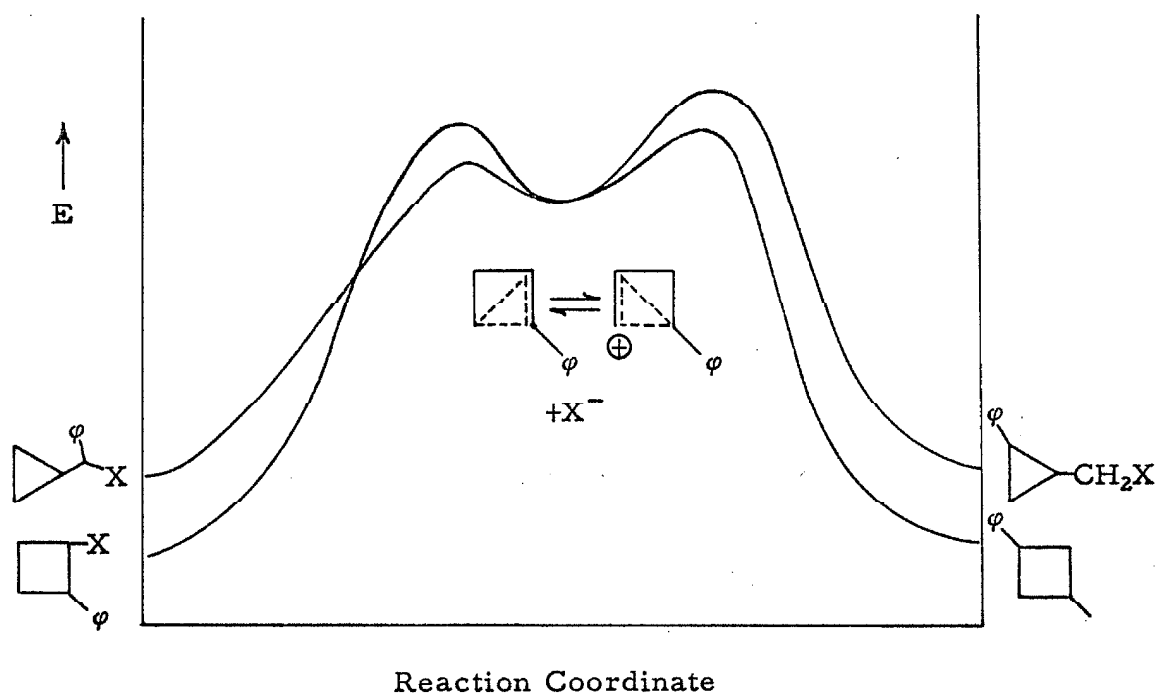
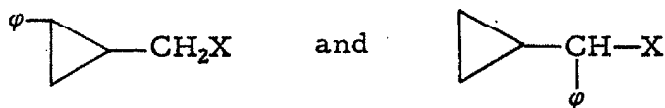


diagram. There are several problems with the argument for electrical effects in the product forming transition state. One must assume nearly equal energies for the two structures



While this seems reasonable as a first approximation, no experimental support is available. Nonetheless, very large perturbations of the electron distribution in the bicyclobutonium ion are not required to explain the product distributions.

In considering substituent effects on the allylcarbiny, cyclopropylcarbiny and cyclobutyl systems, the following conclusions are reached:

- 1) The relative rates will be most sensitive to α -substituents.
- 2) Allylcarbiny systems will be relatively more sensitive to remote substitution than cyclobutyl or cyclopropylcarbiny systems.
- 3) None of the three charged centers of the bicyclobutonium ion are equivalent, so sensitivity to substituent effects will be different for each carbon. Except for the α -position, position 1 should be the most sensitive to substituent effects.

The observed substituent effects, the product distributions, and the label redistributions are all consistent with the proposed solvolytic mechanism involving the non-classical bicyclobutonium ion intermediate. Whether the proposal is a necessary one is a meaningless question unless some reasonable alternate explanation of all the known data is offered.

II. STUDIES OF FLUOROALKADIENES BY NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Introduction

The conformational s-cis-s-trans equilibria of 1,3-butadienes have been investigated by several techniques. Aston, Szasz, Woolery, and Brickwedde, on the basis of a review of earlier spectroscopic studies and extensive calorimetric measurements, concluded that two isomeric forms of symmetries C_{2h} (s-trans) and C_{2v} (s-cis) exist in appreciable concentrations at room temperature, the trans form being more stable by 2.3 kcal/mole (56). Detailed studies of the infrared and Raman spectra of 1,3-butadiene by both English (57) and Russian (58) workers indicate at least 96% of the compound exists in the s-trans form at room temperature. Electron diffraction studies of the vapor require a large predominance of the trans planar form (59).

Substituted 1,3-butadienes have not received much attention. Less detailed infrared and Raman studies have shown the equilibrium mixture of 2,3-dimethylbutadiene to contain ~70% of the s-trans form (58). More recently, microwave studies of 2,3-dimethylbutadiene, fluoroprene and isoprene have yielded no evidence for the presence of more than 2% of the s-cis form (60, 61). (The authors' claim that 2% could have been detected seems overoptimistic). 2,3-Di-t-butyl-1,3-butadiene is reported to exist in a non-transoid conformation (62). Steric interactions from the bulky t-butyl groups prevent it from

adopting either planar form.

E. A. Braude concluded from intensities of u.v. absorption that in 2,4-dimethyl-1,3-pentadiene and 2-chloro-4-methyl-1,3-pentadiene, the favored conformation is $\sim 50^\circ$ from planar while in 1,1,4,4-tetrachloro-1,3-butadiene, the favored conformation is $> 70^\circ$ from planar (85). By infrared and Raman studies, chloroprene, 2,3-dichloro-1,3-butadiene and isoprene have been found to exist predominantly in the s-trans form (86). On the other hand, hexachloro-1,3-butadiene must have a preferred non-planar conformation (86).

From a complete analysis of the infrared and Raman spectra and the polarization ratios of the stronger Raman bands of hexafluoro-1,3-butadiene, I, Nielsen and Albright (63) concluded that "the spectral data are inconsistent with the assumption of molecular symmetry C_{2h} (trans-form) but can be interpreted satisfactorily on the basis of symmetry C_{2v} (cis-form)." From their data they could not rule out a non-planar form. No explanation was offered for this unusual behavior.

The commonly held organic-chemists' view is that the predominance of the s-trans form of butadiene results from H-H non-bonded repulsion in the s-cis form. Assuming the same bond angles and bond distances as found for the s-trans form (59), the calculated cis-cis H-H distance in the s-cis form is 1.93 Å. Since the sum of the van der Waals radii is 2 to 2.4 Å (64), it is questionable whether non-bonded H-H repulsion in the s-cis form could produce the necessary 2.3 kcal destabilization.

Two other explanations have been offered for the predominance

of the s-trans form of butadiene. Parr and Mulliken calculated, using a LCAO-SCF method, the electronic energies of both the s-cis and s-trans forms of butadiene (65). The calculated electronic energy of the s-cis form was less than that of the s-trans form by nearly 20 kcal/mole. Inclusion of the C-C nuclear repulsion terms reversed the relative stabilities making the s-trans favored by ~2.7 kcal/mole. It was therefore concluded that the C-C nuclear repulsion was responsible for the preferred trans form.

More recently Lide (61) has proposed a different explanation. From microwave studies of fluoroprene he concluded that the rotational potential function had a non-cisoid minimum in addition to the transoid minimum. He proposed a two part potential function of the form:

$$V(\Theta) = \frac{1}{2} V_2 (1 - \cos 2\Theta) + \frac{1}{2} V_3 (1 - \cos 3\Theta)$$

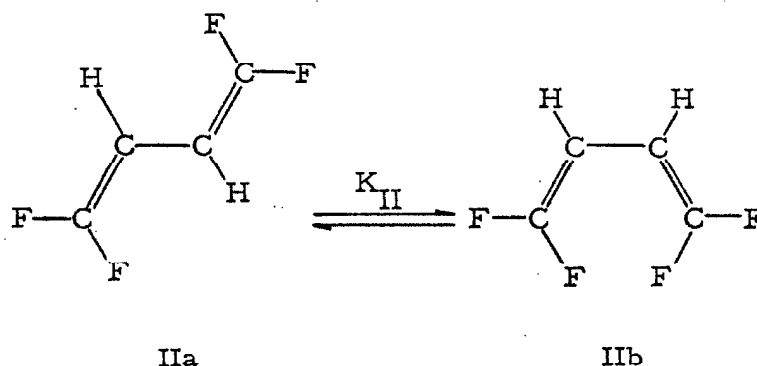
The first term is associated with the diene resonance energy and has minima at $\Theta = 0^\circ$ (trans) and $\Theta = 180^\circ$ (cis); the second term is a rotational potential term similar to that in ethane or propylene and has minima at $\Theta = 0^\circ, 120^\circ$, and 240° . The sum of these yields two out-of-plane minima (in addition to the trans minimum) which approach the cis form as V_2/V_3 is increased.

Since this function which allows for a non-planar isomer in butadiene-type molecules gives a reasonable explanation of all the available data, he concludes that the existence of a stable non-planar form seems at least as probable as the cis. It also explains the "predominance of the trans form of butadiene without the necessity of

introducing rather dubious steric interactions" (61).

A few cyclic compounds contain 1,3-butadiene systems with a non-transoid configuration. In 2,3-dimethylenenorbornane, 1,2-dimethylenecyclobutane and 1,2-dimethylenecyclopentane, the exocyclic double bonds are forced to be cis-planar by the rigid ring systems and have $\gamma_{\max} = 248 \text{ m}\mu$. However, in 1,2-dimethylenecyclohexane, the angle between the double-bond axes can approach 60° without significant distortion of the ring. Since $\lambda_{\max} = 220 \text{ m}\mu$ for this compound, Blomquist and Longone concluded that the exocyclic double bonds were non-planar. Whether this is due to a preferred conformation for the diene or for the ring systems is uncertain (66).

The reports by Anderson, Putnam and Sharkey that the 40 Mcps fluorine nuclear magnetic resonance of 1,1,4,4-tetrafluoro-1,3-butadiene, II, exhibited a broad but unresolvable band in the range of -575 to -315 cps, and that at temperatures of -80 to -120° the spectrum sharpened somewhat, led us to speculate that a slow conformational equilibrium between the s-trans form IIa and s-cis form, IIb, occurs (67). The broad band could then be the result of a slow exchange of the



fluorine nuclei between the magnetically non-equivalent environments in IIa and IIb; the sharpening at low temperature could result from "freezing" the molecule into the s-trans and/or s-cis form.

This work was undertaken in order to provide a better understanding of the anomalous conformational behavior of the halobutadienes.

Results and Discussion

The F^{19} and H^1 nuclear magnetic resonance spectra of 1,1,4,4-tetrafluoro-1,3-butadiene, II, (Fig. 7) were highly complex but not broad bands as previously reported.* In Fig. 7, the F^{19} - $\{H^1\}$ spectrum is compared with the calculated spectrum.** The average line positions determined from ten independent spectra were used in the detailed analysis of the F^{19} spectrum. The experimental energy levels and the n.m.r. parameters were determined using the iterative technique of Swalen and Reilly (69). The results are summarized in Table XIII. The H-H coupling constant for I was obtained from the Cl^{35} satellites of the H^1 - $\{F^{19}\}$ spectrum.

The F^{19} and H^1 n.m.r. spectra of bis-4,5-(difluoromethylene)-cyclohexene, III, prepared by the addition of tetrafluoro-1,2,3-butatriene (70) to 1,3-butadiene, are given in Fig. 8. Both the methylene and vinyl hydrogens were coupled to the fluorine; consequently, a completely decoupled fluorine spectrum could not easily be obtained. However, only the low-field fluorines were coupled to the vinyl hydrogens. The high-field half of the F^{19} n.m.r. spectrum with the methylene hydrogens decoupled (Fig. 9) was used for analysis of the F^{19} chemical shifts and coupling constants. This double-irradiation spectrum was obtained by sweeping the frequency at constant field using

*The previously reported F^{19} spectra (67) were taken at 40 Mc and should have been more complex but not broad bands.

**The notation corresponds to that of reference 68.

Table XIII

N.M.R. Parameters for 1,1,4,4-Tetrafluoro-1,3-butadiene

$$\Delta\nu = 1.461 \text{ ppm}$$

$$J_{AA} = +35.7 \pm 0.2 \text{ cps}$$

$$J_{AB} = +36.6 \pm 0.2 \text{ cps}$$

$$J'_{AB} = + 8.0 \pm 0.2 \text{ cps}$$

$$J'_{BB} = + 4.8 \pm 0.2 \text{ cps}$$

$$J_{HH} = 10.8 \pm 0.2 \text{ cps}$$

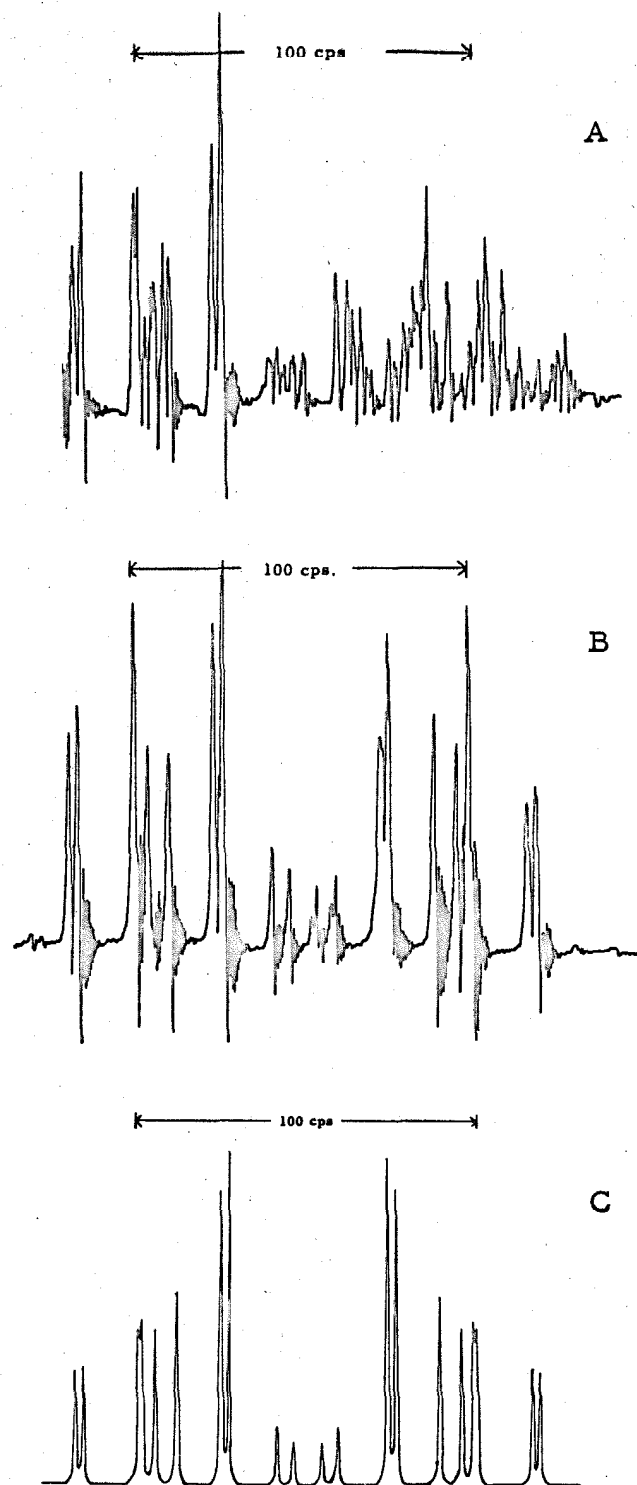


Figure 7. ^{19}F nuclear magnetic resonance spectrum of 1,1,4,4-tetrafluoro-1,3-butadiene; A, observed; B, observed with ^1H decoupling; C, calculated

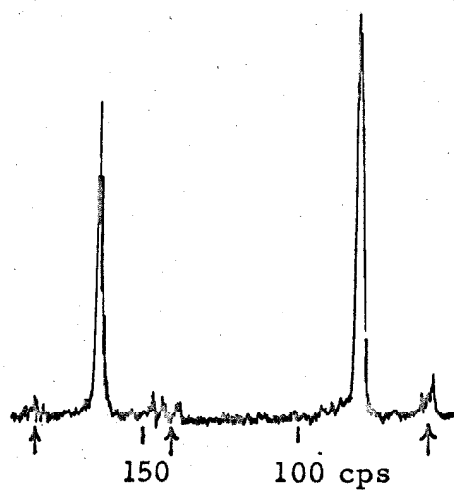


Figure 8. A, H^1 nuclear magnetic resonance spectrum of bis-4, 5-(difluoromethylene)-cyclohexene. Arrows indicate impurities.

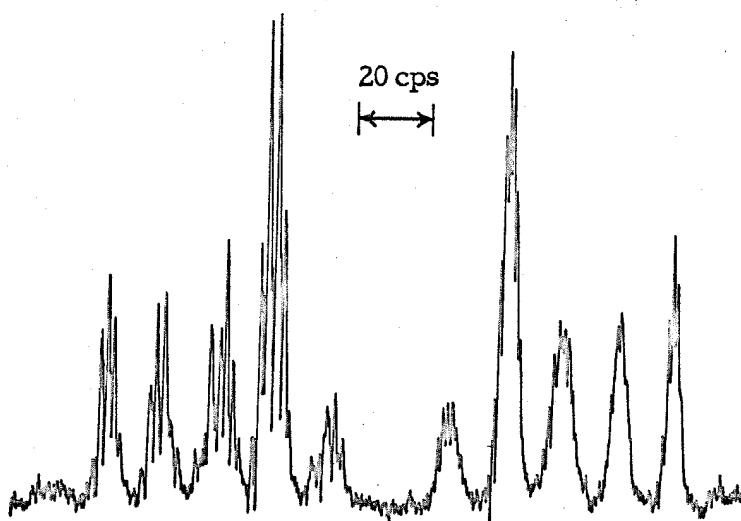


Figure 8. B, F^{19} nuclear magnetic resonance spectrum of bis-4, 5-(difluoromethylene)-cyclohexene.

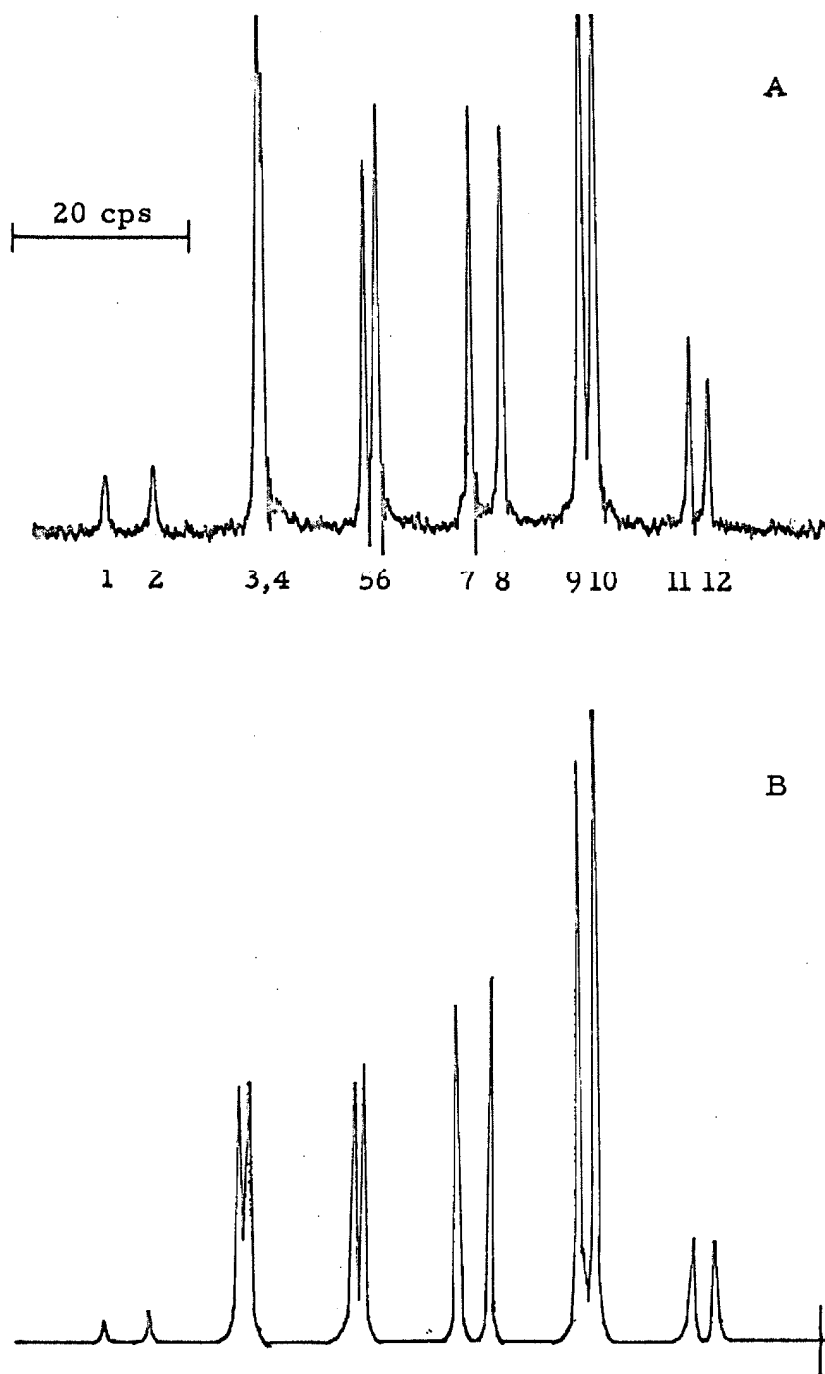


Figure 9. High field portion of $F^{19}\{-H^1\}$ nuclear magnetic resonance spectrum of bis-4, 5-(difluoromethylene)-cyclohexene; A, observed; B, calculated.

the audio side-band phase detection field-lock method (71); the line positions were determined by measurement of the audio frequency with a Hewlett Packard-524 C frequency counter. The experimental energy levels and the n.m.r. parameters were determined by the iterative technique. The results are summarized in Table XIV; the observed and calculated spectra are compared in Fig. 9. F^{19} double-irradiation tickling experiments confirmed the transition assignments. The experimental energy levels together with the corresponding transition assignments are given in Fig. 10. Irradiation of line 6 with a weak r.f. field causes line 12 to decrease in intensity and split while line 7 is slightly enhanced but still broadened (Fig. 11a). The small intensity changes are due to the nuclear Overhauser effect which results when the population of E_7 is decreased and the population of E_4 is increased upon double-irradiation (72).

Freeman and Anderson have described the expected effects of weakly irradiating one transition in a multiplet and give the following rules: 1) Any transition with an energy level in common with the transition irradiated will split into a doublet; 2) If the other two energy levels which are not common for the irradiated and perturbed transitions have the same F_z value then the doublet will be well resolved, if the F_z values differ by 2 then the doublet will be poorly resolved (73).

Using the Freeman-Anderson tickling rules, the location of transition 12 and 7 in the energy level diagram is easily assigned. The spectra obtained on weak irradiation of line 7 and line 8 (Fig. 11b and

Table XIV

N.M.R. Parameters for
Bis-4,5-(-difluoromethylene)-cyclohexene

$$\Delta\nu = 1.746 \text{ ppm}$$

$$J_{AA} = +31.4 \pm 0.2 \text{ cps}$$

$$J_{AB} = +39.0 \pm 0.2 \text{ cps}$$

$$J'_{AB} = +4.8 \pm 0.2 \text{ cps}$$

$$J'_{BB} = +3.3 \pm 0.2 \text{ cps}$$

$$J_{H_1F_A} + J_{H_2F_A} = 2.0 \text{ cps}$$

$$J_{H_1F_B} + J_{H_2F_B} = 0.2 \text{ cps}$$

$$J_{H_3F_B} + J_{H_4F_B} = 3.2 \text{ cps}$$

$$J_{H_3F_A} + J_{H_4F_A} = 1.3 \text{ cps}$$

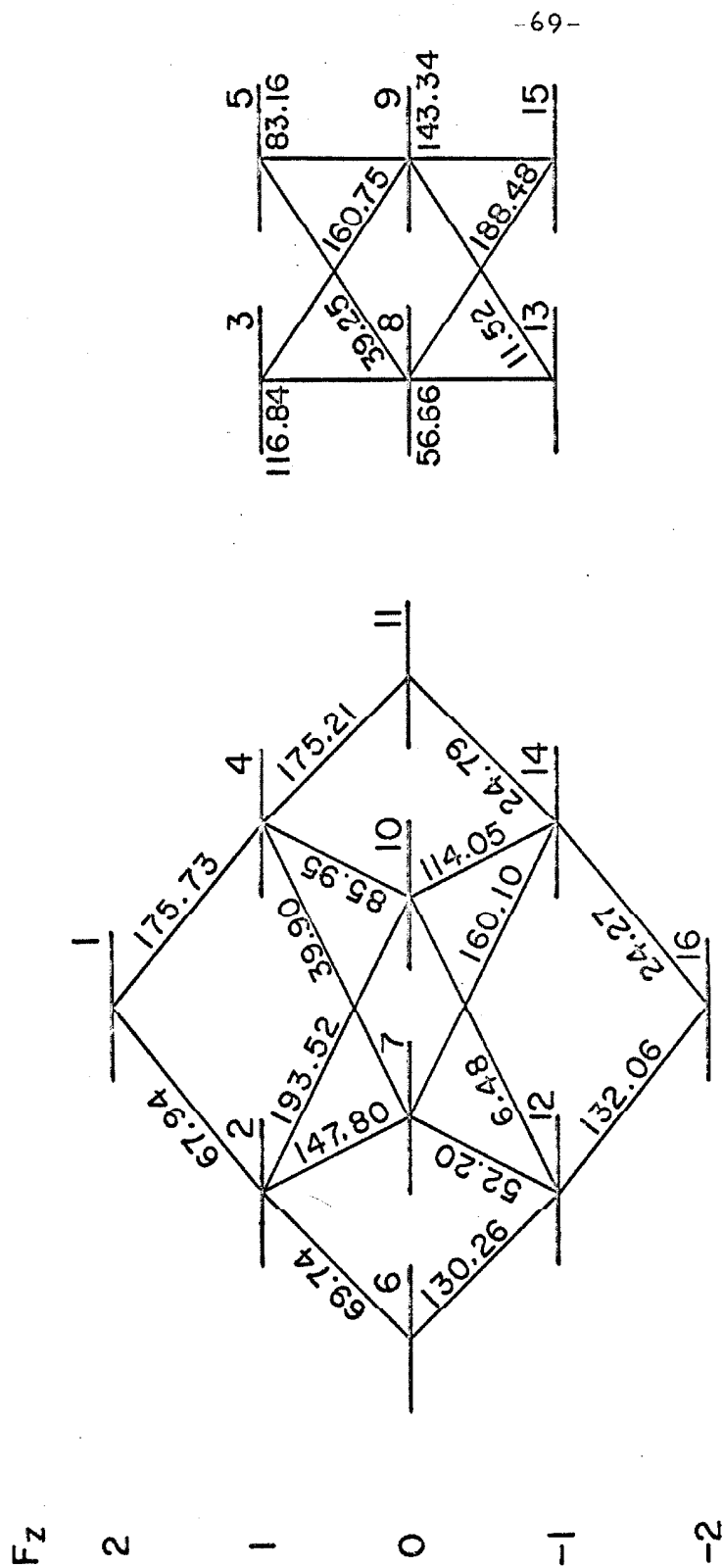
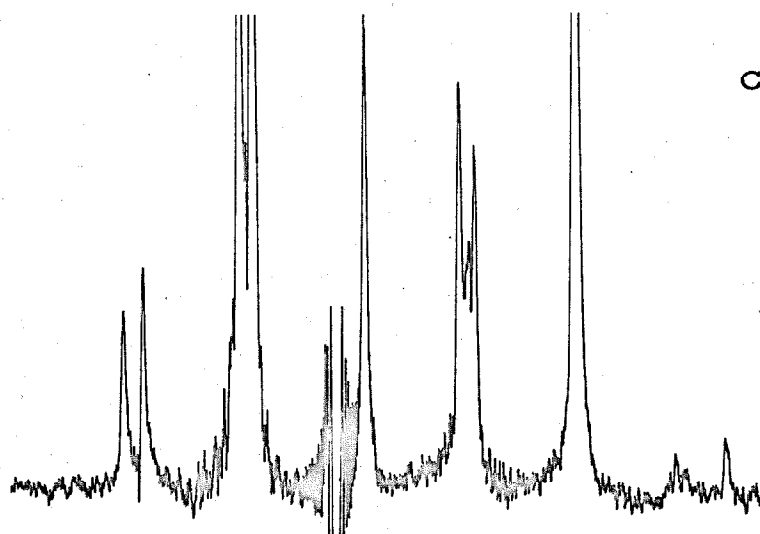
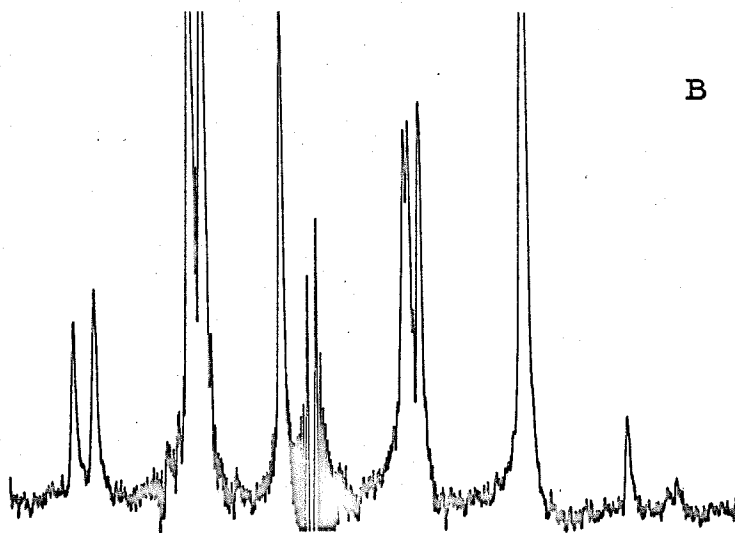
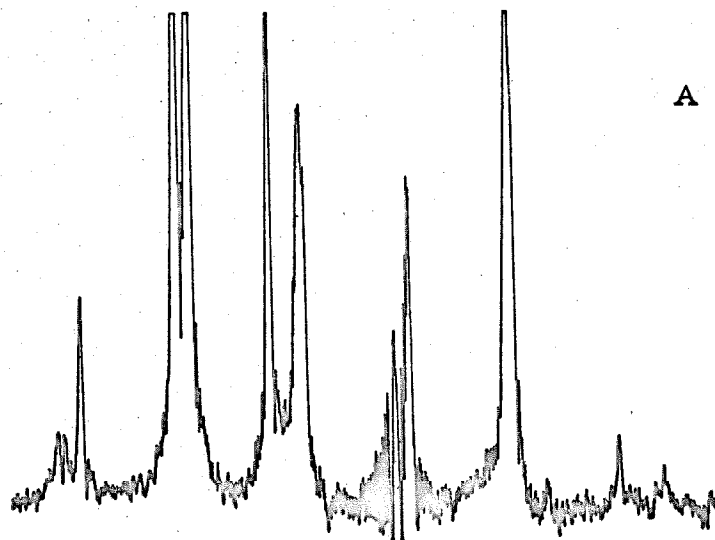


Figure 10. Energy Level Diagram for Bis-4, 5-(difluoromethylene)-cyclohexene

Figure 11. High-field portion of $F^{19}-\{H^1\}$ nuclear magnetic resonance spectrum of bis-4, 5-(difluoromethylene)-cyclohexene with fluorine-fluorine decoupling; A, line 6 irradiated; B, line 7 irradiated; C, line 8 irradiated.

-70a-



11c) are interpreted similarly. These experiments permit a unique set of transition assignments.

The H^1-F^{19} coupling constants of III were determined from the F^{19} n.m.r. spectra. The methinyl proton-fluorine coupling constants were determined from the F^{19} spectrum observed upon decoupling the methylene protons (Fig. 12). The methylene proton-fluorine coupling constants were determined from the F^{19} spectrum with the methinyl protons decoupled (Fig. 12). The fine-structure pattern for these spectra appears the same for both equal and unequal H-F coupling constants when the line width of a component of the observed pattern, $\delta_{\frac{1}{2}}$, is greater than

(74).

$$\frac{(J_{HF} - J_{HF}')^2}{2(J_{FF} - J_{HH})}$$

For these spectra, $\delta_{\frac{1}{2}} \approx 0.5$ cps; $J_{FF} = 35$ or 4 cps; $J_{HH} \approx 10$ cps (for methinyl proton) or 15 cps (for methylene protons). Both J_{FF} values are consistent with any sum of J_{HF} and J_{HF}' equal to the observed line separations.

The ring fluorines and the vinylic fluorines in perfluoro-1,2-dimethylenecyclobutane, IV, (75) were strongly coupled (~ 8 cps). Fluorine-fluorine decoupling was accomplished by a previously unreported technique. The center band frequency was first adjusted to precisely the ring-fluorine resonance frequency; the field was then locked on the hexafluorobenzene resonance (internal) using the audio side-band phase detection field lock system; the vinylic-fluorine

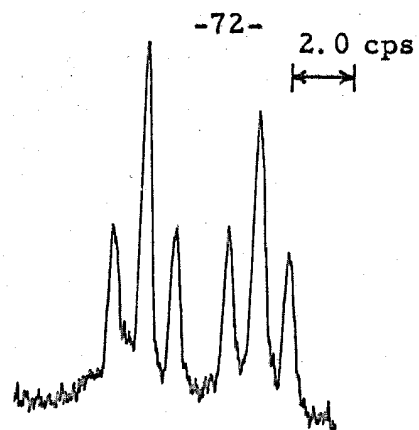


Figure 12A. F^{19} nuclear magnetic resonance spectrum of bis-4, 5-(difluoromethylene)-cyclohexene with irradiation of methylene protons; line 7 and 8 of low-field half of spectrum.

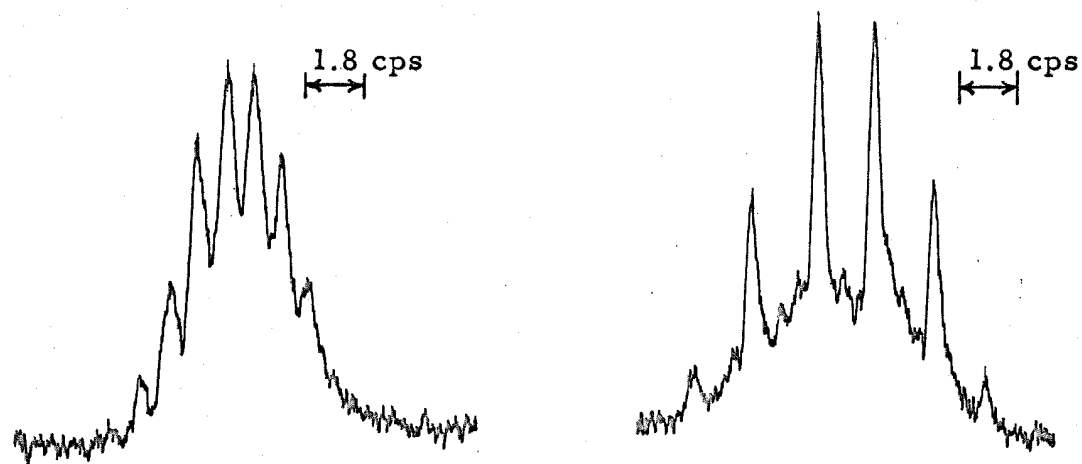


Figure 12B. F^{19} nuclear magnetic resonance spectrum of bis-4, 5-(difluoromethylene)-cyclohexene with irradiation of vinyl protons; Left, lines 9 and 10 of low-field half of spectrum; right, lines 9 and 10 of high-field half of spectrum.

resonances were observed by frequency-sweep using audio side-band detection (Fig. 13). In field-sweep spectra, it is currently impossible to obtain homonuclear decoupling over such a large frequency range since both resonances are swept simultaneously. The conception and performance of this experiment by Drs. S. L. Manatt and D. D. Elleman is greatly appreciated. The line positions were determined by measuring the frequency of the audio side-band used for observation.

The experimental energy levels and the n.m.r. parameters were determined by the iterative technique. The calculated chemical shifts and coupling constants are given in Table XV; the calculated spectrum is included in Fig. 13. Another audio side-band was used to perform the double-irradiation tickling experiments. The experimental energy level diagram with the corresponding transition assignment is given in Fig. 14. Irradiation of line 2 perturbs lines 10, 13 and 15; lines 10 (and 15?) appear as broad doublets while line 13 is a sharp doublet. Irradiations of line 14 perturbs lines 1, 8, and 18; line 1 nearly disappeared, line 18 becomes a low intensity inverted doublet and line 8 is very broadened. Using the Freeman-Anderson rules, these observations conform the given transition assignment.

Attempts to decouple the perfluoromethyl fluorines from the vinylic fluorines in perfluoro-2,3-dimethyl-1,3-butadiene (76) were unsuccessful. The fluorine resonances are separated by only ~ 400 cps (at 56.4 Mc) and are very strongly coupled (the half-width of the CF_3 resonance is ~ 40 cps).

The F^{19} n.m.r. spectrum of II at 56.4 Mc consists of a dense

Table XV

N.M.R. Parameters for
Perfluoro-1,2-dimethylene-cyclobutane

$$\Delta\nu = 1.391 \text{ ppm}$$

$$J_{AA} = +23.2 \pm 0.2 \text{ cps}$$

$$J_{AB} = +14.7 \pm 0.2 \text{ cps}$$

$$J'_{AB} = + 6.7 \pm 0.2 \text{ cps}$$

$$J'_{BB} = + 7.6 \pm 0.2 \text{ cps}$$

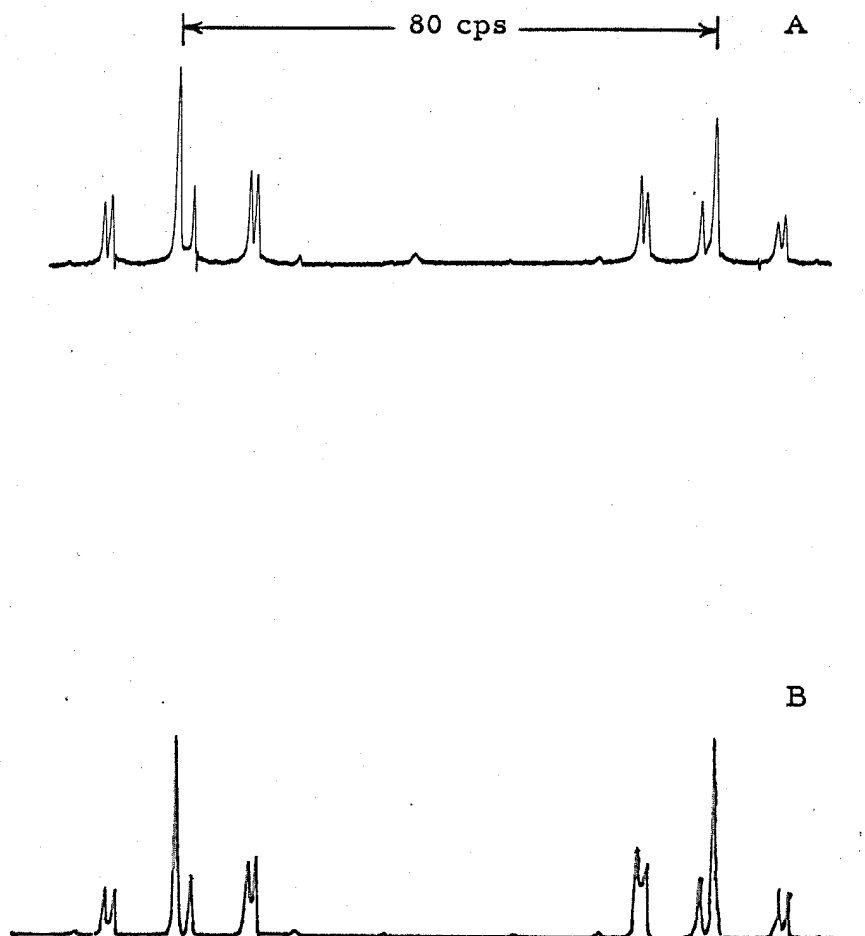


Figure 13. $\text{F}_\text{V}^{19} - \{\text{F}_\text{R}^{19}\}$ nuclear magnetic resonance spectrum of perfluoro-1,2-dimethylenecyclobutane; A, observed; B, calculated.

F_z 2 1 0 -1 -2

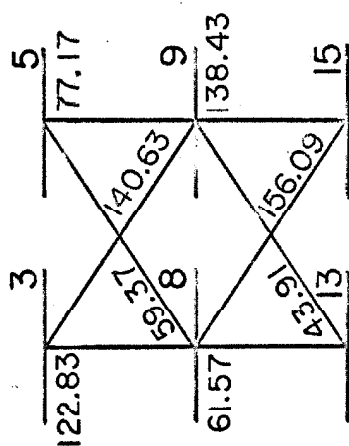
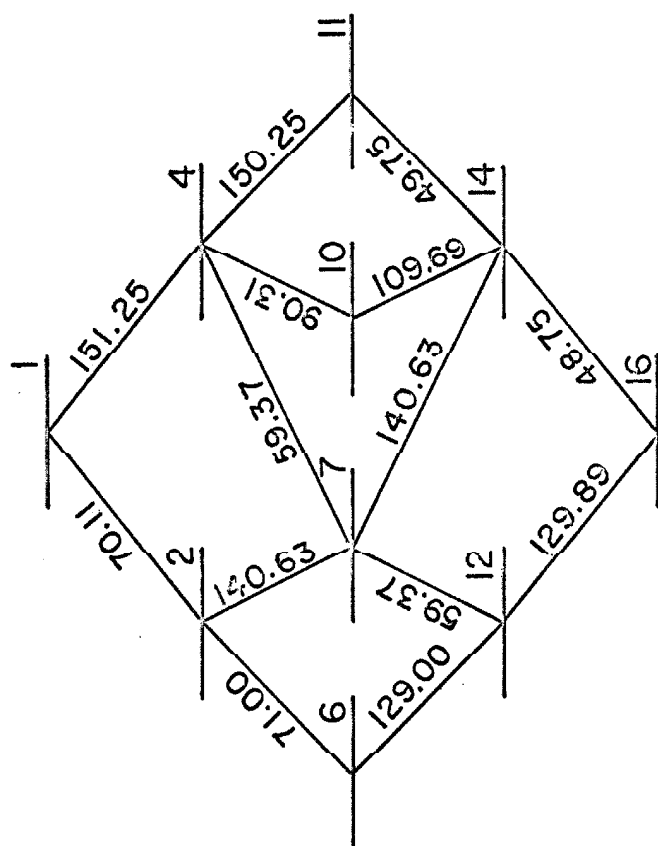
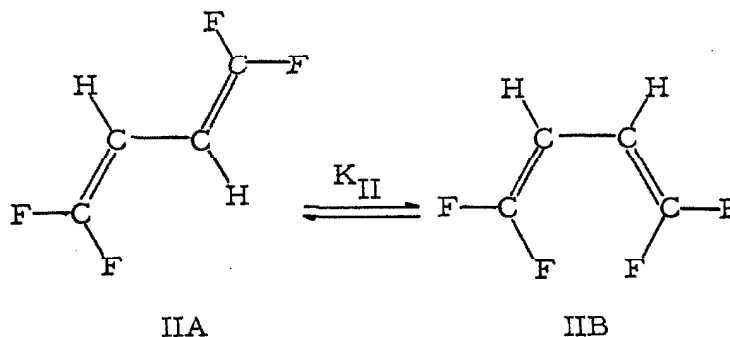


Figure 14. Energy Level Diagram for Perfluoro-1,2-dimethylenecyclobutane

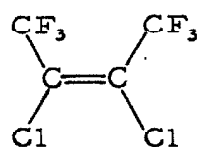
pattern of very sharp lines which upon decoupling simplifies to that of a very tightly coupled AA'BB' system. In addition, no significant change was observed in the decoupled fluorine spectrum down to -80° . The broadness in the previously reported spectra (67) may be partially due to the greater complexity at 40 Mcps but must also be due to poorer resolution. The originally proposed, slowly established cis-trans equilibrium could not be observed. However, a complete analysis of the $F^{19} - \{H^1\}$ spectrum of II does provide interesting information about the magnitude of the equilibrium constant K_{II} .



The very large magnitude (36 cps) of one of the 5-bond fluorine-fluorine coupling constants suggested that II might exist predominantly in the cisoid form, IIB. This original suggestion rested upon the supposition that long-range F-F coupling occurs mainly via through-space interactions.(77). Such interactions are thought to be negligible at fluorine-fluorine distances of greater than 2.7 \AA . Since all of the non-geminal F-F distances in IIA are greater than 2.7 \AA , we concluded that IIB might be the preferred conformation in order to permit such large long-range F-F spin-spin coupling. As will be discussed later, the mechanisms of F-F coupling are not on a sufficiently firm basis

to permit a definite conclusion on the preferred conformation of II. In order to avoid this difficulty, we decided to rest the proof of the conformation of II on what appeared to be a much firmer empirical observation: the sensitivity of long-range coupling constants to the spatial relationship of the two spin-coupled nuclei.

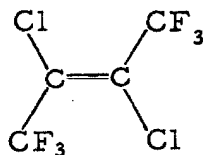
Long-range H-H (78), H-F (79) and F-F (80) coupling constants have all been shown to be very sensitive to the geometrical relationship of the two spin-coupled nuclei. Some illustrative examples for F-F coupling are:



$$J_{FF} = 13.4 \text{ cps}$$

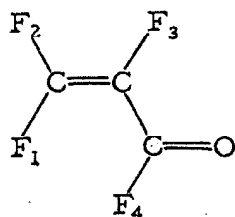
Reference

80c



$$J_{FF} = 1.44 \text{ cps}$$

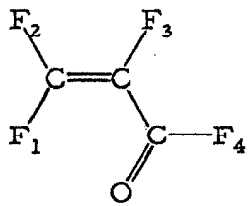
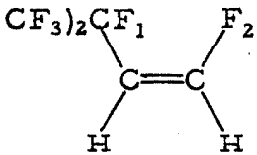
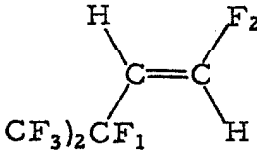
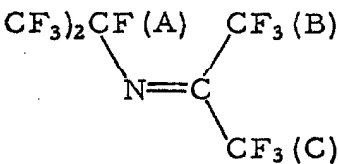
80c



$$J_{14} = 84.5 \text{ cps}$$

80b

$$J_{24} = < 2 \text{ cps}$$

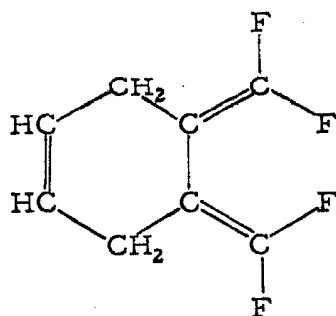
		Reference
	$J_{14} = < 2 \text{ cps}$ $J_{24} = 41.6 \text{ cps}$	80b
	$J_{12} = 31.0 \text{ cps}$	80d
	$J_{12} = 5.5 \text{ cps}$	80d
	$J_{AB} = 38 \text{ cps}$ $J_{AC} = (< 5 \text{ cps ?})$ $J_{BC} = 7 \text{ cps}$	103

The F-F coupling in 1,2-difluoroethylenes is not of the long-range variety but it is nonetheless worthwhile to note that the cis coupling is normally $\sim +70$ cps while the trans coupling is ~ -120 cps (an overall change of ~ 190 cps!) (81).

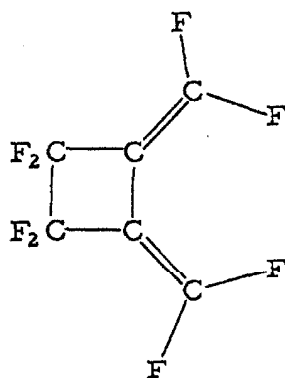
A proof based on the spatial sensitivity of long-range F-F

coupling constants requires model compounds for an empirical basis for magnitudes of F-F coupling constants between fluorines with similar geometrical relationships to those in IIa and IIb. Structurally rigid molecules containing a transoid 1,1,4,4-tetrafluoro-1,3-butadiene fragment are difficult to conceive of. Only the 2,3-positions can be used as handles to tie down the molecule. We therefore sought to examine structurally rigid molecules containing only cisoid 1,1,4,4-tetrafluoro-1,3-butadiene systems. The only previously known compound with this type of structure was perfluoro-1,2-dimethylenecyclobutane, IV (75); since IV must have slightly abnormal bond angles, its coupling constants were expected to be somewhat different from IIb. Bis-4,5-(difluoromethylene)-cyclohexene, III, provides a much better model for cisoid IIb; it is sufficiently rigid to eliminate a transoid conformation but sufficiently flexible to permit a non-planar cisoid conformation as might occur in IIb. In addition it has no highly electronegative substituents which might perturb the electronic structure of the 1,1,4,4-tetrafluoro-1,3-butadiene system.

The F-F coupling constants and chemical shift differences are virtually identical for II and III (see Tables XIII and XIV). The largest change observed is in the geminal (J_{AB}) F-F coupling constant which increases from 33.8 cps in II to 39.0 cps in III. The large five-bond coupling constant (J_{AA}) decreases from 35.7 cps in II to 31.4 cps in III. The change from III to IV (Table XV) is larger. The geminal coupling constant again shows the largest change (to 14.7 cps in IV) but the large five-bond coupling constant also decreases significantly (to 23.2 cps in IV).



III



IV

The variation between the coupling constants for III and IV illustrates the high sensitivity of the F-F coupling constants in this system to structural perturbations. The angle between the carbon-carbon double bond axes increases from 60° in III to about 90° in IV. The hybridization at the olefinic carbon atoms is probably also slightly changed.

One would certainly expect different long-range coupling constants for the very different spatial relationship of the fluorine atoms in IIa and IIb. The occurrence of nearly identical coupling constants in IIa and IIb would not be expected.

Since both III and IV must exist in cisoid like configurations,

the similarity of the long-range five-bond coupling constants for II, III, and IV was thought to be very strong evidence in favor of the cisoid conformation, IIb, of 1,1,4,4-tetrafluoro-1,3-butadiene. The similarity of the chemical shift difference between the two vicinal fluorines could be used to support this conclusion ($\Delta\gamma_{\text{III}} - \Delta\gamma_{\text{II}} = 16$ cps).

The F-F coupling constants of II are plotted as a function of temperature in Fig. 15. The absence of any appreciable temperature dependence requires that K_{II} be very large or very small.

Our conclusion that II exists in a cisoid conformation prompted a microwave study of this compound by R. A. Beaudet. Because the intensities of pure rotational transitions are proportional to the square of the dipole moment, μ , and because the dipole moment of IIa is zero by symmetry, a microwave spectrum is allowed for only IIb. The latter would have a large dipole moment ($\mu \approx 3.0$ D in the s-cis form) and a dense and intense b-type spectrum. Hence a qualitative examination of II for the presence of a pure rotational spectrum should in itself confirm the presence or absence of any appreciable concentration of IIb. The microwave region from 18-22 kmc and from 24.5-25.0 kmc was searched. The sample pressure was about 30 microns and the Stark voltage was kept between 500-1000 V. No pure rotational spectrum was found for this molecule. From intensity considerations, a concentration of 3% of IIb in the sample should have easily been detected. Beaudet therefore concludes that the molecule must exist primarily in the s-trans form (82).

The n.m.r. and microwave studies lead to contradictory

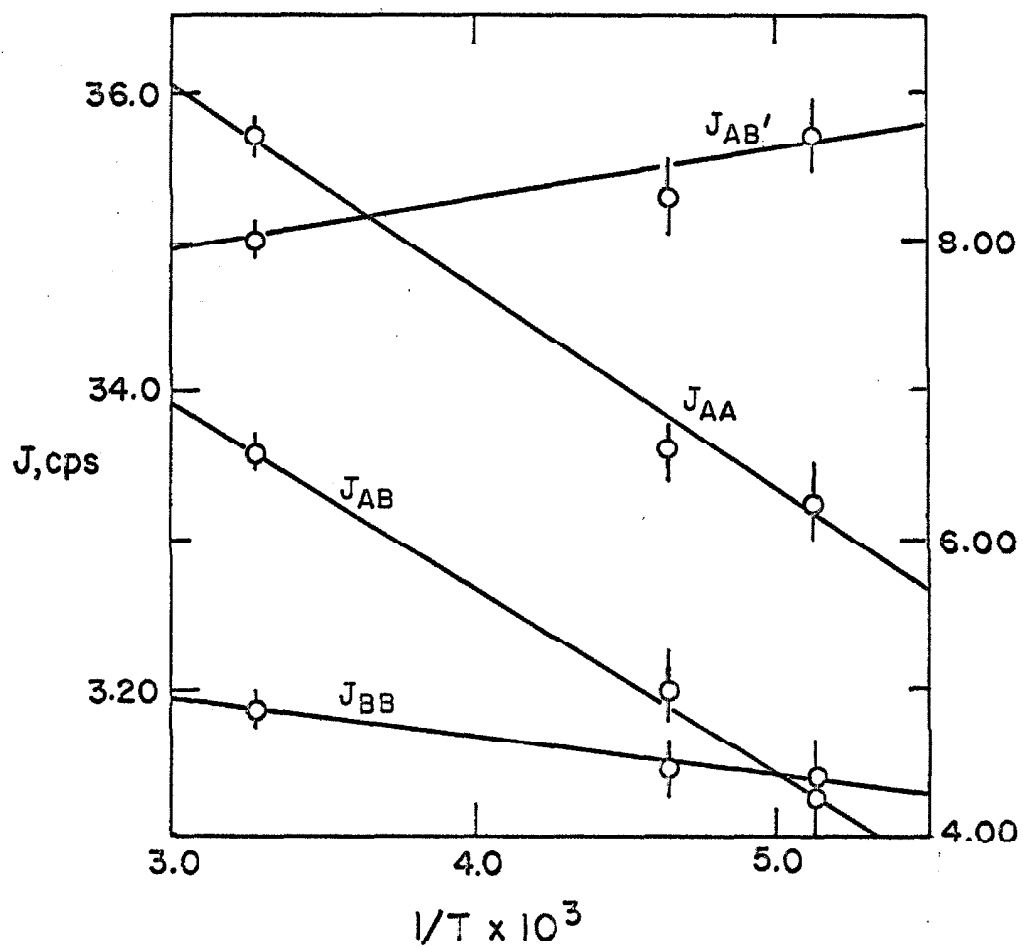


Figure 15. Temperature dependence of F-F coupling constants in 1,1,4,4-tetrafluoro-1,3-butadiene. J_{AA} and J_{AB} left scale, $J_{AB'}$ and J_{BB} right scale.

conclusions which are difficult to reconcile. To eliminate the possibility of a change in preferred conformation on going from the condensed phase (on which the n.m.r. studies were done) to the gas phase (on which the microwave studies were done) the infrared spectrum of II in the gas and condensed phase were determined. The spectra (Fig. 16) show no significant change on going from the gas at 2 mm to the condensed phase, or to carbon disulfide solution. If a change in preferred conformation had occurred, a marked change in the I.R. spectra would have been expected because of the different symmetries of the cis and trans forms. D. A. Dows is currently performing detailed infrared and Raman studies of II which provide additional information on the conformation of II (83).

The infrared spectrum of II shows a doublet in the C-H stretch region and on a doublet in the C=C stretch region. However the Raman spectrum of II shows only a single C-H stretch and a single C-C stretch; the Raman frequencies are different from the infrared frequencies. This implies that one of the infrared bands in the C-H stretch region and one of the infrared bands in the C=C stretch region are combination or overtone bands. The absence of correspondence in the infrared and Raman frequencies favors the C_{2h} symmetry of the s-trans form, IIa. A complete analysis of the Raman and infrared spectra will be required before a final conclusion can be reached.

The dipole moment of II has been measured in carbon tetrachloride solution at 4°. The data are summarized in Table XVI. Both the density and the dielectric constant of the solutions were non-linear

Figure 16. Infrared spectra of 1,1,4,4-tetrafluoro-1,3-butadiene;
A, gas at 2.0 mm; B, gas at 8.0 mm; C, carbon di-
sulfide solution; D, neat liquid.

-85a-

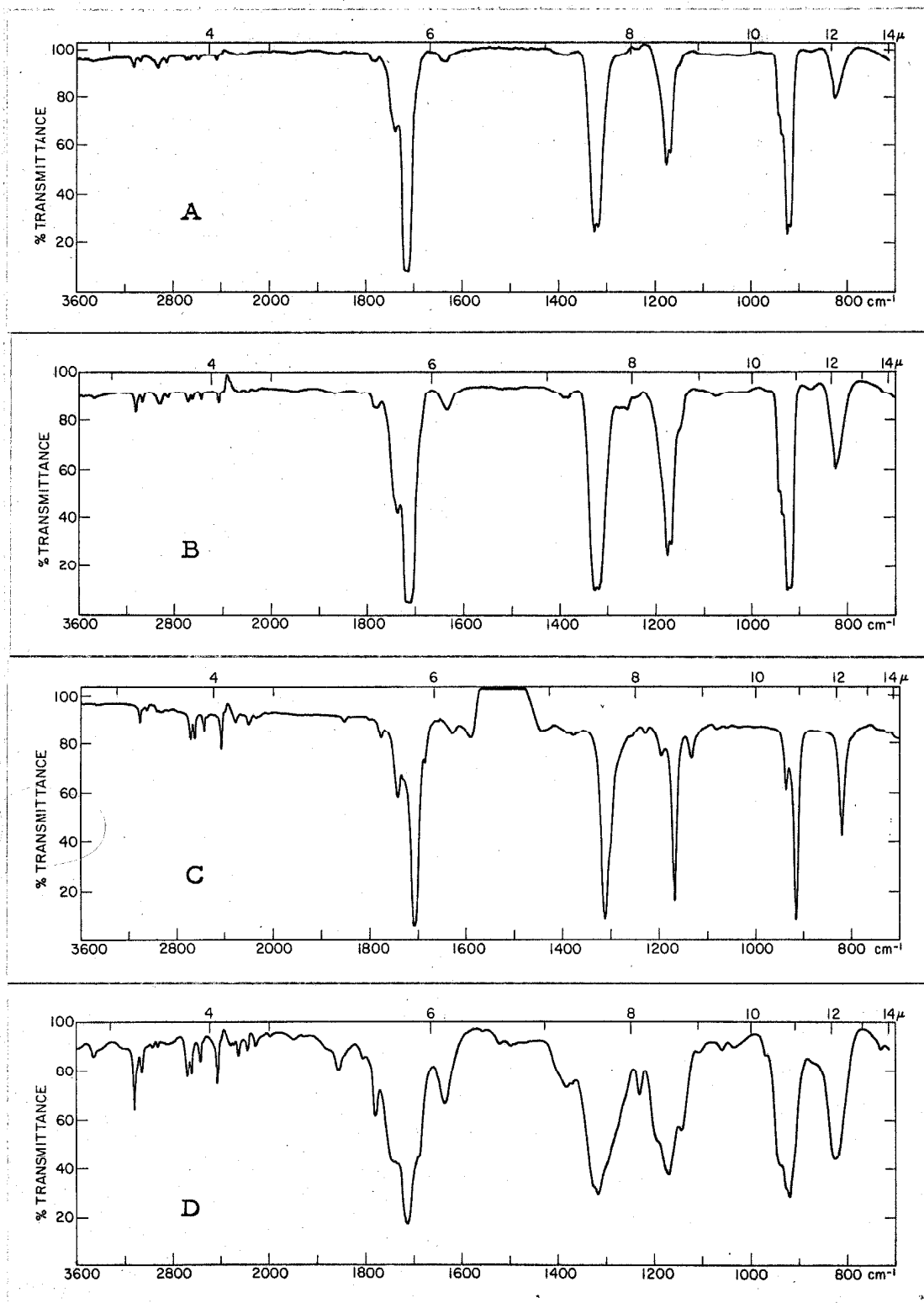


Table XVI

Dipole Moment of 1, 1, 4, 4-Tetrafluoro-1, 3-Butadiene

Conc., Mole Fraction in CCl	P ₂	R ₂	n _D ⁴	d ⁴	ε _{soln.}
0.0232	25.69	27.70	1.4683	1.6113	2.267
0.0345	25.68	20.62	1.4637	1.6080	2.265
0.0685	26.10	20.58	1.4581	1.5945	2.257
0.1072	26.24	20.63	1.4519	1.5180	2.247

Conc., Moles/ml. x 10 ⁴	Δ x 10 ³
2.44	2.29
3.62	13.2
7.19	21.0
11.21	28.4

$$\text{from } P_2^{\circ} = \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \frac{1}{d_1} \left(M_2 - \frac{M_1 b}{d_1} \right) + \frac{3 M a}{(\epsilon_1 + 2) d_1}$$

$$P_2^{\circ} = 25.06$$

P_∞ from P₂ vs C at C=O

$$P_{\infty} = 25.47$$

$$\mu = 0.4 \underline{\underline{D}}$$

from (Δ/C)_{C=O}

$$\mu = 0.4 \underline{\underline{D}}$$

in concentration. Calculation of the dipole moment by the Guggenheim method or by extrapolation of the solute polarization to zero concentration yielded a dipole moment of $\sim 0.4 \text{ D}$. The molar refraction of II obtained ($R_2 = 20.6 \text{ ml/mole}$) agrees reasonably well with that calculated by summing the bond refractions ($R_2^{\text{calc}} = 19.8 \text{ ml/mole}$). The error in very small dipole moments is fairly high since the difference between two large numbers of very similar magnitudes is used as a multiplicative factor in calculating the dipole moment.

The observed dipole moment is not consistent with a cisoid conformation of II. Fisher-Herschfelder models indicate that the angle between the axes of the C=C double bonds can be not more than 120° (trans = 0°). The calculated dipole moment for this conformation (based on the dipole moment of $\text{CH}_2=\text{CF}_2$) is 2.3 D . By assuming $\mu = 0 \text{ D}$ for IIa and $\mu = 2.3 \text{ D}$ for IIb, one can calculate that the equilibrium mixture necessary to produce $\mu = 0.4 \text{ D}$ contains 17% IIb. However, because of the inaccuracy of the data this probably represents an upper limit.

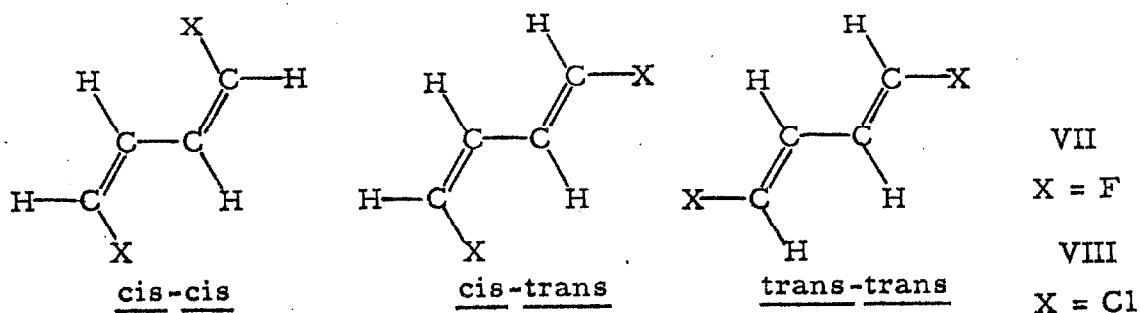
An attempt to determine the conformation of II by photochemical means was unsuccessful. Triplet energy transfer from high energy photosensitizers to dienes is thought to be diffusion controlled. This requires that the ratio of cis- and trans-triplets produced from a 1,3-butadiene system be in the ratio of the s-cis and s-trans equilibrium concentration of the diene. The cis- and trans-triplets from a 1,3-butadiene are thought to lead to different types of dimeric products; a cis-triplet yielding mainly cyclohexene type products and a trans-triplet

mainly cyclobutane type products (84).

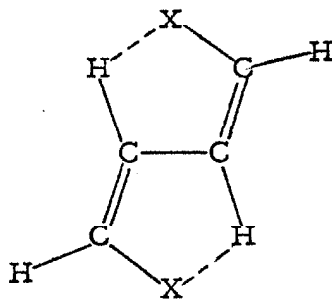
Samples of II containing benzophenone and acetophenone were prepared and irradiated with a 450 watt Hanova Mercury lamp. After 12 hours, the material had formed a white polymeric precipitate. The filtrate obtained upon removal of the solvent left no residue on evaporation. This approach was therefore discontinued.

The existence of II in a non-transoid conformation would not have been entirely unexpected. The other poly-halogenated butadienes, hexafluoro-1,3-butadiene, I, hexachloro-1,3-butadiene, V, and 1,1,4,4-tetrachloro-1,3-butadiene, VI (85), are also reported to be non-transoid. For V, the non-planar form was thought to result from steric interference of the chlorines in either planar form; (86) a similar explanation could account for the non-planarity of I.

For II and VI a different explanation would be required. The cis-cis configuration of both 1,4-difluoro-(VII) and 1,4-dichloro-1,3-butadiene (VIII) is more stable than either the cis-trans or trans-trans configuration (87). Any non-bonded steric interactions which would distabilize the s-trans form of II and VI should also be present in VIII and VII and produce a favored trans-trans configuration. Viehe and Frachimont proposed that the favored cis-cis configuration



of VII and VIII was due to internal hydrogen bonding in the s-trans conformation (88):



There is no reason to expect that the s-trans form of II and VI would not be stabilized by the same interactions. If II and VI prefer non-planar cisoid conformations, cis-cis VII and cis-cis VIII might also be expected to. The s-cis forms of cis-cis VII and cis-cis VIII were ruled out on the basis of their u.v. spectra.

The infrared and Raman studies, the measured dipole moment, and the microwave studies are consistent only with the s-trans conformation, IIa, of 1,1,4,4-tetrafluoro-1,3-butadiene. The contradictory conclusions reached from the n.m.r. data require a reconsideration of the basis for this conclusion. The essential premise for the n.m.r. study was that long-range F-F coupling would be spatially dependent. The basis for this generalization was the observed dependence of F-F couplings on the cis or trans configuration of several model compounds. Very little is known about the conformational dependence of non-vicinal F-F coupling constants for non-rigid fluorocarbons. However, the assumption of a spatial dependence of the F-F coupling constants in the fluoroalkadienes is apparently not

justified.

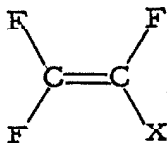
The initial proposal that the large five-bond F-F coupling occurred via a through-space interaction also appears to be incorrect. Before discussing this point in detail, it seems worthwhile to consider the present viewpoints on the various mechanisms of fluorine-fluorine spin-spin couplings.

Theoretical calculations of proton-proton spin-spin coupling constants normally begin with the complete Hamiltonian for the electron-nuclear interactions as was first outlined by Ramsey and Purcell (89) and developed by Ramsey (90). This treatment considers electron-nuclear interaction arising from Fermi contact, magnetic dipolar and electron orbital interactions. Since early calculations indicated that the Fermi contact term was the largest for H-H coupling, both the magnetic dipolar and electron-orbital interactions in later calculations were usually neglected (91-93). H-H couplings have been fairly successfully treated by assuming that the coupling mechanism involves the electron distributions in the intervening bonds and that the contact term dominates the interaction between the protons and the bonding electrons.

The theoretical calculation of F-F couplings is much more complicated since the additional electrons in p-type orbitals must be included. According to McConnell, "nuclear spin coupling between pairs of nuclei other than protons presents a much more complex problem from a theoretical point of view...because, in general, both one-electron orbital and two-electron spin and orbital interactions make significant and sometimes comparable contributions to nuclear spin

coupling" (91). By application of M.O. theory and consideration of only the magnetic dipolar and electron-orbital terms, he obtained coupling constants of the correct order of magnitude for C_2F_4 .

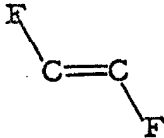
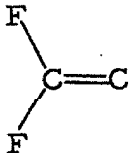
Karplus used the valence bond approach to treat



and neglected all but the contact term (92). He also obtained coupling constants of a reasonable order of magnitude.

Pople has presented a theory of the coupling of nuclear spin in a molecule by the induction of electron orbital currents and derived an approximate expression for the contribution of this effect to the total coupling constant in terms of the anisotropy of the magnetic screening of the nuclei involved. He applied this to the calculation of the F-F coupling constants in fluoroethylenes but obtained values which are an order of magnitude too small (94).

	Magnetic Dipolar and Electron Orbital (91)	Fermi Contact (92)	Electron Orbital Polarization (94)	Observed (95)
	-19 cps	+26 to 62 cps	-1.8 cps	+33 to 58 cps

	Magnetic Dipolar and Electron Orbital (91)	Fermi Contact (92)	Electron Orbital Polarization (94)	Observed (95)
	-46 cps	+53 to 120 cps	+52 cps	-115 to -124 cps
	-64 cps		-13.8 cps	+15 to +87 cps

Williams and Gutowsky attempted to calculate the F-F coupling constants in the three difluorobenzenes using McConnell's procedure (96). The various contributions to the coupling constants are summarized below.

one electron terms	ortho	meta	para
J_{1a}	+ 2.7	+ 0.5	+ 0.3
J_{1b}	-28.8	- 6.4	- 4.4
J_2	- 1.7	+ 1.6	+ 1.7
two electron terms			
J_3	+57	+15	+ 3
$J_2 (p\sigma)$	-20	- 5	+12
$J_2 (p\pi)$	+ 7	+ 7	+ 7

two electron terms	ortho	meta	para
J_{1b}	+44	-22	-22
	+60	- 9	- 2
Observed	∓ 20.8	± 6.9	± 17.2

1a and 1b correspond to electron orbital terms

2 corresponds to dipole-dipole interactions

3 is the Fermi contact term

Since it does not at present appear to be possible to make meaningful calculations of F-F coupling constants, more empirical rationalizations have been offered. Consideration of the available data led Petrakis and Sederholm to propose that F-F coupling did not occur through the bonding electrons but by a through-space mechanism which involved non-bonded (F, F) interaction (97). The magnitudes of the coupling constants were correlated with F-F distance (Fig. 17). This is essentially a three-point plot with adjusted values for J_{13} and J_{14} . Using standard bond lengths and bond angles, the calculated 1,3-F,F distance is 2.51 Å in two of the nine possible conformers of a propane system while in the other 7 conformers the 1,3-F,F distance is greater than 2.73 Å. Since they believed that F-F coupling only occurred at F,F distances of less than 2.7 Å (the sum of the van der Waals radii) they multiplied the observed 1,3-F,F coupling constant by 9/2 to obtain the adjusted value which they plot. Similarly for the 1,4-F,F coupling constant they present the following argument: there are 27

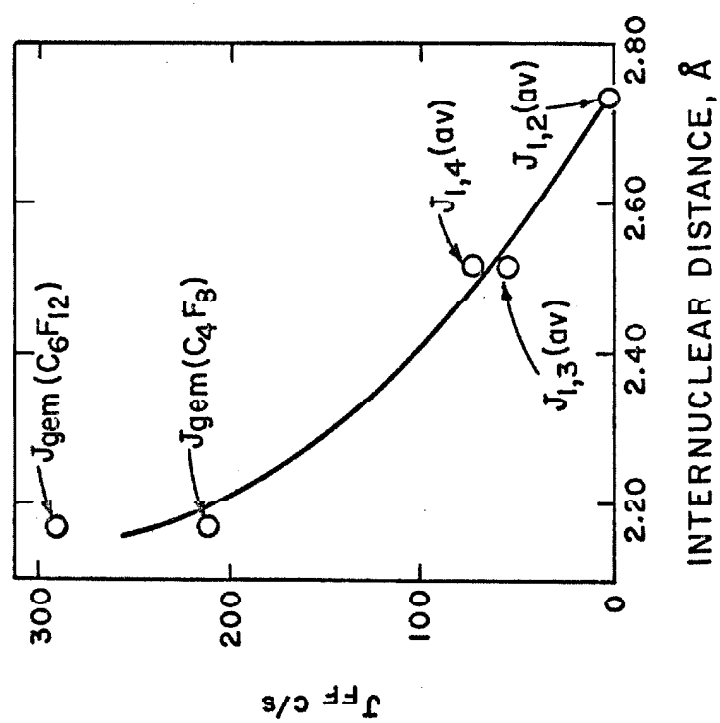
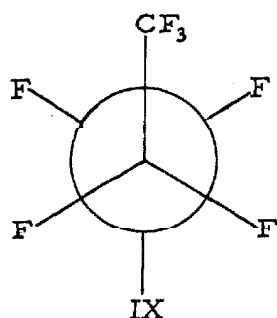


Figure 17. Fluorine-Fluorine Coupling Constant versus Internuclear Distance

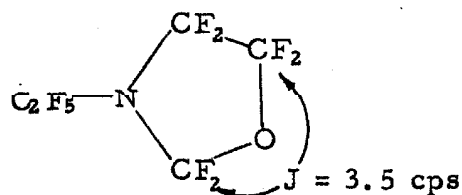
different relative positions for a pair of fluorine atoms on the 1 and 4 carbon atoms; all of the distances between the fluorines are greater than 2.73 Å except for four configurations in which the distances are 1.76 Å (two cases) and 2.46 Å (two cases); the two configurations corresponding to the 1.76 Å distance are neglected in the adjustment since the F-F distance is too small to make these preferred conformations; the observed 1,4-F, F coupling constant is multiplied by 27/2 to obtain the adjusted value for the plot.

The neglect of conformational preferences certainly makes the adjustment procedure suspect; most of the 1,3 values were taken from molecules of the type IX or from



	J_{13} , cps
X = CO ₂ H	9.9
= CO ₂ CH	9.0
= I	10.8
= NF	8.6
= H	< 1

five membered oxygen and nitrogen containing ring system where only one or two of the possible conformations is appreciably populated. Compounds which cannot exist in one of the conformations with the short F, F distance show appreciable coupling, for example:



Small through-bond interactions would produce very large errors in the Petrakis-Sederholm plot.

The points for $J_{FF} = 200$ to 300 cps are for geminally located fluorines. Absolutely no justification can be offered for the assumption that only through-space coupling is important here. The observation that the coupling varies from 15 to 87 cps in 1,1-difluoro-ethylenes certainly implies coupling through the bonding electrons since the F-F distance is little changed in these compounds.

The only other point on the Petrakis-Sederholm plot is for vicinal fluorines. Since the closest F, F distance (2.73\AA) is greater than twice the van der Waals radius of fluorine (2.70\AA) they believed that there was no through-space contribution to vicinal F-F coupling. (Most of the J_{12} values at that time were close to zero). More recent informations forced a modification of this view.

		Ref.
$\text{CF}_2\text{BrCFBr}_2$	$J_{\text{trans}} = -16.2$	98
	$J_{\text{gauche}} = -18.6$	
$\text{CF}_2\text{BrCFBrCl}$	$J_{\text{trans}} = -17$	99
	$J_{\text{gauche}} = -18$	
$\text{CF}_2\text{BrCF}_2\text{Br}$	$J_{\text{trans}} = -1.5$	100
	$J_{\text{gauche}} = -12$	
$\text{CF}_2\text{ClCF}_2\text{Cl}$	$J_{\text{trans}} = +6.6$	100
	$J_{\text{gauche}} = -10.2$	

In order to account for these results Sederholm has recently

proposed that "for vicinal fluorine coupling constants both through-bond and through-space mechanisms are important. The through-space mechanism gives a contribution to the coupling when the fluorines get close to each other in space. The through-bond mechanism ceases to give a contribution when the sum of the electron-withdrawing power of all atoms attached to the C-C skeleton become sufficiently high" (101). The highly electronegative substituents withdraw nuclear-spin-information carrying electrons from the bonds between the interacting nuclei (termed the "vampire effect") and thereby reduce the coupling constants. A plot of J_{FF} versus the sum of the electronegativity of the substituent does show a significant correlation (101).

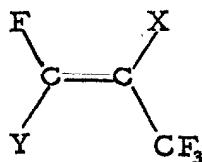
Explanation of 1, 3 F-F coupling by only the through-space mechanism also seems inadequate. In a study of a series of compounds of the type $CF_3)_2X$, Harris found that as the C-X-C angle was varied from $\sim 100^\circ$ to $\sim 180^\circ$, J_{FF} decreased from ~ 9 cps to 5 cps (102). If only the through-space mechanism were operative, J_{13} would be

	J_{13} , cps
$CF_3)_2CF_3$	7.3
$CF_3)_2NNO$	10.8
$CF_3)_2S$	9.7
$CF_3)_2PCl$	8.9
$CF_3)_2Se$	8.5
$CF_3)_2Hg$	5.2

expected to decrease to zero as the C-X-C angle approached 180° .

In addition, fluorine-fluorine couplings as large as 13 cps in systems

of the type



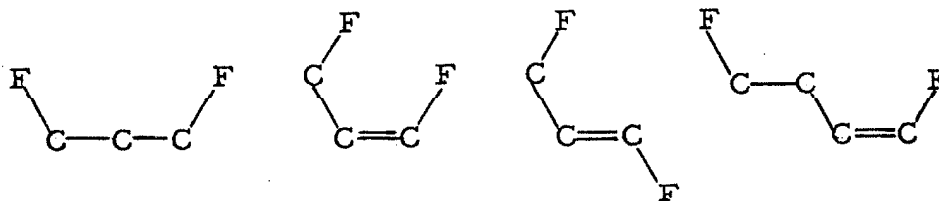
must be due entirely to through-bond coupling (103, 104).

Despite the obvious deficiencies of Sederholms' correlation, the following data suggest that direct-through-space coupling of fluorines separated by four or more bonds might be significant.

		Ref.
	$J_{\text{cis}}^{\text{CF}_3-\text{CF}_3} = 12 \text{ cps}$	103
	$J_{\text{trans}}^{\text{CF}_3-\text{CF}_3} = 1.5 \text{ cps}$	102
	$J_{\text{cis}}^{\text{CF}_3-\text{CF}_3} = 10 \text{ to } 12 \text{ cps}$	101
	$J_{\text{trans}}^{\text{CF}_3-\text{CF}_3} < 1 \text{ cps}$	101
	$J_{\text{AB}} = 38 \text{ cps}$ $J_{\text{AC}} < 5 \text{ cps}$	105

Although this experimental evidence is consistent with the through-space mechanism, very little is known about the magnitude of this interaction and its dependence on the fluorine-fluorine distance.

The F-F coupling constants in several difluoroaromatic compounds were determined by first-order analysis of the C^{13} satellites of the $F^{19}\{-H^1\}$ n.m.r. spectra and are listed in Table XVII. The relative signs are assumed to be the same as was found for several substituted compounds.(106). Manatt and Elleman have shown that 4- and 5-bond F-F coupling in the systems

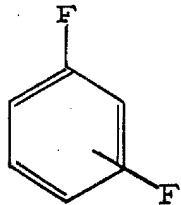
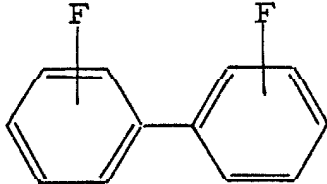
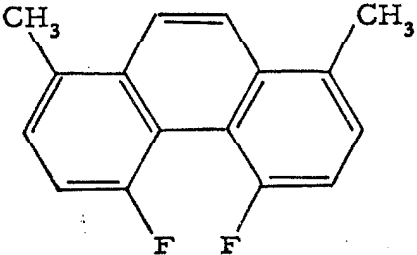


are all positive (relative to geminal F-F coupling). The 4- and 5-bond coupling here are assumed to be of the same sign (107).

In the three fluoroalkadienes, II, III, and IV, J'_{AB} and J_{BB} are also five-bond coupling constants. Since these F-F distances are much longer than the supposed minimums necessary to produce a through-space interaction, the observed couplings must arise from through-bond interactions. These interactions occur through unsaturated systems and may be larger than what would be found in the corresponding saturated system. Nonetheless, it seems clear that through-bond interactions of fluorines even over five-bonds are certainly not negligible.

Table XVII

Fluorine-Fluorine Coupling Constants
in Difluoroaromatic Compounds

	<u>o</u> -	J_{FF} , cps
	<u>m</u> -	-20.8
	<u>p</u> -	+ 6.9
	<u>o, o</u> -	+17.2
	<u>m, m</u> -	16.5
	<u>p, p</u> -	< 1
	<u>p, p</u> -	< 1

Since III and IV exist in cisoid conformations, the resultant cis-cis F-F distance is expected to be nearly as small as will be observed for non-geminal fluorines in a stable molecule. The coupling constant between these fluorines should therefore approach the maximum observable from a through-space interaction. If this F-F distance is less than or equal to that of geminal fluorines, one would predict on the basis of Sederholms' correlation $J_{FF} > 200$ cps. The observed values of 35 and 23 cps respectively are an order of magnitude smaller than the predicted values. The angle between the axes of the carbon-carbon double bonds would have to be greater than 60° before the F-F distance increased to $> 2.70 \text{ \AA}$; this large a distortion of IV does not seem possible. Sederholms' correlation seriously overestimates the magnitude of through-space contributions to F-F coupling.

The similarity of the coupling constants in II and III is puzzling. Even without consideration of the mechanism of F-F nuclear spin correlation, one would have expected a difference in the coupling constants for II and III. No entirely satisfactory explanation can be offered for the lack of conformational dependence of the long-range F-F couplings; but the results seem most consistent with through-bond coupling with the coupling constant either independent of conformation or proportional to a function with similar values at 0° and 180° .

For IIa, no contributions to the coupling from through-space interactions would be expected since all of the F-F distances are greater than $\sim 4.0 \text{ \AA}$. The similarity of the coupling constants in IIa

and III suggests that no significant through-space interaction contributes to the coupling in III. Since III should be a nearly ideal situation for the occurrence of such interactions, serious doubt is cast onto the necessity of invoking through-space coupling in other systems.

The mechanism of long-range spin-spin coupling of fluorine appears to be much more complicated than a simple distance vs. J_{FF} correlation would suggest. Further studies, both empirical and theoretical, will be needed to help resolve this rather confused situation.

III. THE DISSOCIATION CONSTANTS OF METHYL ALKYL KETONE CYANOHYDRINS

Introduction

The structural dependence of the rates of solvolysis of alkyl halides and arylsulfonates has been of major theoretical interest for many years (108). One of the main areas of concern has been the attempt to obtain from the rates of solvolysis information as to the effect of structure on the stability of carbonium ion intermediates. Rigorous study of this structural dependence has been rendered difficult by the transient nature of these reactive intermediates.

As a possible route out of this difficulty, Brown has suggested that ketones might provide reasonably satisfactory models for carbonium ions of related structures (109). On this basis, a structural change which facilitates carbonium ion formation in a reaction where the coordination number of the carbon changes from four to three should hinder addition reactions to ketone where the coordination number changes from three to four. A number of reactions have been utilized in the studies of the effects of structure on the reactivity of ketones. These include the reaction of the ketone with hydroxylamine (113), phenylhydrazine (114), and semicarbazide (115). However, the available evidence indicates that the mechanism of these reactions involves a number of stages and it is not always clear that the same step is rate-determining. The reactions of ketones in isopropanol with

sodium borohydride exhibit simple second-order kinetics and appear to involve a single rate-determining step (116). Cyanohydrin dissociation constants are expected to provide a useful tool for studying structural effects since in these dissociation processes no kinetic problems arise.

To test Brown's hypothesis, the rates of sodium borohydride reduction of a large number of cycloalkanones were determined. These were found to yield a remarkably good linear correlation with the rates of solvolyses of the corresponding tosylates (110) for C_5 to C_{10} compounds. The dissociation constants of the cyanohydrins of the cycloalkanones were also linearly related to the rate of sodium borohydride reduction. These correlations were attributed to the change in internal strain accompanying the change in the coordination number of the ring atom undergoing reaction

	$k_{\text{solv}} \times 10^5,$ sec ⁻¹ , ROTs in HOAc, 70° ^a	$k_{\text{red}} \times 10^4$ l mole ⁻¹ sec ⁻¹ $R_2CO + NaBH_4$ ^b	$K_{\text{diss}}, \text{ mole l}^{-1}$ $R_2COHCN, 22^\circ$ 96% EtOH ^c
C_5	32.2	7.01	0.021
C_6	2.37	161	0.001
C_7	60.0	1.02	0.13
C_8	452	0.078	0.86
C_9	408	0.032	1.70
C_{10}	891	0.013	

a) Ref. 110 and 111

b) Ref. 109

c) Ref. 112

The results of similar studies for the acyclic ketones are far less satisfying. The rates of sodium borohydride addition to the acyclic ketones have been measured (Table XVIII) (117). Since the substituent effects were non-additive, it was concluded that inductive effects were not a major factor. In order to account for the observed rates, Brown considered it necessary to ascribe large steric requirements to aliphatic substituents and use their effects to rationalize the energy of the transition states composed of ketone and borohydride moieties (117).

According to Brown's original proposal, the order of solvolysis of the tosylates $RCH(OBs)CH_3$ should be methyl < ethyl < isopropyl < t-butyl if no factors other than the steric effects were involved. Neither the arylsulfonates (118) or the chlorides (119) exhibit a regular change in reactivity. The acetolysis rates of the secondary alkyl p-bromobenzenesulfonates pass through a maximum at $R =$ isopropyl as R is varied from methyl to t-butyl (Table XVII). For anchimerically unassisted solvolyses, the sequence of rates for the various R groups, methyl < ethyl < isopropyl < t-butyl is predicted on the basis of inductive and steric accelerative effects of R . The opposite order is predicted on the basis of hyperconjugation. The observed reactivity pattern was presented as evidence that solvolysis of $(CH_3)_2CHCH(OBs)CH_3$ was accelerated by a driving force due to hydrogen participation (118).

The rates of ethanolysis of tertiary aliphatic chlorides are even less regular (Table XVIII). The observed order for $RCCl(CH_3)_2$ of

Table XVIII

Effect of Alkyl Groups on Reactivity

R	25°		rel. k_{red} , NaBH ₄	rel. k_{solv} , 80% EtOH	rel. k_{diss} , 96% EtOH	35°	
	rel. k_{solv} , AcOH	RCH(OBz)CH ₃ ^c				rel. k_{diss} , aq. EtOH	RCOH(CN)CH ₃ ^g
	obs.	calc. ^a	0°	25°	20°		
			RCOCH ₃ ^d	RCOCl(CH ₃) ₂ ^e	RCOH(CN)CH ₃ ^f		
				obs.	calc. ^b		
CH ₃	1.0	1.0	1.0	1.0	1.00	1.00	
CH ₃ CH ₂	2.3	2.2	0.417	1.65	2.1	0.87	0.76
(CH ₃) ₂ CH	6.0	5.0	0.195	0.95	4.6	0.51	0.77
(CH ₃) ₃ CH	2.9	13.1	0.0815	1.21	11.5	1.01	1.08
CH ₃ CH ₂ CH ₂				1.58		1.16	1.29

a) $\log k/k_0 = -3.49\sigma^*$; ref. 120b) $\log k/k_0 = -3.3\sigma^*$; ref. 120

c) ref. 118

d) ref. 117

e) ref. 119

f) ref. 121b

g) ref. 122

isopropyl < methyl < t-butyl < ethyl cannot be rationalized by either inductive or hyperconjugative effects alone. The irregularity of this pattern has been used as evidence for acceleration of ionization due to steric strain.

The rough, single-term $\rho^* \sigma^*$ correlation of solvolysis rates (120) fails rather badly to account for the rate sequence in either the tertiary alkyl chlorides or the secondary alkyl p-bromobenzenesulfonates.

The stated similarity of the reaction of ketones with hydrogen cyanide and with sodium borohydride (117) would lead one to expect a linear relationship between the dissociation constants of ketone cyanohydrines and rates of sodium borohydride reduction of methyl alkyl ketones. This expectation is not borne out by the available data in the literature (Table XVIII) (121). These equilibrium constants were obtained by titrating the residual cyanide after "quenching" the equilibrium with nitric acid. In addition, the possibility of side reactions such as hydrate or hemiketal formation rendered the literature data on the cyanohydrin dissociation constants not entirely unquestionable. To avoid these difficulties, the dissociation constants of the methyl alkyl cyanohydrins have been remeasured in situ, by nuclear magnetic resonance spectroscopy.

Results and Discussion

The relative cyanohydrin dissociation constants were determined from solutions of acetone, the methyl alkyl ketone and hydrogen cyanide in methanol at 33°. The H^1 nuclear magnetic resonance spectra were taken with a Varian A-60 spectrometer using a Hewlett-Packard 405 CR D. C. digital voltmeter for integral measurements. The integrated areas of the methyl resonances of the ketone and the cyanohydrin were measured for both acetone and the methyl alkyl ketone. The relative dissociation constants were determined from:

$$K_{\text{diss}}^{\text{rel.}} = \frac{[\text{Area RCOCH}_3]}{[\text{Area RC(CN)OH CH}_3]} \times \frac{[\text{Area (CH}_3)_2\text{C(CN)OH}]}{[\text{Area (CH}_3)_2\text{CO}]} \quad (1)$$

Results are given in Table XIX.

Table XIX

Relative Dissociation Constants of Methyl Alkyl Ketone Cyanohydrins

Ketone	$K_{\text{diss}}^{\text{rel.}}, 33^\circ$	
	MeOH	CCl_4
Acetone	1.00	1.0
Methyl ethyl	0.82	0.8
Methyl <i>n</i> -propyl	1.17	~1.0 ^a
Methyl <i>i</i> -propyl	0.34	-
Methyl cyclopropyl	> 2	-
Methyl <i>n</i> -butyl	~1.1 ^a	-
Methyl <i>i</i> -butyl	> 2	-
Methyl <i>t</i> -butyl	0.95	1.1

a) large errors (± 0.2) due to overlap of the methyl resonance of the cyanohydrin with the alkyl portion of the ketone.

The n. m. r. spectra offered no evidence for formation of hemiketals. However, this does not eliminate the possibility of a rapid, reversible hemiketal formation which would produce a small discrepancy between the real and the apparent concentration of the ketone.* The relative dissociation constants of the cyanohydrins in carbon tetrachloride solution were also determined (Table XIX). The similarity of the relative dissociation constants in methanol and carbon tetrachloride show conclusively that the order of the dissociation constants is not a result of reaction of the ketone with the solvent.

Lapworth and Manske thought that the effect of replacing a β -hydrogen by a methyl group was, in the main, due to the "primary effect of the substituent on the CO or C(OH) · CN groups--a stabilizing 'steric effect' at very close quarters and a destabilizing 'electropolar' effect at points more remote" (121a). They suggested that there was a possible connection between such stabilizing effects at close quarters and the function, \underline{a} , in van der Waals's equation,

$$RT = (p + a/v^2) (v - b)$$

This suggestion was based on the resemblance of these substituent effects to those of ortho substituents on the dissociation constants of cyanohydrins of aromatic aldehydes (121b).

* It is extremely unlikely that the rate of hemiketal formation would be sufficiently fast on the n. m. r. time scale to produce average resonance peaks for the ketone and the hemiketal.

Evans and Young reported the dissociation constants for a large number of alkyl alkyl cyanohydrins (122). These are summarized in Table XX. In going from the alkyl phenyl ketones there is a change from a fully inverted sequence of the groups $\text{Me} > \text{Et} > \text{i-Pr} > \text{t-Bu}$ to the normal sequence of inductive release $\text{Me} < \text{Et} < \text{i-Pr} < \text{t-Bu}$ in the isopropyl or t-butyl alkyl ketones. The seeming regularity of this change is remarkable:

Table XX

Dissociation Constants of the Cyanohydrins of Alkyl Alkyl Ketones

R-COR'		$K_{\text{diss}}, \times 10^2, \text{Aq. EtOH, } 35^\circ \text{ (122)}$					
	R'	Me	Et	<u>n</u> -Pr.	<u>i</u> -Pr.	ϕ	<u>t</u> -Bu
R							
Me		7.03	5.33	9.11	5.42	312	7.61
Et		5.33	4.94	9.96	6.19	148	17.5
<u>n</u> -Pr.		9.11	9.96	13.4	10.9	216	26.9
<u>i</u> -Pr.		5.42	6.19	10.9	19.3	60	808
ϕ	312		148	216	60		21
<u>t</u> -Bu		7.61	17.5	26.9	808	21	

Evans and Young concluded that hyperconjugative electron release was the important factor determining the stability of the ketone relative to the cyanohydrins. They proposed that the steric effect was noticeable only for isopropyl t-butyl ketone. No attempt was made to explain the inversions observed in the alkyl alkyl ketone series except to note that it is likely that a compensation of hyperconjugation and inductive electron release occurs which, coupled with steric effects in the branched-chain compounds, leads to the observed values.

This explanation is not entirely satisfactory. Hyperconjugation and inductive electron release for a given alkyl group should be essentially independent of the second alkyl group of the ketone. One should therefore expect the same relative order of $R = \text{Me, Et, } \underline{i}\text{-Pr, } \underline{t}\text{-Bu}$ for each R' in the dialkyl ketone $RR'\text{CO}$. The only parameter which is sensitive to both alkyl groups is the steric effect; however, this does not appear to be important for any but isopropyl \underline{t} -butyl ketone.

In Fig. 18, the relative rates of solvolysis of the secondary alkyl benzenesulfonates (118) are compared with the relative dissociation constants of the corresponding methyl alkyl ketone cyanohydrins. There appears to be a remarkably close correlation; the negative correlation is even more remarkable. If the transition state for benzenesulfonate solvolysis is presumed to be carbonium ion like, then factors increasing the stability of the carbonium ion should increase the rate of benzenesulfonate solvolysis. Using Brown's proposal that the ketone be used as a model for the carbonium ion, one would predict that factors increasing the stability of the carbonium ion would increase the stability of the ketone and thereby increase the cyanohydrin dissociation constant. Increasing the stability of the carbonium ion should therefore increase both the rate of benzenesulfonate solvolysis and the cyanohydrin dissociation constant. In fact, the observed effect is that a substituent which increases the rate of benzenesulfonate solvolysis decreases the cyanohydrin dissociation constant. The hypothesis that ketones are good models for carbonium ions does not seem very fruitful in this case.

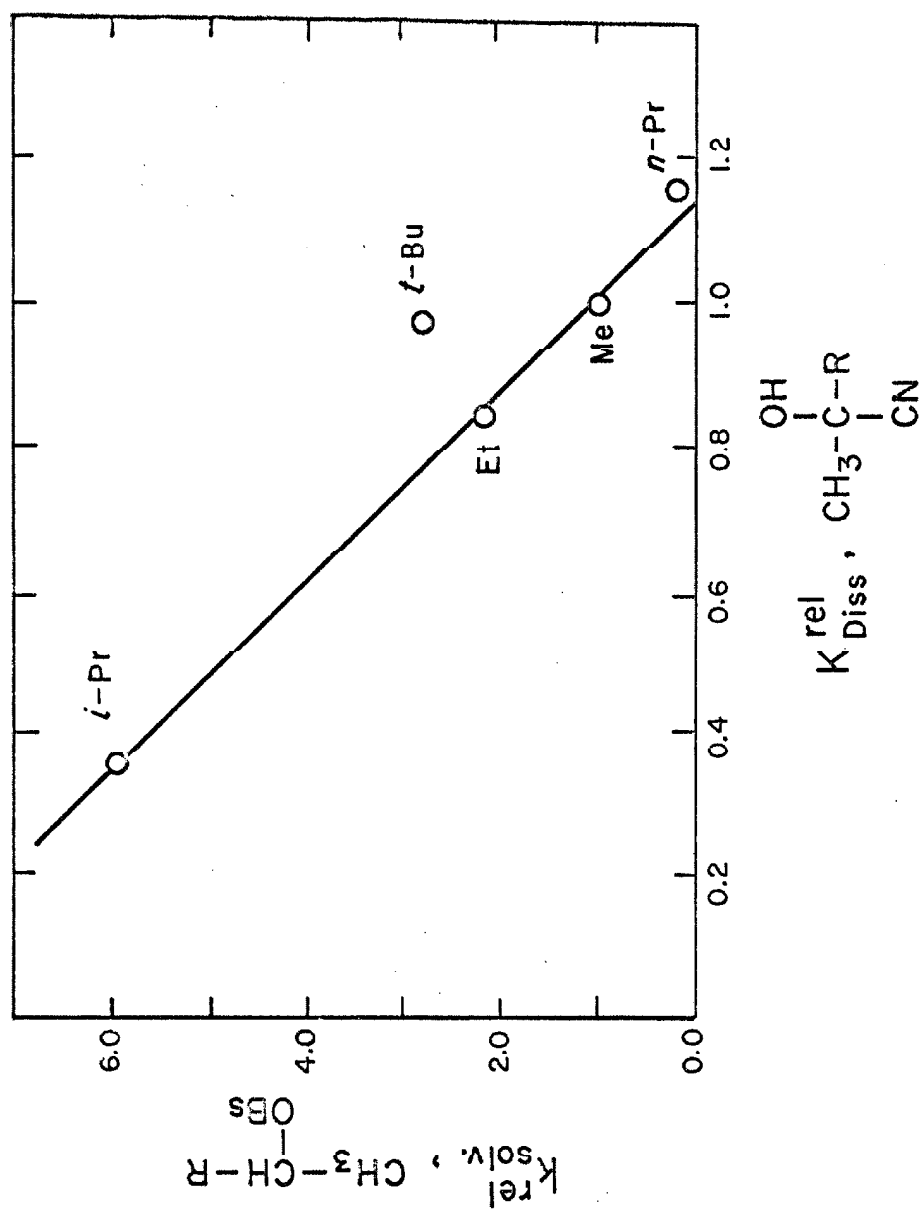
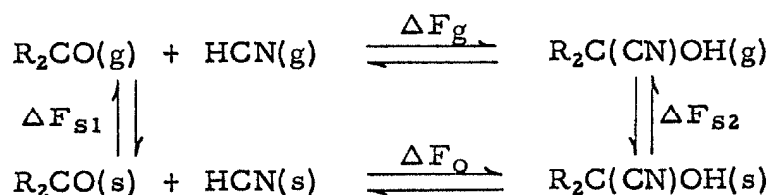


Figure 18. Relationship between the Dissociation Constants of Methyl Alkyl Cyanohydrins and the Rate Constants for the Solvolysis of the Corresponding Benzene Sulfonates

The effect of the substituent on the equilibrium constant can be dissected into three parts: the effect on the free energy of solution of the ketone, the effect on the equilibrium constant for the gas phase reaction, and the effect on the free energy of solution of the cyanohydrin. These effects may be shown by the following energy cycle:



The free energy of dissociation of the cyanohydrin (ΔF_o) is then the sum of the free energy of vaporization of the reactants ($-\Delta F_{s2}$) the free energy of dissociation in the gas phase (ΔF_g), and the free energy of solution of the cyanohydrin (ΔF_{s1}). If one is interested in interpreting the effect of structure on the "intrinsic" reaction rates or equilibria it is most desirable to obtain the appropriate data for the gas-phase reactions where the complications of solvation effects can be ignored since intermolecular interactions are at a minimum.

$$\Delta F_g = \Delta F_o + \Delta F_{s2} - \Delta F_{s1} \quad (2)$$

In actual practice, the desired data are very difficult to obtain for most reactions of interest, gas-phase reaction rates are immeasurably slow and equilibrium conditions difficult to obtain.

The application of equation 2 to equilibrium constants involving the same compound in two different media is straightforward. Since the reactants and products are the same for both media, the identity of the gas-phase standard states is immaterial since gas-phase free

energies will cancel in the differences ($\Delta F'_{s1} - \Delta F_{s1}$) and ($\Delta F'_{s2} - \Delta F_{s2}$). These differences then reduce to the differences in free energies associated with the transfer of the appropriate species from their standard states in the unprimed medium to their standard states in the primed medium.

The application of equation 2 to relative equilibrium constants involving species of different structure in the same medium is ambiguous. The major difficulty involves the choice of standard states. There seems to be no problem in choosing, as the standard states in solution, hypothetical unit concentrations in the concentration dimensions employed in the measurement. For standard states in the gas phase, unit fugacities are commonly employed.* In the application of equation 2, unit fugacities are inappropriate as standard states since then solvation energies vary with molecular weight generally becoming more negative as molecular weight increases and volatility decreases. If the standard state chosen is the fugacity of the vapors in equilibrium with the pure substance, the solvation energy becomes $2.303 RT \log (P/P_0)$ where P_0 is the saturation vapor pressure of the pure substance and P is its partial pressure over the hypothetical unit concentration solution (assuming ideal gas behavior). By this procedure, ΔF_g is the standard free energy change associated with the transfer of the reactants from their pure liquid states to the products in their pure

* This is a natural standard state for gaseous reactions since pressure is the normal concentration dimension.

liquid state. The value of the equilibrium constant defined in this fashion will not in general correspond to any specific gas-phase equilibrium constant. Substituent effects due to solvent-solute interactions can thus be eliminated; however, differential substituent effects on solute-solute interactions (in the pure liquid state) for reactants and products might still be important.

An alternative method for obtaining approximate values for use in equation 2 is to determine heats of solution of the reactants and the products. To obtain the free energies of solution one would need to know the corresponding entropies of solution. However, since we are interested in relative substituent effects on the equilibrium constant we can write:

$$\Delta\Delta F_g = \Delta\Delta F_o - (\Delta\Delta H_{s1} - \Delta\Delta H_{s2}) - T(\Delta\Delta S_2 - \Delta\Delta S_1) \quad (3)$$

According to Hildebrand "differences in intermolecular forces can cause large heats of mixing----which usually overshadow any small entropy corrections" (123). Consequently, one would expect the difference in entropies of solution of the two reactants and their corresponding products to be small. As a first approximation these could be ignored to give:

$$\Delta\Delta F_g \approx \Delta\Delta F_o - (\Delta\Delta H_{s1} - \Delta\Delta H_{s2}) \quad (4)$$

and for the cyanohydrin equilibria

$$\begin{aligned} \Delta F_g^{R_2CO} - \Delta F_g^{R_2'CO} \approx \Delta F_o^{R_2CO} - \Delta F_o^{R_2'CO} + \\ (\Delta H_s^{R_2CO} - \Delta H_s^{R_2'CO}) - (\Delta H_s^{R_2C(CN)OH} - \Delta H_s^{R_2'C(CN)OH}) \end{aligned} \quad (5)$$

The heats of solution of the methyl alkyl ketones and two of the corresponding cyanohydrins in methanol have been measured in a non-isothermal calorimeter (128) (see experimental section for details). The results are summarized in Table XXI. Since the cyanohydrins have half-lives of several hours at room temperature (129), no anomalous heats of solution due to cyanohydrin dissociation are expected. The cyanohydrin of t-butyl methyl ketone was prepared; however, its heat of solution could not be measured since it is a solid.

We had originally proposed that the relative cyanohydrin dissociation constants were determined by the heats of solution of the corresponding ketones. Bulky substituents α to the carbonyl group should perturb the solvent shell and thus decrease the relative stability of the ketone in solution. A similar explanation has been offered for the decrease in pKa with increasing size of the alkyl group for the following series of acids (125):

$\begin{array}{c} R_1 \\ R_2CH-CO_2H \end{array}$		
R_1	R_2	pKa (at 25°C in 50% MeOH)
CH ₃	(CH ₃) ₃ CCH ₂	6.05
CH ₃	(CH ₃) ₃ C	6.25
CH ₃ CH ₂	(CH ₃) ₃ C	6.32
(CH ₃) ₂ CH	(CH ₃) ₂ CH	6.40

On this basis, one would predict the relative dissociation constants to be Me > Et > i-Pr > t-Bu. However, the differences in the heats of solution of the ketones are much smaller than the differences in the

Table XXI

Heats of Solution of Alkyl Methyl Ketones and Cyanohydrins

Compound	ΔH_s , kcal/mole (of compound) ^a
Acetone	0.50
Methyl ethyl ketone	0.56
Methyl <u>i</u> -propyl ketone	0.62
Methyl <u>n</u> -propyl ketone	0.68
Methyl <u>t</u> -butyl ketone	0.67
Methyl <u>i</u> -butyl ketone	0.64
Acetone cyanohydrin	-0.69
Methyl <u>i</u> -propyl ketone cyanohydrin	-0.67

a) heat evolved

free energies of dissociation of the cyanohydrins (see Table XXII).

Furthermore, the differences in heats of solution of the cyanohydrins have not as yet been considered. One would expect the heats of solution of the cyanohydrins to be less sensitive to α -substituents than the ketone because interaction of the cyanohydrin with the solvent will occur predominantly through the cyano- and the hydroxy-groups which are somewhat further removed from the α -substituent than the initial carbonyl group. For the two cyanohydrins (acetone and methyl isopropyl ketone) that have been measured, the difference is only 0.02 kcal/mole.

Table XXII

Free Energy of Dissociation of Methyl Alkyl Ketone Cyanohydrins

<u>Ketone</u>	$\Delta\Delta F_o$ kcal/mole	$\Delta\Delta H_s$ R_2CO kcal/mole ^a	$\Delta\Delta H_s$ $R_2COH(CN)$ kcal/mole ^a	$\Delta\Delta F_g$ kcal/mole
Acetone	0	0	0	0
Methyl ethyl ketone	0.12	0.06	-	-
Methyl i-propyl ketone	0.65	0.12	0.02	0.55
Methyl t-butyl ketone	0.03	0.17	-	-

a) heat absorbed

The resultant free energies for the dissociation in the gas phase are expected to be at most 20% smaller than the observed values in solution. The observed order does not appear to be due only to changes in heats of solution.

It has been proposed that the basis for the Baker-Nathan order is due to steric hindrance to solvation rather than to hyperconjugation (126). Clement has shown that alkyl substituent effects on the rates of solvolysis of benzhydryl chlorides in methanol could be due entirely to differences in the free energies of solution of the substituted benzyl chlorides and therefore proposed that the observed Baker-Nathan order was most readily interpreted as due to steric hindrance to solvation (127).

Steric hindrance to solvation cannot be the cause of the Baker-Nathan sequence in the dissociation constants of these cyanohydrins since the same relative order is predicted for the gas-phase reactions. This appears to be the first instance in which the Baker-Nathan order has been established for a gas-phase reaction.

The observed order can be most readily explained in terms of hyperconjugation and steric effects. As the number of hydrogens α to the ketone decreases the relative stability of the ketone decreases. For the t-butyl compound, one would then have to invoke a steric destabilization of the tetrahedral cyanohydrin with respect to the trigonal ketone. This explanation is consistent with the dissociation constants for all the cyanohydrins of the alkyl alkyl ketones. As the size of the second alkyl group increases, steric destabilization would be expected

to occur sooner in the series Me, Et, i-Pr, t-Bu.

No explanation can be offered for the inverse correlation of the cyanohydrin dissociation constants and the rates of solvolysis of secondary alkyl benzenesulfonates. However, it seems clear that conclusions about the effect of structure on the stability of carbonium ions obtained by studying ketone reactivity should be considered with serious reservations.

EXPERIMENTAL

Boiling points and melting points are uncorrected; melting points were taken with the Hershberg or Buchi melting point apparatus. Vapor chromatograms were obtained using Perkin-Elmer Vapor Fractometers Models 154-C and 800. Preparative vapor phase chromatography was performed on the Beckman Megachrom or the Wilkens Autoprep preparative vapor fractometers. Infrared spectra were obtained with the Beckman Infrared Spectrometer Model IR-7 and Perkin-Elmer Model 137 spectrometers. Elemental analyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Michigan and the West Coast Analytical Laboratory, El Cerrito, California.

Proton nuclear magnetic resonance spectra were obtained at 60 Mcps., using a Varian Associates Model A-60 for the room temperature spectra and a Varian Associates V-4300 B spectrometer with 12-in. magnet, superstabilizer, field homogeneity control coils and Model V3521 integrator and base line stabilizer for variable temperature work.

Fluorine nuclear magnetic resonance spectra were obtained at 56.4 Mcps. using the same Varian Associates V-4300 B spectrometer. Proton decoupling was achieved using a Nuclear Magnetic Resonance Specialties Model SD-60 spin decoupler. Frequency sweep spectra were obtained using the Varian Associates V-4300 B spectrometer at the Jet Propulsion Laboratory which was equipped with a phase sensitive lock-in detector for field stabilization. A variable frequency audio

side-band provided the exciting r.f. signal for observation. Drs. S. L. Manatt and D. D. Elleman kindly assisted with these measurements.

Measurements of line positions in the field-sweep spectra were accomplished by the usual audio-sideband method using a Hewlett-Packard Model 200AB audio-oscillator and Model 521-C frequency counter. In the frequency-sweep spectra, the line positions were measured by determining the frequency of the r.f. field using a Hewlett-Packard Model 524-C frequency counter.

1, 1, 4, 4-Tetrafluoro-1, 3-butadiene (II). - was provided by H. N. Jacobson of duPont. Vapor phase chromatography using columns packed with diisobutyl maleate, diisodecyl phthalate, silver nitrate, silver nitrate-ethylene glycol, Fluorolube and Kel-F No. 3 indicated the material was more than 99% pure.

1, 2-Bis-(difluoromethylene)-4-cyclohexene (III). - 1, 1, 4, 4-tetrafluoro-1, 2, 3-butatriene, prepared by the procedure of Martin and Sharkey (130) was carried by a stream of deoxygenated nitrogen as it was generated through a series of two Dry Ice-acetone cooled traps each of which contained approximately 10 g. of 1, 3-butadiene. After one day at -70° , the traps were warmed to -10° to -20° for two days, then to -5° for two days and then to 25° for one day. The product was purified by preparative v.p.c. on the Megachrom using 12-ft. Carbowax columns at 85° . The infrared spectrum of III (Fig. 19) was consistent with the assigned structure. The absorptions were assigned as follows:

C=CF ₂	stretch		1740 cm ⁻¹
C-F	stretch	1260 and	1268 cm ⁻¹
C=C	stretch		1657 cm ⁻¹
=C-H	stretch		3030 cm ⁻¹
CH ₂	stretch	2970 and	2875 cm ⁻¹

The ultraviolet spectrum of III in cyclohexane had a single absorption maximum at 216 mμ. The H¹ n.m.r. spectrum had resonances at 5.56 and 2.68 ppm in the ratio of 1 to 2. The F¹⁹ n.m.r. spectrum of III is shown in Fig. 8.

Due to the instability of this compound, good combustion analyses could not be obtained. Quantitative hydrogen analysis (135) by n.m.r. of a freshly purified sample gave better agreement with the value calculated for this compound.

Anal. Calcd. for C₈H₆F₄: C, 53.9; H, 3.37.

Found: C, 52.9; H, 7.62.

N.M.R. Analysis: H, 3.5.

2-Methyl-5-fluorobenzaldehyde. - To a 500 ml. three-necked flask was added 3.0 g. of magnesium turnings in 20 ml. of ether. After the magnesium had been activated with iodine, a solution of 25 g. (0.1 mole) of 2-methyl-5-fluoriodobenzene (Aldrich Chemical Company) in 100 ml. of ether was added over 45 min. The mixture was refluxed two hours after the addition was complete. Ethyl orthoformate (20 g.) in 30 ml. of ether was added rapidly and the mixture refluxed five hours.

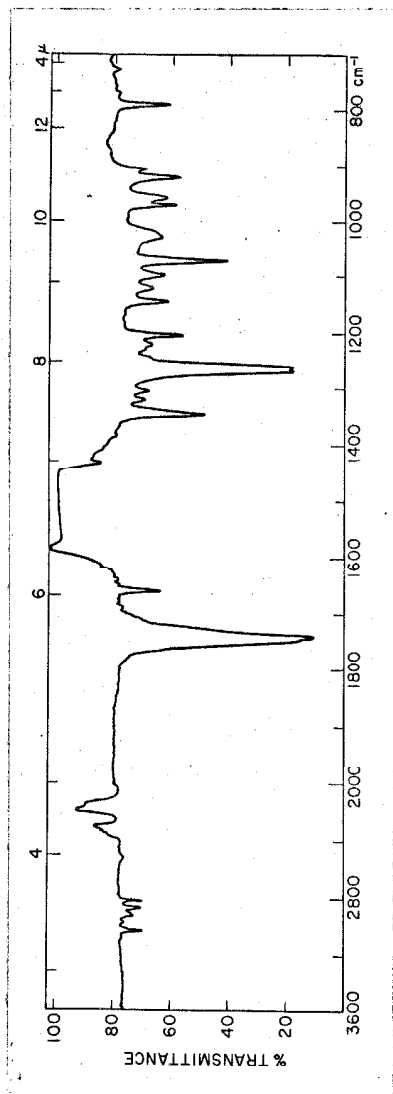


Figure 19. Infrared spectrum of bis-4, 5-(difluoromethylene)-
cyclohexene in carbon disulfide.

The ether was removed on the steam bath to a point where a vigorous reaction began. The flask was immediately immersed in an ice bath and allowed to stand overnight. To the resinous mixture was added 50 g. of ice and 125 ml. of cold 5 N hydrochloric acid. The residual ether was removed on the steam bath and the residue refluxed for 30 mins. under a nitrogen atmosphere. The residue was steam distilled under nitrogen and the distillate extracted with ether. The ether was removed on the steam bath and the residue distilled at reduced pressure to give 8.6 g. of 2-methyl-5-fluorobenzaldehyde, b.p. 70-72° (7 mm). The n.m.r. and infrared spectra of the product were consistent with the assigned structure.

2,2'-Dimethyl-5,5'-difluorobenzoin. - In a 100 ml. round-bottomed flask was placed 0.75 g. potassium cyanide, 15 ml. water, 30 ml. 95% ethanol and 14.0 g. (0.10 moles) of the 2-methyl-5-fluorobenzaldehyde. The mixture was refluxed for two hours on the steam bath using an air-cooled condensor. The solution was extracted with ether. The ether extracts were dried over sodium sulfate and the solvent removed on the rotary evaporator. The residue was chromatographed on alumina. Approximately 35% of the original benzaldehyde was recovered. The eluted benzoin was recrystallized from 80% ethanol to give 6.5 g. of slightly yellow crystals, m.p. 75-76°. The infrared spectrum of the product was consistent with the assigned structure.

2,2'-Dimethyl-5,5'-difluorostilbene. - In a 100 ml. round-bottomed flask was placed 5.2 g. of 2,2'-dimethyl-5,5'-difluorobenzoin

and 5 ml. of thionyl chloride. The mixture was heated on the steam bath for 5 min. after the benzoin had dissolved. The volatile material was removed on the aspirator; 10 ml. of 60-70 petroleum ether was added and then removed on the aspirator. The residue was dissolved in 40 ml. of 95% ethanol, cooled, and 410 mg. of sodium borohydride added. After 10 minutes, 4 ml. of glacial acetic acid and 2 g. of zinc dust were added. The mixture was refluxed for one hour. After cooling, 50 ml. of ether was added. The solution was decanted from the residue and washed with HCl solution (1 ml. in 50 ml. water), 5% sodium carbonate solution and saturated sodium chloride solution. After removal of the solvent on the rotary evaporator, the product was chromatographed on alumina. The eluted product was recrystallized from 95% ethanol to give 1.2 g. of 2,2'-dimethyl-5,5'-difluorostilbene, m.p. 117.5-118°.

Anal. Calcd. for $C_{16}H_{14}F_2$: C, 78.67; H, 5.78; F, 15.56.

Found: C, 78.75; H, 5.87; F, 15.50.

2,8-Dimethyl-4,5-difluorophenanthrene. - The procedure of Mallory and Wood for conversion of stilbene to phenanthrene was used with minor modifications for use with a 450-watt mercury lamp. The yield of 2,8-dimethyl-4,5-difluorophenanthrene from 0.97 g. of 2,2'-dimethyl-5,5'-difluorostilbene was 350 mg. m.p. 102-103.5°.

Sublimation gave 300 mg. of material, m.p. 105.5-106°.

Anal. Calcd. for $C_{16}H_{12}F_2$: C, 79.33; H, 4.99; F, 15.68.

Found: C, 79.40; H, 4.89; F, 16.0.

Tetrafluoroallene. - 1,3-Dibromo-1,1,3,3-tetrafluoropropane

was obtained from Dr. L. Morantz. This was dehydrobrominated by the procedure of Jacobs to give tetrafluoroallene (75).

Perfluoro-1,2-dimethylenecyclobutane. - Approximately 5 g. of tetrafluoroallene and 0.05 g. of hydroquinone were sealed in a heavy-wall glass tube and heated at 40° for 20 hours. The tube was cooled and opened; the contents were distilled to give 1.0 g. of perfluoro-1,2-dimethylenecyclobutane, b.p. 57-63° (lit. 63°) (75). The infrared spectrum was identical with that reported.

Allylcarbinyl Tosylate. - 3-Butenenitrile (47.3 g.) was hydrolyzed to 3-butenic acid with concentrated hydrochloric acid (131). There was obtained 39.7 g. of product, b.p. 68-70° (13 mm.). Lithium aluminum hydride reduction of 27.8 g. of 3-butenic acid gave 11.9 g. of allylcarbinol, b.p. 110-113° (lit. 112.5-113.5°) (132). The reaction of 2.0 g. of allylcarbinol with 7.0 g. of p-toluenesulfonyl chloride in collidine gave 5 g. of allylcarbinyl tosylate, b.p. 150° (~ 6 mm.):

Anal. Calcd. for $C_{11}H_{14}O_3S$: C, 58.38; H, 6.24; S, 14.17.

Found: C, 57.80; H, 5.86; S, 13.44.

n-Butyl Tosylate. - n-Butyl tosylate, b.p. 135° (~ 2.5 mm.) (133) was prepared from n-butyl alcohol.

Cyclobutyl Tosylate. - Cyclobutanol (10.0 g.) was esterified with p-toluenesulfonyl chloride to give 12.4 g. of cyclobutyl tosylate, m.p. 23° (lit. 24.5-25.4°) (134).

1,1-Dideutero-3-butenyl Tosylate. - To 10.0 g. of 3-butenic acid in diethyl ether was added a solution of 4.8 g. of diazomethane in diethyl ether. The solvent was removed and the residue distilled to

give 9.6 g. of methyl 3-butenolate, b.p. 103-105° (745 mm.). To 2.0 g. of lithium aluminum deuteride in 70 ml. of ether was added a solution of 9.6 g. of methyl 3-butenolate in 20 ml. of ether over a one-hour period. The mixture was hydrolyzed with saturated ammonium chloride solution and extracted three times with ether. The combined ether extracts were dried over sodium sulfate. The ether was removed through a 20-cm. Vigreux column and the product distilled through a 30-cm. Hickman column to give 3.6 g. of 1,1-dideutero-3-butenol, b.p. 110-113°. The n.m.r. spectrum of the product was as expected for 1,1-dideutero-3-butenol. The reaction of 3.5 g. of 1,1-dideutero-3-butenol with p-toluenesulfonyl chloride in collidine gave after distillation 2.6 g. of the tosylate. Integration of the area where the 1-protons would fall in the n.m.r. spectrum of the tosylate indicated an isotopic purity of >99%.

(β -Methylallyl)-carbinyl Tosylate. - A sample of crude (β -methylallyl)-carbinol (obtained from Dr. W. B. Kover) was purified by preparative v.p.c. To 0.90 g. (0.0109 moles) of the carbinol in 4 g. of pyridine at 0° was added 1.92 g. (0.108) of p-toluenesulfonyl chloride. The mixture was allowed to stand for one day at 0° and then two hours at room temperature. The mixture was then extracted with 75 ml. of 60-70° petroleum ether. The petroleum ether extract was twice washed with 25 ml. of 1 N hydrochloric acid and once with 25 ml. of water. The ether extracts were dried over magnesium sulfate and the ether removed on the rotary evaporator. The residue was twice extracted into 10 ml. of 30-40° petroleum ether. The ether was

removed on the rotary evaporator. The product was flash distilled to give 1.7 g. of (β -methylallyl)-carbiny l tosylate. This compound could not be obtained in crystalline form. Attempts to fractionally distill this compound led to decomposition. The n.m.r. spectrum (Fig. 20), shows no absorption due to impurities. The measurement of the rate of solvolysis of this compound showed no deviation from linearity up to 60% solvolysis (Table XXX).

cis- and trans-3-Penten-1-ol. - cis- and trans-3-Penten-1-ol (K and K Laboratories) were separated by preparative v.p.c. on the Megachrom using four 12-ft. T.C.E.P. columns. The collected fractions were found to be 98% pure by v.p.c. analysis on a 6-ft. Carbowax column. The material assigned the trans structure had the characteristic infrared absorption band at 955 cm^{-1} . The material assigned the cis structure had the characteristic absorption band at 690 cm^{-1} .

trans-3-Penten-1-yl Tosylate. - To 0.90 g. (0.0105 moles) of trans-3-penten-1-ol in 4 g. of pyridine cooled to 0° was added 1.92 g. (0.0108 moles) of p-toluenesulfonyl chloride. The mixture was allowed to stand for one day at 0° and then for two hours at room temperature. The mixture was extracted with 75 ml. of $60-70^\circ$ petroleum ether. The petroleum ether extract was washed twice with 25 ml. of 1 N hydrochloric acid and then with 25 ml. of water. The extracts were dried over magnesium sulfate and the solvent was removed on the rotary evaporator. The residue was twice extracted with 10 ml. of $30-40^\circ$ petroleum ether and the ether removed on the rotary evaporator. Flash

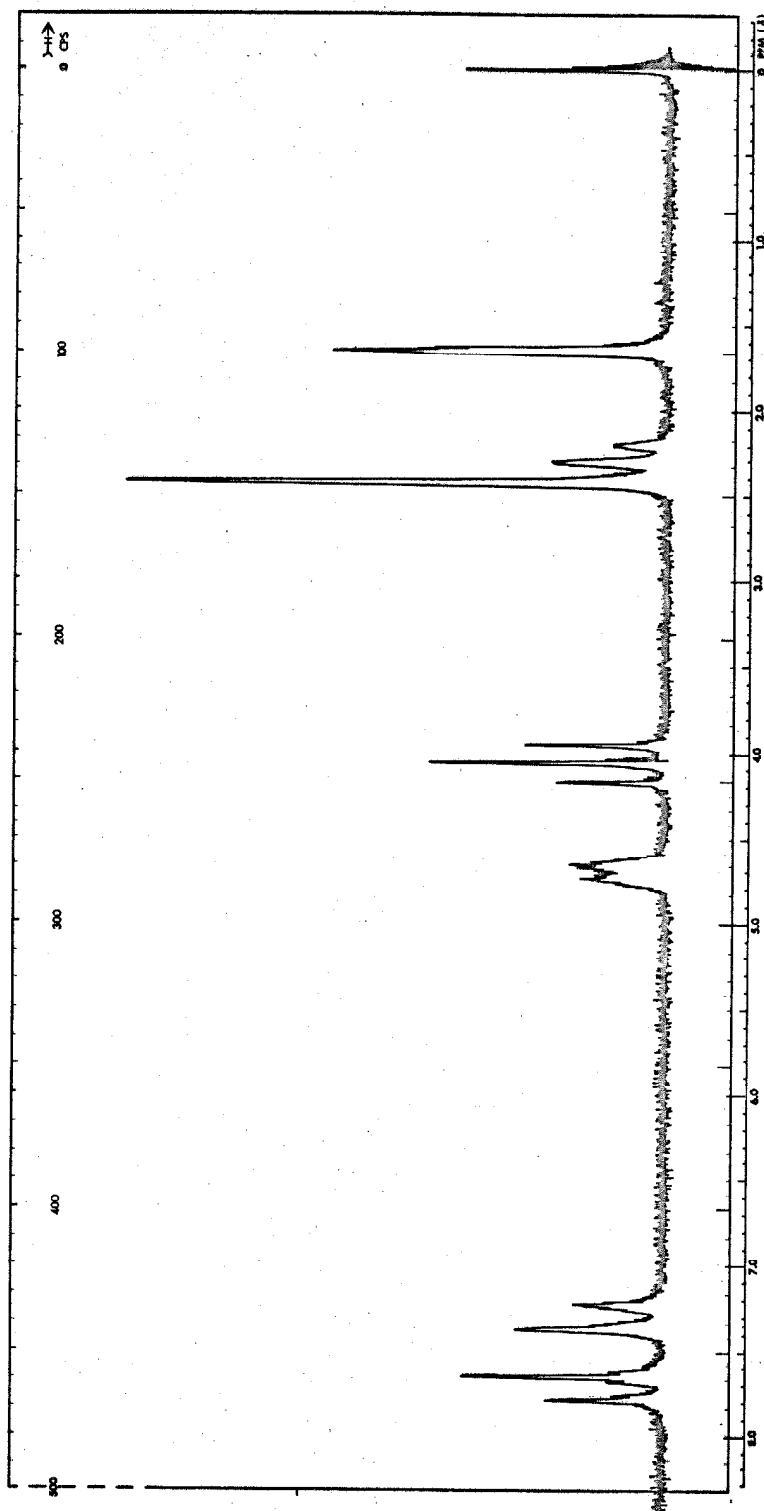


Figure 20. 60 Mcps H^1 nuclear magnetic resonance spectrum of (β -methylallyl)-carbinyI tosylate

distillation of the residue gave 1.7 g. of trans-3-penten-1-yl tosylate, b.p. 140° (~ 1 mm.).

In the n.m.r. spectrum of this compound (Fig. 21) no absorption due to impurities could be detected. The measurement of the rate of solvolysis of this compound showed no deviation from linearity up to 85% solvolysis (Table XXXIII).

cis-3-Penten-1-yl Tosylate. - The procedure used was identical to that for the isomeric trans compound except that 0.50 g. (0.0058 mole) of cis-3-penten-1-ol was used with 1.06 g. (0.0059 mole) of p-toluenesulfonyl chloride. Bulb-to-bulb distillation gave 0.7 g. of cis-3-penten-1-yl tosylate, b.p. 140° (~ 1 mm.).

The n.m.r. spectrum of this compound (Fig. 22) shows only one minor impurity peak at 0.9 ppm. The nature of this minor impurity is not known. The presence of this impurity did not interfere with the determination of the rate of solvolysis. The plot for the rate of solvolysis of this compound was linear up to 70% conversion (Table XXXII).

4-Phenyl-3-butene-1-ol. - In a 1 l three-necked flask equipped with a stirrer, thermometer and an addition funnel was placed 6.5 g. of magnesium and 400 ml. of freshly dried tetrahydrofuran. A Grignard reaction was started by adding 0.5 ml. of methyl iodide and heating to 50°. The solution was then cooled to 25° and a solution of 50.0 g. of freshly distilled β -styrylbromide in 100 ml. of tetrahydrofuran was added at such a rate to maintain the temperature at 30°. After the addition was complete, the mixture was heated at 50° for five minutes and then cooled to 20°. To the cooled solution was added

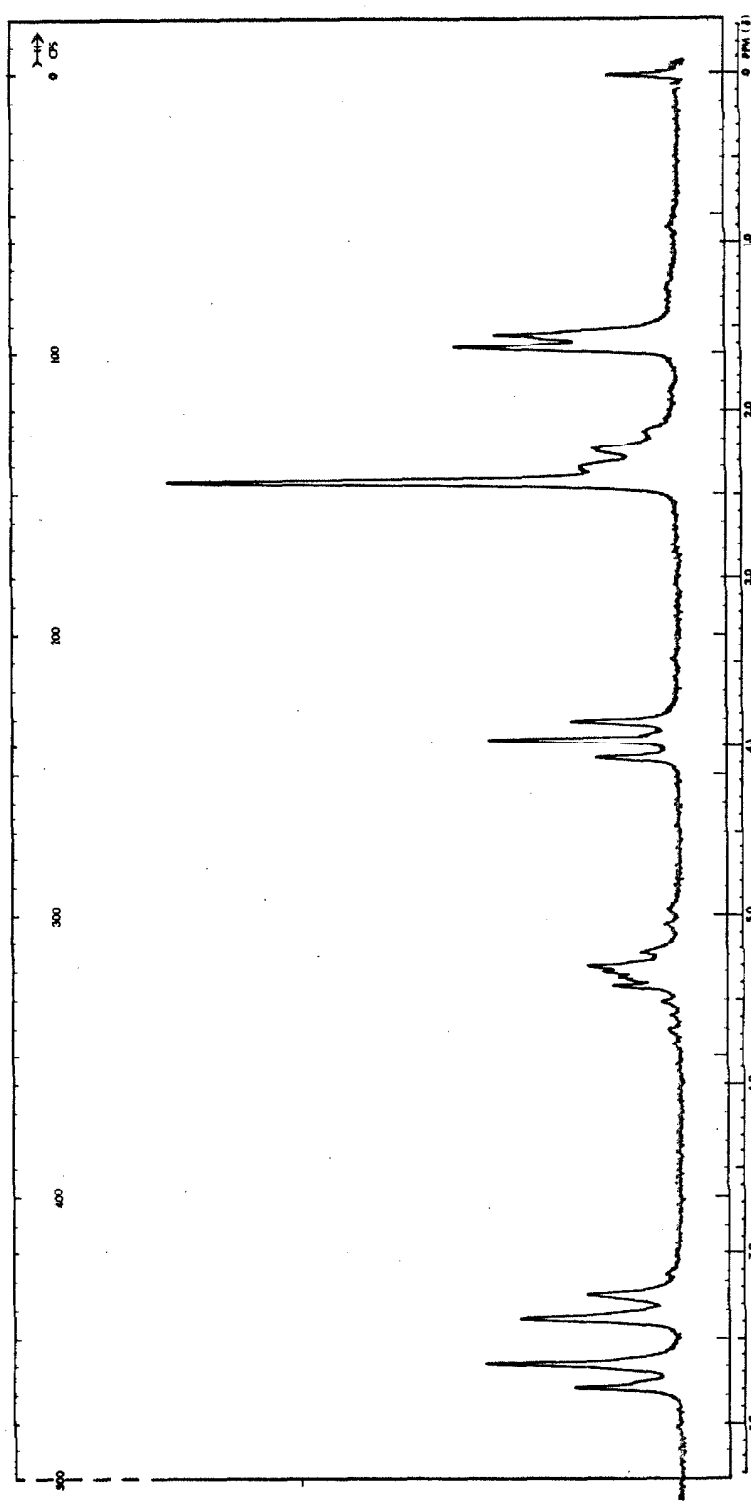


Figure 21. 60 Mcps H^1 nuclear magnetic resonance spectrum of trans-3-pentenyl tosylate.

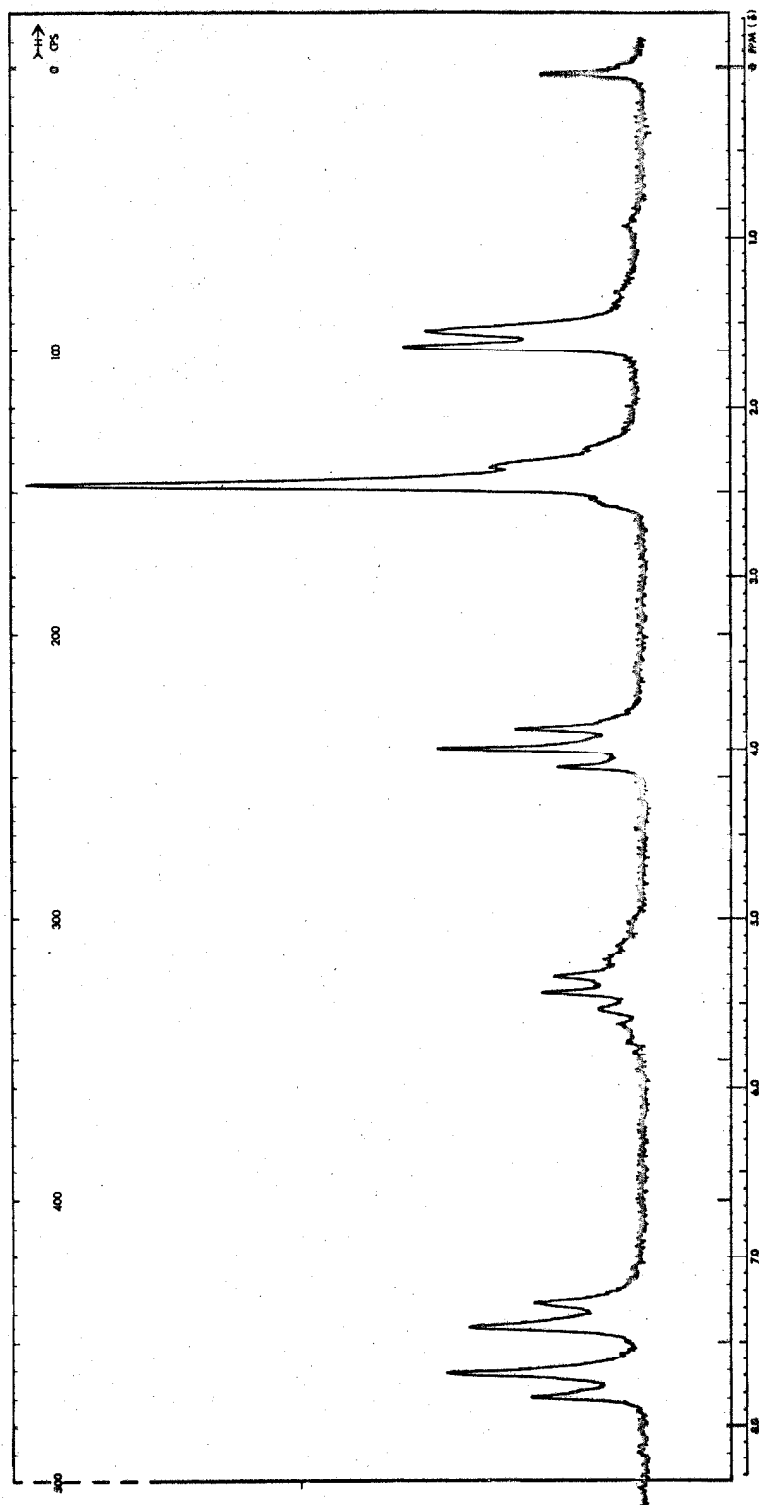


Figure 22. 60 Mcps ^1H nuclear magnetic resonance spectrum of cis-3-pentenyl tosylate

20 g. of ethylene oxide in 100 ml. of tetrahydrofuran. The solution was stirred for 30 minutes and then hydrolyzed with saturated ammonium chloride solution. The solution was filtered and the residue washed with two 50-ml. portions of tetrahydrofuran. The filtrate was evaporated on the rotary evaporator. The residue was distilled through a 5-cm. Vigreux column. After a low-boiling forerun, 24.8 g. of material, b.p. 142° (12 mm.) was obtained. This distillate was redistilled through a 20-cm. wire-spiral column to give 20.2 g. (55% yield) of 4-phenyl-3-buten-1-ol, b.p. 99-103° (2 mm.). The n.m.r. spectrum of the compound was consistent with the assigned structure.

The cis and trans isomers were separated by preparative v.p.c. on the Autoprep using a 20-ft. S.E.-30 column at 170°. The structural assignment was based on analysis of infrared spectra of the 650 to 1000 cm^{-1} region.

trans-4-Phenyl-3-buten-1-yl Tosylate. - To 0.90 g. (0.0061 mole) of trans-4-phenyl-3-buten-1-ol in 4 g. pyridine cooled to 0° was added 1.13 g. (0.0062 mole) of p-toluenesulfonyl chloride. The mixture was allowed to stand at 0° for one day and then at room temperature for two hours. The solution was diluted with 100 ml. of 30-40° petroleum ether and then twice extracted with 25 ml. of 1 N hydrochloric acid and 25 ml. of water. The petroleum ether solution was dried over magnesium sulfate and then evaporated on the rotary evaporator. The residue was twice extracted into the minimal amount of 30-40° petroleum ether and the ether removed on the rotary evaporator. Low-temperature recrystallization from 50:50 ether-petroleum ether

gave white crystals. Three fractions of m.p. 49.8-51.2°, 50.2-51.4°, and 42.2-45.4°, respectively, were obtained by successive recrystallization. The n.m.r. spectra of the first two fractions were consistent with the assigned structure.

Since the n.m.r. spectrum of the second fraction (Fig. 23) showed no detectable absorptions due to impurities, this fraction was used for determination of the solvolytic rate constant. The rate of solvolysis of this compound showed no deviation from linearity up to 75% solvolysis (Table XXXIV).

4-Methyl-3-penten-1-ol. - To 2.5 g. of lithium aluminum hydride in 200 ml. of ether was added a solution of 6.0 g. of 4-methyl-3-pentenoic acid (prepared by C. Rüchardt) in 50 ml. of ether over a two-hour period. The solution was stirred an additional hour after the addition was complete and then hydrolyzed with saturated ammonium chloride solution. The ether layer was decanted off and the residue washed twice with ether. The combined ether fractions were dried over sodium sulfate and the ether removed on the rotary evaporator. The residue was distilled through a 5-cm. Vigreux column to give 4.18 g. of 4-methyl-3-penten-1-ol, b.p. 88-90° (60 mm.). The 4-methyl-3-penten-1-ol was further purified by preparative v.p.c. on the Mega-chrom using eight 6-ft. T.C.E.P. columns.

4-Methyl-3-penten-1-yl Tosylate. - To 1.05 g. (0.0105 moles) of 4-methyl-3-penten-1-ol in 4 g. of pyridine cooled to 0° was added 7.92 g. (0.0108 moles) of p-toluenesulfonyl chloride. The mixture was allowed to stand for one day at 0° and then two hours at room tempera-

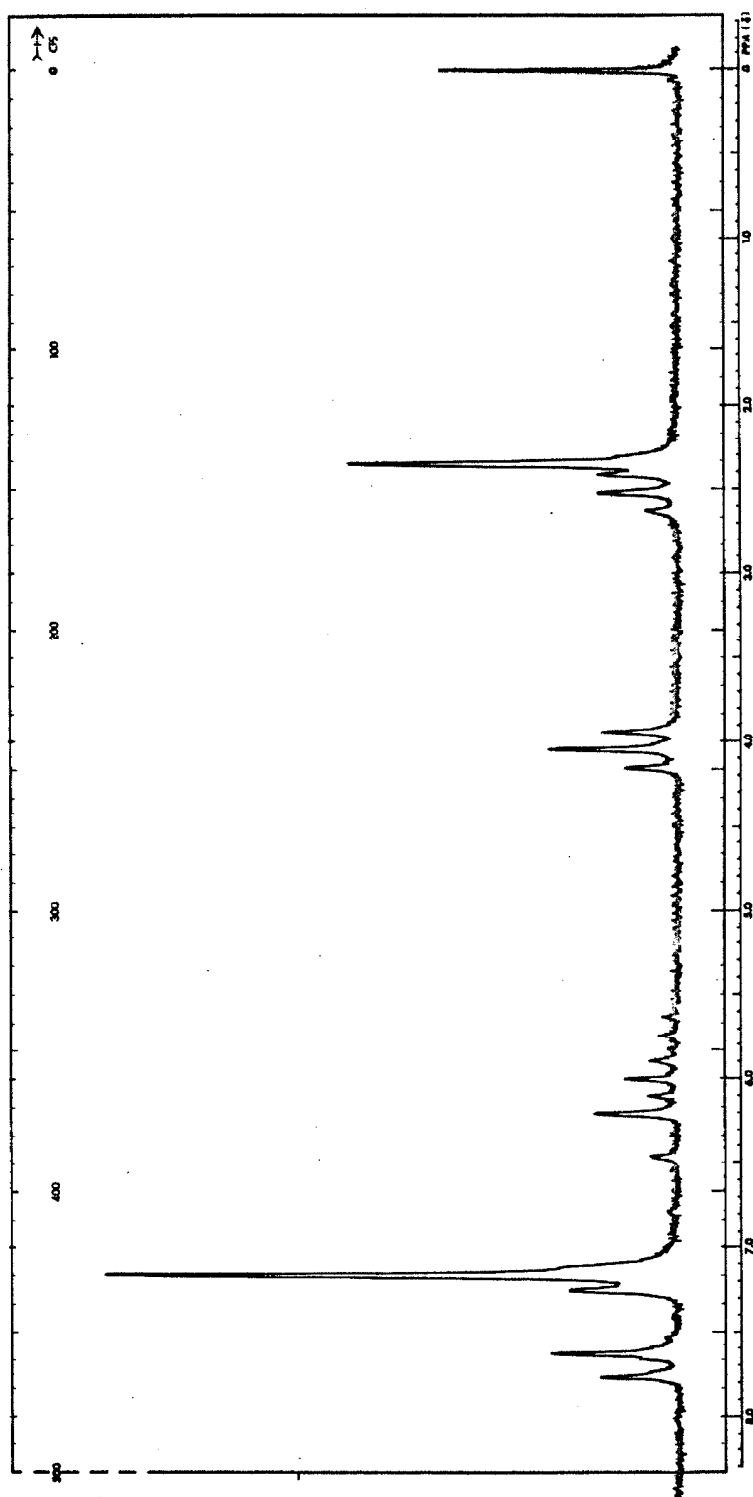


Figure 23. 60 Mcps H^1 nuclear magnetic resonance spectrum of trans-4-phenyl-3-butenyl tosylate.

ture. The mixture was extracted with 75 ml. of 60-70° petroleum ether. The petroleum ether extract was washed twice with 25 ml. of 1 N hydrochloric acid and then with 25 ml. of water. The extract was dried over magnesium sulfate and the solvent was removed on the rotary evaporator. The residue was twice dissolved in 10 ml. of 30-40° petroleum ether and the ether removed on the rotary evaporator. Attempts to bulb-to-bulb distill a portion of the residue at reduced pressure led to decomposition. The remainder of the residue was heated at ~ 50° under vacuum for 5 minutes and gave 1.5 g. of 4-methyl-3-penten-1-yl tosylate.

This compound could not be obtained in crystalline form. The purity of the compound was established by examination of the n.m.r. spectrum of the compound. The n.m.r. spectrum (Fig. 24) shows only one minor absorption due to an impurity at 0.9 ppm. The absence of other impurity absorptions and the location of the resonance suggests that it may be due to a high-boiling hydrocarbon. An equivalent quantity of petroleum ether was evaporated to dryness (one hour at ~50° and 20 mm.) on the rotary evaporator and the flask rinsed with 1 ml. of chloroform. The n.m.r. spectrum of the chloroform rinse did show an absorption at 0.9 ppm. (The same absorption was detected in the n.m.r. spectrum of cis-3-pentenyl tosylate). The high reactivity of this compound made the measurement of the rate of solvolysis somewhat difficult. (The half-life is less than one minute at 50° in 98% formic acid.) The absence of any detectable deviation from linearity in the rate of solvolysis of this compound further substantiates

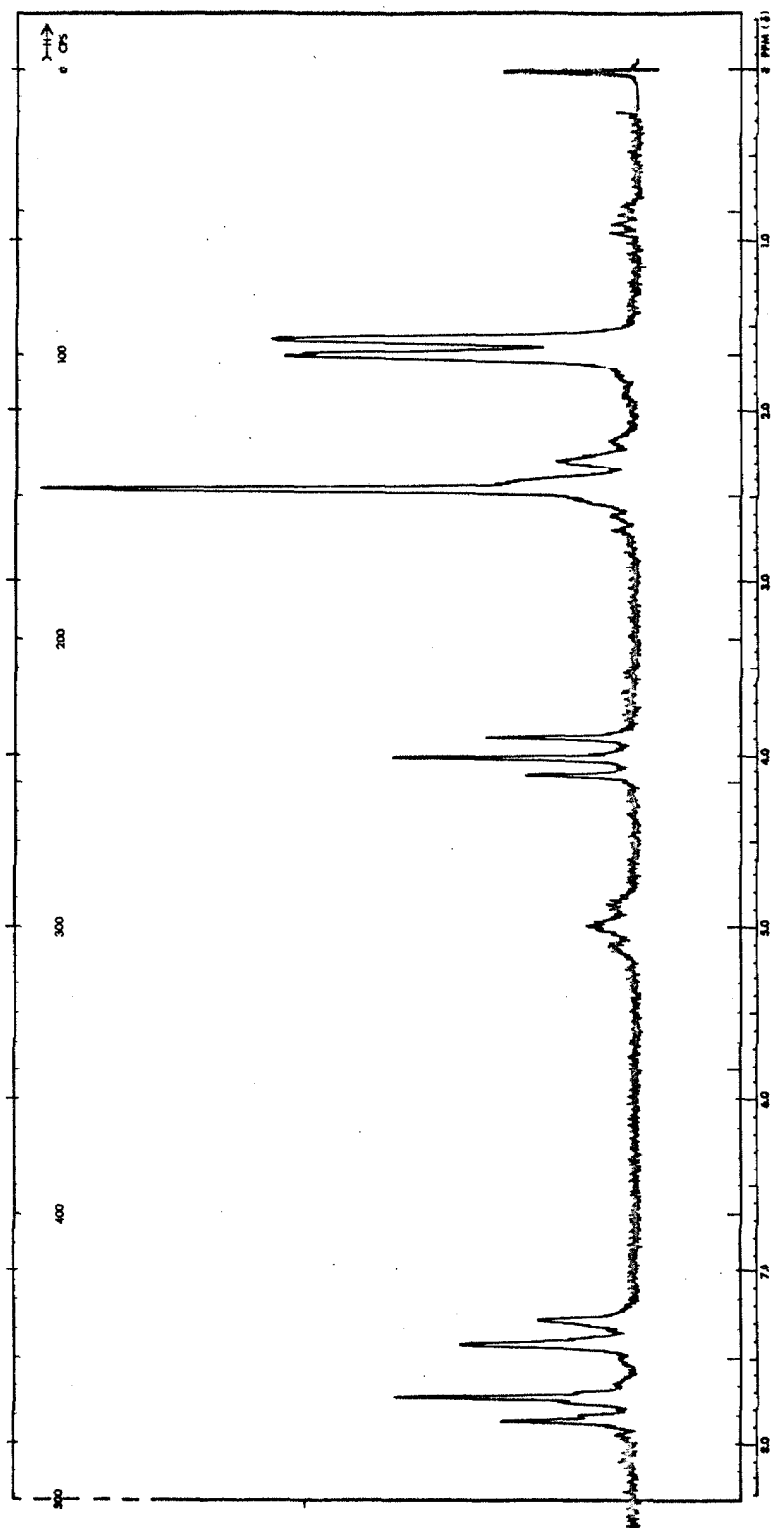


Figure 24. 60 Mcps H^1 nuclear magnetic resonance spectrum of 4-methyl-3-pentenyl tosylate.

its purity (Table XXXV).

Rate of Solvolysis of Allylcarbinyl Tosylates--Procedure A. -

Approximately 0.03 g. of the tosylate was placed in a 4.94-mm. o.d. thin-walled pyrex tube. Approximately 1 ml. of solvent was added and the tubes were sealed. The sealed tubes were placed in a constant-temperature bath. For each measurement the tubes were removed from the oil bath and cooled to -10° in an ice-methanol bath. Immediately before measurement, the tubes were removed from the ice-methanol bath and placed in the probe of the Varian A-60 at 37° C. Seven to ten spectra were taken of each sample for each measurement. After removal from the probe, the tubes were transferred back to the ice bath and then back to the constant temperature bath. For each measurement, the tubes were out of the constant temperature bath for 20 minutes and were in the probe for five minutes.

Procedure B. - A special Teflon cell cap was constructed to provide a completely sealed reaction vessel for the International Instruments Difunctional Recording Titrator. The cap was sealed to the cell by means of a pressure O-ring seal. The electrodes were introduced through O-ring seals. The stirrer was a section of a 1-ml. tuberculin syringe with a glass stirring blade attached to the bottom of the plunger. The stirrer was also introduced through an O-ring seal. The base and substrate were injected through rubber septums.

The glass electrodes were soaked in 98% formic acid for several days before use. After equilibration for 15 minutes, the electrodes showed no drift in pH reading over a three-hour period. Titration of

p-toluenesulfonic acid with sodium formate produced an apparent change of 2 pH units on going from excess acid to excess base. The inflection point on the titration curve was relatively flat.

For the rate studies, approximately 15 ml. of 98% formic acid was introduced into the thermostated cell and the system closed. After 15 minutes, the pH-stat was set to maintain the equilibrium pH.

(This was not very reproducible.) The sample ($\sim 30\mu\text{l}$) was injected through one of the rubber septums. The amount of base (5% sodium formate in formic acid) added to maintain a constant pH was plotted against time. The rates were determined from the usual plot of $\log \frac{a_{\infty} - x}{a_{\infty}}$ versus time.

Procedure C. - Approximately 0.03 g. of the tosylate was placed in a 4.94 mm. o.d. thin-walled pyrex tube. Approximately 1 ml. of solvent was added and the tubes were sealed. The sealed tubes were immediately placed in the variable temperature probe of the HR-60. The probe temperature was controlled with a heated nitrogen system. The rates of solvolysis were then calculated as in Procedure A.

Solvolysis Products of Allylcarbinyl Tosylates. - A sample of the tosylate (~ 0.2 g.) was placed in a pyrex tube (18 x 150 mm.), the solvent was added, the tube was sealed and placed in a constant-temperature bath at 50°. After the specified length of time, the tube was removed from the bath, cooled in Dry Ice, opened, and the contents poured into a 100-ml. round-bottomed flask. A 20% sodium hydroxide

solution was added with cooling until a pH of 8 to 9 was obtained. The mixture was stirred at room temperature for three hours and then continuously extracted with ether for 24 hours. The ether extract was dried over sodium sulfate and the volume reduced to ~5 ml. by removal of the ether through a 20-cm. Vigreux column. The residues were analyzed by v.p.c. on a 20-ft. 1, 2, 3-tris-(2-cyanoethoxy)-propane (T.C.E.P.) column at 120°. The analyses were calibrated by comparisons with known mixtures of similar concentrations.

Cyanohydrin Equilibria. - The ketones (all commercially available) were first distilled and then purified by preparative vapor phase chromatography on the Megachrom. Methanol was dried by distillation from magnesium methoxide. Hydrogen cyanide was prepared from sodium cyanide and sulfuric acid and was dried by passing it through an anhydrous calcium sulfate drying tower and stored in heavy-wall glass cylinder with a Teflon needle valve.

To a Varian precision n.m.r. tube was added methanol (containing 1 drop of triethylamine per 50 ml.) acetone and the ketone. The tube was attached to the vacuum line, cooled, and evacuated; hydrogen cyanide was then distilled into the tube and the tube sealed. The mixtures were allowed to equilibrate several weeks at room temperature before the dissociation constants were measured.

The H^1 nuclear magnetic resonance spectra were taken on the Varian A-60 (probe temperature 33°) using a Hewlett Packard 405 CR D. C. Digital Voltmeter for integral measurements. The integrated areas of the methyl resonances of the ketones and the cyanohydrin were

measured for both acetone and the respective ketone. Numerous integrations were averaged for each sample. The relative dissociation constants were determined from equation 1.

For t-butyl methyl ketone, the methyl resonance was found to be nearly coincident with that of acetone; the areas of the t-butyl resonances in the ketone and the cyanohydrin were measured and used to determine the relative dissociation constant.

The relative dissociation constant of the cyanohydrin of n-butyl methyl ketone could not be accurately determined since the methyl resonance peak of the cyanohydrin overlapped with the resonance of the alkyl portion of the ketone.

The dissociation constants of the cyanohydrins in carbon tetrachloride were determined in a similar fashion.

Heats of Solution. - A non-isothermal calorimeter was constructed from a 500-ml. silvered Dewar encased in a large polystyrene foam block. A Teflon-coated magnetic bar was used for stirring. Temperatures were measured to $\pm 0.002^\circ$ with a Beckmann thermometer. The ketone (10.0 ml.) was contained in a glass tube closed at one end with a disc of aluminum foil sealed on with paraffin wax. The calorimeter containing 200.0 ml. of methanol was assembled and allowed to reach thermal equilibrium. The aluminum foil disc was punctured with a thin glass rod and the temperature change recorded. The heat capacity of the calorimeter and solution was then determined from the temperature change resulting from the input of a known amount of electrical energy. The heater and timing circuits were

similar to those described by Sturtevant (128).

The heat capacities were essentially constant from run to run. The average of several determinations for each ketone was used.

Since the Dewar contained a moderately large air volume, difficulty was encountered in the determination of heats of solution of very volatile ketones. For acetone, the temperature continued to fall for several minutes after mixing due to cooling resulting from vaporization of the ketone.

APPENDIX

The rate constants reported in Tables XXVI to XXXVI have been calculated by the method of least squares. For rates determined by procedures A and C, the least squares values are not as meaningful as those determined graphically. The least squares procedure overweights the points at higher conversion where, because of the analytical method, the errors are larger. In addition, the plot of $\log (1-\underline{C})$ versus time must pass through the origin -- the least squares procedure ignores this restriction. These values have been included for comparison and to provide an estimate of the accuracy of the data.

Table XXIII

Rate of Solvolysis of n-Butyl Tosylate
80% Formic Acid, 51.62°

Time, min	Conc., $\left(\frac{C_0 - C}{C_0}\right)$	Calc., C	Diff.
735.	0.883	0.891	-0.008
1148.	0.848	0.847	0.001
1826.	0.782	0.778	0.004
2415.	0.727	0.724	0.003
3287.	0.651	0.650	0.001
3624.	0.629	0.623	0.006
4002.	0.592	0.595	-0.003
4879.	0.529	0.533	-0.004
5377.	0.499	0.501	-0.002
6954.	0.414	0.412	0.002

$$k = 2.07 \times 10^{-6} \text{ sec}^{-1}$$

$$\text{Calc. Inf. Conc.} = -0.024$$

Table XXIV

Rate of Solvolysis of Allylcarbinyl Tosylate
80% Formic Acid, 51.62°

Time, min.	Conc. $\left(\frac{C_0-C}{C_0}\right)$	Calc., C	Diff.
483.	0.898	0.937	-0.039
1465.	0.805	0.790	0.015
1789.	0.763	0.747	0.016
2158.	0.706	0.700	0.006
2738.	0.649	0.633	0.016
3374.	0.568	0.567	0.001
4247.	0.471	0.487	-0.016
5103.	0.420	0.420	0.000

$$k = 2.90 \times 10^{-6} \text{ sec}^{-1}$$

Calc. Inf. Conc. = 0.019

Table XXV

Rate of Solvolysis of n-Butyl Tosylate
80% Formic Acid, 79.1°

Time, min.	Conc., $\left(\frac{C_0-C}{C_0}\right)$	Calc., C	Diff.
60.0	0.862	0.865	-0.003
120.0	0.766	0.761	0.005
180.0	0.671	0.670	0.001
240.0	0.591	0.590	0.001
300.0	0.515	0.519	-0.004
360.0	0.455	0.457	-0.002
420.0	0.404	0.402	0.002

$$k = 3.55 \times 10^{-5} \text{ sec}^{-1}$$

$$\text{Calc. Inf. Conc.} = -0.016$$

Table XXVI
Rate of Solvolysis of Allylcarbinyl Tosylate
80% Formic Acid, 79.1°

Time, min	Conc., $\left(\frac{C_0-C}{C_0}\right)$	Calc., C	Diff.
60.0	0.797	0.790	0.007
120.0	0.647	0.642	0.005
180.0	0.500	0.521	-0.021
240.0	0.434	0.423	0.011

$$\underline{k} = 5.78 \times 10^{-5} \text{ sec}^{-1}$$

$$\text{Calc. Inf. Conc.} = -0.027$$

Table XXVII

Rate of Solvolysis of n-Butyl Tosylate
98% Formic Acid, 50.28°

Time, min	Conc., $\left(\frac{C_0-C}{C_0}\right)$	Calc. C	Diff.
1080.	0.939	0.944	-0.005
2680.	0.869	0.872	-0.003
4170.	0.801	0.809	-0.008
5670.	0.750	0.751	-0.001
7475.	0.697	0.687	0.010
9805.	0.619	0.612	0.007
27420.	0.254	0.255	-0.001

$$\underline{k} = 8.27 \times 10^{-7} \text{ sec}^{-1}$$

$$\text{Calc. Inf. Conc.} = -0.004$$

Table XXVIII
Rate Solvolysis of Allylcarbinyl Tosylate
98% Formic Acid, 50.28°

Time, min	Conc., $\left(\frac{C_0-C}{C_0}\right)$	Calc. C	Diff.
240.	0.950	0.985	-0.035
810.	0.880	0.877	0.003
1485.	0.810	0.764	0.046
2975.	0.550	0.563	-0.013
4510.	0.410	0.411	-0.001

$$\underline{k} = 3.41 \times 10^{-6} \text{ sec}^{-1}$$

$$\text{Calc. Inf. Conc.} = 0.034$$

Table XXIX

Rate of Solvolysis of Allylcarbinyl Tosylate
10% Pyridine-Formic Acid, 50.21°

Time, min	Conc. $\left(\frac{C_0-C}{C_0}\right)$	Calc., C	Diff.
556.	0.964	0.949	0.015
1444.	0.882	0.886	-0.004
2152.	0.823	0.839	-0.016
3577.	0.752	0.751	0.001
5029.	0.675	0.672	0.003
7644.	0.550	0.549	0.001

$$k = 1.28 \times 10^{-6} \text{ sec}^{-1}$$

$$\text{Calc. Inf. Conc.} = 0.010$$

Table XXX

Rate of Solvolysis of β -(Methylallyl)-Carbinyl Tosylate
10% Pyridine-Formic Acid, 50.21°

Time, min	Conc. $\left(\frac{C_0-C}{C_0}\right)$	Calc. C	Diff.
486.	0.893	0.891	0.002
995.	0.788	0.779	0.009
1955.	0.595	0.605	-0.010
2386.	0.544	0.540	0.004
2784.	0.473	0.486	-0.013
3599.	0.400	0.392	0.008

$$\underline{k} = 4.4 \times 10^{-6} \text{ sec}^{-1}$$

Calc. Inf. Conc. = 0.012

Table XXXI
Rate Solvolysis of trans-3-Pentenyl Tosylate
10% Pyridine-Formic Acid, 50.5°

Time, min.	Conc. $\left(\frac{C_0-C}{C_0}\right)$	Calc. C	Diff.
6.0	0.824	0.854	-0.030
8.0	0.824	0.828	-0.004
15.0	0.726	0.744	-0.018
18.0	0.754	0.711	0.043
26.0	0.673	0.629	0.044
33.0	0.562	0.566	-0.004
35.0	0.553	0.548	0.005
40.0	0.488	0.508	-0.020
42.0	0.474	0.493	-0.019
52.0	0.413	0.423	-0.010
54.0	0.428	0.410	0.018

$$k = 2.56 \times 10^{-4} \text{ sec}^{-1}$$

$$\text{Calc. Inf. Conc.} = -0.066$$

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Table XXXII

Rate Solvolysis of cis-3-Pentenyl Tosylate
10% Pyridine-Formic Acid, 50.5°

Time, min.	Conc. $\left(\frac{C_0-C}{C_0}\right)$	Calc. C	Diff.
15.	0.989	0.974	0.015
19.	0.970	0.960	0.010
22.	0.949	0.949	-0.000
25.	0.926	0.939	-0.013
34.	0.934	0.908	0.026
36.	0.890	0.901	-0.011
49.	0.857	0.859	-0.002
53.	0.854	0.846	0.008
58.	0.828	0.831	-0.003
65.	0.806	0.809	-0.003
71.	0.799	0.791	0.008
88.	0.756	0.743	0.013
90.	0.739	0.738	0.001
96.	0.704	0.721	-0.017
107.	0.675	0.693	-0.018
127.	0.624	0.643	-0.019
138.	0.615	0.617	-0.002
152.	0.593	0.586	0.007
163.	0.567	0.563	0.004
193.	0.506	0.503	0.003
211.	0.460	0.471	-0.011
224.	0.456	0.449	0.007
246.	0.412	0.414	-0.002
327.	0.311	0.306	0.005

$$k = 6.18 \times 10^{-3} \text{ sec}^{-1}$$

$$\text{Calc. Inf. Conc.} = 0.029$$

Table XXXIII

Rate of Solvolysis of trans-3-Pentenyl Tosylate
.98% Formic Acid, 49.6°

Time, min.	Conc. $\left(\frac{a_{\infty}-a}{a_{\infty}}\right)$	Calc. Conc.	Diff.
1.18	0.963	0.961	0.002
2.54	0.935	0.934	0.001
3.93	0.905	0.909	-0.004
5.38	0.878	0.882	-0.004
7.44	0.843	0.846	-0.003
9.90	0.799	0.805	-0.006
13.48	0.758	0.749	0.009
17.48	0.705	0.691	0.014
21.56	0.643	0.636	0.007
24.56	0.605	0.599	0.006
27.88	0.563	0.560	0.003
31.96	0.520	0.516	0.004
35.88	0.478	0.476	0.002
39.20	0.451	0.446	0.005
44.50	0.377	0.400	-0.023
50.30	0.351	0.356	-0.005
53.70	0.322	0.332	-0.010
58.70	0.299	0.300	-0.001
64.00	0.273	0.270	0.003
70.80	0.238	0.235	0.003
83.00	0.189	0.184	0.005
95.30	0.143	0.143	-0.000

$$k = 3.37 \times 10^{-4} \text{ sec}^{-1}$$

Calc. Inf. Conc. = - 0.016

Table XXXIV

Rate of Solvolysis of trans-4-Phenyl-3-butenyl Tosylate
98% Formic Acid, 50.1°

Time, min.	Conc. $\left(\frac{a_{\infty}-a}{a_{\infty}}\right)$	Calc. Conc.	Diff.
4.15	0.944	0.955	-0.011
5.92	0.923	0.934	-0.011
8.95	0.907	0.898	0.009
11.90	0.864	0.865	-0.001
14.00	0.832	0.842	-0.010
17.10	0.817	0.809	0.008
21.30	0.780	0.767	0.013
26.90	0.720	0.714	0.006
30.70	0.674	0.680	-0.006
34.80	0.649	0.646	0.003
40.90	0.608	0.597	0.011
45.20	0.568	0.565	0.003
48.20	0.534	0.544	-0.010
53.00	0.513	0.512	0.001
61.90	0.468	0.457	0.011
69.50	0.392	0.414	-0.022
75.80	0.385	0.382	0.003
86.10	0.333	0.335	-0.002
95.50	0.314	0.297	0.017
102.40	0.263	0.272	-0.009

$$k = 2.13 \times 10^{-4} \text{ sec}^{-1}$$

Calc. Inf. Conc. = 0.007

Table XXXV

Rate of Solvolysis of 4-Methyl-3-pentenyl Tosylate
98% Formic Acid, 49.94°

Time, min.	Conc. $\left(\frac{a_{\infty}-a}{a_{\infty}}\right)$	Cal. Conc.	Diff.
0.10	0.909	0.850	0.059
0.20	0.828	0.798	0.030
0.30	0.788	0.750	0.038
0.40	0.737	0.704	0.033
0.50	0.692	0.662	0.030
0.60	0.636	0.622	0.014
0.80	0.485	0.549	-0.064
1.00	0.404	0.484	-0.080
1.40	0.348	0.377	-0.029
1.80	0.288	0.294	-0.006
2.20	0.237	0.229	0.008
2.60	0.197	0.178	0.019

$$\underline{k} = 1.04 \times 10^{-2} \text{ sec}^{-1}$$

$$\text{Calc. Inf. Conc.} = -0.100$$

Table XXXVI

Rate of Solvolysis of Cyclobutyl Tosylate
98% Formic Acid, 15.0°

Time, min	Conc. $\left(\frac{a_{\infty}-a}{a_{\infty}}\right)$	Calc. Conc.	Diff.
0.5	0.970	0.986	-0.016
1.0	0.952	0.967	-0.015
2.3	0.923	0.919	0.004
3.3	0.891	0.884	0.007
10.0	0.692	0.683	0.009
11.3	0.648	0.649	-0.001
13.5	0.598	0.596	0.002
15.1	0.548	0.560	-0.012
16.3	0.534	0.535	-0.001
18.1	0.497	0.499	-0.002
21.1	0.457	0.444	0.013
22.7	0.418	0.418	0.000
26.8	0.363	0.357	0.006
31.0	0.304	0.303	0.001
35.6	0.258	0.254	0.004
40.8	0.211	0.208	0.003
44.2	0.163	0.182	-0.009
54.6	0.122	0.122	0.000

$$k = 6.44 \times 10^{-4} \text{ sec}^{-1}$$

$$\text{Calc. Inf. Conc.} = 0.005$$

Table XXXVII

Observed and Calculated $F^{19} - \{H^1\}$ N. M. R. Spectrum
of 1, 1, 4, 4-Tetrafluoro-1, 3-butadiene

Obs. Freq., cps.	Calc. Freq., cps.	O-C
612.1	612.07	0.03
614.5	614.39	0.11
630.5	630.19	0.31
630.5	631.00	-0.50
634.8	634.69	0.11
640.8	640.96	-0.16
653.7	653.62	0.08
656.3	656.20	0.10
670.1	670.26	-0.16
675.2	674.95	0.25
682.8	683.05	-0.25
687.9	687.74	0.16
701.7	701.80	-0.10
704.3	704.38	-0.08
717.2	717.04	0.16
723.2	723.31	-0.11
727.5	727.00	0.50
727.5	727.81	-0.31
743.5	743.61	-0.11
745.9	745.93	-0.03

Table XXXVIII

Observed and Calculated $F_v^{19} - \{F_r^{19}\}$ N. M. R. Spectrum
of Perfluoro-1, 2-dimethylenecyclobutane

Obs. Freq., cps	Calc. Freq., cps	O-C
43.91	43.967	0.063
48.75	48.624	0.126
49.75	49.872	-0.122
59.37	59.166	0.204
59.37	59.470	-0.100
59.37	59.520	-0.150
61.57	61.551	0.019
70.11	70.013	0.097
71.00	71.096	-0.096
77.17	77.104	0.066
90.31	90.401	-0.091
109.69	109.593	0.097
122.83	122.890	-0.060
129.00	128.898	0.102
129.89	129.981	-0.091
138.43	138.443	-0.013
140.63	140.474	0.156
140.63	140.524	0.106
140.63	140.828	-0.198
150.25	150.122	0.128
151.25	151.371	-0.121
156.09	156.027	0.063

Table XXXIX

Observed and Calculated F^{19} N. M. R. Spectrum
of Bis-4, 5-(-difluoromethylene)-cyclohexene

Obs. Freq., cps	Calc. Freq., cps	O-C
6.48	6.617	-0.137
11.52	12.274	0.750
24.27	24.237	0.033
24.79	25.117	-0.327
39.25	38.754	0.496
39.90	40.199	-0.299
52.20	52.057	0.143
56.66	56.584	0.076
67.94	68.019	-0.079
69.74	69.959	-0.219
83.16	83.064	0.096
85.95	85.639	0.311
114.05	114.361	-0.311
116.84	116.936	-0.096
130.26	130.041	0.219
132.06	131.981	0.079
143.34	143.416	-0.076
147.80	147.943	-0.143
160.10	159.801	0.299
160.75	161.246	-0.496
175.21	174.883	0.327
175.73	175.763	-0.033
188.48	187.726	0.750
193.52	193.383	0.137

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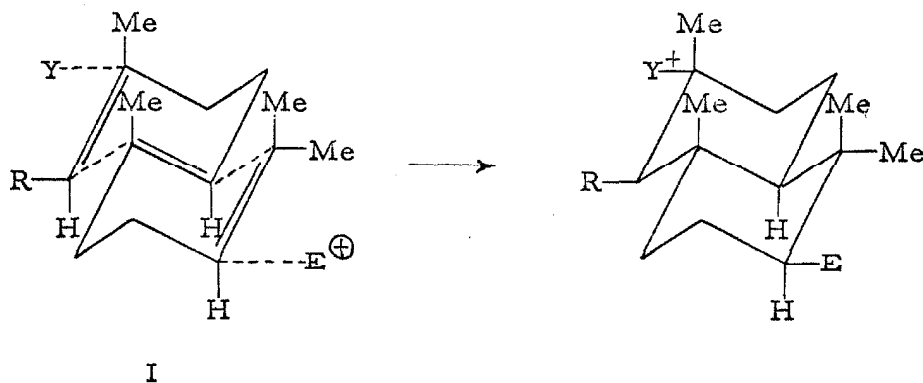
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Proposition 1

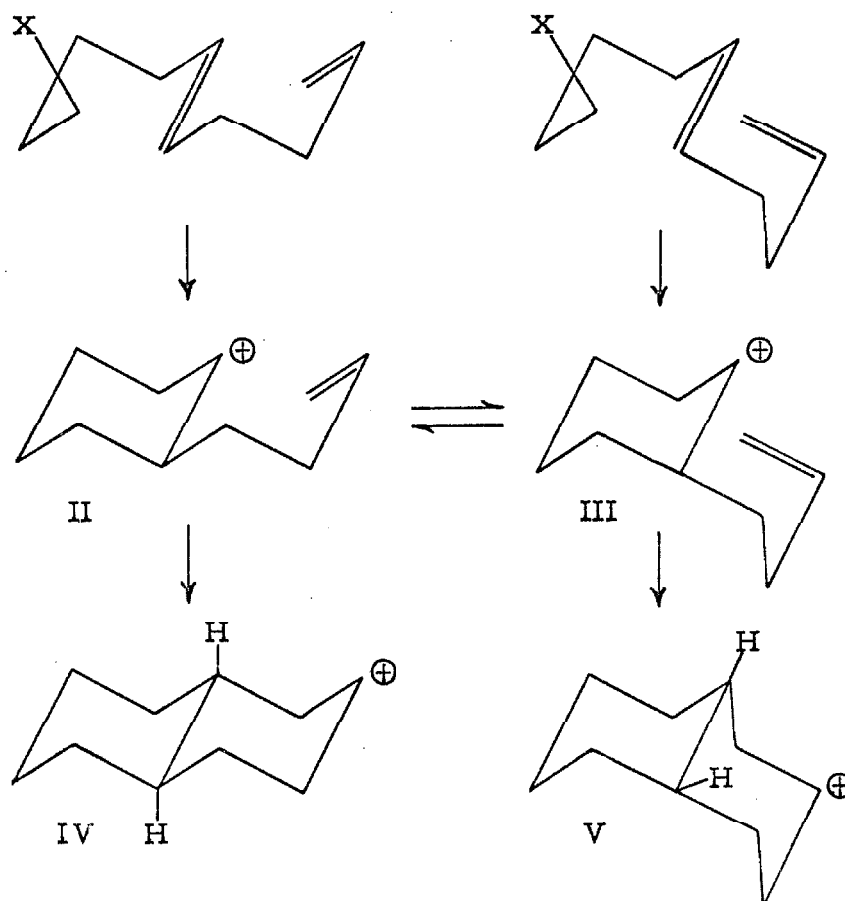
Experiments are proposed to clarify the mechanism of cationic cyclization in the formation of trans-fused rings.

In the stereorotational theory of Stork (1) and Eschenmoser (2) for the biogenesis of the polycyclotriterpenoids and steroids, the trans-fused ring systems result from a synchronous ring closure initiated by electrophilic attack on an all trans-fused polyene such as I.



Johnson and coworkers have found considerable evidence in support of this hypothesis (3). The formolysis of 5-hexenyl p-nitrobenzenesulfonate in 98% formic acid proceeds with participation of the olefinic bond at a rate which is about twice that of the hexyl ester to produce predominantly ring-closed products (3d). Formolysis of trans-5,9-decadienyl p-nitrobenzenesulfonate yielded decalols with exclusively trans-fused rings (3b) while formolysis of cis-5,9-decadienyl p-nitrobenzenesulfonate yielded decalols with exclusively cis-fused rings (3a). These observations eliminate a common cationic intermediate in these

reactions but do not require synchronous closure of both rings. The trans-5,9-decadienyl derivative might yield initially the monocyclic cationic intermediate II while the cis-5,9-decadienyl derivative might yield III. Since interconversion of II and III requires an inversion of the cyclohexane ring, there should be an energy barrier of ~ 10 kcal for the $\text{II} \rightleftharpoons \text{III}$ interconversion. If ring closure to the cations

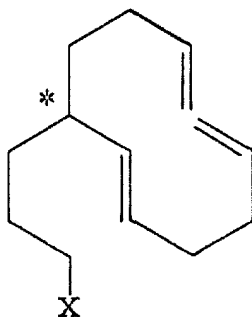


IV and V competes favorably with interconversions of II and III, formation of monocyclic cationic intermediates predicts the same product stereochemistry as a synchronous closure of both rings.

Other attempts to rule out formation of monocyclic cationic

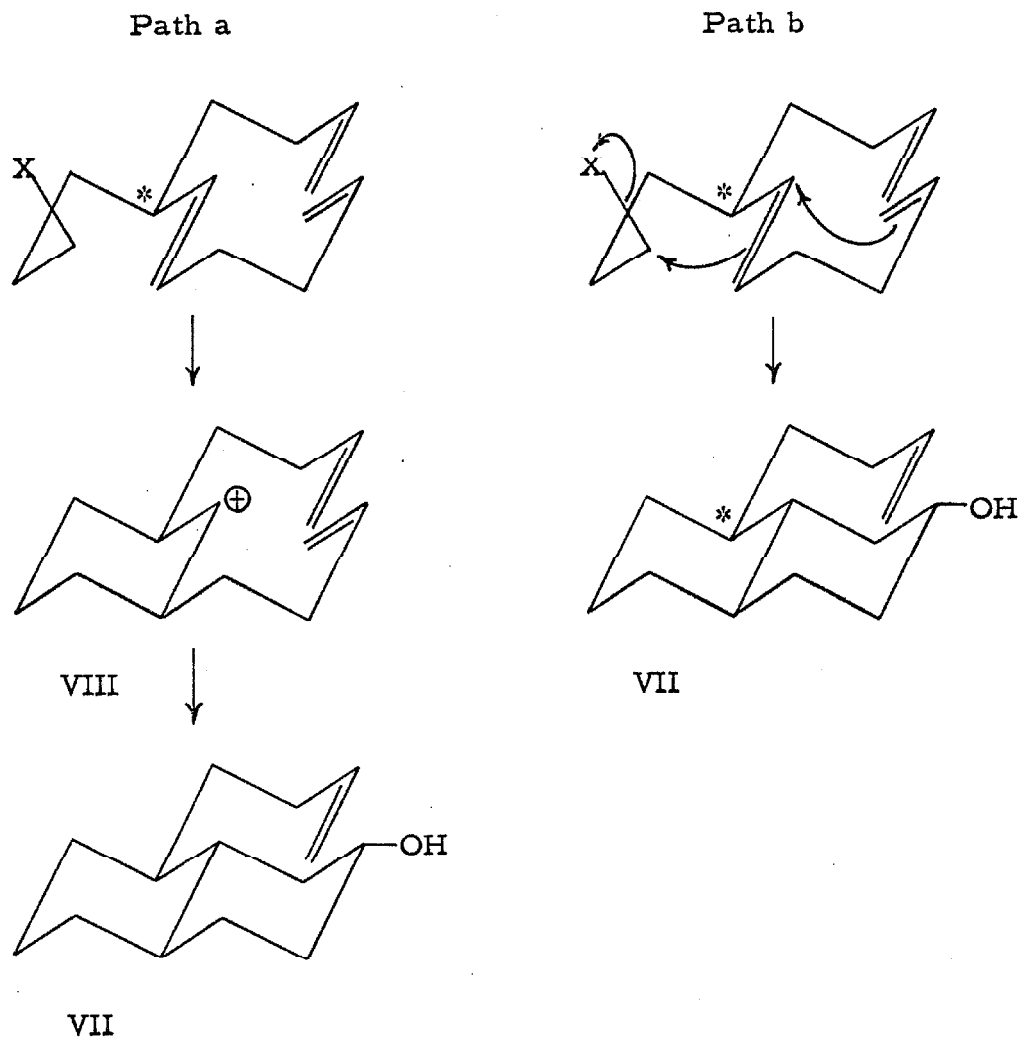
intermediates in similar reactions have not been conclusive (4). Formation of cis-decalin derivatives from acid catalyzed cyclization of Δ^3 -butenylcyclohexene may also result from formation of intermediate III as a result of conformational control of the direction of protonation (3c, 5).

Determination of the optical activity of the equatorially substituted trans-2-decalol from the solvolysis of optically active VI should permit a decision between the two proposed mechanisms. Solvolysis



VI

by way of monocyclic cationic intermediate (path a) should yield optically inactive VII. A totally concerted synchronous solvolytic mechanism (path b) should produce optically active VII. Formation of optically active VII would conclusively eliminate the formation of the intermediate monocyclic cation VIII and provide strong evidence for the stereorotational theory of Stork and Eschenmoser.



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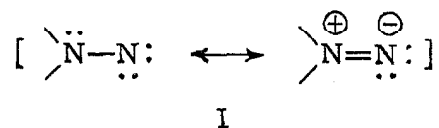
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Proposition 2

Studies of the label distribution in the acetaldehyde ethylhydrazone obtained from the decomposition of 1, 1-diethyl-2-benzenesulfonylhydrazine-1-¹⁵N sodium salt are proposed to determine the mechanism of the diazene-hydrazone rearrangement.

The oxidation of 1, 1-disubstituted hydrazines (1), the thermal decomposition of 1, 1-disubstituted 2-sulfonylhydrazine salts (2, 3, 7), the reduction of nitrosamines (4, 5), and the base-catalyzed decomposition of 1, 1-disubstituted 2-chlorohydrazines (6) have been proposed to proceed through aminonitrene(diazene) intermediates, I. The products

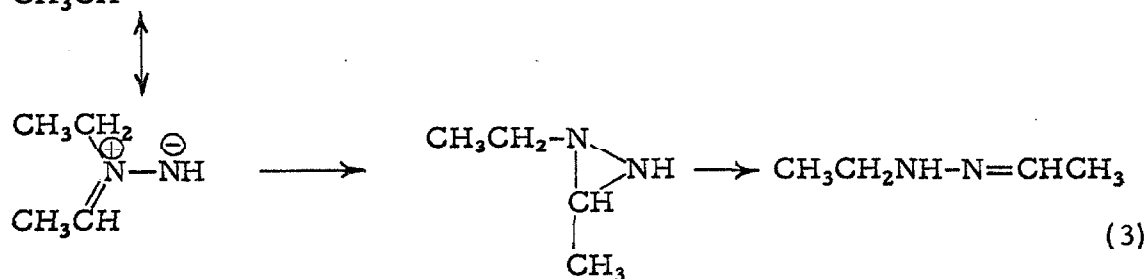
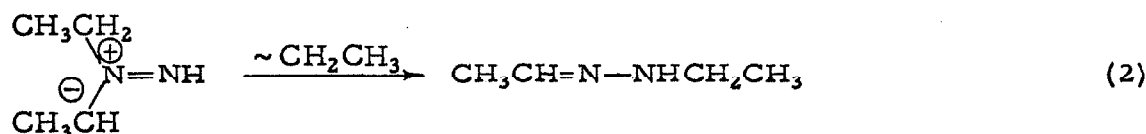
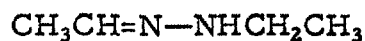
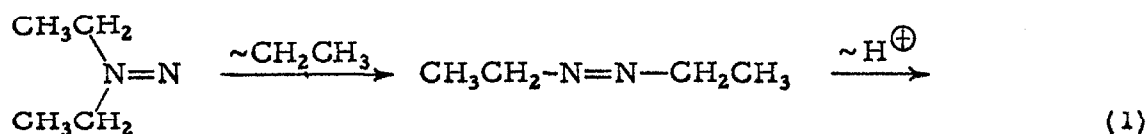


of these reactions are solvent dependent; tetrazenes are the usual products in inert solvents but cleavage of the carbon-nitrogen bond with formation of molecular nitrogen accompanied by disproportionation, coupling and fragmentation is frequently observed (1-7).

In the decomposition of 1, 1-disubstituted 2-benzenesulfonylhydrazines in basic hydroxylic solvents, rearrangement of the intermediate diazene to hydrazones occurs competitively with or to the exclusion of tetrazene formation (2, 7).

Three mechanisms have been proposed for the diazene-hydrazone rearrangement. The most obvious pathway for the rearrangement would be a 1, 2-shift of an alkyl group followed by base-catalyzed tautomerization of the resulting azo compound (mechanism 1) (7).

(1, 1-Diethyldiazene is used for illustrating the mechanisms.) An alternative mechanism requires 1, 2-migration of an alkyl group in an initially formed zwitterionic intermediate, II, (mechanism 2) (8). The third possibility is ring closure of the zwitterionic intermediate to an isohydrazone (diaziridine) followed by ring opening to the hydrazone (mechanism 3) (2).

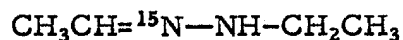


II

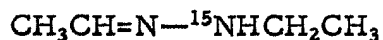
A priori, mechanism 1 would appear to be the most likely possibility. Mechanism 2 has some very dubious features. Alkyl group migration in the zwitterionic intermediate, II, is formally similar to the Stevens rearrangement; however, in the latter reaction, simple alkyl group migration normally does not occur (9). Furthermore, in a typical Stevens ylid intermediate, the negative charge resides only on the carbon while the charge is delocalized in the zwitterion, II. In

addition, if mechanism 2 is correct, rearrangement of II must not only occur but must also be very rapid in comparison to ring closure to form the diaziridine. Despite these objections, mechanism 2 is currently favored for the diazene-hydrazone rearrangement (2).

Determination of the label distribution in the acetaldehyde ethylhydrazone from the decomposition of 1, 1-diethyl-2-benzenesulfonylhydrazine-1-¹⁵N sodium salt will permit a clear choice between the three possible mechanisms. Mechanism 2 will give only III and mechanism 3 will give only IV while a mixture of equal amounts of III and IV will be obtained if mechanism 1 is correct (10). The label distribution in these compounds can be easily ascertained by ¹⁵N analysis of



III



IV

the ethylhydrazine obtained upon hydrolysis of the acetaldehyde ethylhydrazone.

References

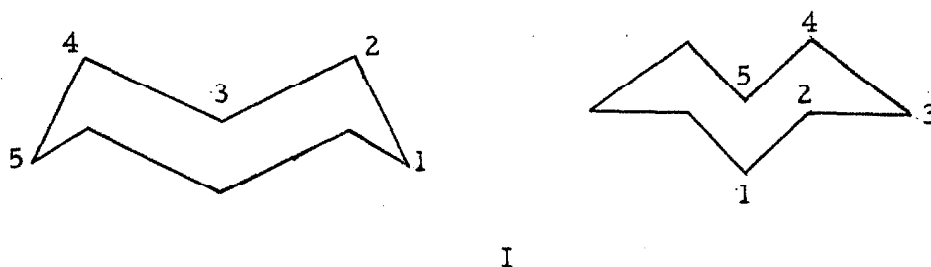
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10. The rearrangement has been shown to be intramolecular for benzylphenylhydrazine (ref. 7). This should be verified for the dialkylhydrazine by determining the products from the decomposition of 1-methyl-1-ethyl-2-benzenesulfonylhydrazine sodium salt.

Proposition 3

Infrared studies of deuterated cyclooctanes are proposed to distinguish between the stretched-crown and saddle conformations of the cyclooctane ring system.

The conformations of the cyclooctane ring system have been the subject of a number of recent papers (1-4). The basic conformation of the cyclooctane ring system is generally assumed to be that of a stretched crown (I), although no really compelling evidence has been presented. Dipole moment studies have shown that for 5-heterocyclooctanones (5) the group moments are nearly parallel while for 5-p-chlorophenylcyclooctanones (6) the angle between the dipoles is about 60° . These have been interpreted as evidence for the stretch crown form with the carbonyl at C-1 (7).



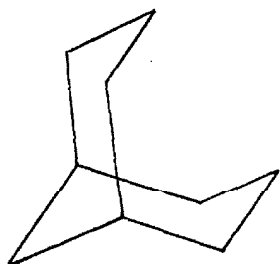
Infrared and Raman studies have eliminated a number of possible conformations, but because of the complexity of the system involved they were also consistent with several other possible conformations (8). The approximate nature of the ring system of aza-cyclooctane hydrobromide has been deduced from X-ray diffraction studies and appears to be of the crown form (9).

One of the strongest arguments for the stretched-crown conformation has been that three methylene scissoring bands are observed in the infrared spectrum at 1450, 1470 and 1477 cm^{-1} . These authors state that "the appearance of n bands in the $\delta(\text{CH}_2)$ region means that the molecule possesses at least n different types of CH_2 groups" (10). This rule does not appear to be generally valid. Bicyclo [3.3.1]-nonane (II) whose unique conformation has now been established as being that of two-fused cyclohexane chairs (11) contains three types of methylene groups but its infrared spectrum shows four CH_2 scissoring bands at 1445, 1455, 1462 and 1485 cm^{-1} (4). These authors propose that the two identical methylene groups in the 3- and 7-position being forced strongly towards each other, "give rise by mechanical coupling to a splitting of their infrared bands" (4).

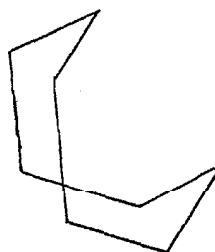
All of the available data, except for the infrared, appears consistent with the saddle conformation (III) of the cyclooctane ring whose carbon skeleton follows the diamond lattice. The dipole moment studies are readily interpretable on this basis as are the relative stabilities of the cis- and trans-isomers of 1,3-dialkylcyclooctanones.

The ability of cyclooctane, but not cyclodecane, to form solid solutions with adamantane (IV) and bicyclo [3.3.1]-nonane has been presented as evidence in favor of the saddle conformation (12). The observed intensity distribution from wide-angle X-ray scattering studies of liquid cyclooctane is stated to fit better with the scattering function of the saddle than with that of the crown conformation (4).

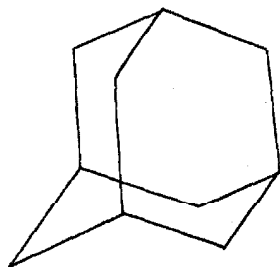
Infrared studies of $(\text{CD}_2)_7\text{CH}_2$ should provide a means of distinguishing between these two conformations. For the stretched-crown conformation, the same three methylene scissoring bands should be observed since the equilibrium distribution should contain a CH_2 group in each of the three possible non-equivalent positions. For the saddle conformation, one should observe only two CH_2 bands since coupling of the 3- and 7-methylene groups will no longer be possible.



II



III



IV

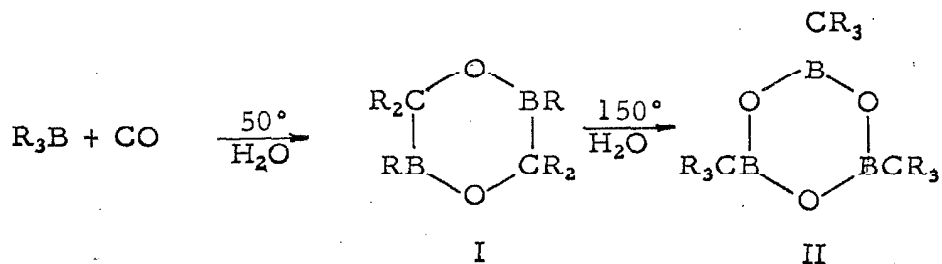
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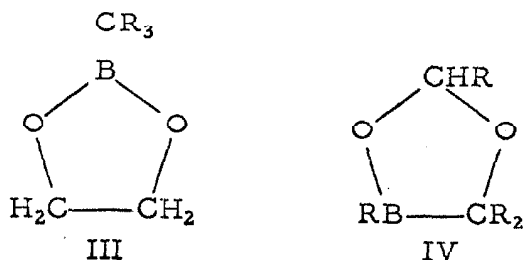
Proposition 4

Experiments are proposed to elucidate the nature of the intermediate involved in the carbonylation of organoboranes.

During the last few years, much attention has been directed toward the synthesis of organoborane derivatives (1); however, relatively little is known about the reaction mechanisms and the intermediates involved in many of these reactions (1c). The reaction of trialkylboranes with carbon monoxide has been reported to give a variety of products in which novel rearrangements of the alkyl groups from boron to carbon have occurred. In hydroxylic solvents, hexaalkyl-2, 5-dibora-1, 4-dioxanes (I) or trialkylcarbinyl-boronic anhydrides (II) are formed depending on reaction temperature (2). In the presence of ethylene glycol, 2-trialkylcarbinyl-2-bora-1, 3-



dioxolanes (III) are formed (3) while addition of aldehydes gives 4-bora-1, 3-dioxolanes (IV) (4).

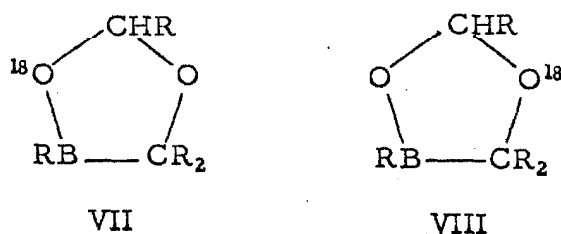


The trialkylboron carbonyls (6), analogous to the known borane carbonyl (H_3BCO) (5), are presumed to be unstable intermediates which isomerize to either the dialkylacylboranes (V) or to the intermediate VI before further reaction. Reaction of V with aldehyde by a 1, 3-dipolar addition reaction would give an unstable



charge separated intermediate which could then rearrange to the 4-bora-1, 3-dioxolane. The intermediate VI could react with the aldehyde directly (again by a 1, 3-dipolar addition) to produce the 4-bora-1, 3-dioxolane directly (7). On the basis of present evidence, both intermediates appear equally attractive.

It is proposed that the use of ^{18}O labeled aldehyde will permit a choice between the two possible intermediates in the carbonylation of organoboranes. If the labeled aldehyde is used then reaction proceeding through intermediate V will yield the 4-bora-1, 3-dioxolane VII but reactions proceeding through the intermediate VI would yield VIII (7). Examination of the mass spectral cracking pattern of the resultant 4-bora-1, 3-dioxalanes should permit determination of the location of the ^{18}O label in the product and provide information on the nature of the intermediate.



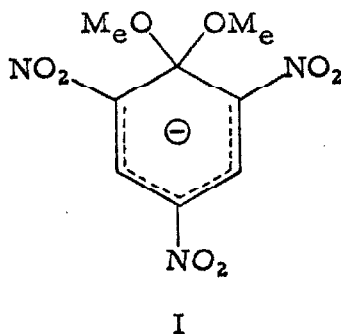
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7. The ring closed form should react in the same fashion.

Proposition 5

Investigations of the structure of some Meisenheimer complexes using nuclear magnetic resonance spectroscopy are proposed.

The formation of highly colored solutions from the reaction of aromatic nitro compounds with bases has long been known and solid products can sometimes be isolated. The interpretation of the color in relation to possible structures of the complex has remained a subject of interest for over 80 years. The commonly accepted structural formulation of the addition complex of methyl picrate and methoxide ion is written as I and termed a Meisenheimer complex (1, 2). This

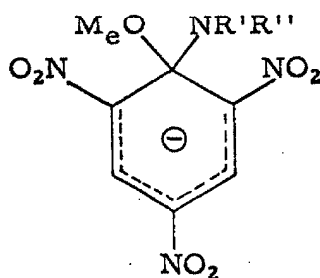


structure is based on infrared (3), ultraviolet (4), and nuclear magnetic resonance spectroscopic evidence (5).

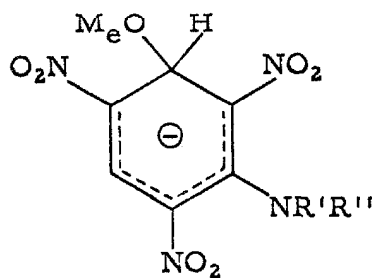
Picramide is an aromatic amine with potentially acidic hydrogen atoms and has been used as one of the indicators in establishing the H_+ scale in basic media on the assumption that its indicator behavior is due to proton loss from the amino group (6). The N,N-dimethyl derivative does not contain acidic hydrogens but both compounds give

intensely colored solutions on addition of sodium methoxide.

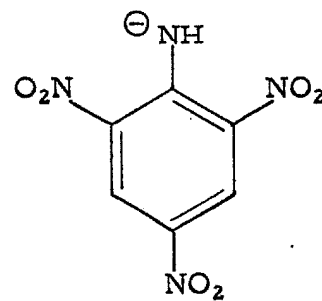
The structures of these 1:1 complexes of picramide and dimethylpicramide remain a point of current controversy. Farmer suggested II for complexes of this kind (7). His observation that both the reaction of methylpicrate with methylamine and the reaction of N-methylpicramide with methoxide yielded, on acid decomposition, only N-methylpicramide does not require this formulation. Gold has presented arguments in favor of structure III based on the similarity of the equilibrium constants for complex formation of trinitrobenzene and dimethylpicramide with methoxide and on the rate of formation of methyl picrate (8). Gold also concluded from similar arguments that the complex of picramide existed ~ 20% as structure IV and 80% as structure III (8).



II



III



IV

A thorough investigation of the species by nuclear magnetic resonance spectroscopy is proposed. Since the rate of establishment of equilibrium is nearly slow enough to measure (5), difficulty with observing individual species should not be encountered. The number of different resonances and the chemical shift for the aromatic protons should permit definite conclusions as to the structures of these complexes.

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