PART I

3-PHENYLCYCLOBUT-2-ENONE AND 3-PHENYLCYCLOBUTANONE DERIVATIVES

PART II

CALCULATION OF THE DELOCALIZATION ENERGIES OF SOME SMALL-RING SYSTEMS EMPLOYING THE SIMPLE MOLECULAR ORBITAL TREATMENT

THESIS BY

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ABSTRACT

PART I

Catalytic hydrogenation of either 1,1-difluoro-2,2-dichloro-3-phenylcyclobutene or 1,1-difluoro-2,2-dichloro-3-phenylcyclobutane gives 1,1-difluoro-3-phenylcyclobutane. Bromination of this compound with N-bromosuccinimide followed by dehydrobromination with one mole of ethanolic potassium hydroxide gives good yields of 1,1-difluoro-3-phenylcyclobut-2-ene. Careful hydrolysis of this material with concentrated sulfuric acid gives 3-phenylcyclobut-2-enone. Treatment of 3-phenylcyclobut-2-enone with dilute aqueous sodium hydroxide opens the ring to give benzoylacetone. Ring-opening of 3-phenylcyclobut-2-enone in acetic acid gives β-methylcinnamic acid. Reduction of 3-phenylcyclobut-2-enone by sodium borohydride in methanol gives 3-phenylcyclobut-2-enol.

The reaction of phosphorus pentachloride with several 3-phenylcyclobut-2-enones was found to give good yields of _gem_-dichlorides. Concentrated sulfuric acid hydrolysis of these _gem_-dichlorides in most cases regenerated the corresponding 3-phenylcyclobut-2-enone.

Catalytic reduction of 2-chloro-3-phenylcyclobut-2-enone gives 3-phenylcyclobutanone. The reduction of this ketone by several reagents is described. Reduction of 2-chloro-3-phenylcyclobut-2-enone by sodium borohydride in methanol gives 2-chloro-3-phenylcyclobut-2-enol. Catalytic hydrogenation of this alcohol gives _cis_-3-phenylcyclobutanol.

The rates of the acid-catalyzed hydrolysis, in "80%" acetone-water, of the 4-nitrobenzoates of cinnamyl alcohol, methylstyrylcarbinol, cyclobutanol, *cis*- and *trans*-3-phenylcyclobutanol, 2-chloro-3-phenylcyclobut-2-enol, and 3-phenylcyclobut-2-enol, are described. The importance of 1,3-interaction in the 3-phenylcyclobut-2-enyl carbonium ion is discussed. It has been concluded that the acid-catalyzed hydrolysis of 4-nitrobenzoate esters is not a satisfactory means of studying relative carbonium ion stabilities.

PART II

The simple molecular orbital method (LCAO) has been used to calculate the electron delocalization energies of a number of small-ring compounds in order to see which might be predicted to be reasonably stable on theoretical grounds. Included are a number of phenyl-substituted cyclobutadienes, benzocyclobutadienes, cyclobutadienoquinones, cyclobutenes, cyclobutenones, methylenecyclopropenes, cyclopropenones, phenyl-substituted cyclopropenyl cations, and several miscellaneous cyclobutenyl cations. The qualitative significance of the results is discussed.

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PART I

3-PHENYLCYCLOBUT-2-ENONE AND 3-PHENYLCYCLOBUTANONE DERIVATIVES

INTRODUCTION

Until a few years ago difficulties in the syntheses of cyclobutane and its derivatives (1,2) precluded extensive studies of the chemical and physical properties of these small-ring compounds. The rather recent discovery of the thermal cycloaddition of fluorinated ethylenes with themselves, acetylenes, olefins and dienes (3,4,5,6) has provided synthetic pathways to a variety of halogen-substituted cyclobutanes and cyclobutenes. More recently cyclo-addition reactions of allenes with suitably substituted non-halogenated olefins have been found to give good yields of cyclobutanes (7,8).

The polyhalogenated cyclobutane derivatives obtained by cycloaddition reactions at first seemed chemically inert, and their conversion to non-fluorine-containing cyclic substances did not seem practical (9). However, Roberts, Kline and Simmons were able to transform halogenated-cyclobutanes, obtained by the thermal cycloaddition reactions defined above, to halogen-free four-membered ring compounds (10). Smutny and Roberts (11) and Silversmith and Roberts (12) have extended this work, which is of such importance to the present research that it will be discussed in some detail.

Phenylacetylene undergoes cycloaddition reactions with either 1,1,2-trifluoro-2-chloroethylene (11) or 1,1-difluoro-2,2-dichloroethylene (10) at 100-130° to give 1:1 adducts in high yields. The structure of the latter adduct has been established beyond doubt as 1,1-difluoro-2,2-dichloro-3-phenylcyclobutene (I) (10,13,14,15). The other cycloaddition isomer of I, 1,1-difluoro-2,2-dichloro-4-phenylcyclobutene (II), has been synthesized in the present work and will be described later. The hydrolysis of I with concentrated sulfuric acid at 100° to give 2,2-dichloro-3-phenylcyclobutenone (III) in 85% yield has proved to be its most unusual and useful reaction (10). The structure of III has also been firmly established (10,13,14,15). Both I and III were shown to isomerize when heated with triethylamine to give 1,1-difluoro-2,4-dichloro-3-phenylcyclobutene (IV) and 2,4-dichloro-3-phenylcyclobutenone (V), respectively (10). With concentrated sulfuric acid IV is converted to V. The postulated structures for IV and V have been positively confirmed (10,13,14,15). Both catalytic and Clemmensen reduction of the 2,2-dichloroketone III gave 3-phenylcyclobutanone (VI) (10). Catalytic reduction of the 2,4-dichloroketone V gave VI, but Clemmensen reduction of V gave phenylcyclobutane (VII) (10).

The adduct of phenylacetylene and 1,1,2-trifluoro-2-chloroethylene, 1,1,2-trifluoro-2-chloro-3-phenylcyclobutene (VIII), on mild hydrolysis with concentrated sulfuric acid yielded 2-fluoro-2-chloro-3-phenylcyclobutenone (IX) while more vigorous hydrolysis yielded phenylcyclobutenedione (X) (2,11). IX can also be hydrolyzed to X. Clemmensen reduction of X gave phenylcyclobutane (VII), and oxidation with hydrogen

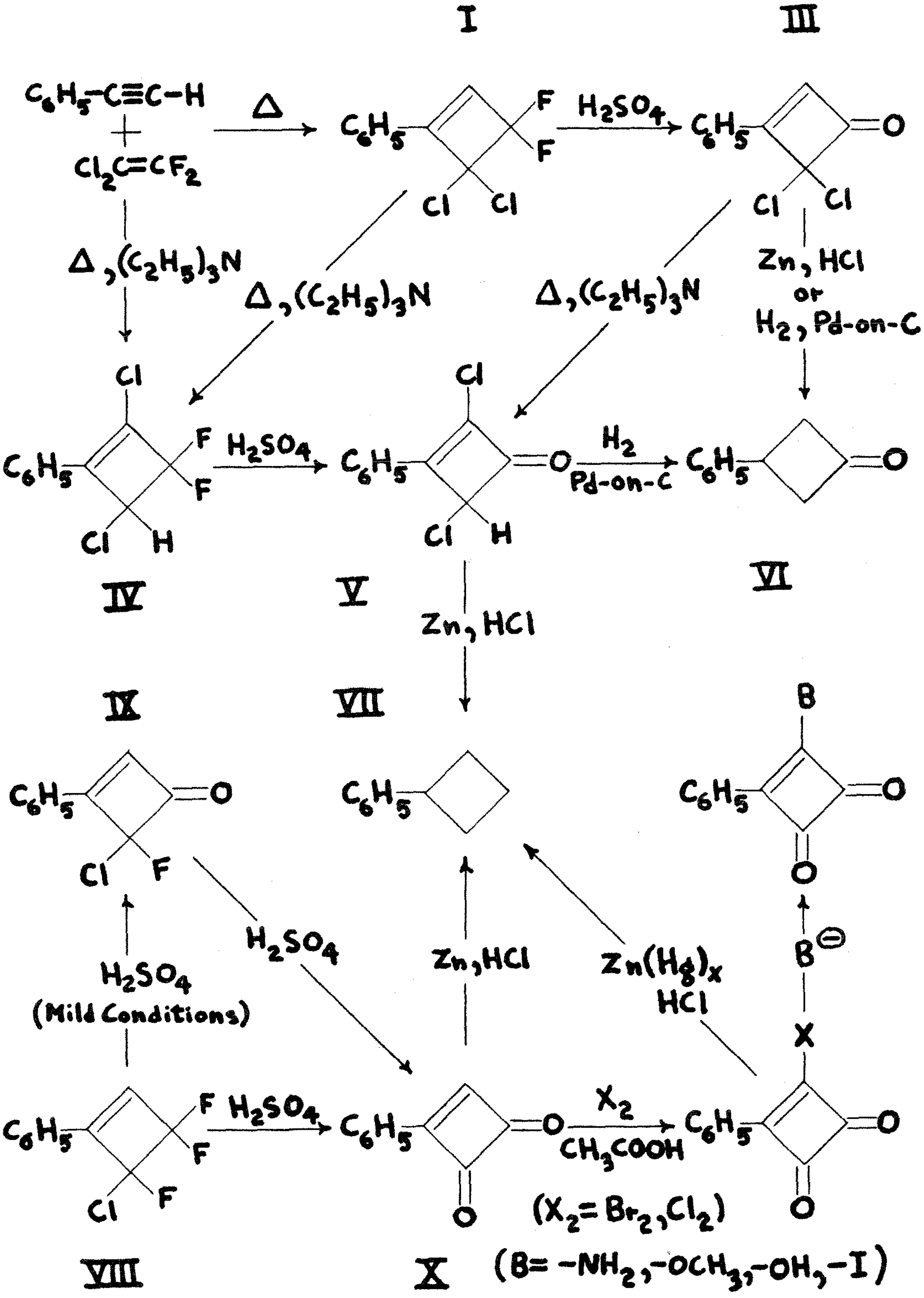

I
III
$C_6H_5-C\equiv C-H$ + $Cl_2C=CF_2$
Δ
H_2SO_4
Δ, $(C_2H_5)_3N$
Δ, $(C_2H_5)_3N$
Δ, $(C_2H_5)_3N$
Zn, HCl or H_2, Pd-on-C
H_2SO_4
H_2 / Pd-on-C
IV
V
VI
Zn, HCl
IX
VII
B
H_2SO_4 (Mild Conditions)
H_2SO_4
Zn, HCl
$Zn(Hg)_x$ HCl
$B^{\ominus}$
H_2SO_4
X_2 / CH_3COOH
$(X_2 = Br_2, Cl_2)$
VIII
X
$(B = -NH_2, -OCH_3, -OH, -I)$

Fig. 1

peroxide gave phenylmaleic anhydride (11). X could not be successfully reduced by catalytic hydrogenation. The vinylic hydrogen of X was easily substituted by bromine or chlorine in acetic acid. The bromo compound on Clemmenson reduction gave phenylcyclobutane (VII) which demonstrated the presence of the four-membered ring. The bromo compound underwent a displacement reaction with ammonia, solvolysis in methanol, and hydrolysis in aqueous acetic acid to yield the corresponding amine, methyl ether and hydroxyquinone, respectively (11). 4-Hydroxy-3-phenylcyclobutenedione (XI) appears to be the strongest known acid of the electrically neutral carbon-hydrogen-oxygen compounds having an ionization constant of 0.5 in water solution (11). XI gives a magenta color with ferric chloride solution (enol test).

Styrene undergoes cycloaddition reactions with both 1,1,2-trifluoro-2-chloroethylene and 1,1-difluoro-2,2-dichloroethylene at 100-130° to give high yields of 1,1,2-trifluoro-2-chloro-3-phenylcyclobutane (XII) and 1,1-difluoro-2,2-dichloro-3-phenylcyclobutane (XIII), respectively. The structures of both XII and XIII have been well established (12,15,16,17). Treatment of XII with excess potassium hydroxide in ethanol gave 1,1-difluoro-2-ethoxy-3-phenylcyclobut-2-ene (XIV). XIV was hydrolyzed by concentrated sulfuric acid to 2-ethoxy-3-phenylcyclobut-2-enone (XV) (12). Treatment of XII with excess potassium _t_-butoxide in _t_-butyl alcohol gave 1,1-difluoro-2-_t_-butoxy-3-phenylcyclobut-

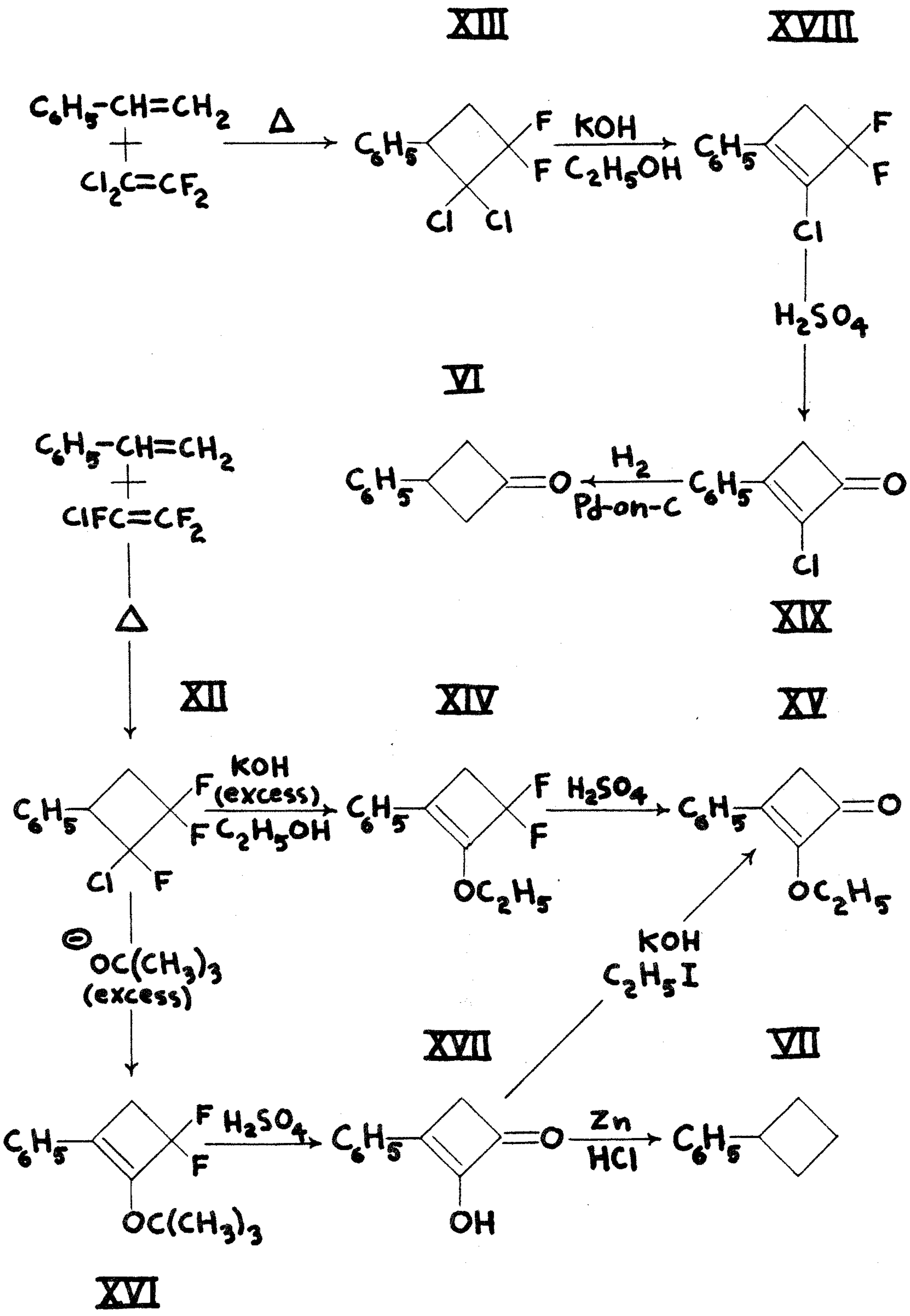

XIII
XVIII
C6H5-CH=CH2
+
Cl2C=CF2
Δ
C6H5
F
F
Cl
Cl
KOH
C2H5OH
C6H5
F
F
Cl
H2SO4
VI
C6H5-CH=CH2
+
ClFC=CF2
Δ
C6H5
=O
H2
Pd-on-C
C6H5
=O
Cl
XIX
XII
XIV
XV
C6H5
F
F
Cl
F
KOH
(excess)
C2H5OH
C6H5
F
F
OC2H5
H2SO4
C6H5
=O
OC2H5
⊖OC(CH3)3
(excess)
KOH
C2H5I
XVII
VII
C6H5
F
F
OC(CH3)3
H2SO4
C6H5
=O
OH
Zn
HCl
C6H5
XVI

Fig. 2

2-ene (XVI). Hydrolysis of XVI by sulfuric acid gave 2-hydroxy-3-phenylcyclobut-2-enone (XVII)(12). XVII was converted to XV by alkali and ethyl iodide. Clemmensen reduction of XVII gave phenylcyclobutane (VII). XVII gives a dark color with ferric chloride solution (enol test). The pK_A of XVII was 6.25 as compared with the pK_A's of 2-hydroxy-2-cyclohexenone and 2-hydroxy-2-cyclopentenone of 10.30 and 9.14, respectively (12). The major difference in the pK_A's between these three compounds has been attributed to the varying degree of stabilization of the anions by π-type interaction between electrons in the *p*-orbitals on the 1- and 3-position, and this effect should increase as the 1,3-distance decreases (12,18).

The adduct 1,1-difluoro-2,2-dichloro-3-phenylcyclobutane (XIII) was found to dehydrochlorinate readily on treatment with potassium hydroxide (1 mole) in ethanol to give 1,1-difluoro-2-chloro-3-phenylcyclobut-2-ene (XVIII). XVIII on hydrolysis with concentrated sulfuric acid gave 2-chloro-3-phenylcyclobut-2-enone (XIX). Catalytic hydrogenation of XIX gave 3-phenylcyclobutanone (VI) (15).

The present research deals with the syntheses of 3-phenylcyclobut-2-enone (XX) and 3-phenylcyclobut-2-enol (XXI) starting from the adduct 1,1-difluoro-2,2-dichloro-3-phenylcyclobutene (I) or 1,1-difluoro-2,2-dichloro-3-phenylcyclobutane (XII). The importance of π-type interactions between electrons in the *p*-orbitals on the 1- and 3-positions in 3-phenylcyclobut-2-enone and the 3-phenylcyclobut-2-enyl cation is discussed. The reactivity of the 2-chloro-3-phenylcyclobut-2-enyl and 3-phenylcyclobut-2-enyl 4-nitrobenzoate esters was studied. The reaction of 3-phenylcyclobut-2-enones with phosphorus pentachloride in benzene has been studied. The synthesis of 3-phenylcyclobutanone (VI) from the adduct XII, described above, has been improved, and the reduction of VI by several reagents is described.

SECTION 1

3-Phenylcyclobut-2-enone and 3-Phenylcyclobut-2-enol.

Simmons (19) first unsuccessfully attempted the synthesis of 3-phenylcyclobut-2-enone (XX) by the thermal cycloaddition reaction of phenylacetylene and ketene at 100°. He obtained only red tars. However, it is now known that any XX formed would have been destroyed under these conditions. The possibility of obtaining XX by allowing phenylacetylene and ketene to stand at temperatures below 40°, either alone or with an appropriate catalyst, has not yet been investigated.

A possible synthesis of XX is suggested by the discovery that a <u>gem</u>-difluoro group in the 1-position of a 3-phenylcyclobut-2-ene can be hydrolyzed by concentrated sulfuric acid at 100° to give the corresponding ketone (10). The <u>gem</u>-difluoro compound required for synthesis of XX is 1,1-difluoro-3-phenylcyclobut-2-ene (XXII). The synthesis of XXII from the already known 1,1-difluoro-3-phenylcyclobutane (XXIII) in two steps, halogenation in the 3-position and the dehalogenation, seemed to be the most direct route. This possibility was first investigated by Knutson (20) and then by Vogel (21). A further study of the synthesis of XX by this reaction sequence is described below.

Roberts, Kline and Simmons found that catalytic hydrogenation of 1,1-difluoro-2,2-dichloro-3-phenylcyclobutene (I) gave 1,1-difluoro-3-phenylcyclobutane (XXIII) in 22% yield (10). Knutson was able to raise the yields of the hydrogenation to 30-60% (20). Vogel obtained 80-85% of XXIII by carrying out the hydrogenation at about 60 psi with sodium acetate as a buffer in place of sodium carbonate (21). In the present work, yields of 78-83% of XXIII were obtained from I following Vogel's procedure. However, it was found that XXIII could be obtained in yields of 80-88% by hydrogenolysis of 1,1-difluoro-2,2-dichloro-3-phenylcyclobutane (XIII). The hydrogenolysis of XIII proceeded much faster than the hydrogenation of I, and XIII, being made from styrene instead of phenylacetylene, is much cheaper than I.

Knutson (20) and Vogel (21) attempted the bromination of XXIII by N-bromosuccinimide in carbon tetrachloride, but they were never able to isolate the expected product, 1,1-difluoro-3-bromo-3-phenylcyclobutane (XXIV), in pure form. In the present research, material having the correct elemental analysis for XXIV was obtained in 91-99% yields by working carefully with the rather unstable product. The possibility that any significant amount of 1,1-difluoro-2-bromo-3-phenylcyclobutane (XXV) was present in the product was ruled out by the proton nuclear magnetic resonance (NMR) spectrum which showed only peaks characteristic of phenyl and methylene hydrogens in the weight of 5:4. The methylene peak was a broad triplet. The NMR spectrum of two pairs of two equivalent nuclei, designated as an A_2X_2 system, such that the chemical shift between the A and X nuclei is very large relative to the various spin-coupling constants involved, has been treated theoretically by Pople, Schneider and Bernstein (89). The theory predicts a triplet for both the A and X regions of the spectrum if both A's are coupled equally to both X's. The 1,1-difluoro-3-bromo-3-phenylcyclobutane (XXIV) molecule appears to be approximated as an $A_2X_2A_2$ system where the two A_2 groups are not coupled. In this circumstance, the proton spectrum of XXIV may be described as two superimposed triplets. The form of the fluorine spectrum should be a quintet (90). The two methylene protons *cis* to the bromine atom should show some chemical shift relative to the two protons *trans*. If the degree of this non-equivalence is small, each peak of the triplet will be split into several closely spaced bands which could possibly only be resolved under high resolution. The proton spectrum of XXIV is consistent with this interpretation. The proton NMR spectrum of 1,1-difluoro-2-bromo-3-phenylcyclobutane (XXV) would be expected to show four kinds of hydrogens and to be extremely complicated due to the various possibilities for spin-spin coupling of the magnetic nuclei on the four-membered ring.

The infrared and ultraviolet spectra of XXIV were consistent with the proposed structure. XXIV gave an immediate precipitate with alcoholic silver nitrate solution and did not react with bromine or permanganate.

Knutson (20) attempted the dehydrobromination of impure XXIV with potassium hydroxide in ethanol and with quinoline or pyridine, but only small yields of impure product were obtained. The crude products partially decomposed on distillation to give colored fractions, which fumed in air and eventually deposited a black solid. Knutson found that his impure product reacted readily with bromine in carbon tetrachloride and with potassium permanganate in acetone, but did not give an immediate reaction with alcoholic silver nitrate; on catalytic hydrogenation 96% of the theoretical amount of hydrogen for one double bond was taken up, and the product was shown to be 1,1-difluoro-3-phenylcyclobutane (XXIII) from its index of refraction and infrared spectrum (10). Vogel dehydrobrominated impure XXIV with pyridine and obtained yields of impure product as high as 75%. Again, decomposition of the material to vividly colored mixtures was observed.

In the present research it was found that the dehydrobromination of XXIV could be carried out very satisfactorily with a solution of potassium hydroxide in ethanol. Careful isolation and purification of the product as described later gave 89-95% yields of a colorless product which had the correct elemental analysis for 1,1-difluoro-3-phenylcyclobut-2-ene (XXII). During distillation of several preparations of XXII, decomposition occurred in the manner described by Knutson and Vogel; however, this decomposition could be eliminated by using mineral oil as a still base. XXII is quite unstable and is sensitive to air, moisture, acid, and etched glassware. It can only be kept sealed under vacuum for a few hours at room temperature, a few days at 0°, or a few weeks at Dry Ice temperatures. The intense purple-colored products of decomposition mixture were investigated, but no single substance could be isolated or identified. When a sealed sample of XXII decomposed, considerable hydrogen fluoride pressure developed after about a day. Addition of an organic base to a sample of XXII definitely slowed its rate of decomposition. It was not determined whether one or two moles of hydrogen fluoride were liberated on decomposition.

Pure XXII was found to react readily with bromine in carbon tetrachloride and potassium permanganate in acetone, but to be inert to alcoholic silver nitrate, as was observed by Knutson (20). The ultraviolet spectrum of XXII in cyclohexane had λ_{max} 253.0 mμ (ϵ 16,000), λ_{max} 215.5 mμ (ϵ 14,300), λ_{max} 209.0 mμ (ϵ 19,200) and λ_{max} 204.0 mμ (ϵ 17,600). This spectrum compares favorably with the styrene spectrum for the bands between 200 and 225 mμ; styrene had λ_{max} 248.0 mμ (ϵ 13,000), λ_{max} 215.0 mμ (ϵ 12,600), λ_{max} 208.0 mμ (ϵ 21,600) and λ_{max} 205.0 mμ (ϵ 24,200). The band in the 250 mμ region in XXII was shifted 5.0 mμ to longer wavelength than in styrene. Since the unhalogenated or unsubstituted 1-phenylcyclobutene chromophore has never been described, one cannot assay the exact interplay of ring-strain, phenyl conjugation, and the electrical effects of the <u>gem-</u>

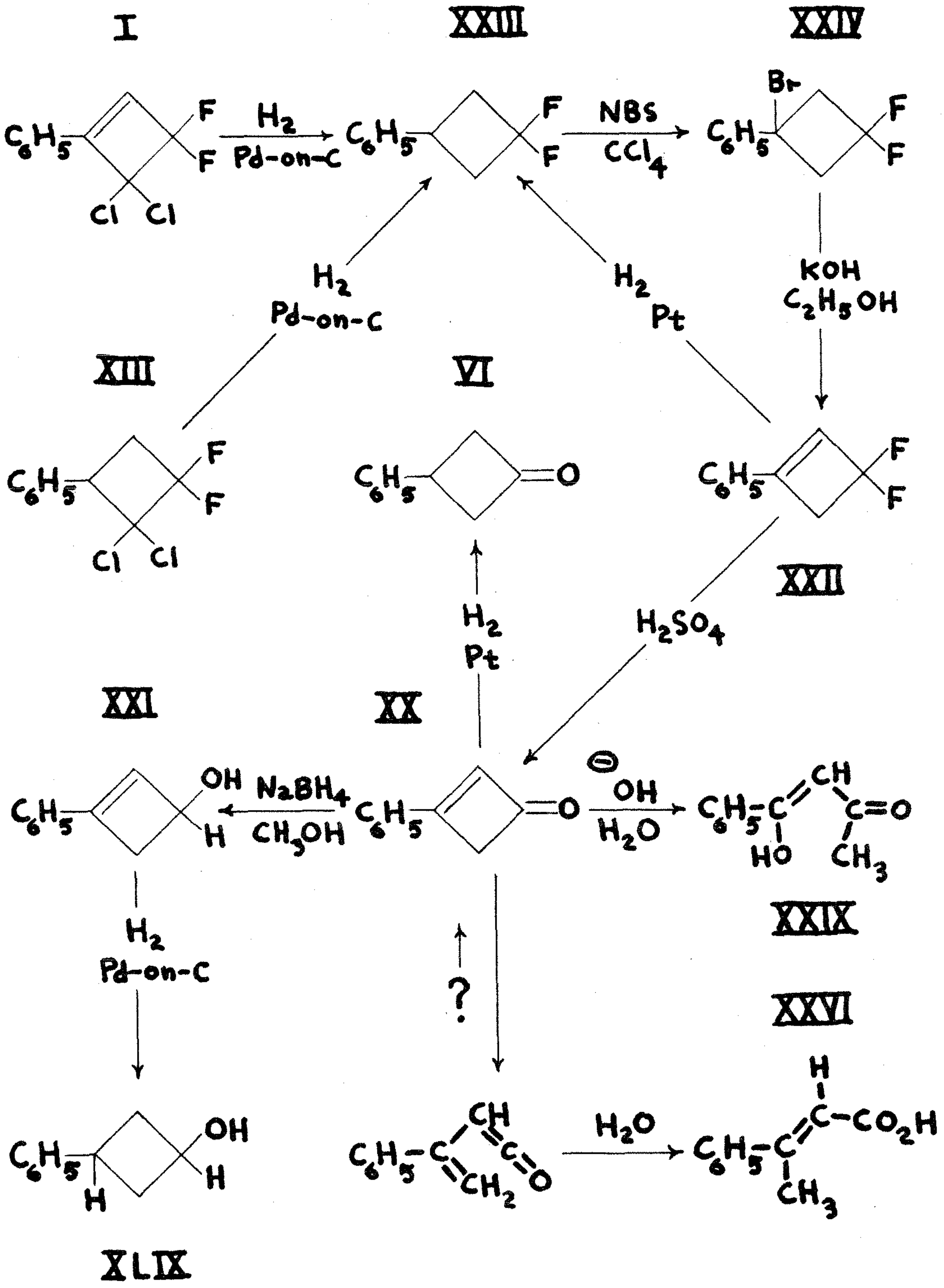

I
XXIII
XXIV
C_6H_5
F
F
Cl Cl
H_2
Pd-on-C
NBS
CCl_4
Br
KOH
C_2H_5OH
H_2
Pd-on-C
H_2
Pt
XIII
VI
XXII
H_2SO_4
H_2
Pt
XXI
XX
OH
H
$NaBH_4$
CH_3OH
O
$OH^{\ominus}$
H_2O
CH
HO
CH_3
XXIX
H_2
Pd-on-C
?
XXVI
C_6H_5-C
CH_2
C=O
H_2O
$C-CO_2H$
XLIX

Fig. 3

difluoro group in XXII. The infrared spectrum of XXII showed a band at 6.16 μ assigned to C=C stretching and a band at 6.97 μ characteristic of C-H methylene deformation.

The proton NMR spectrum of 1,1-difluoro-3-phenylcyclobut-2-ene (XXII) showed the expected resonance singlets characteristic of phenyl, methylene and vinyl hydrogens in the intensity ratio of 5:2:1, respectively. As has been observed for a number of other fluorine-substituted phenylcyclobutenes (22), the adjacent hydrogen-fluorine couplings are very small as there were no multiplets observed in the case of the methylene and vinyl protons of XII. The fluorine NMR spectrum was not observed.

Although Knutson (20) and Vogel (21) were unable to obtain pure 1,1-difluoro-3-phenylcyclobut-2-ene (XXII), each found that sulfuric acid hydrolysis of their preparations gave small quantities of a solid ketonic product, m.p. 48-51°. From vacuum sublimation of the crude product, Knutson obtained a small amount of white crystalline material having the correct elemental analysis for 3-phenylcyclobut-2-enone (XX). The product from the catalytic hydrogenation of this material gave a 2,4-dinitrophenylhydrazone which had the same melting point as the 2,4-dinitrophenylhydrazone of 3-phenylcyclobutanone (10). Vogel improved the yield of the hydrolysis step to about 50%. He attempted to purify his crude product by recrystallization from ethanol, but found XX to be quite soluble in this solvent and to undergo partial decomposition when heated in solution. On recrystallization from ethanol he sometimes obtained material which melted at 56° and two other unknown substances which he did not investigate. In the present research, the infrared spectrum of his material m.p. 56° has been found to be identical with that of benzoylacetone (XXIX). The infrared spectrum of one of his other unknown substances is very similar to that of cis-β-methylcinnamic acid (XXVI).

In the present research the hydrolysis of 1,1-difluoro-3-phenylcyclobut-2-ene (XXII) with concentrated sulfuric acid was carried out many times, and it soon became apparent that the amount of crude product was very dependent on the temperature and the duration of the reaction. A procedure was developed which gave 66-89% yields of crude product. The thermal instability of 3-phenylcyclobut-2-enone (XX) precluded its purification by recrystallization in the usual manner. However, high-vacuum sublimation at temperatures below 40° gave large colorless needles (44-59% yields, m.p. 51.4-52.7°) which had the correct elemental analysis for XX. XX gave a 2,4-dinitrophenylhydrazone (m.p. 240.9-241.5° with decomposition) also having the correct elemental analysis. With potassium permanganate in acetone XX gave an immediate reaction and produced benzoic acid (XXVII). XX decolorized bromine in carbon tetrachloride only slowly. XX was found to be very irritating to the skin. After standing open to the air for several days XX became very wet. It darkened when exposed to strong light and was stored most satisfactorily in the dark under vacuum. From samples of decomposed XX, good yields of cis-β-methylcinnamic acid (XXVI) were isolated. As reported by Knutson (20), catalytic hydrogenation of XX gave 3-phenylcyclobutanone which was identified by its infrared spectrum and 2,4-dinitrophenylhydrazone derivative.

The proton NMR spectrum of XX showed singlet bands characteristic of phenyl, vinyl and methylene hydrogens in the intensity ratio of 5:2:1; the chemical shifts were not measured. The infrared spectrum of XX showed absorption bands at 5.65 μ (C=O stretch), 6.39 μ (C=C stretch) and 7.05 μ (methylene deformation). In agreement with Vogel (21), the ultraviolet spectrum of XX was found to have λ_{max} 286.0 mμ (ϵ 23,000), λ_{max} 222.5 mμ (ϵ 11,600) and λ_{max} 217.0 mμ (ϵ 13,000). Cinnamaldehyde and benzalacetone have conjugated systems nearly identical with that of XX; the former has λ_{max} 287.5 mμ (ϵ 25,000) (23), λ_{max} 228.5 mμ and λ_{max} 220.5 mμ, and the latter has λ_{max} 287.5 mμ (ϵ 25,000) (23), λ_{max} 226.5 mμ and λ_{max} 221.5 mμ. Thus the ultraviolet spectrum of 3-phenylcyclobut-2-enone (XX) appears to be nearly normal for an α,β-unsaturated -β-phenylketone. However, the possibility that the observed maxima result from near cancellation of a hypsochromic displacement due to ring strain by a bathochromic displacement resulting from π-type interactions between the electrons on the 1- and 3-position of the cyclobutene ring is not ruled out. The ultraviolet spectrum of the unknown 1-phenylcyclobutene would perhaps provide the necessary information as to the effect of ring strain on light absorption in the cyclobutene system.

Treatment of 3-phenylcyclobut-2-enone (XX) with hot dilute aqueous base was found to give three products: benzoic acid (XXVII), acetophenone (XXVIII) and benzoylacetone (XXIX). The amounts of XXVII and XXVIII increased as the concentration of base was increased, and the initial product is assumed to be XXIX. XXIX is known to give XXVIII under the basic conditions employed (24), presumably by a retrograde Claisen condensation involving initial attack of hydroxide ion on the carbonyl carbon atom γ to the phenyl ring followed by subsequent cleavage to acetic acid and acetophenone enolate anion (see Figure 4). XXVII could arise from XXIX by a similar mechanism involving attack of hydroxide ion on the carbonyl carbon α to the phenyl ring followed by subsequent cleavage to give benzoic acid and the enolate of acetone. The mechanism of the ring-opening of XX could involve a single and/or a multiple-step mechanism. A possible one-step mechanism would involve attack of hydroxide ion on the electron deficient 3-position of XX concerted with cleavage between carbons 3 and 4 to give an enolate anion of benzoylacetone. As a multiple-step mechanism, the first step could involve attack (possibly reversible) of hydroxide ion on the electron deficient 3-position (but without concerted ring-cleavage) to give the enol anion of 3-phenylcyclobutan-3-ol-1-one (XXX) (see Figure 4). XXX could then undergo subsequent ring-opening to a benzoylacetone enolate anion, or it could pick up a proton from the solvent to give the

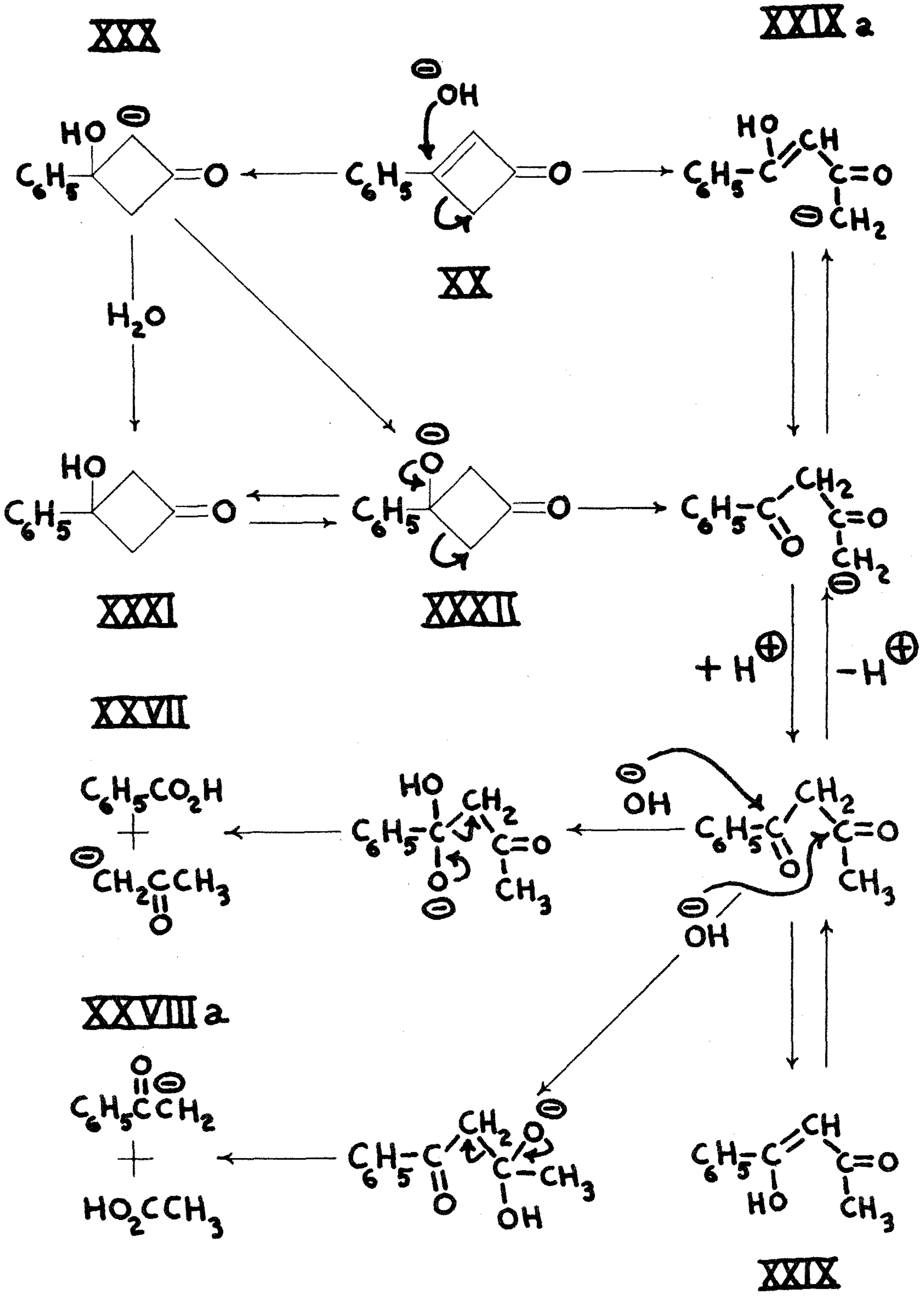


Fig. 4

neutral intermediate 3-phenylcyclobutan-3-ol-1-one (XXXI). Since the enolate anion of XXXI would be expected to be a much stronger base than the alkoxide of XXXI (25), the next step could be the reversible removable of the alkoxyl hydrogen by hydroxide ion to give 3-phenylcyclobutan-3-ol-1-one alkoxide (XXXII) which could undergo irreversible ring-opening to an enolate anion of benzoylacetone. Experiments designed to trap any intermediate such as XXXI were not carried out in the present research. Attack by hydroxide ion at carbon-1 would be expected to result in formation of a carboxylic acid derivative as the initial ring-opening product, but no such product was isolated. All three reaction mechanisms proposed above are reasonable on the basis of the products formed.

Ring-opening of 3-phenylcyclobut-2-enone (XX) in acetic acid gave a good yield of _cis_-β-methylcinnamic acid. The acetic acid ring-opening reactions of a number of halogen-substituted 3-phenylcyclobut-2-enones have been studied, and these reactions have been shown to proceed through vinyl-ketene intermediates which undergo either 1,2- or 1,4-addition to carboxylic acid derivatives (13,15). In those cases where the bulkiness of the attached groups are such that the ketene and vinyl groups cannot achieve coplanarity and therefore maximum conjugation, the ketene adds acetic acid in a 1,2-manner as if it were an isolated group. When the groups present are not too bulky for the ketene and vinyl groups to achieve coplanarity with maximum conjugation, 1,4-

addition to the ketene is observed (15). The ring-opening of XX falls in this latter category.

Reduction of 3-phenylcyclobut-2-enone (XX) with sodium borohydride gave an alcohol, m.p. 66.4-68.6°, having the correct elemental analysis for 3-phenylcyclobut-2-enol (XXI). XXI proved to be unstable and could only be kept under nitrogen or vacuum at 0° in the dark. A sample of XXI exposed to air becomes yellowish and oily within a few minutes. XXI gave a solid 4-nitrobenzoate ester, m.p. 146.2-148.4°, and on catalytic hydrogenation gave cis-3-phenylcyclobutanol (XLIX) (see Section 4). XXI reacted immediately with bromine in carbon tetrachloride and potassium permanganate in acetone.

The infrared spectrum of XXI showed absorption bands at 3.03 μ (O-H stretching) and 6.99 μ (methylene deformation). There does not seem to be any band in the region 5.5-6.5 μ which can be assigned to the C=C in the four-membered ring. The infrared spectra of cinnamyl alcohol and methylstyrylcarbinol only show a very weak band at about 6.0 μ which could be attributed to C=C stretch. The ultraviolet spectrum of XXI had λ_{max} 255.0 mμ (ϵ 19,000), λ_{max} 217.5 mμ and λ_{max} 211.0 mμ and was quite similar to the ultraviolet spectrum of cinnamyl alcohol which had λ_{max} 251.5 mμ, λ_{max} 219.5 mμ and λ_{max} 213.5 mμ. The λ_{max} 255.0 mμ in XXI decreases with time. The effect of oxygen or hydrogen ion on this change was not investigated.

Extra stabilization due to π-type interactions between electrons in the p-orbitals on the 1- and 3-positions in the four-membered ring of the anions of 2-hydroxy-3-phenylcyclobut-2-enone (XVII) and 4-hydroxy-3-phenylcyclobutenedione (XI) has been suggested (12,18) as responsible for the great acidity of these systems, pK_A's 6.25 (12) and <1 (11), respectively. The pK_A's of 2-hydroxy-2-cyclohexenone and 2-hydroxy-2-cyclopentenone are 10.30 and 9.14, respectively (12). From the effect of substitution of a phenyl group on the acidity of several phenols, it appears that the phenyl group can account for only about 0.5 pK_A units of the observed acidity differences. Similar 1,3-interactions would be expected to stabilize the undissociated enols, but to be less significant because of the associated charge separation (12). This type of stabilization is probably responsible for the remarkable stability of phenylcyclobutenedione (11).

Smutny (18) has estimated the 1,3-interaction effect by the simple molecular orbital treatment (LCAO) for cyclobutenone (XXXIII), cyclobutenedione (XXXIV) and several of the enol anions mentioned above. For XXXIII and XXXIV he used 1,3-exchange integrals (β_{13}) of 0.2-0.5β, where β is -20 kcal./mole. He took the carbon-oxygen exchange integral as $\sqrt{2}\beta$ and the oxygen Coulomb integral as $\alpha+2\beta$ where α is the Coulomb integral of carbon (27). The delocalization energy (DE) of XXXIII without 1,3-interaction was 0.4927β or about 9.9 kcal./mole. With a β_{13} of 0.2β the DE was 0.6277β or about 12.3 kcal./mole, and with β_{13} of 0.5β it was 0.8694β or 17.4 kcal./mole. The DE of XXXIV without

1,3-interaction was 1.2375 β or 24.8 kcal./mole, while with both β_{13} and β_{24} equal to 0.5 β the DE was increased to 1.9863 β or 39.7 kcal./mole. Smutny's calculations employing the LCAO-MO method suggest that even in the ground states 1,3-interaction makes a substantial contribution to the electron DE.

One of the purposes of the present research was to determine how 1,3-interaction is manifest in the 3-phenylcyclobut-2-enone (XX) system. Figure 5 shows a π-orbital drawing of XX illustrating 1,3-interaction. However, before the properties of small-ring compounds are contrasted with those of the corresponding acyclic derivatives, the importance of σ-bond strain and other destabilizing effects due to the close proximity of the ring atoms must be realized. Good quantitative estimates of these effects for the cyclobutene system have not been made (26). Estimates of the σ-bond strain for cyclobutene and cyclobutenone by a crude theoretical method described in Section IV are 45 and 53 kcal./mole, respectively. Estimates by this method are probably too high (26).

The exact effect of 1,3-interaction to be expected on light absorption is unknown. The ultraviolet spectrum of 3-phenylcyclobut-2-enone was very similar to those of the corresponding acyclic systems, cinnamaldehyde and benzalacetone. The ultraviolet spectrum of 3-phenylcyclobut-2-enol showed a small shift to longer wave lengths over that of cinnamyl alcohol (shift of 3.5 mμ). This small effect might

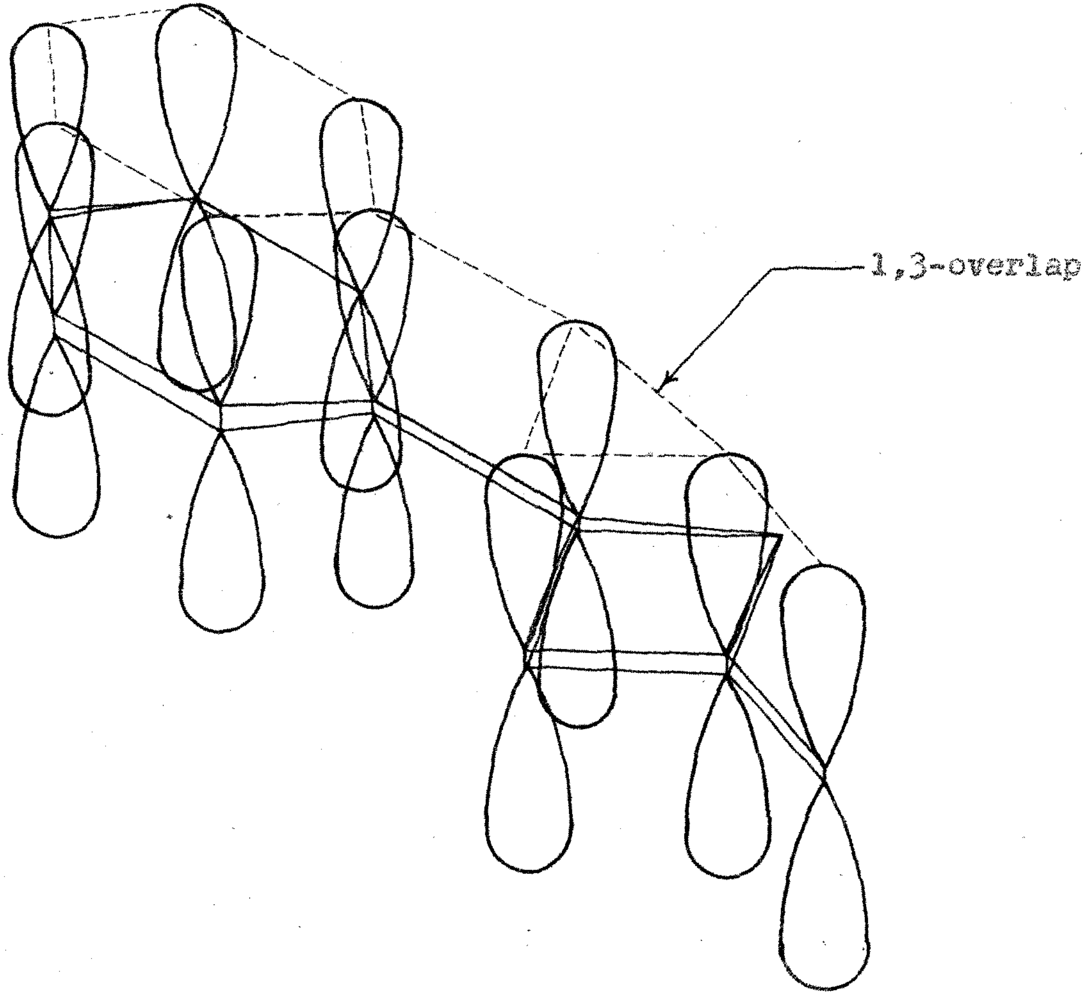


Fig. 5. An illustration of the *p*-orbital overlap and 1,3-*p*-overlap for 3-phenylcyclobut-2-enone.

indicate that the steric strain in the excited state is less than in the ground state.

The magnitude of steric strain in the cyclobutene and cyclobutenone systems could be most directly measured by heats of hydrogenation and combustion, but as yet only one such study for these systems has been reported (91). 1,3-Interactions in the 3-phenylcyclobut-2-enyl cation will be discussed further in Section 5.

SECTION 2

Reaction of 3-Phenylcyclobut-2-enones with Phosphorus Pentachloride

The reaction of phosphorus pentachloride with 3-phenylcyclobut-2-enones was first carried out by Kline with 2,2-dichloro-3-phenylcyclobutenone (III) and 2,4-dichloro-3-phenylcyclobutenone (V) (28). The same reactions were also studied by Knutson (20), Smutny (18) and Vogel (21). This work will be reviewed in some detail below along with the results of the present research with III and V. The reaction of phosphorus pentachloride with several other 3-phenylcyclobut-2-enones has been studied and is also described below.

The first ketone to be subjected to treatment with phosphorus pentachloride in the present research was 2,2-difluoro-3-phenylcyclobutenone (XXXV). XXXV was first obtained by Smutny from the sulfuric acid hydrolysis of 1,1,2,2-tetrafluoro-3-phenylcyclobutene (XXXVI) (18). He found that either XXXVI or XXXV could be hydrolyzed to phenylcyclobutenedione (X) under more vigorous conditions. The structure for XXXV proposed by Smutny was shown to be consistent with the chemical, NMR, ultraviolet and infrared evidence obtained in the present research. Treatment of XXXV with phosphorus pentachloride in benzene gave an 89% yield of a colorless product with an elemental analysis corresponding to that for 1,1-difluoro-2,2-dichloro-4-phenylcyclobutene (II). All of the properties of II were different from those

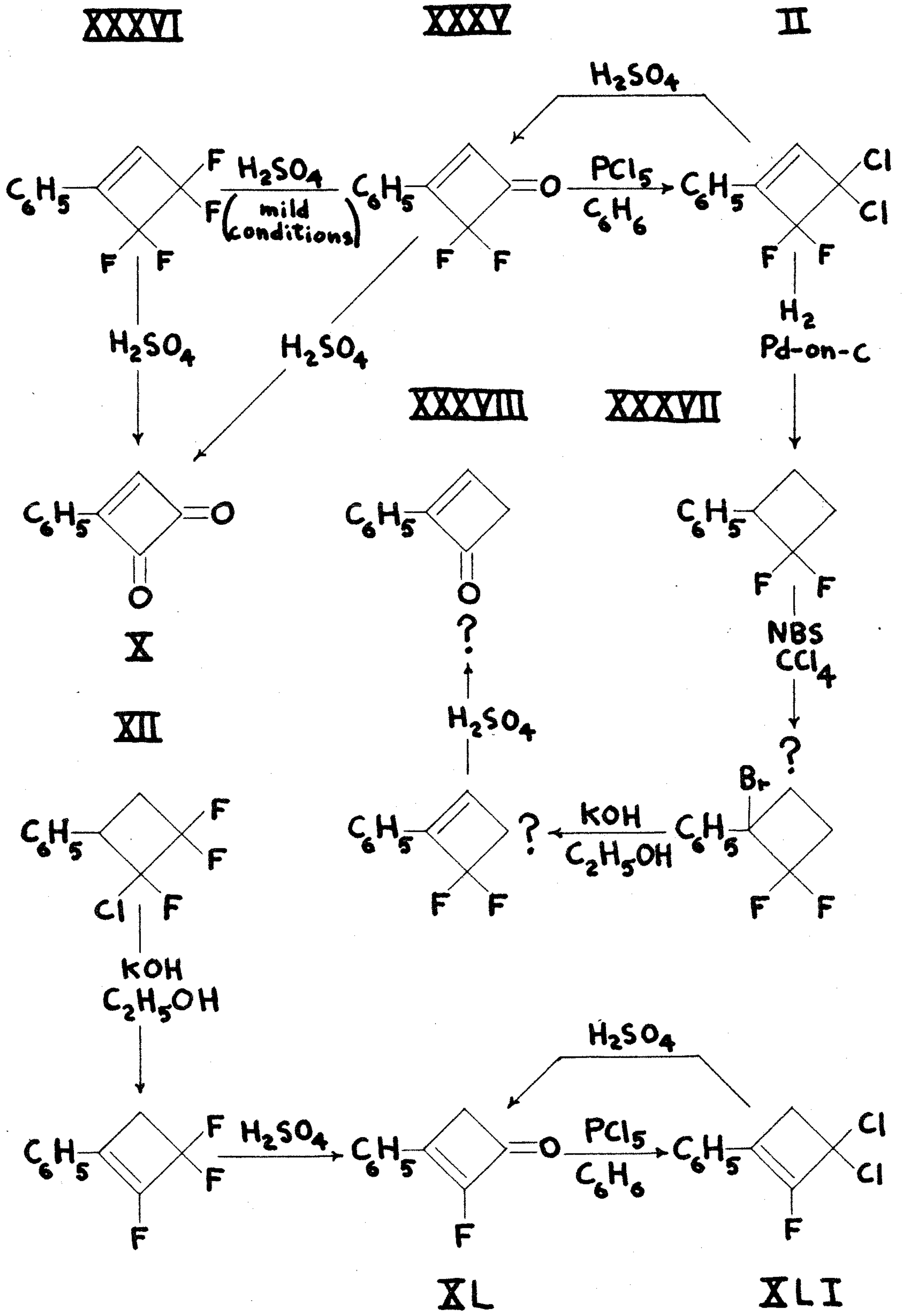

XXXVI
XXXV
II
H_2SO_4
C_6H_5
F
F
F
F
H_2SO_4
(mild conditions)
C_6H_5
=O
F
F
PCl_5
C_6H_6
C_6H_5
Cl
Cl
F
F
H_2SO_4
H_2SO_4
H_2
Pd-on-C
XXXVIII
XXXVII
C_6H_5
=O
O
X
C_6H_5
O
?
C_6H_5
F
F
NBS
CCl_4
?
XII
H_2SO_4
Br
C_6H_5
F
F
Cl
F
?
KOH
C_2H_5OH
C_6H_5
F
F
F
F
KOH
C_2H_5OH
H_2SO_4
C_6H_5
F
F
F
H_2SO_4
C_6H_5
=O
F
PCl_5
C_6H_6
C_6H_5
Cl
Cl
F
XL
XLI

Fig. 6

of 1,1-difluoro-2,2-dichloro-3-phenylcyclobutene (I). The infrared spectrum of II had a band at 6.28 μ assigned to C=C stretch; in I the corresponding band was 6.12 μ. II reacted immediately with permanganate in acetone and with alcoholic silver nitrate; I, in contrast, reacted very slowly with the latter reagent. This difference in reactivity suggests that there is considerable activation imparted to substituents in the 1-position of the 3-phenylcyclobut-2-ene system. The proton NMR spectrum of II showed peaks characteristic of phenyl and vinyl hydrogens in the relative intensity ratio of 5:1. The vinyl peak was a triplet presumably due to cross-ring spin-spin coupling of fluorine and hydrogen (22). The fluorine NMR spectrum was a doublet which is in line with the explanation above and the spectrum of ketone XXXV (22). II was readily hydrolyzed back to XXXV with sulfuric acid. This compound was the first of its type to show hydrolysis of a gem-dichloro group in preference to a gem-difluoro group to give the corresponding ketone in good yields. This fact points up again the increased reactivity of substituents in the 1-position of the 3-phenylcyclobut-2-ene system. Catalytic hydrogenation of I gave material with the correct elemental analysis for 1,1-difluoro-2-phenylcyclobutane (XXXVII). The infrared spectrum, index of refraction and NMR spectrum of XXXVII were all different from those of 1,1-difluoro-3-phenylcyclobutane (XXIII). XXXVII proved to be somewhat unstable also. XXXVII could be a possible intermediate in the synthesis of 2-phenylcyclobut-2-enone (XXXVIII) by a series of reactions similar to those utilizing XXIII for the synthesis of 3-phenylcyclobut-2-enone (XX) (see Figure 6). However, no further work was done with XXXVII.

2-Chloro-3-phenylcyclobut-2-enone (XIX) gave a gem-dichloride, 1,1,2-trichloro-3-phenylcyclobut-2-ene (XLIX), which could be hydrolyzed back to XIX by sulfuric acid in nearly quantitative yield. XLIX reacted readily with permanganate in acetone, alcoholic silver nitrate and bromine in carbon tetrachloride. On catalytic hydrogenation, XLIX gave a 52% yield of phenylcyclobutane (VII) along with considerable partially hydrogenated material. The infrared, ultraviolet and proton NMR spectra of XLIX were in accord with the proposed structure.

The gem-dichloride from 2-fluoro-3-phenylcyclobut-2-enone (XL), 2-fluoro-1,1-dichloro-3-phenylcyclobut-2-enone (XLI), was a solid, m.p. 56-60°, and it also gave a quantitative yield of ketone XL on sulfuric acid hydrolysis. XLI reacted readily with permanganate in acetone, alcoholic silver nitrate and bromine in carbon tetrachloride. The infrared spectrum was consistent with the assigned structure.

2-Fluoro-2-chloro-3-phenylcyclobutenone (XLII) gave a gem-dichloride, assigned the structure 2-fluoro-1,1,2-trichloro-3-phenylcyclobutene (XLIII), which reacted readily with permanganate in acetone and alcoholic silver nitrate,

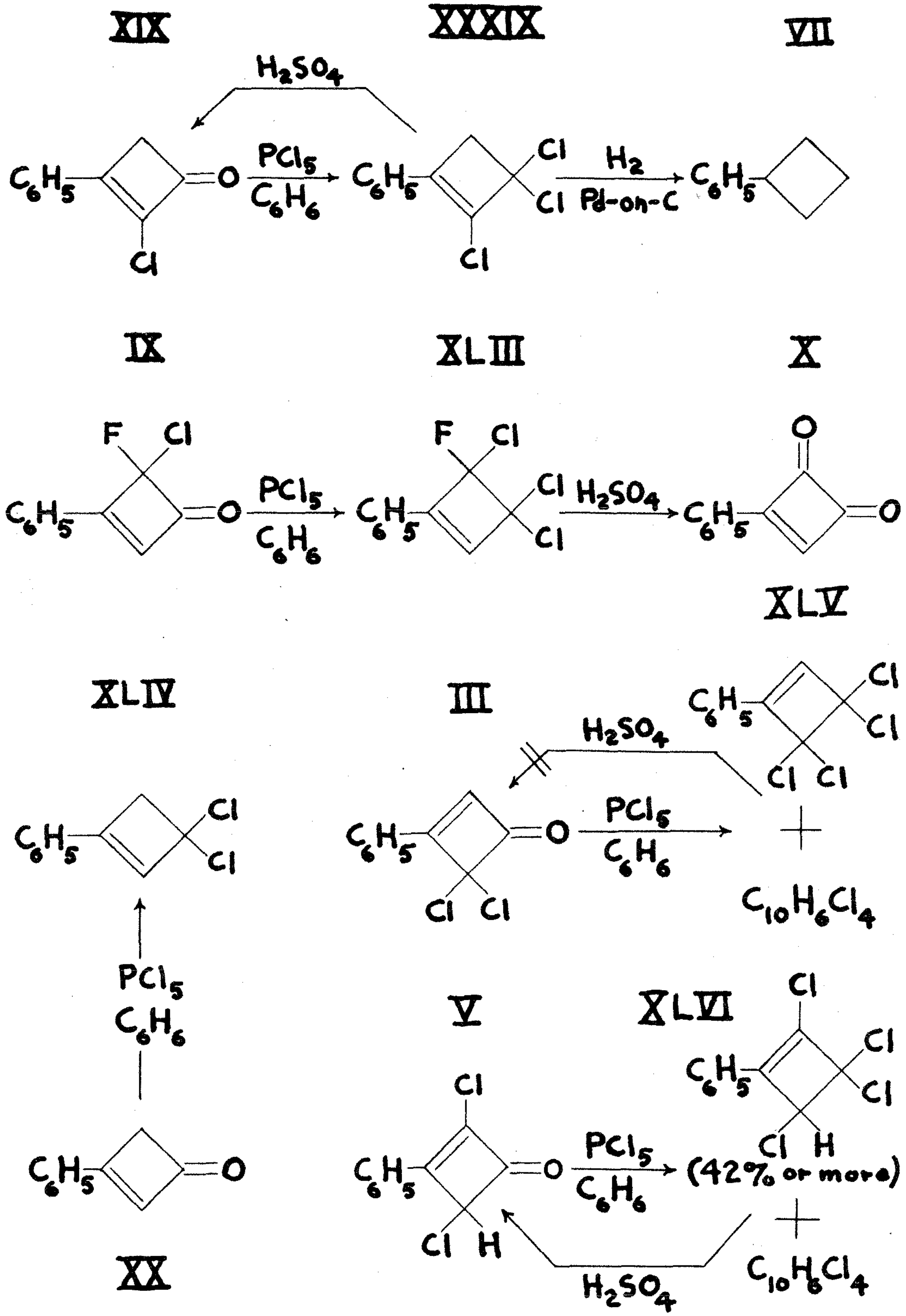

XIX
XXXIX
VII
H₂SO₄
PCl₅
C₆H₆
H₂
Pd-on-C
IX
XLIII
X
XLV
XLIV
III
C₁₀H₆Cl₄
V
XLVI
(42% or more)
XX

Fig. 7

but only slowly with bromine in carbon tetrachloride. Sulfuric acid hydrolysis of XLIII gave a 78% yield of phenylcyclobutenedione (X). The infrared spectrum of XLIII was consistent with the assigned structure.

The gem-dichloride obtained from 3-phenylcyclobut-2-enone, 1,1-dichloro-3-phenylcyclobut-2-ene (XLIV), was a solid, m.p. 37-40°. XLIV reacted readily with permanganate in acetone, alcoholic silver nitrate and bromine in carbon tetrachloride. XLIV decomposed rapidly in air to give a wet, light-brown solid. The ultraviolet and infrared spectra of XLIV were consistent with the assigned structure.

Kline (28), Knutson (20), Smutny (18), and Vogel (21) all studied the reactions of phosphorus pentachloride with 2,2-dichloro-3-phenylcyclobutenone (III) and 2,4-dichloro-3-phenylcyclobutenone (V), which gave materials tentatively assigned the structures of "1,1,2,2-tetrachloro-3-phenylcyclobutene" (XLV) and "1,1,2,4-tetrachloro-3-phenylcyclobutene" (XLVI), respectively. They were unable to show satisfactorily whether the tetrachloro products still had the cyclobutene structure or were open-chain isomers of $C_{10}H_6Cl_4$ or mixtures of both. This problem has not been solved in the present work for LXV, but an experiment to be described below suggests the LXVI contains at least 42% of the 2,4-tetrachlorocyclobutene isomer. The work mentioned above will be reviewed before the miscellaneous experiments carried out in the present work are described.

Kline (28) was unable to hydrolyze XLV with sulfuric acid back to III. However, he was able to hydrolyze XLVI to ketone V in 11% yield. Catalytic hydrogenation of XLVI gave a 25% yield of n-butylbenzene. Reduction of XLV with zinc in alcohol gave a compound which was characterized only by its infrared spectrum.

Knutson (20) treated XLV with triethyl amine, but he did not take the infrared spectrum of the product. He could isolate no ketonic material after treatment of XLV with concentrated sulfuric acid. Under similar conditions from XLVI he isolated a small amount of material, m.p. 79-80°, which was probably V. Treatment of XLVI with zinc or magnesium dust in alcohol resulted in the recovery of starting material which contained impurities which he could not separate by distillation.

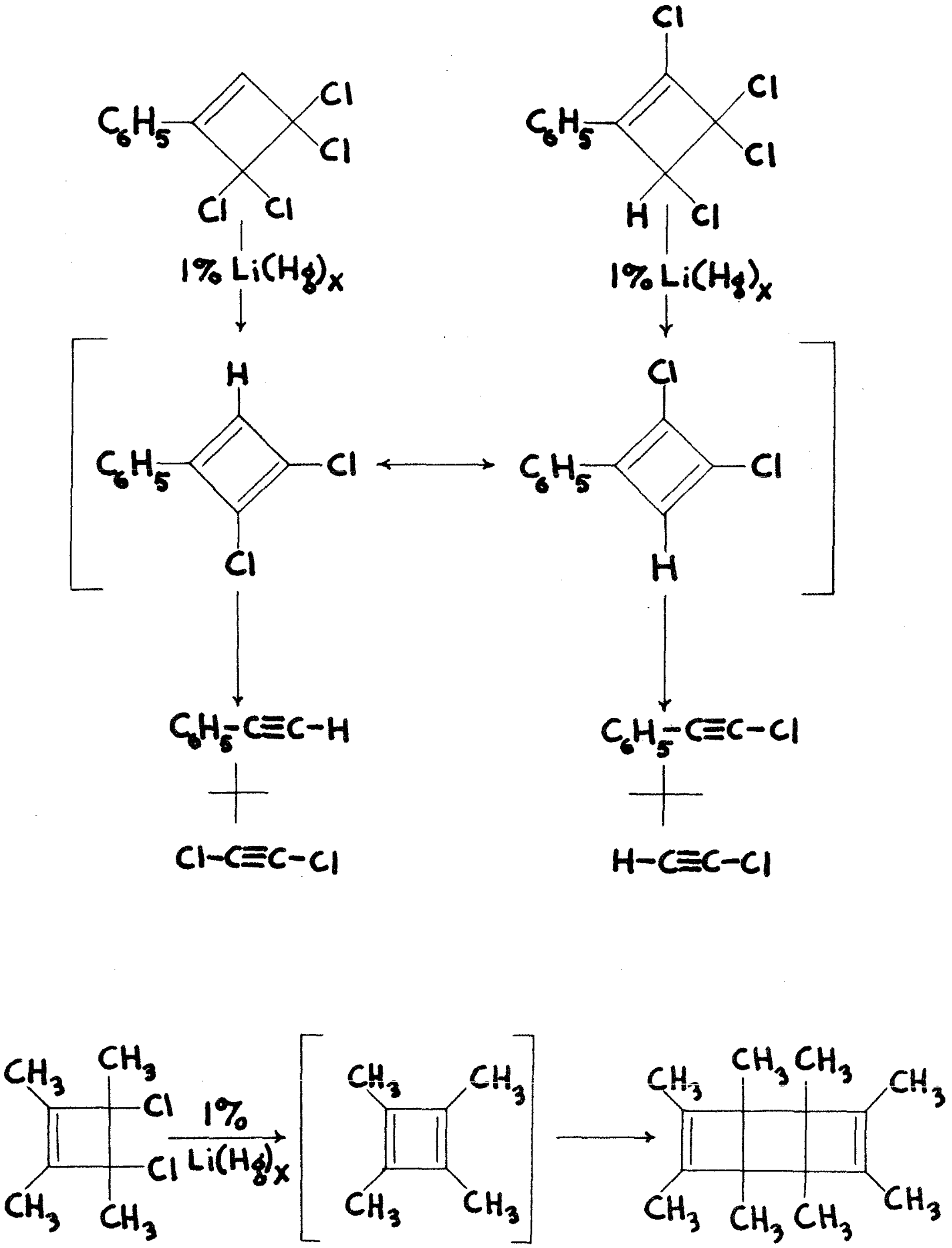
Smutny (18) found that both XLV and XLVI did not immediately decolorize bromine in carbon tetrachloride, although decolorization occurred after several minutes. Both compounds gave negative 2,4-dinitrophenylhydrazine tests; both gave precipitates with alcoholic silver nitrate, and both reacted slowly with sodium iodide in acetone. Treatment of XLV with zinc dust in alcohol gave material having strong acetylenic bands in the infrared, but no pure acetylenic substance could be isolated. Similar treatment of XLVI gave starting material contaminated with some acetylenic material. Ozonization of both XLV and XLVI gave benzoic acid as the only isolable product.

Vogel (21) attempted the reduction of XLV by several reagents, but he never succeeded in obtaining any well-defined products except unreacted starting material.

In the present work, the tetrachloro materials XLV and XLVI were prepared by treatment of the corresponding ketone with a slight excess of phosphorus pentachloride in benzene; the yields were 81% and 92%, respectively. The elemental analyses of both these products were correct for $C_{10}H_6Cl_4$. The tetrachloro materials obtained in the present research may have been somewhat purer than those obtained previously since the infrared spectra showed fewer weak bands such as might be attributed to impurities. Both XLV and XLVI reacted quite slowly with bromine in carbon tetrachloride but rapidly with permanganate in acetone and alcoholic silver nitrate.

The infrared spectra of XLV and XLVI had complex band structures between 6.0-7.0 μ, not characteristic of the other known gem-dichlorides (see Table I below). One surprising feature of the spectrum of XLV (the "2,2-tetrachloro" material) is a strong, sharp band at 5.55 μ. This band cannot be due to a carbonyl group since the elemental analysis rules this out, and XLV does not react with 2,4-dinitrophenylhydrazine reagent. From the infrared spectra of XLV and XLVI it is seen that XLV has every band present in "pure" XLVI and could be a mixture. The presence of XLV in XLVI is ruled out by the absence of the strong band at 5.55 μ.

XLV XLVI



[R. Criegee and G. Louis, Ber. 90, 417-424 (1957)]

Fig. 8

The ultraviolet spectra of both XLV and XLVI are quite different from those of the other gem-dichlorides. The former showed no fine structure in the region 200-220 mμ.

Attempts to hydrolyze "1,1,2,2-tetrachloro-3-phenylcyclobutene" (XLV) to the corresponding ketone, III, with sulfuric acid failed. Treatment of XLV with lithium chloride in acetone resulted in partial isomerization to "1,1,2,4-tetrachloro-3-phenylcyclobutene" (XLVI) as shown by the infrared spectrum. Treatment of a benzene solution of XLV with dilute aqueous potassium carbonate in the isolation procedure of XLV gave a product showing a strong band at 4.74 μ. This is about the normal position for the C≡C stretching band in phenylacetylene. The C≡C stretching band in chlorophenylacetylene falls at 4.52 μ.

XLVI hydrolyzed in concentrated sulfuric acid and gave a 42% yield of the corresponding ketone, 2,4-dichloro-3-phenylcyclobutenone (V). This indicates at least the minimum percentage of four-membered-ring material present. About 30% of a colorless liquid, different from XLVI as shown by the infrared spectrum, was recovered. Its structure was not investigated. Treatment of XLVI with potassium t-butoxide resulted in extensive polymerization. Some material having a sharp band at 4.55 μ in the infrared was isolated. The material also had bands at 3.35 μ which could be attributed to aliphatic C-H stretch.

XLV on treatment with 1% lithium amalgam in ether gave a product which was quite different from the starting material. The strong band in the infrared at 5.55 μ was missing. There were bands at 3.02, 4.56, and 4.77 μ which suggested that small amounts of phenylacetylene and chlorophenylacetylene were present in the ratio 2:1, respectively. Similar treatment of XLVI gave mostly unchanged starting material, but small amounts of phenylacetylene and chlorophenylacetylene were present in the relative ratio of 1:5, respectively, as shown by infrared. Under the conditions of these experiments a cyclobutadiene intermediate could be formed, and its decomposition might account for the formation of the acetylenes. It has been reported that similar treatment of a cyclobutene 3,4-vicinal dihalide appears to liberate very reactive cyclobutadiene intermediates (69) (see Figure 8).

SECTION 3

Infrared Spectral Correlations for 3-Phenylcyclobut-2-ene Derivatives

In the course of the present research on 3-phenylcyclobut-2-enes, several spectral correlations have been made. These will now be discussed briefly. In Table I are listed the positions of the C=C stretching mode, C=C aromatic in-plane vibrations, C=O stretching modes, C-H stretching modes (aliphatic, vinyl and aromatic), and methylene deformation modes for twenty-nine phenylcyclobutene derivatives and several other pertinent compounds.

It is seen that the double bond stretching modes fall into four groups. The first group contains the 3-phenylcyclobut-2-enes with no substituent in the 2-position and no carbonyl group. These absorb in the region from 6.12-6.27 μ. The second group contains the ketones corresponding to the latter compounds, and they all show absorption from 6.20-6.45 μ. The members of the third group each have a substituent in the 2-position, but no carbonyl group, and all these absorb in the region 5.85-6.11 μ. The last group includes the ketones with substituents in the 2-position, and they show absorption from 6.05-6.26 μ. It is well known that conjugation of a double bond with a carbonyl group results in shifts to longer wave lengths and an increase in intensity of the C=C stretching mode (29). Substituents in the 2-position appear to cause a shift of the C=C stretching band to shorter wave lengths and splitting of the carbonyl absorption. The reason for this splitting is unknown. All of the carbonyl absorption bands lie between 5.50 and 5.73 μ; this is the general region for cyclobutanones (10,29). The ketones with halogen substituents in the 2-position have split carbonyl bands, and the reason for this, as stated above, is unknown. All of the compounds studied had absorption in the C-H stretching region at 3.24-3.32 μ, assigned to aromatic and vinyl hydrogens, and 3.39-3.47 μ assigned to methylene hydrogen if present. All of the compounds have a pair of strong bands at 6.71±0.05 μ and 6.88±0.06 μ which are assigned to aromatic C=C skeletal in-plane vibrations. There is another pair of bands appearing at about 6.21±0.06 μ and 6.32±0.08 μ whose intensity varies greatly from compound to compound. Sometimes the C=C absorption partially obscures one or both of these bands. The latter bands seem to be characteristic of a substituted styrene system, and their origin is also ascribed to aromatic C=C skeletal in-plane vibrations. A band at 6.94-7.04 μ is found only in the compounds having a methylene group, and its origin is ascribed to C-H deformation modes. There are two cases where this band falls quite low, at 6.56 and 6.70 μ. The first case is 1,1,2-trifluoro-3-phenylcyclobut-2-ene. Molecules containing several fluorine atoms are known to show many drastic deviations from the normal due to strong interaction effects (29). The second case is that of the corresponding trichloro compound, and it is known that in the case of chlorine atoms there are also interaction effects, but they are usually less than in the case of fluorine (29).

TABLE I

An Infrared Spectra Correlation for a Number of Phenylcyclobutenes and Several Related Compounds

Band Assignments in Microns
(vs, very strong; s, strong; m, medium; w, weak)

Compound	C=C Stretch	Aromatic C=C Stretch	CH_2 Deformation	C=O Stretch	C-H Stretch
1,1-Difluoro-3-phenylcyclobut-2-ene	6.16 (s)	6.27(w), 6.34(m), 6.70(s), 6.90(s)	6.97(s)		3.28(m), 3.40(m)
1,1-Dichloro-3-phenylcyclobut-2-ene	6.17(s)	6.27(m), 6,34(m), 6.71(s), 6.91(s)	7.04(s)		3.27(m), 3.41(m)
1,1-Difluoro-2,2-dichloro-3-phenylcyclobutene	6.12(s)	6.18(m) (shoulder), 6.32(m), 6.68(s) 6.82(s)			3.30(m)
1,1-Difluoro-2,2-dichloro-4-phenylcyclobutene	6.27(vs)	6.15(m), 6.32(s) (shoulder), 6.71(s), 6.91(s)			3.27(m)
1,1,2-Trifluoro-2-chloro-3-phenylcyclobutene	6.12(vs)	6.20(m)(shoulder), 6.30(s), 6.67(vs), 6.86 (vs)			3.26(m)
2-Fluoro-1,1,2-trichloro-3-phenylcyclobutene	6.14(s)	6.26(m), 6.34(m), 6.70(s), 6.90(s)			3.26(m)
1,1,2-Trifluoro-3-phenylcyclobut-2-ene	5.87(s)	6.24(m), 6.35(w), 6.69(m), 6.93(s)	6.56(m)		3.30(m), 3.41(m)

TABLE I (Continued)

Band Assignments in Microns
(vs, very strong; s, strong; m, medium; w, weak)

Compound	C=C Stretch	Aromatic C=C Stretch	CH_2 Deformation	C=O Stretch	C-H Stretch
2-Fluoro-1,1-dichloro-3-phenylcyclobut-2-ene	5.85(s)	6.25(m), 6.34(w), 6.67(m), 6.89(s)	6.94(m)		3.28(m), 3.39(m)
1,1-Difluoro-2-chloro-3-phenylcyclobut-2-ene	6.08(s)	6.25(m), 6.36(w), 6.71(s), 6.91(s)	6.98(vs)		3.31(m), 3.42(m)
1,1,2-Trichloro-3-phenylcyclobut-2-ene	6.11(s)	6.26(m), 6.35(w), 6.72 (s), 6.92(s)	6.70(s) (shoulder)		3.32(m), 3.41(m)
1,1-Difluoro-2,4-dichloro-3-phenylcyclobutene	6.09(s)	6.25(m), 6.35(w), 6.68(s), 6.88(s)			3.26(m)
"1,1,2,4-Tetrachloro-3-phenylcyclobutene"	6.09(m)	6.71(s), 6.93(s), 6.32(s), 6.36(s)			3.26(m)
"1,1,2,2-Tetrachloro-3-phenylcyclobutene"	5.55(s) (?)	6.71(s), 6.92(s), 6.18(s), 6.31(s)			3.26(m)
1,1-Difluoro-2-t-butoxyl-3-phenylcyclobut-2-ene*	5.96(s)	6.23(w), 6.68(w), 6.89(s)	6.77(m), 7.16(s)		3.26(m) (shoulder), 3.35(s), 3.47(m) (shoulder)
1,1-Difluoro-2,2-diethoxyl-3-phenylcyclobutene	5.92(m)	6.69(m), 6.89(m) 6.13(m), 6.33(m)	7.12(m) (shoulder), 7.20(s)		3.26(m) (shoulder), 3.36(s), 3.45(s)

TABLE I (Continued)

Band Assignments in Microns

(vs, very strong; s, strong; m, medium; w, weak)

Compound	C=C Stretch	Aromatic C=C Stretch	CH_2 Deformation	C=O Stretch	C-H Stretch
Cinnamyl Alcohol	6.03(w)	6.25(m), 6.34(w), 6.69(s), 6.90(s)	?		3.30(s), 3.39(s), 3.51(s)
Methylstyrylcarbinol	6.03(w)	6.25(m), 6.34(w), 6.69(s), 6.90(s)	?		3.25(m) (shoulder), 3.30(s), 3.36(s), 3.49(s), 3.42(s)
3-Phenylcyclobut-2-enol	?	6.27(w), 6.36(w), 6.72(s), 6.91(s)	6.99(s)		3.27(s), 3.44(s)
2-Chloro-3-phenylcyclobut-2-enol	6.08(s)	6.25(m), 6.35(w), 6.71(s), 6.91(s)	6.98(s)		3.27(s), 3.43(s)
2,4-Dichloro-3-phenylcyclobutenol	6.08(m)	6.25(w), 6.33(w), 6.68(s), 6.89(s)			3.26(w), 3.32(m), 3.43(m)
Cyclobutanone			7.17(s)	5.58(vs)	3.36(s), 3.40(s) (shoulder)

TABLE I (Continued)

Band Assignments in Microns

(vs, very strong; s, strong; m, medium; w, weak)

Compound	C=C Stretch	Aromatic C=C Stretch	CH_2 Deformation	C=O Stretch	C-H Stretch
3-Phenylcyclobutanone		6.23(m), 6.69(m), 6.88(s)	7.24(s)	5.58(vs)	3.28(m), 3.32(s), 3.38(m), 3.44(m)
3-Phenylcyclobut-2-enone	6.38(s)	6.21(s), 6.29(s), 6.71(s), 6.88(s)	7.04(s)	5.67(vs)	3.26(m), 3.41(m)
2-Hydroxyl-3-phenylcyclobut-2-enone*	6.05(s)	6.24(w), 6.34(w), 6.89(s)	?	5.73(vs)	?
2-Fluoro-3-phenylcyclobut-2-enone	6.06(s)	6.69(m), 6.89(s), 6.13(m)(shoulder) 6.25(m)	6.98(m)	5.50(s), 5.61(vs)	--
2-Chloro-3-phenylcyclobut-2-enone	6.23(s) or 6.17(m) (shoulder)	6.71(m), 6.89(m), 6.34(m), 6.17(m) (shoulder) or 6.23(s)	7.03(m)	5.58(vs), 5.65(vs)	3.28(w), 3.44(w)
2,2-Dichloro-3-phenylcyclobutenone	6.39(s)	6.24(s), 6.32(s), 6.72(s), 6.89(s)		5.57(vs)	--

TABLE I (Continued)

Band Assignments in Microns

(vs, very strong; s, strong; m, medium; w, weak)

Compound	C=C Stretch	Aromatic C=C Stretch	CH_2 Deformation	C=O Stretch	C-H Stretch
2,2-Difluoro-3-phenylcyclobutenone	6.20(vs)	6.27(vs), 6.35(vs), 6.69(s), 6.86(s)		5.57(vs)	3.31(m)
2-Fluoro-2-chloro-3-phenylcyclobutenone	6.38(vs)	6.24(vs), 6.31(vs), 6.72(s), 6.89(s)		5.57(vs)	3.25(m)
2,4-Dichloro-3-phenylcyclobutenone	6.29(s)	6.40(s), 6.22(m) (shoulder) 6.76(s), 6.94(s)		5.58(vs), 5.65(vs)	3.31(m)
1,1-Difluoro-2-phenylcyclobutenone	6.20(s)	6.30(m), 6.36(m), 7.72(s), 6.89(s)		5.62(vs)	3.24(m)
Phenylcyclobutenedione*	6.45(s)	6.25(s), 6.34(w), 6.75(s), 6.90(m)		5.62(vs)	3.31(w)

*Spectra taken in chloroform. All other spectra in carbon tetrachloride or pure liquid. Difference between pure liquid spectra and spectra in carbon tetrachloride was only ± 0.02u.

SECTION 4

Derivatives of 3-Phenylcyclobutanone

3-Phenylcyclobutanone (VI) was first synthesized by Roberts, Kline and Simmons by catalytic reduction of either 2,2-dichloro-3-phenylcyclobutenone (III) or 2,4-dichloro-3-phenylcyclobutenone (V) and by Clemmensen reduction of III. The yields by these procedures were poor, and the product usually had to be purified through the semicarbazone (10,30). A large quantity of VI was required for heat of combustion studies and as an intermediate in a proposed synthesis of 1-phenylcyclobutene (30). A procedure which would give better yields of pure VI than had been obtained previously from III or V was desired.

Silversmith prepared 2-chloro-3-phenylcyclobut-2-enone (XIX) by treatment of 1,1-difluoro-2-chloro-3-phenylcyclobut-2-ene (XVIII) with concentrated sulfuric acid (15). XVIII is the dehydrochlorination product of the adduct XIII of styrene and 1,1-difluoro-2,2-dichloroethylene. In the course of the structure proof of XIX, he reported a 75% yield of 3-phenylcyclobutanone (VI) from the catalytic hydrogenation of XIX. The four-step synthesis of VI from the styrene via the adduct XIII, 1,1-difluoro-2,2-dichloro-3-phenylcyclobutane, seemed quite practical if the yields in each step could be increased. In the present research this was accomplished, and the overall yields of VI from styrene were 41-62%. The only step that could not be improved was the cycloaddition reaction which only gave 61-72% yields of XIII. It was found to be desirable in the hydrogenation step to use 20-30% palladium-on-charcoal catalyst since less active catalysts gave poorer yields. The infrared spectrum of VI freshly prepared by this procedure was identical with that of the ketone prepared from the semicarbazone (10,30). VI was somewhat unstable even when sealed in ampoules under nitrogen and allowed to stand in ordinary light for several weeks. Pure VI could not be recovered by distillation of the partially decomposed mixtures.

VI reacted with phenylmagnesium bromide to give a viscous oil which gave a crystalline acetate having the correct elemental analysis for 1,3-diphenylcyclobutanyl acetate (XLVII). The ultraviolet and infrared spectra of XLVII were in accord with this structure. XLVI was hydrolyzed at 100.2° in "80%" acetone-water which was 0.0951 N in perchloric acid. The infinity titer was 102% of the calculated. The pseudo-first-order hydrolysis constant was 18.7±0.7 hr.$^{-1}$. After about 90% reaction, the rate fell off rapidly. The uncatalyzed rate was not measured or was the nature of the hydrolysis product(s) determined. No equivalent hydrolysis rate studies on acetates have been reported. No further work was done with XLVII.

Reduction of 2-chloro-3-phenylcyclobut-2-enone (XIX) by sodium borohydride in methanol gave 2-chloro-3-phenylcyclobut-

2-enol (XLVIII). XLVIII reacted immediately with aqueous permanganate and bromine in carbon tetrachloride, but it did not give a precipitate with alcoholic silver nitrate. XLVIII was unstable in air and decomposed in several days to an oily brown liquid smelling of hydrogen chloride. A urethan derivative of XLVIII could not be prepared. Treatment of XEVIII with an acid chloride in pyridine gave highly-colored, polymeric products. A 4-nitrobenzoate ester was finally prepared from XLVIII and the acid chloride in benzene with an equivalent amount of pyridine. The acid-catalyzed hydrolysis of this ester is described in Section 5. Numerous unsuccessful attempts were made to obtain a sulfonate ester of XLVIII. The infrared spectrum of XLVIII was consistent with the assigned structure.

XLVIII took up two equivalents of hydrogen on catalytic hydrogenation to give a non-halogen-containing alcohol which has been assigned the <u>cis</u>-3-phenylcyclobutanol (XLIX) structure. This alcohol reacted rapidly with aqueous permanganate and slowly with bromine in carbon tetrachloride. XLIX gave an α-naphthylurethan, m.p. 125-127° and a 4-nitrobenzoate ester, m.p. 131-132°. The acid-catalyzed hydrolysis of the latter derivative is described in Section 5. The proton NMR spectrum of XLIX showed unsplit phenyl hydrogens, unsplit hydroxyl hydrogens, two types of tertiary hydrogens widely split, and methylene hydrogens split into

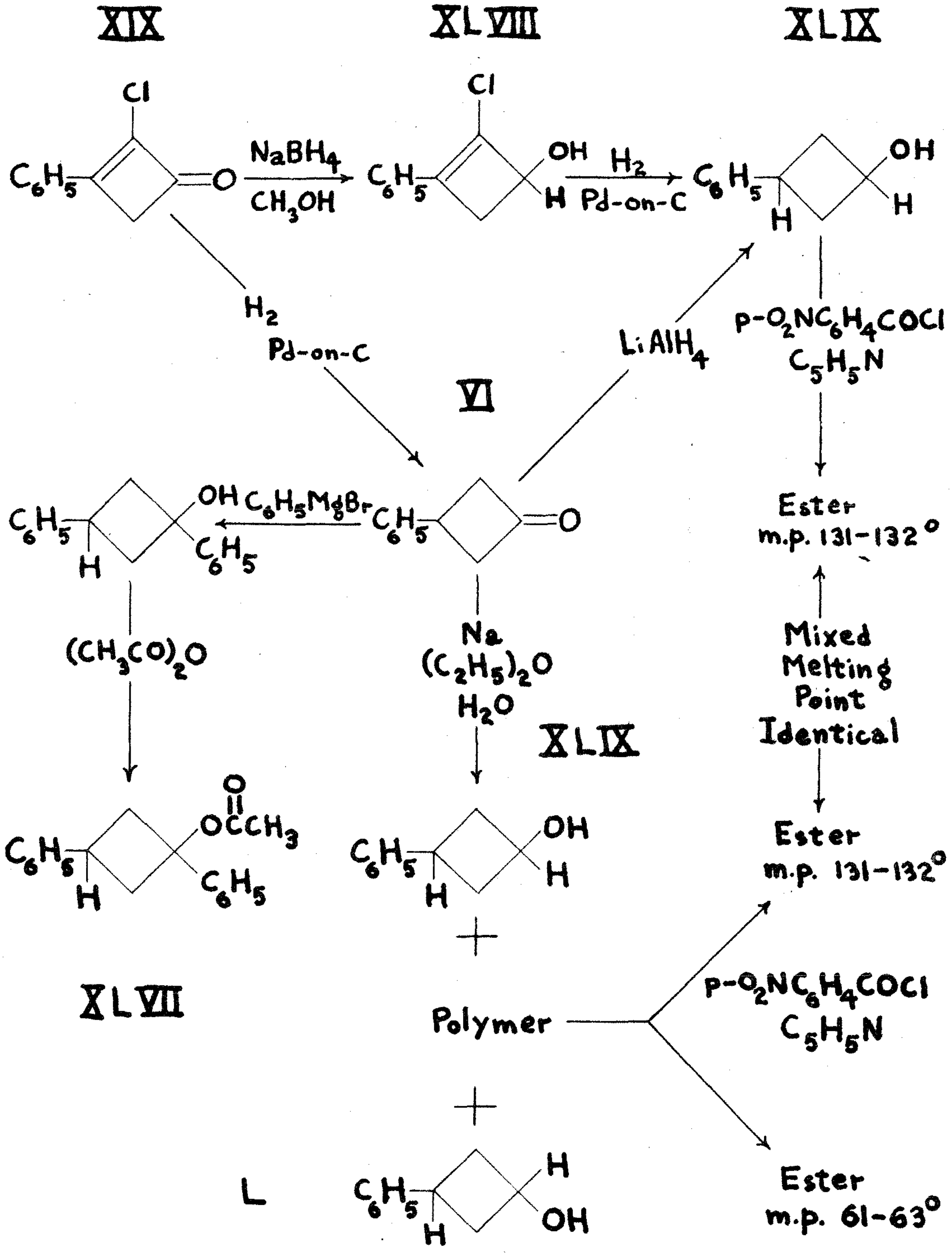

XIX
XLVIII
XLIX
Cl
C6H5
O
NaBH4
CH3OH
OH
H
H2
Pd-on-C
LiAlH4
p-O2NC6H4COCl
C5H5N
VI
C6H5MgBr
Ester
m.p. 131-132°
(CH3CO)2O
Na
(C2H5)2O
H2O
Mixed
Melting
Point
Identical
OCCH3
XLVII
Polymer
L
Ester
m.p. 61-63°

Fig. 9

either four or five peaks. The kinds and number of different protons observed is consistent with the 3-phenylcyclobutanol structure. The infrared spectrum of XLIX was also consistent with this structure.

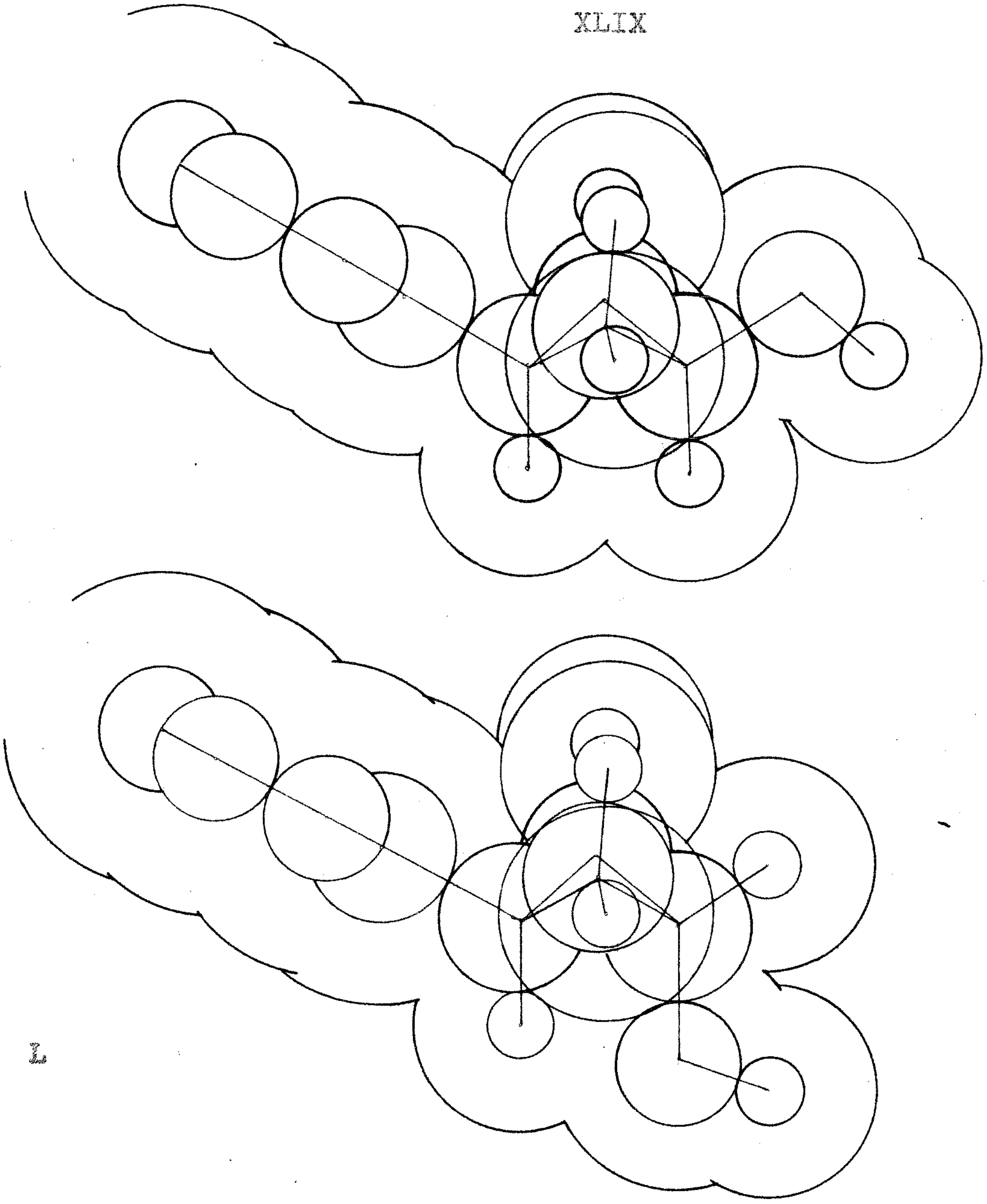
Reduction of 3-phenylcyclobutanone (VI) with lithium aluminum hydride gave only XLIX. Reduction of VI with sodium in wet ether gave mostly white polymer, and small yields of distillable material which appeared to be a mixture of starting material and several alcohols. The starting material (VI) employed in the sodium reductions was impure even though freshly distilled for each reaction, since at the time it was not realized that VI decomposed to a large extent on standing. Pure VI could not be recovered satisfactorily by distillation of the decomposition mixture. The infrared spectrum of the alcoholic product from the first such reduction carried out was different from that of XLIX but consistent with that expected for the 3-phenylcyclobutanol structure except for a strong sharp band at 5.75 μ. This material had been extracted with bisulfite and did not give a reaction with 2,4-dinitrophenylhydrazine reagent, so it would seem that this band was not due to carbonyl absorption. The origin of the band at 5.75 μ is unknown. The material gave a 4-nitrobenzoate ester, m.p. 61-63°, which had the correct elemental analysis for the corresponding 3-phenylcyclobutanol derivative. The acid-catalyzed hydrolysis of the ester is described in Section 5. Several of the crude products obtained from the sodium in wet ether reductions were treated directly with 4-nitrobenzoyl chloride in pyridine, and oily mixtures of esters were obtained. From these oils, the ester, m.p. 131-132°, was isolated by fractional crystallization. After evaporation of the solvent from the mother liquors, the remaining oil deposited after several days to several weeks small amounts of the ester m.p. 61-63°. The ultraviolet spectra of these two esters were identical, but they were very different from the spectrum of the corresponding ester of 3-phenylcyclobut-2-enol (XXI) which contained the substituted phenylcyclobutene chromophore. The latter compound had three sharp bands in the region 200-220 mμ which are characteristic of the styrene chromophore and of the other 3-phenylcyclobut-2-enes observed in the present work. The ultraviolet spectrum of the two former compounds had no fine structure in this region at all. The ester m.p. 61-63° has been assigned the <u>trans</u>-3-phenylcyclobutanyl (L) structure.

XLIX, <u>cis</u>-3-phenylcyclobutanol, was treated under conditions which have been employed to equilibrate isomeric alcohols in the norbornyl series (31) but only a 25% recovery of distillable material was realized. Another 60% of the product was accounted for as polymer. The liquid product gave an α-naphthylurethan, m.p. 85-89°, which did not have the correct elemental analysis for the corresponding isomer of XLIX. The infrared spectrum of the isomerization product was characteristic of an alcohol but different from those of the starting material and the alcoholic materials from the sodium in wet ether reductions having several strong bands which were either very weak or completely absent in the latter materials.

The assignment of the cis-structure to the alcohol obtained from the catalytic reduction of 2-chloro-3-phenylcyclobut-2-enol (XLVIII) was made because cis-addition of hydrogen to a double bond has usually been observed (32), and the approach of the molecule to the catalyst surface with the side having the hydroxyl group up should be unfavorable. If the approach to the catalyst took predominantly this course with subsequent cis-addition of hydrogen, a trans relation of the phenyl and hydroxyl groups would result. The opposite approach would result in a cis relation of these two groups. The stereochemistry and exact mechanism of the subsequent hydrogenolysis of the chlorine atom is assumed not to effect the configuration of the phenyl and the hydroxyl groups. There is no evidence bearing on this point in the literature. The reduction of 3-phenylcyclobutanone (VI) by lithium aluminum hydride gave only the cis-alcohol (XLIX). This result suggests that the 3-phenyl group provides considerable steric hindrance to approach of the relatively small lithium aluminum hydride molecule and thus the hydride can essentially only attack the carbonyl group on one side. This type of situation has been termed "steric approach control" (33). The reduction of VI by sodium in wet ether should give the thermodynamically most stable isomer, which at first sight was assumed to be the trans isomer in the 3-phenylcyclobutanol system.

The fact that mixtures of the two isomers were apparently formed in the sodium in wet ether reduction of VI suggests that perhaps the configurations are of nearly equal energy because of the puckering of the four-membered ring. Figure 10 illustrates the conformations of XLIX and L if the cyclobutane ring is non-planar. Cyclobutane itself is known to be non-planar from electron diffraction studies (38). Figure 10 suggests the two isomers might not differ very much in energy. The main difference is the 1,3-interaction of hydroxyl and hydrogen present in the trans-isomer. Figure 11 illustrates the conformations of XLIX and L if the cyclobutane ring is nearly planar. All the groups must be eclipsed in the four-membered ring. The trans-isomer (L) might be the more thermodynamically stable because of the 1,3-interaction of the hydroxyl group and the bulky phenyl group which should be present in the cis-isomer.

Figures 10 and 11 are approximately to scale with the small circles representing the covalent radii (87) and the large concentric circles the van der Waals radii given by Pauling (87).



XLIX

L

Fig. 10. Conformation of XLIX and L if cyclobutane ring is non-planar

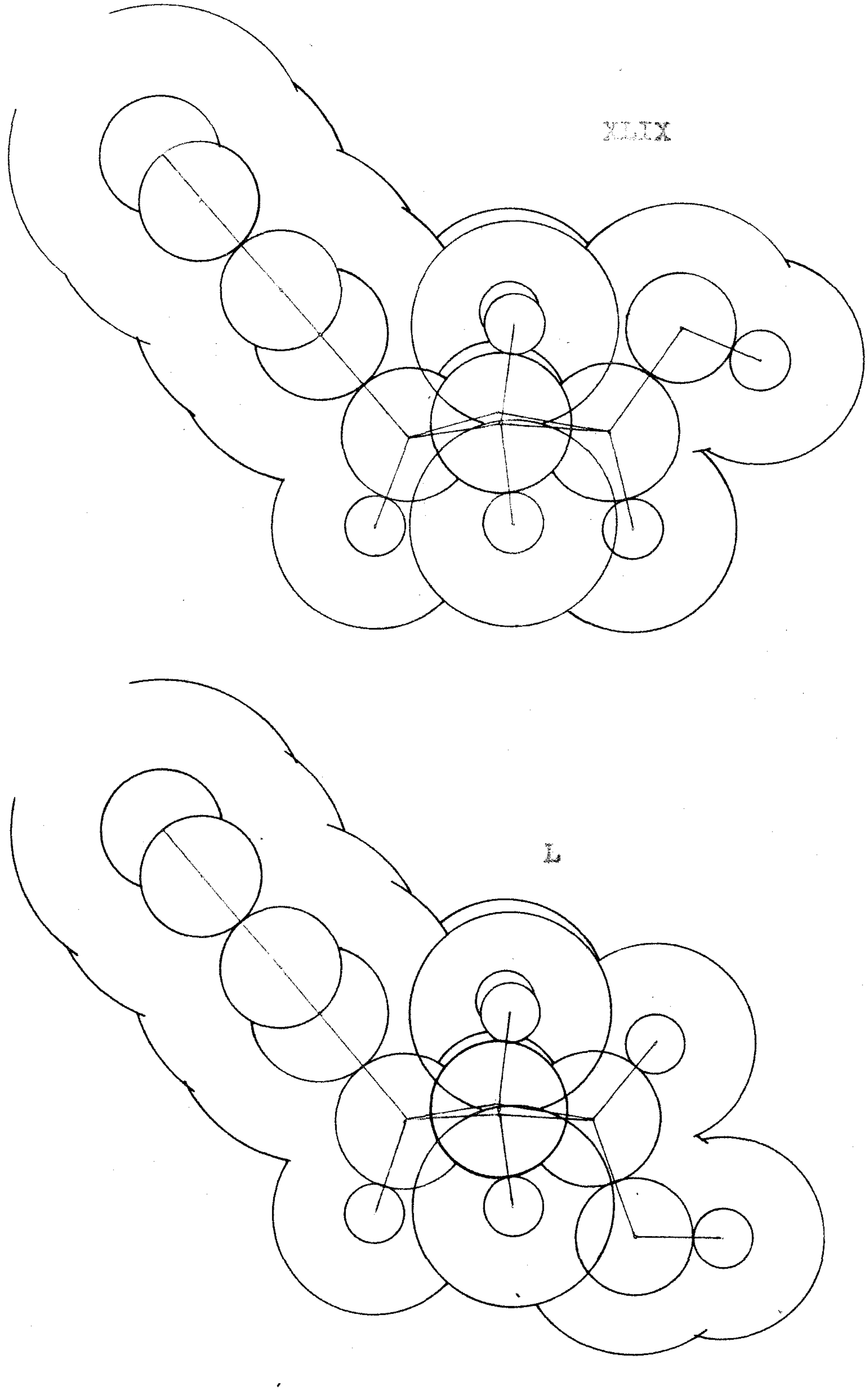


Fig. 11. Conformations of XLIX and L if cyclobutane ring is nearly planar

SECTION 5

Solvolysis of Some 3-Phenylcyclobutyl and 3-Phenylcyclobut-2-enyl 4-Nitrobenzoates

3-Phenylcyclobut-2-enyl System.--The importance of 1,3-overlap of a pair of 2p-orbitals of carbon has been treated theoretically by the molecular orbital method for several simple systems. Simmonetta and Winstein (34) have shown that for the 3-vinyl, 3-dienyl, and 3-phenyl systems the 1,3-orbital interaction of a π-electron system with a developing 2p-orbital at C-1, the reaction center, is predicted to provide significant stabilization of the carbocation formed. A similar treatment of the 7-norbornenyl carbocation by Woods, Carboni and Roberts (35) predicts a net stabilization energy greater than that computed for the most favorable open-chain "homoallylic" carbocation discussed by Simmonetta and Winstein. The geometries of the "homoallylic" and 7-norbornenyl systems are such that the axes of the 1- and 3-2p-orbitals can never be parallel in the conformations in which the internuclear distance between C-1 and C-3 is smallest and the steric strain the least. Thus maximum π-overlap is impossible since two 2p-orbitals must have their axes parallel for maximum overlap at a given internuclear distance. The effect on the stabilization of the types of systems discussed above by a change of hybridization at the 1- and/or 3-positions resulting in sp^m-p or sp^n-sp^o overlap (m, n and o designating the percentage of p-character of the hybrid bond) instead of p-p overlap has not been considered from a theoretical point of view.

There are numerous cases in the literature (36) of solvolysis reactions in a series of related compounds where the rate differences and products of the systems having π-electron systems attached to C-2 can best be explained by some sort of 1,3-interaction. For example, anti-7-norbornenyl tosylate reacts 10^{11} times faster in acetolysis than 7-norbornyl tosylate (37). With the corresponding chlorides in 50% ethanol-water, the rate difference is greater than 10^5 (38).

In the nearly planar four- and five-membered carbon ring systems, two 2p-orbitals in a 1,3-relation can only have their axes very near to parallel unless the ring is substantially warped. For a given 1,3-internuclear distance, 1,3-π-overlap is predicted to be a maximum when the 1- and 3-2p-orbitals are parallel. The planar 3-methylenecyclobutyl system has favorable geometry for this type of interaction. A simple molecular orbital calculation on this system employing as the 1,3-resonance integrals either 0.2β and 0.5β leads to the prediction that the "homoallylic" carbocation should have stabilization energy greater than the classical carbocation by 0.0396β and 0.2360β or 0.8 and 4.7 kcal./mole, respectively, where β is taken as -20 kcal./mole.

In the cyclobut-2-enyl system a slightly different type of 1,3-interaction than was discussed above is possible. Here the 1- and 3-2p-orbitals of an allylic system could overlap. Simple molecular calculations were carried out employing as before either 0.2β or 0.5β for the 1,3-resonance integral. The delocalization energy of the carbocation is predicted to be 20.7 to 27.5 kcal./mole, respectively. These values are significantly greater than the stabilization predicted for the allyl cation (16.6 kcal./mole). These results suggest that if 1,3-interaction is not nullified by other electrical interactions, then a suitable cyclobut-2-enyl derivative should undergo solvolysis reactions relatively more easily than a normal secondary allylic derivative. More specifically, it was predicted that a 3-phenylcyclobut-2-enyl derivative should show a significant rate enhancement in solvolysis over that of an α-methyl-γ-phenylallyl derivative.

It should be pointed out that several very important factors have been completely neglected in the discussion presented above. The magnitude of σ-bond strain in the cyclobut-2-enyl system might be such that any direct experimental comparison of reactivity with the corresponding open-chain derivative would be deceptive. Several theoretical treatments of the strain energies of cyclobutane and cyclopropane have been made (26), but only one such treatment for the cyclobutene system has been reported (39). Experimental evidence in the form of heat of combustion studies for the cyclobutene system is lacking. A heat of hydrogenation study has been reported (91) for 1-methylenecyclobutene, 1-methylcyclobutene, 1,3-dimethylenecyclobutane and 1-methyl-3-methylenecyclobutene. Schomaker and coworkers have discussed the importance of interelectronic repulsion of non-bonded carbon atoms in both cyclobutane (38) and cyclobutene (39).

They ascribed the slight increase in C-C bond lengths in cyclobutane to interelectronic repulsions and the normal C-C bond lengths in cyclobutene to the balancing of interelectronic repulsions by hyperconjugation. The interplay of these two effects in the cyclobut-2-enyl and cyclobut-2-enone systems is unknown. All the molecular orbital calculations made above neglect configurational interactions, σ-bond compressions, and σ-π-interactions. Repulsions between pairs of hydrogens in the eclipsed positions would be expected to increase the energy of the four-membered ring systems (26). Of all the effects mentioned above, σ-bond strain and H-H repulsions are thought to be the most important (26) and probably amount to about 90% or greater of the total destabilizing energy for cyclobutane and cyclobutene systems.

The σ-bond strain has been estimated to make up about 80% of the steric strain of the four-membered ring system (26). It is possible to make a crude estimate of the increase due to this source when a cyclobut-2-enyl derivative ionizes to the carbonium ion. The C_4-C_1-C_2 angle of cyclobutene is about 86.0° (39). This represents a bond bending of about 23.5° from the normal angle of 109.5° for sp^3 hybridization. For the cyclobut-2-enyl carbocation the bond bending from 120° (normal sp^2 hybridization) (46) to about 86.0° amounts to an angle strain of 34.0°. Force constant data suggest that the strain energy per angle is given by $17.5^{\circ}\ \theta^2$ cal./mole, where

θ is the angle of bending in degrees (26). This relation gives the increase in strain energy on going to the carbocation as 10.5 kcal./mole which is of the same order of magnitude as the extra stabilization predicted for 1,3-interaction (4.1 to 10.9 kcal./mole) in the cyclobut-2-enyl carbocation and suggests that the two effects might nearly cancel or that the strain could be somewhat more important (perhaps 4-6 kcal./mole greater) than 1,3-interaction. A similar estimate of the increase in strain energy for the cyclobutyl system gives 9.2 kcal./mole which suggests that rates of displacement reactions on the cyclobutyl system would be lower than for secondary aliphatic derivatives. If this increase in energy was pure energy of activation then this would correspond to a rate retardation of 6.6×10^6 at 25°C. This prediction has been verified for those cyclobutyl systems where anchimeric assistance with rearrangement does not occur. The solvolysis of 1-chloro-1-methylcyclobutane and the displacement of cyclobutyl bromide by iodide ion are both significantly slower than the corresponding reaction of aliphatic compounds (47).

To demonstrate experimentally the interplay of the various factors discussed above in the cyclobut-2-enyl system, the 4-nitrobenzoates of 3-phenylcyclobut-2-enol, 2-chloro-3-phenylcyclobut-2-enol, cinnamyl alcohol and methylstyrylcarbinol were prepared, and their acid-catalyzed hydrolysis in "80%"

TABLE II

Summary of Kinetic Data for Some 4-Nitrobenzoates on Hydrolysis in "80%" Acetone-water at 100.20±0.02°

Alcohol	k_1', hr.$^{-1}$ (1)	k_1, hr.$^{-1}$ x 10^2
Cinnamyl Alcohol	0.0831±0.0049	
Methylstyrylcarbinol	7.81±0.22 (2)	
Cyclobutanol	0.0402±0.0020	
cis-3-Phenylcyclobutanol	0.0369±0.0026	
trans-3-Phenylcyclobutanol	0.0457±0.0063 (2)	
2-Chloro-3-phenylcyclobut-2-enol	0.0376±0.0025	
3-Phenylcyclobut-2-enol	1.006±0.019	2.63±0.13 (2)
cis-5-Methylcyclohex-2-enol	0.799 (3)	1.24 (3)
trans-5-Methylcyclohex-2-enol	4.51 (3)	1.33 (3)

(1) Perchloric acid concentration at 100° of 0.0862 N.

(2) Results from only one kinetic run.

(3) From the work of H. L. Goering and E. F. Silversmith, J. Am. Chem. Soc., _77_, 6249-6253 (1955).

acetone-water at 100.2° were carried out in the present research. The results are summarized in Table I, and the relative rates are 12.1, 0.45, 1.00 and 94, respectively. These results suggest that 3-phenylcyclobut-2-enyl derivatives do not react as fast as acyclic α-methyl-γ-phenylallyl derivatives. Introduction of an α-methyl group into the γ-phenylallyl system appears to bring about a 94-fold increase in the rate, and this is in agreement with the effects produced by similar substitution in other systems. The rate difference between the 3-phenylcyclobut-2-enyl and the 2-chloro-3-phenylcyclobut-2-enyl systems is easily explained as due to the strong inductive effect of the vinyl chlorine atom in the latter. This inductive effect will be discussed in more detail later.

There are no kinetic studies in the literature on the acid-catalyzed hydrolyses of other γ-phenylallyl 4-nitrobenzoate esters, but Goering and Silversmith (48) have made an extensive study of the acid-catalyzed hydrolyses of the <u>cis</u>- and <u>trans</u>-5-methyl-3-cyclohexenyl 4-nitrobenzoates under conditions nearly identical to those employed in the present work. The relative rates for these compounds based on that of the cinnamyl ester are 9.6 and 54, respectively. <u>A priori</u> it would be predicted that these two substances should have nearly the same hydrolysis rates unless some configurational or solvation effect is important. Goering and coworkers had previously examined these same systems by the uncatalyzed solvolyses of the chlorides (49) and the acid-phthalates (50). In no case did they observe a rate difference between the cis- and trans-systems approaching that observed in the acid-catalyzed hydrolyses of the 4-nitrobenzoates. Goering and Silversmith also investigated the uncatalyzed solvolyses of the cis- and trans-4-nitrobenzoates in "80%" acetone-water at 100° and found the rates to be nearly the same, 1.24×10^{-2} $hr.^{-1}$ and 1.33×10^{-2} $hr.^{-1}$, respectively. The observed polarimetric rates were $2.18 \times 10^{-2} hr.^{-1}$ and $2.04 \times 10^{-2} hr.^{-1}$, thus indicating considerable internal return (48). In the acid-catalyzed hydrolyses they observed no internal return. Apparently the factor responsible for the rate differences in the catalyzed hydrolyses is not present in the uncatalyzed reactions. The rate of the uncatalyzed solvolysis of 3-phenylcyclobut-2-enyl-4-nitrobenzoate was found to be 2.63×10^{-2} $hr.^{-1}$. This is an initial rate constant since the rate decreases with time due to an apparent isomerization or a mass-law effect; neither of these possibilities was investigated. Thus the 3-phenylcyclobut-2-enyl system is about twice as reactive as the cyclohexenyl systems discussed above. A priori without consideration of 1,3-interaction or steric strain, the 3-phenylcyclobut-2-enyl system would be predicted to be more reactive than the cyclohexenyl system because simple molecular orbital calculations show that introduction of a phenyl group into an allylic system increases the delocalization energy of the carbonium ion from 16.6 kcal./

mole to about 27.7 kcal./mole (see Part II). If the significance of the unknown factors influencing the rates of the acid-catalyzed hydrolyses had been realized earlier in the present study, more attention would have been directed toward measurement of the uncatalyzed solvolyses rates. It would have been interesting to know the rate for the uncatalyzed solvolysis of methylstyrylcarbinol 4-nitrobenzoate, a good acyclic analog of the 3-phenylcyclobut-2-enyl system.

The difference between the rates of acid-catalyzed hydrolysis of the 2-chloro-3-phenylcyclobut-2-enyl and 3-phenylcyclobut-2-enyl 4-nitrobenzoates would seem to be too small for reactions in which carbonium ion intermediates are formed. The rates relative to cinnamyl 4-nitrobenzoate are 0.45 and 12, respectively, or a rate ratio of 1:27. Based on the work of Winstein, Grunwald and Ingraham (51) with the *cis*- and *trans*-2-substituted cyclohexyl brosylates in acetolysis, this rate difference would be expected to be about 1:2x10^3 at 100°. These authors evaluated the increase of electrostatic energy due to dipole-dipole repulsion between a *trans*-2-substituted electro-negative group and the dipole of the partially broken C-O bond in the cyclohexyl system. Since the model used in the treatment above was the assumed transition state, the energy obtained is a part of the energy of activation and can be used to calculate relative rates by the relation $\Delta F^* - \Delta F_o^* = RT \ln k/k_o$. The left side of this equation is the electrostatic energy calculated from the relationship

$\Delta F^*-\Delta F_o^* = 1.439\times10^{13}\ M_1M_2D_E^{-1}r^{-3}\ (\cos e-3\cos\theta\cos\theta')$ kcal./mole where M_1 is the dipole moment due to the partially broken C-O bond, M_2 the dipole of the neighboring group, D_E the dielectric constant taken as 1.23 (51), r the length of the vector joining centers of the dipoles, angle e the angle between M_1 and M_2, θ the angle between M_1 and r, and θ' the angle between M_2 and r. In a similar calculation for the 2-chloro-3-phenylcyclobut-2-enyl system, M_1 was taken to be 4.6 Debye, one-half the moment of 9.2 Debye calculated for complete ionization at the assumed transition-state distance of 1.93 Å for the C-O bond (51). The four-membered ring was assumed to be planar, and the dimensions and angles were taken from the electron diffraction work of Goldish, Medberg and Schomaker (39) on cyclobutene. The C-Cl dipole was taken as 1.44 Debye (52). The electrostatic energy obtained is 6.14 kcal./mole, and this is equivalent to a relative rate ratio of $1:4.1\times10^3$ at 100° for the 2-chloro-3-phenylcyclobut-2-enyl and 3-phenylcyclobut-2-enyl systems, respectively. This calculation is for the uncatalyzed reaction, and the assumed transition-state gave good results in the case of the *cis*-2-substituted cyclohexyl brosylates (51).

In the acid-catalyzed reactions studied in the present research, the proton is assumed to add to the carbonyl group of the ester group (88). The interaction energy of the positive charge and the chlorine dipole can be estimated by the formula $\Delta F^*-\Delta F_o^* = 1.439\times10^{13}\ qM_2D_E^{-1}r^{-2}$ where q is the charge. Several different models of the transition-state have been investigated. If the charge is well developed at the transition-state then it can be considered to be either at C-1 or about one-half at C-1 and one-half at C-3. The energy calculated for these two cases should not differ by much because of the geometry of the four-membered ring. A calculation for the former model gives a value of 14 kcal./mole or a rate ratio of 1:1.7x10^8 at 100°. This result suggests that the charge development at C-1 is not very great. If a model is assumed with the center of charge at the location of the C-O dipole with geometry of the transition-state the same as that used in the paragraph above for the uncatalyzed reaction then the electrostatic energy is still 8.1 kcal./mole or a rate ratio of 1:5.9x10^4 at 100°. When the center of the positive charge is taken as the location of the oxygen atom of the C-O bond and the C-O bond length taken as 1.46 Å, the energy is 5.3 kcal./mole corresponding to a relative rate ratio of 1:1.3x10^3. These results suggest that the transition-state is very close to the proton addition step. The positive charge after proton addition can be considered to be about one-half on each oxygen atom of the ester group. The average location of the center of positive charge is then at a point farther from the four-membered ring than has been assumed so far. Electrostatic calculations were made for two other models of the transition-state in which the center of positive charge was assumed to be in the

C-O bond direction and at distances of 1.80 and 2.20 Å. The corresponding electrostatic energies are 4.2 and 3.1 kcal./mole or rate ratios of about 1:290 and 1:68, respectively. The observed rate ratio of 1:27 for the acid-catalyzed hydrolysis is more in line with the latter calculation. The experimental results and the calculations presented above suggest that perhaps acyl-oxygen cleavage is more important than alkyl-oxygen cleavage. Unfortunately, no other studies of β-chlorallyl derivatives in solvolysis or hydrolysis reactions have been reported in the literature so no other comparisons can be made at present.

The results of the present study with the 3-phenylcyclobut-2-enyl system suggest that it is less reactive than an α-methyl-γ-phenylallyl system and more reactive than the cyclohexenyl system. The simple theories presented above predict that the strain energy might slightly override any extra stabilization due to 1,3-interaction. The observation that the acid-catalyzed rates of hydrolysis are subject to some unknown conformational or solvation effects not present in the uncatalyzed solvolysis reactions or possibly do not proceed by alkyl-oxygen cleavage suggests that the former method is not very satisfactory for estimating relative carbonium ion (or ion pair) stabilities. Aryl sulfonate esters and halides have proved in general to be the most satisfactory leaving groups to employ when estimating carbonium ion stabilities. Numerous attempts were made in the present research to prepare arylsulfonates of several γ-phenylallyl alcohols without success, and thus the 4-nitrobenzoate esters had to be used. 1,1-Dichloro-3-phenylcyclobut-2-ene, 1,1,2-trichloro-3-phenylcyclobut-2-ene, and several other 3-phenylcyclobut-2-enyl gem-dichlorides (see Section II) were synthesized in the present work. Kinetic studies with these chlorides might show much more about the nature of the 3-phenylcyclobut-2-enyl system than the present study with 4-nitrobenzoates, particularly because the solvolysis rates of a great number of allylic chlorides and several gem-dichlorides have been reported in the literature (84).

3-Phenylcyclobutyl System.--The cyclobutyl, 1-, 2-, and 3-methylcyclobutyl systems have been extensively studied in solvolytic reactions (36,53). In an attempt to assay the effect of phenyl substitution on the reactivity of the cyclobutyl system, the acid-catalyzed hydrolyses in "80%" acetone-water at 100° of cyclobutyl, cis- and trans-3-phenylcyclobutanyl 4-nitrobenzoates were studied. The relative rates are 1.00, 0.92 and 1.1, respectively. These rates are the same within experimental error. Using Taft's polar substituent constant for the $C_6H_5(CH_2)_2$- group as 0.080 and the ρ for solvolysis of brosylates as -4.29 (54), the rate retarding inductive effect of phenyl is predicted to be about 2.2 for an ionization mechanism. The abnormally large solvolytic reactivities of other cyclobutyl systems have been adequately explained in terms of non-classical unsymmetrical "bicyclobutonium" intermediates (36,53). It might be possible that a phenyl group increases the stabilization of these intermediates to such an extent that the inductive effect predicted above is canceled.

The 3-phenylcyclobutanol system could more profitably be studied by the methods used earlier with the cyclobutyl- and cyclopropylcarbinyl systems (53).

SECTION 6

Experimental

Analyses were performed by Dr. Adalbert Elek, Elek Microanalytical Laboratories, Los Angeles, California. Infrared absorption spectra were determined using a Perkin-Elmer double-beam infrared spectrometer, Model 21. Ultraviolet absorption spectra were obtained using a Cary recording spectrophotometer, Model 11M. Vapor chromatograms were obtained with a Perkin-Elmer Vapor Fractometer, Model 154-B. The nuclear magnetic resonance spectra were obtained at 40 mc. with the Varian Associates high resolution spectrometer (V-4300B) with 12-inch magnet.

1,1-Difluoro-2,2-dichloro-3-phenylcyclobutene.--A mixture of 45 g. (0.441 mole) of phenylacetylene (Farchan Research Laboratories) and 63.2 g. (0.461 mole) of 1,1-difluoro-2,2-dichloroethylene (Genetron 1112a, General Chemical Division) was heated in a sealed glass combustion tube at 130° for 12 hours. The tube was cooled in a Dry Ice bath and opened. The thick black syrup was distilled slowly through a 12-cm. Vigreux column. The product (83-91 g., 80-88%) had b.p. 66-69° (0.5-0.6 mm.) and $n^{25}D$ 1.5423; lit., b.p. 109-111° (5 mm.), $n^{25}D$ 1.5435 (10).

1,1-Difluoro-2,2-dichloro-3-phenylcyclobutane.--A mixture of 52 g. (0.500 mole) of styrene and 74 g. (0.552 mole) of 1,1-difluoro-2,2-dichloroethylene was heated in a sealed glass combustion tube at 130° for 24 hours. The tube was cooled in a Dry Ice bath and opened, and the light-tan syrup was distilled through a 12-cm. Vigreux column. The product (72-88 g., 61-72%) had b.p. 78-82° (1 mm.) and $n^{25}D$ 1.5105; lit., b.p. 73.8-74.2° (1 mm.), $n^{25}D$ 1.5103 (15). Considerable light-brown polymeric residue remained in the distillation pot.

1,1,2-Trifluoro-2-chloro-3-phenylcyclobutene.--A mixture of 35 g. (0.343 mole) of phenylacetylene and 45 g. (0.348 mole) of 1,1,2-trifluoro-2-chloroethylene (Genetron 1113, General Chemical Division, and experimental samples from E. I. du Pont de Nemours and Co., Inc.) was heated in a sealed glass combustion tube at 130° for 12 hours. The tube was cooled and opened as described above. Distillation of the thick black mixture through a 12-cm. Vigreux column gave 61-66 g. (81-88%) of colorless product, b.p. 51-54° (1 mm.), $n^{25}D$ 1.5517; lit., b.p. 88-90° (0.4 mm.), $n^{25}D$ 1.5499 (11); Smutny gives $n^{25}D$ 1.5515 (19).

1,1-Difluoro-2-chloro-3-phenylcyclobut-2-ene.--In a 2-l. round-bottomed flask 133 g. (2.01 moles) of potassium hydroxide (assay 86%) was dissolved in 1 l. of 95% ethanol. The solution was cooled, the flask equipped with an Allihn condenser filled with water, and 462.5 g. (1.95 moles) of 1,1-difluoro-2,2-dichloro-3-phenylcyclobutane was poured slowly with vigorous swirling through the condenser into the alcoholic base solution at such a rate that the exothermic reaction did not get out of control. External cooling was occasionally necessary. After the addition was complete (about 5 minutes), the mixture was swirled intermittently and allowed to stand 12 hours. The mixture was poured into about 2 l. of water, and the resulting two-phase mixture was allowed to stand in the refrigerator for an hour. The lower organic layer was separated and the water layer extracted four times with ether (total volume about 1.5 l.). The extracts were combined with the organic layer, and the resulting ether solution was dried in four stages with anhydrous magnesium sulfate. After the ether had been distilled through a straight distilling head, the residue was fractionated through a 20-cm. Vigreux column to give 356-372 g. (91-95%) of colorless product, b.p. 44-48° (0.6 mm.), $n^{25}D$ 1.5388; lit., b.p. 66-67° (1 mm.), $n^{25}D$ 1.5390 (15).

<u>1,1,2-Trifluoro-3-phenylcyclobut-2-ene</u>.--To a solution of 31 g. (0.47 mole) of potassium hydroxide (assay 86%) in 150 ml. of 95% ethanol, 100 g. (0.454 mole) of 1,1,2-trifluoro-2-chloro-3-phenylcyclobutane (prepared by Franco Scardiglia) was added at such a rate that the reaction did not get out of control. Sometimes external cooling was necessary. After the addition was complete, the mixture was swirled several times during a period of five hours and then worked up in the manner described for 1,1-difluoro-2-chloro-3-phenylcyclobut-2-ene. The last traces of solvent remaining

in the residue after distillation of the ether were removed under reduced pressure. Some mineral oil was added to the product as a still base, and the mixture was distilled through a 12-cm. Vigreux to give 74.5 g. (91%) of colorless product, b.p. 38-42° (1 mm.), $n^{25}D$ 1.4990, m.p. 18-20°; lit., b.p. 64.0-65.5° (1.2 mm.) (15). This material decomposes on standing at room temperature for any extended period of time, but a sample was kept for a year in the refrigerator without any apparent decomposition.

1,1-Difluoro-3-phenylcyclobutane. A. From 1,1-Difluoro-2,2-dichloro-3-phenylcyclobutene.--In a citrate bottle were placed 111 g. (0.471 mole) of 1,1-difluoro-2,2-dichloro-3-phenylcyclobutene, 75 g. (0.914 mole) of anhydrous sodium acetate, 3 g. of 10% palladium-on-charcoal catalyst, and 150 ml. of reagent methanol. The mixture was hydrogenated at about 60 psi until the calculated amount of hydrogen had been taken up, i.e., about a week. With more active catalyst, the hydrogen uptake was much more rapid. The catalyst and solids were removed by filtration and washed several times with methanol. The methanol solution was poured into 500 ml. of water, and this mixture was extracted six times with ether (total volume about 1 l.). The ethereal solution was dried in four stages with anhydrous magnesium sulfate, and the ether was distilled through a straight distilling head. The residue was distilled to give 61-66 g. (80-83%) of colorless product, b.p. 32-40° (0.8-1.0 mm.),

$n^{25}D$ 1.4840 (lit., b.p. 80.1-88.3° at 20 mm., $n^{25}D$ 1.4828 for 1,1-difluoro-3-phenylcyclobutane) (10) and 12 g., b.p. 52-65° (0.8-1.0 mm.), $n^{25}D$ 1.5050, which is a mixture of chlorofluorohydrocarbons. The latter material can be rehydrogenated to give more of the desired product.

B. From 1,1-Difluoro-2,2-dichloro-3-phenylcyclobutane.-- In a citrate bottle 30 g. (0.447 mole) of potassium hydroxide (assay 86%) was dissolved in 100 ml. of reagent methanol. After cooling this solution, 100 g. (0.420 mole) of 1,1-difluoro-2,2-dichloro-3-phenylcyclobutane was added with swirling at such a rate that the vigorous exothermic reaction did not get out of control; sometimes cooling with an ice bath was necessary. After the addition was complete, the bottle was flushed with nitrogen, and 3 g. of 10% palladium-on-charcoal catalyst was added. This mixture was hydrogenated at 60 psi until approximately one equivalent of hydrogen had been taken up, and then 28 g. (0.413 mole) more of potassium hydroxide was added. The mixture was hydrogenated until the second equivalent of hydrogen had been taken up. Usually it took about 6 hours for the uptake of two equivalents of hydrogen. The mixture was worked up as described above. Distillation through a 10-cm. Vigreux column gave 55-62 g. (79-88%) of colorless product, b.p. 69-71° (7.5 mm.), $n^{25}D$ 1.4840 (lit., $n^{25}D$ 1.4828) (11) and 3-9 g. of material b.p. 78° and higher (7.5 mm.), $n^{25}D$ 1.5170.

<u>1,1-Difluoro-3-bromo-3-phenylcyclobutane.</u>--In a dry 500-ml. standard-taper round-bottomed flask fitted with a reflux condenser were placed 50 g. (0.297 mole) of 1,1-difluoro-3-phenylcyclobutane, 53 g. (0.298 mole) of N-bromosuccinimide (Arapahoe Chemical, Inc.), 250 ml. of reagent carbon tetrachloride, and 0.5 g. of benzoyl peroxide. The mixture was heated until the vigorous exothermic reaction started, and then the heating mantle was removed until the reaction no longer refluxed from its own heat. The reaction mixture was refluxed for two hours, cooled, the succinimide removed by filtration, and the carbon tetrachloride distilled under reduced pressure at a temperature below 40°. A series of Dry Ice cooled traps in the system facilitated the latter process. The residue was distilled through a 10-cm. Vigreux column using a magnetic stirrer and an oil bath. A heating mantle should not be used as decomposition may result from overheating; a pressure of about 1 mm. or less should be used. Glass apparatus with etched walls can cause the product to decompose. On distillation, 66-73 g. (91-99%) of colorless 1,1-difluoro-3-bromo-3-phenylcyclobutane, b.p. 49-53° (less than 1 mm.), $n^{25}D$ 1.5276, was obtained. This material can be kept for several months in the refrigerator under nitrogen without any apparent decomposition.

<u>Anal</u>. Calcd. for $C_{10}H_8BrF_2$: C, 48.61; H, 3.67; Br, 32.34. Found: C, 48.51; H, 3.60; Br, 32.26.

The infrared spectrum of 1,1-difluoro-3-bromo-3-phenylcyclobutane has four very strong bands at 7.69, 8.02, 8.65 and 9.10 μ which are assigned to C-F vibrations (29). There are two other strong bands at 10.31 and 10.92 μ whose origin is unknown. A large number of infrared spectra of organofluorine compounds have been reported, but no general correlations have been formulated due to the complexities of the spectra. It has been observed that the intensity of the C-F absorption is exceptionally high, and interaction effects are very great, resulting in large high-frequency shifts in adjacent C-H, C=C, and C=O stretching vibrations (29). One anomalous feature in the spectrum is the weakness of the band at about 6.2 μ, which is very sharp in 1,1-difluoro-3-phenylcyclobutane and phenylcyclobutane, and which is assigned to C=C skeletal in-plane vibration of the aromatic ring. In 1,1-difluoro-2,2-dichloro-3-phenylcyclobutane the 6.2 μ band is present, but much lower in intensity than the other bands from 6.6-7.2 μ.

The ultraviolet spectrum of 1,1-difluoro-3-bromo-3-phenylcyclobutane in cyclohexane shows a broad plateau, λ_{max} 238.5 mμ (ϵ 5,800), with a sharp rise at 217.5 mμ and λ_{max} 202.0 mμ (ϵ 17,300).

The nuclear magnetic resonance (NMR) proton spectrum shows lines characteristic of phenyl and methylene hydrogens approximately in the ratio of 5:4, respectively. The methylene protons are split into a symmetric triplet with relative peak heights of 1:2:1. The fluorine spectrum was not observed.

<u>1,1-Difluoro-3-phenylcyclobut-2-ene.</u>--To a solution of 12.8 g. (0.191 mole) of potassium hydroxide (assay 86%) in 125 ml. of denatured ethanol, 41 g. (0.17 mole) of 1,1-difluoro-3-bromo-3-phenylcyclobutane was added slowly with swirling. After the initial exothermic reaction was complete, the mixture was refluxed for one hour and then poured into 500 ml. of water. The resulting mixture was extracted five times with ether (a total of about 700 ml.). The ether was dried in four stages with anhydrous magnesium sulfate and distilled until the head temperature rose to about 45°. The residue was transferred to a distilling flask fitted with a 10-cm. Vigreux column and stirred magnetically while the last traces of solvent were removed by pumping. The product decomposes quite rapidly when in contact with etched glassware or when in contact with air at room temperature. The product was distilled with a mineral oil heating bath and mineral oil as a still base. One fraction, 24.5-26.2 g. (89-95%), was obtained, b.p. 43-46° (0.7-0.8 mm.), $n^{25}D$ 1.5130, m.p. 5-6°; Knutson (20) gives $n^{25}D$ 1.5144, and Vogel (21) gives $n^{25}D$ 1.5192.

<u>Anal.</u> Calcd. for $C_{10}H_8F_2$: C, 72.28; H, 4.85. Found: C, 72.26; H, 5.01.

The infrared spectrum of 1,1-difluoro-3-phenylcyclobut-2-ene shows sharp bands at 3.28 and 3.40 μ which are assigned to vinyl and methylene stretching vibrations, respectively. A sharp band at 6.16 μ is attributed to C=C stretching. A band at 6.97 μ is assigned to C-H deformation of the ring methylene group. There are two pairs of bands, one at 6.27 and 6.34 μ and the other at 6.70 and 6.89 μ which are attributed to C=C skeletal in-plane vibrations of the aromatic ring (29). There are four very intense bands at 7.70, 7.90, 8.67 and 9.05 μ whose origin is probably due to C-F stretch (29). The band assignments above are made on the basis of the spectra of a number of cyclobutane and cyclobutene derivatives which have been correlated in Table I above.

The ultraviolet spectrum in cyclohexane has λ_{max} 253.0 mμ (ϵ 16,000), λ_{max} 215.5 mμ (ϵ 14,300), λ_{max} 209.0 mμ (ϵ 19,200), and λ_{max} 204.0 mμ (ϵ 17,600).

The proton NMR spectrum of 1,1-difluoro-3-phenylcyclobut-2-ene showed the expected lines characteristic of phenyl, unsplit methylene, and unsplit vinyl hydrogens in the ratio 5:2:1. The fluorine spectrum was not observed but it should be a single peak.

<u>3-Phenylcyclobut-2-enone.</u>--In a 200-ml. conical flask, 20 g. (0.12 mole) of 1,1-difluoro-3-phenylcyclobut-2-ene was cooled in an ice bath, and 100 ml. of concentrated sulfuric

acid (assay 98%) was added slowly with vigorous swirling. This operation was done in a hood since a large amount of hydrogen fluoride was given off. When the addition was complete, the deep purple-colored mixture was swirled and heated on a steam bath for four minutes and then poured with vigorous stirring onto ice. The mixture was immediately filtered by suction, and the solid, which contained pieces of ice, was washed twice with water, three times with dilute sodium bicarbonate solution to remove the last traces of acid, and once more with water. The cream-colored product was sucked dry and then pumped under vacuum. The yield of crude cinnamon-smelling product, m.p. 44-50°, was 11.5-15.4 g. (66-89%). Recrystallization of this crude material from a great number of different solvent systems was explored without success due to the thermal instability of the compound. The only satisfactory method of purification was high-vacuum sublimation at a temperature below 40°. By this method 7.6-10.2 g. (44-59%) of large, colorless crystals, m.p. 51.4-52.7°, was obtained.

Anal. Calcd. for $C_{10}H_8O$: C, 83.31; H, 5.59. Found: C, 83.33; H, 5.47.

The residue in the sublimation tube was black. By extracting this residue with boiling water, cis-β-methylcinnamic acid could be isolated, m.p. 96-97° (lit., m.p. 98.5°) (40).

3-Phenylcyclobut-2-enone becomes dark when exposed to strong light. It decomposes slowly in the presence of moist air to give a colorless oil. From decomposed samples good yields of cis-β-methylcinnamic acid were isolated. 3-Phenylcyclobut-2-enone can be kept in vacuo at Dry Ice temperature for long periods of time without any apparent decomposition.

The 2,4-dinitrophenylhydrazone was very insoluble in all solvents, but was obtained from ethyl acetate as very fine red crystals, m.p. 240.9-241.5° (decomposition to a black tar).

Anal. Calcd. for $C_{16}H_{12}O_4N_4$: C, 59.26; H, 3.73. Found: C, 59.21; H, 3.79.

The infrared spectrum of 3-phenylcyclobut-2-enone has a band at 3.26 μ which is assigned to vinyl C-H stretching. The doublet at 3.39 and 3.42 μ is assigned to methylene C-H stretch. The carbonyl band is very strong and falls at 5.65 μ. The four bands at 6.21, 6.30, 6.72 and 6.88 μ are assigned to C=C stretching of the aromatic ring. The C=C stretching of the four-membered ring falls at 6.39 μ. The band at 7.05 μ is assigned to methylene deformation. There seems to be some disagreement (12) as to whether the band at 6.88 μ should not be attributed to the methylene deformation instead of that at 7.05 μ. A survey of a number of phenylcyclobutene compounds encountered in the present work indicates that a band at 6.88±0.10 μ is present in every 3-phenylcyclobut-2-ene derivative whether or not it has a methylene group. A band at about 6.9-7.3 μ is present only in those compounds having methylene groups.

The ultraviolet spectrum in 95% ethanol was found to have λ_{max} 286.0 mμ (ϵ 23,000), λ_{max} 222.5 mμ (ϵ 11,600) and λ_{max} 217.0 mμ (ϵ 13,000).

The proton NMR spectrum of 3-phenylcyclobut-2-enone in carbon tetrachloride solution showed resonance lines characteristic of phenyl, unsplit vinyl, and unsplit methylene hydrogens in the respective ratios of 5:2:1. The chemical shifts were not measured.

Catalytic Hydrogenation of 3-Phenylcyclobut-2-enone.--In a citrate bottle were placed 3.0 g. (0.021 mole) of crude 3-phenylcyclobut-2-enone, 10 ml. of reagent methanol and 0.1 g. of Adam's catalyst. The mixture was hydrogenated for about two hours at 60 psi and then poured into 50 ml. of water. The cream-colored emulsion resulting was extracted with ether three times, and the ether extracts were dried over anhydrous magnesium sulfate in four stages. The ether was stripped, and the residue was distilled through a 5-cm. Vigreux column at reduced pressure to give 2.5 g. (75%) of a slightly yellowish liquid. The product was redistilled through a glass tube, 12-mm. I.D. by 10-cm. long, packed with glass wool. A colorless, pleasant-smelling liquid was obtained which had an infrared spectrum identical with that of 3-phenylcyclobutanone (10). This material gave a 2,4-dinitrophenylhydrazone, m.p. 150-151° (lit., m.p. 148.5-150°) (10).

Reaction of 3-Phenylcyclobut-2-enone with Aqueous Sodium Hydroxide.--A. To 30 ml. of 1.5 N sodium hydroxide was added 3 g. (0.021 mole) of 3-phenylcyclobut-2-enone (m.p. 47.0-49.5°), amd the mixture was heated on a steam bath. After 7 minutes only one phase was present, but after 10 minutes there were two phases again. At this point, 0.5 g. more of sodium hydroxide was added, and the mixture was heated for 10 minutes, cooled, and acidified with 6 N hydrochloric acid. The reddish oil was separated from the aqueous layer by decantation. The infrared and ultraviolet spectra indicated the oil to be a mixture of benzoic acid and acetophenone. This material was washed several times with dilute sodium bicarbonate solution, and part of the oil dissolved. An oil settled out on acidification of the bicarbonate washings and partially crystallized on standing in the refrigerator overnight. The crystals were collected and, after several recrystallizations from 30-60° petroleum ether, gave small cream-colored needles, m.p. 120.7-122.1°; the mixed melting point with benzoic acid was 121.4-121.5°. Both the infrared and the ultraviolet spectra of this material were identical to those of benzoic acid.

The oil which was insoluble in bicarbonate was taken up in ether. The ether was dried with anhydrous magnesium sulfate and then evaporated in a stream of air. The infrared and ultraviolet spectra indicated a mixture of acetophenone and benzoic acid. From the residue, two derivatives were obtained, a 2,4-dinitrophenylhydrazone, m.p. 248.5-249.1°, from ethyl acetate, and a 4-nitrophenylhydrazone, m.p. 183.4-185.0°, from ethanol-water. A sample of acetophenone 2,4-dinitrophenylhydrazone, m.p. 248.6-249.3° (lit., m.p. 250°) (41), gave a mixed melting point of 247.1-248.1° with the unknown 2,4-dinitrophenylhydrazone above. The literature melting point for acetophenone 4-nitrophenylhydrazone is 184-185° (41).

B. To 3.0 g. (0.021 mole) of 3-phenylcyclobut-2-enone was added 30 ml. of 1.5 N (0.045 mole) sodium hydroxide, and the mixture was heated on a steam bath with swirling for a period of 10 minutes. After five minutes, a cream-colored emulsion had formed, but after eight minutes the mixture was brown and homogeneous. An excess of 6 N hydrochloric acid was added immediately, and the resulting emulsion was placed in the refrigerator for several hours. One drop of the mixture gave a deep purple color with ferric chloride solution. Some light-reddish solid precipitated out of the cold mixture. The mixture was made basic and extracted several times with ether, and on evaporation this extract yielded 0.8 g. of oily brown crystals (A). These crystals also gave a positive ferric chloride test, and the odor of acetophenone was evident. After the ether extractions, the basic solution above was made acidic and extracted with ether. A drop of the ether extract gave a positive ferric chloride test. After removal of the ether, 1.5 g. of a cream-colored solid (B) was obtained, m.p. 56-60° (lit. m.p.

for benzoylacetone 61°) (41). The ultraviolet and the infrared spectra of samples A and B were taken and compared with the corresponding ones for acetophenone, benzoylacetone, benzoic acid, and 3-phenylcyclobut-2-enone. Comparison of the spectra indicated that A was a mixture of much benzoylacetone with a little acetophenone, and that B was a mixture of much benzoylacetone and a little benzoic acid. Probably a significant amount of acetophenone was lost when the ether was removed from the basic extraction by pumping overnight. Fraction A distilled at 1 mm. pressure through a glass tube, 12-mm. I.D. by 10-cm. long, packed with glass wool, to give a white crystalline solid, m.p. 57.5-58.4°. Fraction B distilled through the same apparatus to give a white crystalline solid, m.p. 59.0-60.8°. When mixed with an authentic sample of benzoylacetone (Eastman White Label), m.p. 57.0-58.0°, the melting point of A was 57.0-58.0°, and that of B was 56.5-57.8°. The infrared spectra of A and B were identical to that of authentic benzoylacetone.

Acetolysis of 3-Phenylcyclobut-2-enone.--Fifty-five ml. of glacial acetic acid and 2.5 g. (0.017 mole) of 3-phenylcyclobut-2-enone were refluxed in a 100-ml. round-bottomed flask. After 12 hours, 1 ml. of the solution was pipetted and added to 5 ml. of water. A cream-colored emulsion resulted, and some colorless needle-like crystals were obtained, m.p. 96.5-97.3° (lit. m.p. 98.5° for β-methylcinnamic acid) (40).

The ultraviolet spectrum in 95% ethanol was characteristic of an α,β-unsaturated acid, having λ_{max} 265.5 mμ (λ_{max} 274.0 mμ for cinnamic acid). After 48 hours at reflux, 10 ml. of water was added to the remainder of the mixture, and the refluxing continued for three hours. The mixture was then poured into 300 ml. of water. The cream-colored solid was collected by suction filtration and washed several times with water. Recrystallization from water gave long colorless needles, m.p. 97.0-97.9°. The infrared spectrum was consistent with the β-methylcinnamic acid structure.

Neutral equiv. Calcd. for $C_{10}H_{10}O_2$: 162.18. Found: 162.

3-Phenylcyclobut-2-enol.--In a 25-ml. conical flask, 2.0 g. (0.0134 mole) of sublimed 3-phenylcyclobut-2-enone was dissolved in about 5 ml. of reagent methanol. The solution was cooled to about 0° in an ice bath, and 0.5 g. (0.0132 mole) of sodium borohydride (Metal Hydrides Incorporated) was added with swirling and cooling over a five-minute period. After five minutes longer, the mixture was heated two minutes at 70° and poured into a 125-ml. flask filled with crushed ice, at which point white microscopic platelets precipitated. The slurry was swirled, and as the ice melted, more was added until the volume of liquid was about 100 ml. The solid was collected by filtration and washed twice with ice water. The crude product was pumped under high vacuum overnight in the dark to remove the last traces of water, and 1.7 g. (75%) of white material was obtained. One recrystallization of 0.5 g. of the latter material from pentane gave 0.4 g. of long white needles, m.p. 66.4-68.6°.

__Anal.__ Calcd. for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 81.89; H, 6.99.

Good yields of the alcohol were obtained only when the 3-phenylcyclobut-2-enone used was very pure. The alcohol was quite unstable to light, heat and air. The crude material could only be stored in the dark under high vacuum at Dry Ice temperature. The recrystallized material can be stored satisfactorily in an evacuated ampule in a refrigerator.

The infrared spectrum of 3-phenylcyclobut-2-enol shows a strong band at 3.02 μ assigned to O-H stretch, a strong band at 3.27 μ assigned to vinyl C-H stretch, and a strong band at 3.38 μ assigned to C-H stretch of the methylene group. There are four bands at 6.27, 6.36, 6.72 and 6.91 μ which are assigned to aromatic C=C stretching. A band at 6.99 μ is assigned to methylene deformation. There does not seem to be any band in the region 5.5-6.5 μ which can be assigned to C=C stretch in the four-membered ring. In 2-chloro-3-phenylcyclobut-2-enol, to be described below, there is a strong band at 6.08 μ which has been assigned to olefinic C=C stretch.

The ultraviolet spectrum in 95% ethanol has λ_{max} 255.0 mμ (ε 19,000), λ_{max} 217.5 mμ and λ_{max} 211.0 mμ. The λ_{max}

255.0 mμ decreases with time. The spectrum of cinnamyl alcohol has λ_{max} 251.5 mμ, λ_{max} 213.5 mμ and λ_{max} 219.5 mμ.

3-Phenylcyclobut-2-enol 4-nitrobenzoate was prepared from the alcohol and the acid chloride in a benzene solution with the calculated amount of pyridine added. The customary pyridine method for preparation of esters from an alcohol and an acid chloride failed (41). To an ice-cooled solution of 0.30 g. (0.0021 mole) of 3-phenylcyclobut-2-enol and 0.20 g. of pyridine, a solution of 0.40 g. (0.0023 mole) of recrystallized 4-nitrobenzoyl chloride in dry benzene was added at once. The mixture was stirred for 30 minutes at 0°. The solvent was evaporated in a stream of nitrogen with gentle warming, and the solids remaining were extracted twice with hot ethyl acetate. The insoluble residue, which was water soluble, was discarded. The ethyl acetate solution was evaporated to a volume of 3-5 ml., and on cooling, cream-colored platelets were obtained, m.p. 145-146°. Recrystallization from hexane-ethyl acetate gave material of m.p. 146.2-148.4°.

Anal. Calcd. for $C_{17}H_{13}O_4N$: C, 69.14; H, 4.44. Found: C, 69.05; H, 4.60.

Catalytic Hydrogenation of 3-Phenylcyclobut-2-enol.--A methanol solution of 0.65 g. of partially decomposed crude alcohol shaken with hydrogen over 10% palladium-on-charcoal catalyst gave a mixture of products whose vapor phase chromatogram showed three components. One component made up 89% of the total. The infrared spectrum of the product mixture was identical with that of cis-3-phenylcyclobutanol to be described below.

Reaction of 3-Phenylcyclobut-2-enone with Phosphorus Pentachloride.--In a 50-ml. round-bottomed flask fitted with a condenser and a soda-lime drying tube, 3.0 g. (0.021 mole) of 3-phenylcyclobut-2-enone, 4.8 g. (0.023 mole) of phosphorus pentachloride, and 20 ml. of reagent benzene were refluxed for 20 hours. After the mixture had cooled, it was poured into an ice-filled separatory funnel and shaken. After the ice had melted, the benzene layer was separated, and the water layer was extracted twice with ether. The organic phases were combined and washed three times with cold water. The solvent was dried in two stages with anhydrous magnesium sulfate and then evaporated in a stream of nitrogen with gentle heating from a steam bath. The residue was pumped at reduced pressure to remove the last traces of solvent, and distillation gave 3.2 g. (81%) of a nearly colorless liquid, b.p. 64-67° (1 mm.), m.p. 37-40°. A small sample was redistilled for analysis.

Anal. Calcd. for $C_{10}H_8Cl_2$: C, 60.33; H, 4.05; Cl, 35.62. Found: C, 60.16; H, 4.23; Cl, 35.12.

This material turns brown readily in air and is stored most satisfactorily in an evacuated ampule in the refrigerator.

The ultraviolet spectrum in cyclohexane had λ_{max} 259.5 mμ (ϵ 20,400), λ_{max} 218.0 mμ (ϵ 13,500), λ_{max} 212.0 mμ (ϵ 18,000) and λ_{max} 206.5 mμ (ϵ 17,100). In 95% ethanol the ultraviolet absorption maxima decreased drastically with time.

The infrared spectrum of this compound is summarized in Table I. All the experimental facts are consistent with the 1,1-dichloro-3-phenylcyclobut-2-ene structure.

2-Chloro-3-phenylcyclobut-2-enone.--In a 200-ml. conical flask, 10 g. (0.0494 mole) of 1,1-difluoro-2-chloro-3-phenylcyclobut-2-ene and 5 ml. of concentrated sulfuric acid (assay 98%) were heated on a steam bath. After about two minutes, 55 ml. more acid was added, and the deep-red mixture was heated and swirled until it was homogeneous (5-15 minutes). Considerable gas evolution took place. The solution was then poured slowly onto ice with vigorous stirring. The white solid was collected by filtration, washed twice with water and three times with dilute sodium bicarbonate solution, and dried under vacuum overnight to give 7.7-8.7 g. (87-99%) of crude dirty-white product, m.p. 63-67°. Recrystallization from 30-60° petroleum ether after treatment with Norite gave 6.9-7.9 g. (78-90%) of long white needles, m.p. 67.8-69.2° (lit., m.p. 67.2-68.2°) (15). This reaction was run several times on a two-mole scale with yields of crude product of about 90-95%.

<u>1,1,2-Trichloro-3-phenylcyclobut-2-ene.</u>--In a 500-ml. round-bottomed flask fitted with a reflux condenser and a calcium chloride drying tube, were placed 44.0 g. (0.249 mole) of 2-chloro-3-phenylcyclobut-2-enone, 58 g. (0.280 mole) of phosphorus pentachloride and 250 ml. of dry benzene. This mixture was refluxed for eighteen hours. After the reaction mixture had cooled, it was poured onto ice and the slurry shaken in a separatory funnel. After the ice had melted, the benzene layer was separated, washed four times with ice water, and then dried twice with anhydrous potassium carbonate and once with anhydrous magnesium sulfate. The benzene was evaporated with an air stream while the flask was heated on a steam bath. The residue was pumped under vacuum for two hours to remove the last traces of solvent and then distilled slowly through a 10-cm. Vigreux column to give one fraction (51.4 g., 88%), b.p. 71-75° (less than 1 mm.), $n^{25}D$ 1.6042.

<u>Anal.</u> Calcd. for $C_{10}H_7Cl_3$: C, 51.43; H, 3.02; Cl, 45.55. Found: C, 51.64; H, 3.17; Cl, 45.40.

The ultraviolet spectrum of 1,1,3-trichloro-3-phenylcyclobut-2-ene in cyclohexane had λ_{max} 267.5 mμ (ϵ 25,900), λ_{max} 219.5 mμ (ϵ 13,700), λ_{max} 213.5 mμ (ϵ 17,700) and

λ_{max} 208.0 mμ (ε 17,000). In 95% ethanol the λ_{max} 267.5 mμ decreased with time, and the other peaks became smoothed out. The infrared spectrum is summarized in Table I above. The proton NMR spectrum showed only phenyl and methylene hydrogens in the ratio 5:2.

1,1,2-Trichloro-3-phenylcyclobut-2-ene and concentrated sulfuric acid gave a purple solution which was heated on a steam bath for five minutes and then poured onto ice. The white solid was removed by filtration. Recrystallization from 60-70° petroleum ether gave a nearly quantitative yield of long, white needles, m.p. 69.3-70.3°. The mixed melting point with a sample of 2-chloro-3-phenylcyclobut-2-enone, m.p. 71.4-72.4° was 70-71°. The infrared spectrum of the product was identical with that of 2-chloro-3-phenylcyclobut-2-enone.

<u>Phenylcyclobutane</u>.--In a citrate bottle were placed 51.4 g. (0.220 mole) of 1,1,2-trichloro-3-phenylcyclobut-2-ene, 63 g. of anhydrous sodium acetate, 2.5 g. of 10% palladium-on-charcoal catalyst, and 150 ml. of reagent methanol. The mixture was hydrogenated at about 60 psi until 0.965 mole (110% of the theoretical) of hydrogen had been taken up. The catalyst was removed by filtration, and the filtrate was poured into 500 ml. of water. The mixture was extracted three times with ether (total volume 400 ml.), and the extracts were dried in three stages with a mixture of

anhydrous sodium carbonate and anhydrous magnesium sulfate. The ether was removed by distillation through a straight distilling head, and the residue distilled through a 12-cm. Vigreux column to give 0.8 g., b.p. 56-62° (7.6-10.1 mm.), $n^{25}D$ 1.5121; 14.6 g., b.p. 62-68° (7.6-10.1 mm.), $n^{25}D$ 1.5210; and 6.2 g., b.p. 70° and up (8.0 mm.), $n^{25}D$ 1.5453. The distillate residue (14.7 g.) was a brown liquid which became hard overnight. The reported $n^{25}D$'s for phenylcyclobutane are 1.5281 (42) and 1.5277 (10). The infrared spectrum of the second fraction was almost identical with that of the material obtained by Clemmensen reduction of 2,4-dichloro-3-phenylcyclobutenone (10) except that the former spectrum showed fewer weak bands. The vapor chromatogram of the first fraction indicated that it contained three components with retention times of 2.6, 2.9, and 3.4 minutes, respectively. The latter component made up 80% of the total and was assumed to be phenylcyclobutane. The second fraction showed six components with retention times 2.5, 2.8, 3.3 (86% of the total from the peak area), 4.6, 6.1 and 6.8 minutes (Perkin-Elmer Column C, 225°, flow 3.8). The first and second fractions made up a total of 16.4 g. (52%).

<u>2-Chloro-3-phenylcyclobut-2-enol</u>.--In a 500-ml. conical flask, 50.5 g. (0.283 mole) of 2-chloro-3-phenylcyclobut-2-enone was dissolved in 150 ml. of reagent methanol. The solution was cooled in an ice bath, and 11.6 g. (0.283

mole) of sodium borohydride was added slowly with vigorous swirling at such a rate that the evolution of gas did not get out of control. The temperature was kept below 5°. After the addition of the sodium borohydride was complete, the solution was allowed to stand twenty minutes at room temperature and then poured onto crushed ice. The resulting mixture was placed in the refrigerator for two hours. The white solid product was removed by suction filtration, the filter cake washed several times with water, and the crude product dried by pumping under vacuum overnight to give 35.8-44.7 g. (70-86%) of white material, m.p. 76-78°. Recrystallization from pentane three times gave white cottony material, m.p. 79.0-79.8°. An analytical sample was prepared by precipitating a sample three times from a methanol solution by addition of ice followed by filtration of the solid and pumping three days under high vacuum.

Anal. Calcd. for $C_{10}H_9OCl$: C, 66.86; H, 4.49; Cl, 19.74. Found: C, 66.71; H, 4.64; Cl, 19.65.

The infrared spectrum of 2-chloro-3-phenylcyclobut-2-enol shows a sharp band at 2.79 μ which is assigned to free O-H stretching, a strong band at 3.01 μ assigned to associated O-H, a band at 3.27 μ assigned to vinyl C-H stretching and a band at 3.43 μ characteristic of methylene C-H stretching. A sharp band at 6.08 μ is assigned to C=C stretch. There are four bands at 6.25, 6.35 (weak), 6.71 and 6.90 μ which are characteristic of the aromatic ring and due to C=C stretching. A sharp band at 6.98 μ is assigned to methylene C-H deformation (29). The ultraviolet and NMR spectra of this compound were not taken.

2-Chloro-3-phenylcyclobut-2-enol decomposes slowly to give a yellow oil if exposed to air, moisture, heat or light, but can be stored quite satisfactorily *in vacuo* in the dark.

The *4-nitrobenzoate of 2-chloro-3-phenylcyclobut-2-enol* was prepared from the alcohol, pyridine, and the acid chloride in benzene in a manner similar to that described above for the 4-nitrobenzoate of 3-phenylcyclobut-2-enol. Recrystallization of the ester from ethyl acetate gave cream-colored platelets, m.p. 172-173.2°.

Anal. Calcd. for $C_{17}H_{12}O_4NCl$: C, 61.92; H, 3.67; Cl, 10.75. Found: C, 62.10; H, 3.80; Cl, 10.71.

The customary pyridine method for preparation of an ester from an alcohol and acid chloride gave only highly-colored, polymeric products. Attempts to prepare an α-naphthylurethan of this alcohol failed.

cis—3-Phenylcyclobutanol.--In a citrate bottle were placed 40.0 g. (0.222 mole) of crude 2-chloro-3-phenylcyclobut-2-enol, 18.2 g. of sodium acetate, 3 g. of 10% palladium-on-charcoal catalyst, and 150 ml. of reagent methanol. The mixture was hydrogenated at 60 psi. In twenty hours, a pressure drop of 38 psi, corresponding to 0.52 mole of hydrogen, occurred. The solids were removed by filtration and washed first with methanol and then with water. To the resulting cloudy mixture, 11 g. of sodium hydroxide was added with vigorous swirling to saponify any acetate ester present and to neutralize the acetic acid formed in the hydrogenolysis. After the mixture had stood at room temperature for three hours, it was poured into 600 ml. of water, and the resulting emulsion was extracted six times with a total volume of 600 ml. of ether. The ether was dried in three stages with anhydrous magnesium sulfate and evaporated in an air stream on a steam bath. Distillation of the material remaining gave one fraction (30 g., 92%), b.p. 80-84° (less than 1 mm.), $n^{25}D$ 1.5453. A sample for analysis was distilled through a 30-cm. Holzman column (43), b.p. 62-64° (less than 1 mm.).

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.83; H, 8.18.

The α-naphthylurethan of cis-3-phenylcyclobutanol was prepared by a published procedure (41) and had m.p. 125.2-127.4°, after recrystallization from 60-70° petroleum ether.

Anal. Calcd. for $C_{21}H_{19}O_2N$: C, 79.46; H, 6.03. Found: C, 79.50; H, 6.00.

The 4-nitrobenzoate of cis-3-phenylcyclobutanol was prepared from the alcohol and acid chloride in pyridine (41), long white needles, m.p. 131.1-131.6°, after recrystallization from ethyl acetate-hexane.

Anal. Calcd. for $C_{17}H_{15}O_4N$: C, 68.67; H, 5.09. Found: C, 68.80; H, 5.23.

The infrared spectrum of *cis*-3-phenylcyclobutanol shows a sharp band at 2.78 μ characteristic of free O-H stretch and a very strong broad band at 3.03 μ characteristic of associated O-H stretch. The band structure from 3.2-3.5 μ was very similar to that of 3-phenylcyclobutanone with a pair of bands of equal intensity at 3.39 and 3.44 μ and a pair at 3.24 and 3.27 μ (strongest). These bands are assigned to C-H stretch. There are three bands at 6.25, 6.71 and 6.92 μ which are characteristic of aromatic C=C in-plane stretch. A somewhat broad band at 7.03 μ is attributed to methylene C-H deformation.

The proton NMR spectrum showed unsplit phenyl hydrogens, unsplit hydroxyl hydrogen, two widely split tertiary hydrogens and methylene hydrogens split into either four or five peaks.

Isomerization of cis-3-Phenylcyclobutanol.--In a 100-ml. round-bottomed flask were placed 0.20 g. of sodium, 0.20 g. of fluorenone, 5.0 g. of *cis*-3-phenylcyclobutanol and 50 ml. of dry reagent benzene. The mixture was refluxed for 72 hours and then the benzene was evaporated in an air stream. The gelatinous residue was treated with 50 ml. of water, and the mixture was extracted three times with ether. The ether was dried over anhydrous magnesium sulfate and evaporated in an air stream. The residue was transferred to a small distilling flask and pumped for several hours to remove the last traces of solvent. On distillation, 1.3 g. of a slightly yellow material was obtained. The distillate residue amounted to 3 g. of yellowish polymer soluble in carbon tetrachloride or ether. A total of 85% of the starting material was accounted for.

The infrared spectrum of the distillable product had a broad band at 2.99 μ assigned to associated O-H stretch. Two pairs of bands, one at 3.29 and 3.32 μ and the other at 3.40 and 3.47 μ, made up a structure similar to that found in the starting material. There were three bands at 6.24, 6.69 and 6.88 μ characteristic of aromatic C=C stretch and a band at 6.99 μ assigned to methylene deformation. There was a strong band at 7.27 μ which was not present in the starting material. Two strong bands present in the starting material at 7.56 and 8.13 μ were absent in the isomerization product. The strong band in the starting material at 9.1 μ appeared to be shifted to 9.63 μ. There were three new bands at 10.12, 11.05, and 11.80 μ. A band at 10.55 μ was similar in shape and intensity to a band at 10.49 μ in the starting material.

An attempt to prepare a 4-nitrobenzoate of the isomerization product failed. An α-naphthylurethan was prepared by a published procedure (41). Five recrystallizations of this material from hexane gave material, m.p. 86.0-89.2°, which did not, however, have the correct analysis for $C_{21}H_{19}O_2N$.

Anal. Calcd. for $C_{21}H_{19}O_2N$: C, 79.46; H, 6.03. Found: C, 78.60; H, 6.75.

3-Phenylcyclobutanone.--In a citrate bottle were placed 50.0 g. (0.283 mole) of 2-chloro-3-phenylcyclobut-2-enone, 24 g. (0.29 mole) of anhydrous sodium acetate, 200 ml. of reagent methanol, and 4.0 g. of freshly prepared 20-30% palladium-on-charcoal catalyst. The mixture was hydrogenated at 60 psi for ten hours, and then 2.0 g. more catalyst was added. The hydrogenation was allowed to proceed until the uptake of hydrogen ceased. The catalyst and solids were removed by filtration and washed with methanol and then with water. To the filtrate, 700 ml. of water was added, and the milky mixture was extracted six times with ether (total volume 700 ml.). The ether was dried in four stages with anhydrous magnesium sulfate and then distilled through a 30-cm. Vigreux column until the head temperature rose to 45°. The crude material was pumped under high vacuum for several hours to remove the last traces of solvent and distilled through a 10-cm. Vigreux column to give 35.1-37.6 g. (85-91%) of a colorless liquid product, b.p. 69-76° (1-2 mm.); lit., b.p. 93-95° (1.5 mm.), $n^{25}D$ 1.5423 (10).

The *2,4-dinitrophenylhydrazone of 3-phenylcyclobutanone*, prepared in the usual manner (42), had m.p. 150.8-151.8° (from ethyl acetate); lit., m.p. 148.5-150° (10).

Anal. Calcd. for $C_{16}H_{14}O_4N_4$: C, 58.89; H, 4.32. Found: C, 59.03; H, 4.27.

The infrared spectrum of 3-phenylcyclobutanone had four sharp bands at 3.28, 3.32, 3.38 and 3.44 μ. The first two bands are assigned to aromatic C-H stretch, and the latter pair are ascribed, respectively, to the in-phase and out-of-phase C-H stretching modes (29). There are three very sharp bands at 6.23, 6.69 and 6.88 μ which are assigned to C=C in-plane vibration of the aromatic ring. A strong band due to C=O stretching is at 5.58 μ. A strong band at 7.24 μ is assigned to methylene C-H deformation. The infrared spectrum of freshly prepared material was identical with that of material prepared from the semicarbazone (30).

The proton NMR spectrum showed unsplit phenyl, methylene, and tertiary hydrogens in the ratio 5:4:1. The ultraviolet spectrum shows a broad λ_{max} 254.0 mμ.

3-Phenylcyclobutanone slowly became yellow on standing in light for several weeks and took on a very sweet odor. The infrared spectrum showed a new strong band at 5.75 μ and a band at 6.97 μ. The band at 7.24 μ was much weaker. The vapor phase chromatogram showed several components. Distillation failed to effect a satisfactory separation as indicated by the infrared spectrum, although the vapor phase chromatogram showed only one major component.

Reduction of 3-Phenylcyclobutanone with Sodium in Wet Ether.--In a 200-ml. three-necked round-bottomed flask fitted with a mechanical stirrer, dropping funnel, and reflux condenser were placed 5.7 g. of freshly cut pieces of sodium and 20 ml. of ether. The stirrer was started, and a solution of 5.0 g. (0.034 mole) of freshly distilled 3-phenylcyclobutanone in 30 ml. of wet ether was added slowly. It was necessary to add several drops of water occasionally to maintain the evolution of hydrogen from the sodium. After the addition of the ketone solution was complete (1 hour), the mixture was stirred until the remainder of the sodium had dissolved. A solution of 14 g. of ammonium chloride in 100 ml. of water was added, and the ether layer was separated. The water phase was extracted three times with ether, and the combined ether phases were dried with anhydrous magnesium sulfate. The ether was evaporated in a stream of air, and the residue distilled through a 10-cm. Vigreux column to give 4.0 g. of colorless material, b.p. 64-81° (1 mm.), $n^{25}D$ 1.5268. The infrared spectrum showed that a significant amount of the starting material was present. The product was dissolved in ethanol, and an alcoholic solution of sodium bisulfite was added with cooling. After the mixture had stood for five minutes, the solid was removed by filtration, and the filtrate was treated with another portion of bisulfite solution. After about fifteen minutes the small amount of precipitate was removed by filtration, and the filtrate extracted four times with ether. The ether extracts were dried with anhydrous magnesium sulfate. The ether was evaporated in an air stream, and the residue was distilled through a glass tube, 12-mm. I.D. by 10-cm. long, packed with glass wool, to give 2.0 g.

of colorless product, b.p. 87-96° (1 mm.), $n^{25}D$ 1.5280. This material did not give a satisfactory analysis for a $C_{10}H_{12}O$ isomer and did not give a reaction with 2,4-dinitrophenylhydrazine reagent.

The infrared spectrum had a sharp band at 2.78 μ characteristic of free O-H stretch and a broad band at 3.00 μ characteristic of associated O-H. There were four bands at 3.28, 3.31 (shoulder), 3.38 and 3.41 μ giving a structure similar to that found in cis-3-phenylcyclobutanol and due to the various C-H stretching vibrations. There were three bands at 6.23, 6.69 and 6.89 μ assigned to aromatic C=C stretch. A band at 6.96 μ was assigned to methylene C-H deformation. There was a very strong, sharp band at 5.75 μ whose origin is unknown. There was no broad band at 10.65 μ which was present in the cis-isomer. A band at 8.60 μ, missing in the cis-isomer, was present. A strong broad band at 9.2 μ may correspond to the strong broad band in the cis-isomer at 9.1 μ. The band structure from 7-8 μ was quite different from that of cis-3-phenylcyclobutanol which had only one strong band at 7.58 μ; a multiplicity of bands was present in this region.

A 4-nitrobenzoate ester was prepared by the pyridine method (41) and had m.p. 60.7-63.0° after recrystallization from absolute alcohol.

Anal. Calcd. for $C_{17}H_{15}O_4N$: C, 68.67; H, 5.09. Found: C, 68.62; H, 5.05.

Several of the products from other sodium and wet ether reductions (in some cases a small amount of ethanol being added) were treated directly with 4-nitrobenzoyl chloride in pyridine. Oily mixtures of 4-nitrobenzoate esters were obtained, and by fractional crystallization poor yields of an ester, m.p. 131-132° were obtained. This material gave no melting point depression on admixture with an authentic sample of the 4-nitrobenzoate of *cis*-3-phenylcyclobutanol. The mother liquors were evaporated to give yellowish oils from which long needle-like crystals were deposited after about three months. These crystals were washed with a small amount of pentane and had m.p. 61-63°. They gave no melting point depression with the analytical sample above having m.p. 60.7-63.0°.

The ultraviolet spectrum in cyclohexane of the ester m.p. 60.7-63.0° had λ_{max} 259.0, $\lambda_{\text{inflection}}$ 219.0 and $\lambda_{\text{inflection}}$ 209.5 mµ. This spectrum was identical with the corresponding one of the 4-nitrobenzoate of *cis*-3-phenylcyclobutanol, m.p. 131-132°. The ultraviolet spectrum of the 4-nitrobenzoate of 3-phenylcyclobut-2-enol had λ_{max} 258.0, λ_{max} 217.5, λ_{max} 211.5 and λ_{max} 205.0 mµ. The latter three bands were very sharp and typical of many of the 3-phenylcyclobut-2-ene systems studied in the present research.

Reduction of 3-Phenylcyclobutanone with Lithium Aluminum Hydride.--In a 300-ml. three-necked round-bottomed flask fitted with a reflux condenser, mechanical stirrer, and dropping funnel, 2.7 g. (0.071 mole) of freshly ground lithium aluminum hydride (Metal Hydrides Incorporated) was placed under 100 ml. of anhydrous ether. A solution of 10 g. (0.069 mole) of 3-phenylcyclobutanone in 30 ml. of anhydrous ether was added with stirring at such a rate that there was gentle reflux. After the addition was complete, the mixture was refluxed for 45 minutes. The excess lithium aluminum hydride was decomposed with a concentrated solution of ammonium chloride, and when the hydrogen evolution ceased, 6 N hydrochloric acid was added until the solid hydroxides just dissolved. The ether layer was separated, and the aqueous layer was extracted three times with ether. The combined ether phases were dried in two stages with anhydrous magnesium sulfate and evaporated in a stream of air. The residue was pumped several hours under high vacuum to remove the last traces of solvent and then distilled to give 8.0 g. (80%) of colorless product, b.p. 82-94° (1 mm.), $n^{25}D$ 1.5385. The infrared spectrum was nearly identical with that of cis-3-phenylcyclobutanol. The product gave a 4-nitrobenzoate, m.p. 131-132°, which showed no melting point depression when admixed with an authentic sample of the 4-nitrobenzoate of cis-3-phenylcyclobutanol.

The Reaction of 3-Phenylcyclobutanone with Phenylmagnesium Bromide.--In a 200-ml. three-necked round-bottomed flask, fitted with a stirrer, reflux condenser, dropping funnel, and flushed with nitrogen, was placed 1.46 g. (0.0599 mole) of oven-dried magnesium turnings. The apparatus was flame dried and allowed to cool protected from atmospheric moisture with a calcium chloride drying tube. With vigorous stirring, 10.0 g. of redistilled reagent bromobenzene in 75 ml. of anhydrous ether was added slowly. After the addition was complete, the brownish mixture was refluxed for 30 minutes. To the Grignard mixture, 5.0 g. (0.034 mole) of 3-phenylcyclobutanone in 30 ml. of anhydrous ether was added at such a rate that the reaction did not become too vigorous. After the addition of the ketone was complete, the mixture was refluxed on a water bath for 45 minutes. Concentrated aqueous ammonium chloride was slowly added until the evolution of hydrogen ceased, and then enough 6 N hydrochloric acid was added to make the two phases clear. The ether phase was decanted, and the water phase was extracted several times with ether. The combined ether extracts were dried over anhydrous magnesium sulfate and evaporated in an air stream. A gummy yellowish residue remained. This material was pumped under high vacuum with gentle heating for several hours to remove the last traces of solvent. The viscous oil was placed in the refrigerator for several weeks but nothing crystallized. To the product 30 ml. of acetic anhydride and 5 g. of pyridine were added. This solution was allowed to stand for one day, and then the excess reagents were evaporated in an air stream. The oily residue was chromatographed on acid-washed activated alumina with benzene. Six fractions, each of about 200 ml., were taken, but only the second one (the largest) crystallized on removal of the solvent. Recrystallization three times from pentane gave 2.0 g. of long, white needles, m.p. 86-88°. One more recrystallization from pentane gave material m.p. 88.9-90.6°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.02; H, 6.93.

The infrared spectrum showed four bands in the C-H stretch region at 3.29, 3.32, 3.36 and 3.42 μ. There was a strong carbonyl band at 5.75 μ, three sharp bands at 6.25, 6.70 and 6.92 μ assigned to aromatic C=C stretch, and a strong band at 7.01 μ assigned to methylene deformation.

The ultraviolet spectrum of the crystalline acetate in cyclohexane showed $\lambda_{shoulder}$ 220.0 mμ (ϵ 16,000), $\lambda_{shoulder}$ 216.5 mμ (ϵ 22,000) and λ_{max} 211.0 mμ (ϵ 24,600). The ultraviolet spectrum of phenylcyclobutane had almost the same shape, but the intensity of absorption was only about half that of the acetate above.

The acetate was hydrolyzed at 100.20±0.02° in "80%" acetone-water 0.0951 N in perchloric acid. The pseudo-first-order rate constant was 18.7±0.7 hr.$^{-1}$. After about 90%

reaction the rate fell off rapidly.

Hydrolysis equiv. Calcd. for $C_{18}H_{18}O_2$: 266.32. Found: 271.

2,2-Difluoro-3-phenylcyclobutenone.--In a 300-ml. conical flask, 23.0 g. (0.113 mole) of 1,1,2,2-tetrafluoro-3-phenylcyclobutene was cooled in an ice bath, and 100 ml. of concentrated sulfuric acid (assay 98%) was added. The reddish-orange mixture was heated and swirled vigorously on a steam bath for a period of ten minutes. The homogeneous, dark reddish-brown solution was poured slowly onto crushed ice. The cream-colored solid which precipitated was removed by suction filtration and washed with water, dilute sodium bicarbonate solution, and again with water. The solid was pressed dry, transferred to a large test tube, and pumped under high vacuum overnight to give 19.5 g. (95%) of gray material, m.p. 59-61°. Recrystallization from ethanol, 30-60° petroleum ether or high vacuum sublimation (18) gave material, m.p. 60.4-61.4°.

Anal. Calcd. for $C_{10}H_6OF_2$: C, 66.66; H, 3.36. Found: C, 66.63; H, 3.37. (Analysis from unpublished research of Dr. E. J. Smutny).

The infrared spectrum showed strong carbonyl absorption at 5.57 μ and a strong band at 6.30 μ assigned to four-membered ring C=C stretch. The four strong bands at 6.20, 6.27, 6.69 and 6.87 μ were characteristic of aromatic C=C stretching. At 3.31 μ there is a band characteristic of aromatic C-H stretch. The band at 2.82 μ may be due to an overtone of the carbonyl fundamental since a band at approximately this wavelength in the infrared was observed in 2-fluoro-2-chloro-3-phenylcyclobutenone and 2,2-dichloro-3-phenylcyclobutenone. The infrared spectra of both these latter compounds have the same number of bands as 2,2-difluoro-3-phenylcyclobutenone from 2.0-7.9 μ, the only differences being small shifts in wavelengths and changes in relative intensities.

The ultraviolet spectrum in 95% ethanol had λ_{max} 280.5 mμ (ϵ 28,100), λ_{max} 220.0 mμ (ϵ 10,900) and λ_{max} 215.5 mμ (ϵ 11,800). The ultraviolet spectrum of 2,2-dichloro-3-phenylcyclobutenone had λ_{max} 288 mμ (ϵ 24,000) (28). The ultraviolet spectrum of 1,1-difluoro-2-phenylcyclobutenone in 95% ethanol (sample supplied by Dr. Yoshio Kitahara) had λ_{max} 261.2 mμ (ϵ 15,900), λ_{max} 218.5 mμ (ϵ 10,000) and λ_{max} 212.2 mμ (ϵ 11,300).

The proton NMR spectrum of 2,2-difluoro-3-phenylcyclobutenone showed singlet phenyl and triplet vinyl hydrogens. The splittings in the latter case were 12 c.p.s. (22). The fluorine NMR spectrum showed a doublet with coupling of 12 c.p.s. These spectra show cross-ring spin-spin coupling of hydrogen and fluorine which has also been observed in a number of other phenylcyclobutene derivatives (22).

The 2,4-dinitrophenylhydrazone was prepared in the usual manner (41) and had m.p. 224.2-225.8° after recrystallization from ethyl acetate.

Anal. Calcd. for $C_{16}H_{10}O_4N_4F_2$: C, 53.34; H, 2.80. Found: C, 53.36; H, 2.75.

1,1-Difluoro-2,2-dichloro-4-phenylcyclobutene.--In a 200-ml. round-bottomed flask fitted with a reflux condenser and a calcium chloride drying tube, a mixture of 21.6 g. (0.120 mole) of 2,2-difluoro-3-phenylcyclobutenone, 25.2 g. (0.120 mole) of phosphorus pentachloride and 120 ml. of dry benzene was refluxed for 24 hours. After the mixture had cooled, enough ice was added to make the volume about 200 ml. The mixture was extracted with 100 ml. of ether, and then the aqueous layer was discarded. The ether-benzene layer was washed twice with water, twice with dilute potassium carbonate solution and then three more times with water. The organic phase was dried in three stages over anhydrous magnesium sulfate, and then the solvent was evaporated in an air stream on a steam bath. After the residue had been pumped under high vacuum for an hour to remove the last traces of solvent, distillation gave one fraction (25.3 g., 89%), b.p. 71-74° (1.5 mm.), $n^{25}D$ 1.5328.

Anal. Calcd. for $C_{10}H_6F_2Cl_2$: C, 51.08; H, 2.57; Cl, 30.17. Found: C, 51.30; H, 2.68; Cl, 30.40.

The infrared spectrum showed a band at 3.28 μ assigned to vinyl and aromatic C-H stretch, a strong band at 6.28 μ assigned to C=C stretch of the four-membered ring and four bands at 6.15, 6.32 (shoulder), 6.71 and 6.91 μ assigned to aromatic C=C stretching.

The proton NMR spectrum showed singlet phenyl and triplet vinyl hydrogens. The fluorine NMR spectrum showed a doublet. These spectra show strong cross-ring spin-spin coupling of hydrogen and fluorine (22).

With concentrated sulfuric acid, 1,1-difluoro-2,2-dichloro-4-phenylcyclobutene gave a deep purple solution. This solution was heated on a steam bath for five minutes and was then poured onto ice. The white precipitate was collected by suction filtration, washed with water, and dried under high vacuum overnight. Recrystallization from 30-60° petroleum ether gave long, white needles, m.p. 63.0-63.8°. The melting point of an admixture with an authentic sample of 2,2-difluoro-3-phenylcyclobutenone, m.p. 60.4-61.4°, was 60.8-61.4°. A 2,4-dinitrophenylhydrazone was prepared in the usual manner (41); m.p. 224-226° after recrystallization from ethyl acetate. The mixed melting point with an authentic sample of the corresponding derivative of 2,2-difluoro-3-phenylcyclobutenone showed no depression.

1,1-Difluoro-2-phenylcyclobutane.--In a citrate bottle, a mixture of 25.0 g. (0.106 mole) of 1,1-difluoro-2,2-dichloro-4-phenylcyclobutene, 18 g. of anhydrous sodium acetate, 125 ml. of reagent methanol, and 2 g. of 10% palladium-on-charcoal catalyst was hydrogenated at 60 psi until 130% of the theoretical amount of hydrogen had been taken up. The mixture was poured into 500 ml. of water, and solid sodium hydroxide was added to neutralize the acetic acid present. After removal of the catalyst by suction filtration, the two-phase mixture was extracted six times with ether (total volume 700 ml.). The ether extracts were combined and dried in three stages with anhydrous magnesium sulfate. The ether was distilled, and the residue was pumped for one hour at reduced pressure to remove the last traces of solvent. Distillation gave two fractions: 10.8 g. (61%), b.p. 84-92° (11-14 mm.), $n^{25}D$ 1.4920 and 3.2 g., b.p. 92° and up (11 mm.), $n^{25}D$ 1.5130. There was a polymeric still residue of about 4-5 g. The vapor phase chromatogram of the first fraction indicated that it was greater than 92% one component. Distillation of 1 g. of this material through a glass tube, 12-mm. I.D. by 10-cm. long, packed with glass wool, gave 0.5 g. of material, $n^{25}D$ 1.4890. The vapor phase chromatogram showed this material to be at least 96% one component.

Anal. Calcd. for $C_{10}H_{10}F_2$: C, 71.41; H, 5.99. Found: C, 71.25; H, 6.30.

The infrared spectrum of 1,1-difluoro-2-phenylcyclobutane was identical with that of 1,1-difluoro-3-phenylcyclobutane in the C-H stretching region, showing bands at 3.32 μ and 3.38 μ. Both substances have bands at 6.23, 6.67 and 6.90±0.02 (shoulder) μ assigned to aromatic C=C stretching. In the former substance there were bands at 6.86 and 7.01 μ which could be assigned to methylene deformations of the two types of methylene groups in the molecule. In the region 7.5-10.0 μ there were a number of strong bands whose origin has been assigned to C-F vibrations (29).

The proton NMR spectrum showed unsplit phenyl hydrogens, and extremely split tertiary and methylene hydrogens. The fluorine NMR spectrum was not taken.

1,1-Difluoro-3-phenylcyclobutane became cloudy after only one or two minutes' exposure to air. This material turned yellowish after standing several hours at room temperature, but a sample which had stood for a year still had a vapor phase chromatogram indicating that it was at least 88% one component.

2-Fluoro-3-phenylcyclobut-2-enone.--In a 300-ml. conical flask, a mixture of 35.0 g. (0.190 mole) of 1,1,2-trifluoro-3-phenylcyclobut-2-ene and 150 ml. of concentrated sulfuric acid (assay 98%) was heated and swirled on a steam bath until the mixture became homogeneous. The solution was slowly poured onto ice with vigorous stirring, and the white solid which precipitated was collected by suction filtration, washed twice with water, four times with dilute aqueous sodium bicarbonate, and then twice more with water. The crude air-dried product was pumped under high vacuum overnight to give 28.6 g. (93%) of material, m.p. 76-80°. Two recrystallizations from 60-70° petroleum ether (Norite) gave white needles, m.p. 79.2-80.8°; lit., m.p. 82.0-83.0° (15).

2-Fluoro-1,1-dichloro-3-phenylcyclobut-2-ene.--A mixture of 25.0 g. (0.154 mole) of 2-fluoro-3-phenylcyclobut-2-enone, 33.6 g.(0.160 mole) of phosphorus pentachloride, and 180 ml. of dry benzene was refluxed for twelve hours. After the reaction mixture had cooled, it was poured into 500 ml. of ice-water slurry and swirled several minutes. The benzene layer was diluted with ether and separated from the aqueous phase. The organic layer was washed several times with water, twice with dilute aqueous potassium carbonate, and then twice more with water. After being dried in two stages over anhydrous magnesium sulfate, the solvent was distilled. As the last traces of the benzene were being removed under reduced pressure with gentle heating, the product began to sublime. The heating was stopped, and on cooling the residue solidified to a cream-colored solid (30.9 g., 92%), m.p. 52-57°. The infrared spectrum of this material revealed that it contained none of the starting material. Sublimation of a small amount of the crude material gave cream-colored needles, m.p. 56-60°. Repeated sublimation failed to sharpen the melting point.

Anal. Calcd. for $C_{10}H_7FCl_2$: C, 55.33; H, 3.25; Cl, 32.67. Found: C, 55.40; H, 3.32; Cl, 32.47.

The infrared spectrum is summarized in Table I above. The ultraviolet and **NMR** spectra were not observed.

When 2-fluoro-1,1-dichloro-3-phenylcyclobut-2-ene was mixed with concentrated sulfuric acid, a purple mixture resulted. This mixture was heated for several minutes on a steam bath and then poured into a test tube filled with ice. The white precipitate was collected by filtration and recrystallized from 60-70° petroleum ether. The product, m.p. 80-81°, gave an infrared spectrum identical with that of 2-fluoro-3-phenylcyclobut-2-enone. The melting point of an admixture with an authentic sample of the latter, m.p. 79.2-80.8°, showed no depression.

2-Fluoro-1,1,2-trichloro-3-phenylcyclobutene.--In a 100 ml. round-bottomed flask fitted with a reflux condenser and closed to moisture with a calcium chloride drying tube, 9.0 g. (0.045 mole) of 2-fluoro-2-chloro-3-phenylcyclobutenone (prepared by Dr. Marjorie Caserio), 10.0 g. (0.048 mole) of phosphorus pentachloride and 50 ml. of dry benzene were refluxed for 24 hours. After the mixture had cooled, it was poured into an ice-water slurry. Ether (50 ml.) was added to break the emulsion, and the organic layer was separated, washed four times with water and dried in two stages with anhydrous magnesium sulfate. The solvent was evaporated in an air stream, and distillation of the residue through a 10-cm. Vigreux column gave 10.0 g. (87%) of a colorless liquid, b.p. 79-83° (less than 1 mm.). The infrared spectrum showed that the product contained about 5% of the starting material. The product was chromatographed on acid-washed activated alumina using hexane as the eluent. The first 150 ml. of the eluate contained the product. The solvent was evaporated in an air stream, and the residue was distilled to give 9.0 g. of colorless product, b.p. 61-66° (less than 1 mm.), $n^{25}D$ 1.5798. The infrared spectrum showed complete absence of carbonyl absorption at 5.57 μ due to starting material.

Anal. Calcd. for $C_{10}H_6FCl_3$: C, 47.75; H, 2.40; Cl, 42.29. Found: C, 47.74; H, 2.51; Cl, 42.28.

The infrared spectrum is summarized in Table I above. The ultraviolet and NMR spectra were not observed.

2-Fluoro-1,1,2-trichloro-3-phenylcyclobutene (0.20 g., 0.00079 mole) was mixed with concentrated sulfuric acid, and a light-brownish, two-phase mixture resulted. This mixture was heated on a hot plate with swirling. There was slight gas evolution, and the mixture became deep brown. A yellow solid precipitated when the reaction mixture was poured onto ice. The solid was collected and dried under high vacuum to give 0.10 g. (78%) of yellow powder, m.p. 130-145°. Sublimation of a portion of this material under high vacuum gave bright-yellow micro needles, m.p. 150-152°. The infrared and ultraviolet spectra of this material were identical with those of phenylcyclobutadienoquinone (11), and the mixed melting point with an authentic sample of phenylcyclobutadienoquinone (prepared by Dr. C. M. Sharts) showed no depression.

2,4-Dichloro-3-phenylcyclobutenone.--In a 300-ml. conical flask, 80 g. of concentrated sulfuric acid (assay 98%) was heated on a steam bath until the temperature was about 75°. Then 40.0 g. (0.170 mole) of 1,1-difluoro-2,4-dichloro-3-phenylcyclobutene was added at once. Heating and stirring wewe continued for about 25 minutes. The mixture was poured with vigorous stirring onto crushed ice. The tan solid was collected by suction filtration, washed four times with water, three times with dilute aqueous sodium bicarbonate (total volume 300 ml.), and then three more times with water. The solid was sucked dry and pumped under vacuum overnight. The crude yield was 32.9 g. (91%). Recrystallization from denatured ethanol gave 27 g. (75%) of light-tan needles, m.p. 73-76°. Repeated recrystallization from denatured ethanol gave white needles, m.p. 77.0-78.6°; lit., m.p. 78-80° (10).

"1,1,2,4-Tetrachloro-3-phenylcyclobutene".--In a 300-ml. round-bottomed flask protected from moisture by a calcium chloride drying tube, a mixture of 27.0 g. (0.127 mole) of 2,4-dichloro-3-phenylcyclobutenone, 29.0 g. (0.138 mole) of phosphorus pentachloride, and 150 ml. of dry benzene was refluxed for 24 hours. After the reaction mixture had cooled, it was poured onto crushed ice. When the ice had melted, the benzene layer was separated, washed twice with water, twice with dilute aqueous sodium bicarbonate, finally three more times with water and dried in two stages with anhydrous magnesium sulfate. The benzene was evaporated in a stream of air on a steam bath, and the residue was pumped for one hour at reduced pressure to remove the last traces of solvent. Distillation through a 10-cm. Vigreux column gave 31.3 g. (92%) of slightly yellow, viscous liquid, b.p. 92-97° (less than 1 mm.), $n^{25}D$ 1.6036. The infrared spectrum of some preparations showed the presence of starting material which could be removed by chromatography on acid-washed activated alumina with benzene or hexane as the eluent.

Anal. Calcd. for $C_{10}H_6Cl_4$: C, 44.82; H, 2.26; Cl, 52.93. Found: C, 45.04; H, 2.20; Cl, 52.14.

The infrared spectrum showed a band at 3.26 μ due to aromatic C-H stretch, a band at 6.09 μ assigned to C=C stretch and six bands at 6.24, 6.32, 6.36, 6.42 (shoulder), 6.71 and 6.93 μ whose origin is most probably due to aromatic C=C stretch. In all the other 3-phenylcyclobutenes studied at most four bands have been found in this region.

The ultraviolet spectrum in cyclohexane had λ_{max} 271.0 mμ (ϵ 14,300), $\lambda_{shoulder}$ 210.0 mμ (ϵ 15,300) and $\lambda_{shoulder}$ 203.5 mμ (ϵ 19,400). This spectrum had numerous inflection points, and the series of sharp bands observed for other phenylcyclobutenes between 200 and 225 mμ were absent.

In a large test tube, a mixture of 1.5 g. (0.0056 mole) of "1,1,2,4-tetrachloro-3-phenylcyclobutene" and 5 ml. of concentrated sulfuric acid was heated with stirring in a boiling water bath. At intervals during a period of three hours, the lower brownish acid layer was removed with a dropper and replaced with fresh acid. The acid extracts were added to ice, and a cream-colored solid precipitated. After three hours, only a cream-colored emulsion resulted when the acid extract was added to ice. All of the solid previously obtained was collected by suction filtration, washed with water and dried under vacuum to give 0.50 g. (42%) of crude material which after recrystallization from ethanol (Norite) gave tan needles, m.p. 74-76°. The infrared spectrum was identical with that of 2,4-dichloro-3-phenylcyclobutenone. The melting point of a mixture with an authentic sample of 2,4-dichloro-3-phenylcyclobutenone, m.p. 77.0-78.6°, was 75.0-77.8°. Water was added to the residue remaining after the removal of the last acid extract, and this mixture was extracted once with ether. The ether was dried and evaporated in an air stream to give 0.45 g. (30%) of colorless liquid. The infrared spectrum of this material showed no band at 6.09 μ (present in the starting material and ascribed to $C=C$ stretch), but the band structure from 6.2-7.0 μ was identical with the starting material. In the starting material there was a strong band at 11.67 μ, but in this product the band was weaker by a factor of ten. No new bands were present.

To an excess of potassium t-butoxide in t-butyl alcohol, 3.0 g. of "1,1,2,4-tetrachloro-3-phenylcyclobutene" was added at once. There was a very vigorous exothermic reaction, and the mixture turned dark brown immediately. The mixture was refluxed for eight hours. Water was added, and the whole extracted with ether. The ether was dried and on evaporation gave a black tarry residue. Distillation through a glass tube packed with glass wool gave a very small amount of sweet-smelling colorless liquid. The infrared spectrum showed a band at 4.55 μ, which could be due to the presence of acetylenic material, and a band at 3.35 μ, which could be due to aliphatic C-H stretching. There was a band at 6.07 μ ascribed to $C=C$ stretch, but the band structure from 6.2-6.4 μ was weaker by a factor of four from that of the starting material. Careful redistillation did not yield any low-boiling acetylenic material.

2,2-Dichloro-3-phenylcyclobutenone.--A mixture of 20 g. (0.085 mole) of 1,1-diflucro-2,2-dichloro-3-phenylcyclobutene and 40 g. of concentrated sulfuric acid (assay 98%) was heated and swirled on a steam bath for eleven minutes and then poured slowly with vigorous stirring onto crushed ice. The precipitate was collected by filtration, washed with water twice, dilute aqueous sodium bicarbonate solution twice, and then twice more with water. Recrystallization from alcohol gave 10.8 g. of tan needles, m.p. 74-75°; lit., m.p. 79.5-80.5° (10). A second crop, 3.3 g. (total yield 78%), was obtained; m.p. 74-75°.

"1,1,2,2-Tetrachloro-3-phenylcyclobutene".--In a 250-ml. round-bottomed flask protected from moisture by a calcium chloride drying tube, a mixture of 19.3 g. (0.092 mole) of 2,2-dichloro-3-phenylcyclobutenone and 22.0 g. (0.105 mole) of phosphorus pentachloride in 150 ml. of dry benzene was refluxed for 24 hours. The reaction mixture was worked up as described above for the preparation of "1,1,2,4-tetrachloro-3-phenylcyclobutene." Distillation gave 21.7 g. (88%) of slightly yellow liquid, b.p. 94-101° (less than 1 mm.), $n^{25}D$ 1.6137. The infrared spectrum showed that about 5-10% of the starting material was present in the product, and a band at 4.73 μ suggested that some acetylenic material was present. The product was chromatographed on acid-washed activated alumina with hexane. The first 250 ml. of eluate contained 20.0 g. (81%) of material, b.p. 92-96° (less than

1 mm.), $n^{25}D$ 1.6082. The infrared spectrum of this product showed the absence of starting material. This product did not react with 2,4-dinitrophenylhydrazine reagent.

Anal. Calcd. for $C_{10}H_6Cl_4$: C, 44.82; H, 2.26; Cl, 52.93. Found: C, 45.01; H, 2.34; Cl, 52.78.

The infrared spectrum showed a band at 3.27 μ assigned to aromatic C-H stretch, a strong band at 5.55 μ, and a complex band structure from 6.0-6.9 μ having four principal bands at 6.18, 6.31, 6.71 and 6.92 μ assigned to aromatic C=C stretching. The origin of the band at 5.55 μ is unknown, but it cannot be due to C=O stretching since the elementary analysis of the tetrachloro material indicated that it contained essentially no oxygen.

The ultraviolet spectrum in cyclohexane had λ_{max} 271.0 mμ (ε 14,300), $\lambda_{shoulder}$ 210.0 mμ (ε 15,300) and $\lambda_{shoulder}$ 203.5 mμ (ε 19,400). The region 200-220 mμ showed no fine structure characteristic of other 3-phenylcyclobutenes. The ultraviolet spectrum in 95% ethanol changed markedly with time.

Attempts to hydrolyze the product with concentrated sulfuric acid to a solid carbonyl derivative in a manner similar to that described for "1,1,2,4-tetrachloro-3-phenylcyclobutene" failed.

A mixture of 1.0 g. of "1,1,2,2-tetrachloro-3-phenylcyclobutene", 1.0 g. of solid lithium chloride and 50 ml. of dry acetone was refluxed for 72 hours. The solid was removed by filtration, and the filtrate evaporated in a stream of nitrogen. The residue was taken up in ether, and the ether was removed in a stream of nitrogen to give some yellowish oil which was pumped under vacuum to remove the last traces of solvent. The infrared spectrum showed a number of changes. The C-H stretching region showed only one band at 3.27 µ as in the starting material. There was a sharp doublet at 5.58 and 5.61 µ, a sharp band at 6.08 µ, and a sharp band at 6.25 µ. The intensity of the band at 5.55 µ and the appearance of the doublet at 5.58 and 5.61 µ are consistent with the partial isomerization to the 2,4-tetrachloro compound and partial hydrolysis of this latter material by water present in the lithium chloride employed in this experiment to give some 2,4-dichloro-3-phenylcyclobutenone. The spectrum is also consistent with hydrolysis of some of the tetrachloro compound to the corresponding ketone which is then isomerized to 2,4-dichloroketone. A sharp band at 6.25 µ had previously been observed several times in preparations of the "1,1,2,2-tetrachloro" material before they were chromatographed. There is a band in the corresponding ketone at this position, but it has been shown that this ketone would have been isomerized readily to the 2,4-dichloro ketone under the conditions employed above (44). Thus the origin of the band at 6.25 µ is unknown.

Several preparations of "1,1,2,2-tetrachloro-3-phenylcyclobutene" in benzene solution were washed with dilute aqueous potassium carbonate in the isolation procedure. The infrared spectrum of the distilled products showed a sharp band at 4.74 μ which is about the normal position for the C≡C stretching in phenylacetylene. The C≡C stretching in chlorophenylacetylene falls at 4.52 μ. No pure acetylenic material could be isolated either by careful distillation or chromatography on alumina.

Preparation of 1% Lithium Amalgam.--In a pyrex combustion tube 60-cm. long, were placed 50 g. of mercury and 0.5 g. of freshly cut lithium wire. Helium was slowly blown over the metals, and the mixture was lowered into a Wood's metal bath heated to 200°. A vigorous exothermic reaction began after about 15 seconds, and the mercury refluxed for about one minute. The reaction was completed by shaking and poking the slush at the bottom of the tube with a thick glass rod. After the contents of the tube had cooled, the tube was cut near the bottom, and the semi-solid product was removed with a spatula. The amalgam was stored under dry ether in a glass-stoppered flask. The amalgam was very lumpy. It was found later that the amalgam formed with 50 g. of mercury and 0.25 g. of lithium (0.5% amalgam) is much more homogeneous.

Reaction of "1,1,2,4-Tetrachloro-3-phenylcyclobutene" with 1% Lithium Amalgam.--In a 125-ml., oven-dried, glass-stoppered flask 25 g. (0.036 mole) of 1% lithium amalgam and 3.0 g. (0.011 mole) of "1,1,2,4-tetrachloro-3-phenylcyclobutene" in 50 ml. of dry ether were allowed to stand at room temperature. The mixture turned brown after several minutes.

No gas had been evolved after the mixture had stood for two days, but considerable tan precipitate had formed. The excess amalgam and precipitate were removed by filtration, and the ether was distilled through a 30-cm. Vigreux column until only about 2-3 ml. of liquid remained. The residue was pumped under reduced pressure to remove the last traces of solvent. The brown oil remaining was distilled to give 1.5 g. of cloudy, yellowish liquid and considerable black still residue. Redistillation only resulted in further decomposition. The infrared spectrum of this material indicated that it was mostly starting material but contained some acetylenic material since there were bands at 3.03 μ characteristic of ≡C-H stretch and 4.56 μ characteristic of C≡C stretch in chlorophenylacetylene. Attempts to trap some of the acetylenic material by redistilling at a lower temperature and higher pressure gave nothing and only resulted in further decomposition. If phenylacetylene and chlorophenylacetylene were the two acetylenic derivatives present, the infrared spectrum indicated that they were present in about the ratio of 1:5, respectively.

Reaction of "1,1,2,2-Tetrachloro-3-phenylcyclobutene" with 1% Lithium Amalgam.--The procedure and quantities of materials used were identical with those of the previous experiment. The mixture darkened much more rapidly than in the case of the "1,1,2,4-tetrachloro" material, but there was no evolution of gas. The mixture was worked up as described above. Distillation gave 0.8 g. of brown, cloudy liquid and considerable black tar in the still. The infrared spectrum was quite different from that of the starting material. The strong band at 5.55 μ was completely absent. The region 6.0-6.5 μ was the same general shape as in the starting material but only about one-half as intense. There were strong bands at 3.02 and 4.56 μ and a weak band at 4.77 μ. Attempts to isolate any acetylenic material by redistillation failed. The bands at 3.02 and 4.77 μ are of the correct position and relative intensities to be assigned to the ≡C-H stretch and the C≡C stretch in phenylacetylene. The band at 4.56 μ is assigned to the C≡C stretch of chlorophenylacetylene. The infrared spectrum indicated that phenylacetylene and chlorophenylacetylene were present in the ratio of 2:1, respectively.

<u>Methylstyrylcarbinol</u>.--In a 200-ml. conical flask, 34.8 g. (0.238 mole) of benzalacetone (Eastman White Label) was dissolved in 100 ml. of absolute ethanol, and the solution was cooled to 0°. Sodium borohydride, 9.05 g. (0.238 mole), was added slowly over a period of ten minutes with vigorous swirling to the ice-cooled solution. After the addition of the borohydride was complete, the solution was heated and swirled on a steam bath for one minute and then allowed to stand for fifteen minutes. The solution was poured onto an ice-water slurry. When the ice had melted, the two-phase

system was extracted three times with ether, and the ether extracts were dried in four stages with anhydrous magnesium sulfate. The ether was distilled until the temperature rose to 50°, and then the residue was pumped at reduced pressure to remove the last traces of solvent. Distillation through a 10-cm. Vigreux column gave 29.6 g. (82%) of a colorless liquid, b.p. 73-81° (less than 1 mm.), $n^{25}D$ 1.5594; lit., b.p. 106° (18 mm.) (45). The infrared spectrum showed no carbonyl absorption. There was a broad band at 3.0 μ characteristic of O-H stretch. There were three bands at 3.30, 3.39 and 3.51 μ assigned to the various C-H stretching vibrations. The bands at 6.25, 6.34, 6.69 and 6.90 μ were assigned to aromatic C=C stretch, and the weak band at 6.03 μ was assigned to C=C stretch. A broad band at 7.1 μ could be due to C-H deformation.

The 4-nitrobenzoate was prepared by the pyridine method (41). Recrystallization of this ester from a number of solvent systems gave only oils which crystallized after standing in the refrigerator for from several days to several weeks. Five "recrystallizations" (the material oiled out) from pentane gave a white powder, m.p. 61-65°; lit., m.p. 60° (55).

Anal. Calcd. for $C_{17}H_{15}O_4N$: C, 68.67; H, 5.09. Found: C, 68.84; H, 5.15.

4-Nitrobenzoate of Cinnamyl Alcohol.--The ester was prepared from the alcohol and acid chloride in pyridine (41) and after three recrystallizations from pentane had m.p. 76.5-

77.0°; lit., m.p. 78° (41).

Anal. Calcd. for $C_{16}H_{13}O_4N$: C, 67.84; H, 4.63. Found: C, 67.62; H, 4.72.

Kinetic Method.--The rate measurements were made by a procedure similar to that described by Goering and Silversmith (48). In all but one case, a weighed amount of ester was washed into an uncalibrated volumetric flask, and the flask was filled to the mark with solvent thermostated to 25.0°. Then 4.987 ml. portions of the ester solution were pipetted into constricted 18 x 150 mm. pyrex test tubes which had been scrupulously cleaned. Experience showed that care had to be taken not to touch the sides of the neck of the ampule in filling. Any material accidentally deposited on the neck of the ampule was carefully wiped out in order to avoid flaming back on sealing. After addition of the ester solution, the ampules were allowed to stand in an ice bath for five minutes before sealing. The 4-nitrobenzoate of 2-chloro-3-phenylcyclobut-2-enol was so insoluble in the solvent at room temperature that individual samples (20-30 mg.) were carefully transferred into test tubes which were then constricted before the addition of 4.987 ml. of solvent.

The solvent was made by mixing 80% by volume of acetone with 20% by volume of boiled, distilled water (56). The acetone was purified by a published method (57). The acid solvent was made in a similar manner, except that a solution of reagent grade perchloric acid in boiled, distilled water was mixed with the acetone. Two different batches of acid solvent were prepared, one being 0.0960 N and the other being 0.0951 N in perchloric acid. Three different batches of 0.02 N sodium hydroxide were prepared, normalities 0.01962, 0.01910 and 0.01894. Two different batches of 0.01 N base were prepared, normalities 0.01155 and 0.01062. The standard solutions used in any individual kinetic run are indicated with the data for that run in Tables IV-XII.

Solvent blanks definitely showed that there was an increase of titer with time. In the first twelve hours the increase was about 0.10 ml. of 0.01 N base, and after about thirty-six hours it was about 0.20 ml. The solvent blanks became quite yellow after 10-12 hours. The solvent system was not investigated spectrophotometrically. Plain "80%" acetone—water was colorless after being kept at 100° for three weeks.

Most of the kinetic runs were 50% complete after 20 hours. Initial rate constants were obtained graphically from plots of $\log (x_o - x/x_o)$ versus time where $\underline{x_o}$ is the initial equivalents of ester present and $\underline{x}$ is the equivalents of acid titrated at time $\underline{t}$. Every run was linear to at least 50% completion.

After each ampule had been placed in the mineral oil bath for the specified time, it was quickly removed and quenched in an ice-water slurry or, in the case of the faster-reacting esters, an isopropyl alcohol-Dry Ice bath. The ampule was warmed to room temperature, wiped with paper towels to remove the mineral oil, scratched with a carborundum point, placed in an ice bath and opened by application of a hot glass rod to the scratch. The contents were transferred to a 150-ml. beaker containing a nitrogen atmosphere and a Teflon-covered magnetic stirring bar. The ampule was washed very carefully with a total of 5-8 ml. of reagent acetone in order to remove the last traces of acid. This is the most important step in the analysis scheme because of the high concentration of acid present relative to the small amount of acid produced. Next, 24.88 ml. of 0.02 N carbonate-free sodium hydroxide solution was pipetted into the beaker. At this point a significant amount of solid usually precipitated, but experience showed that the solid did not affect the titration. The mixture was immediately titrated under nitrogen with 0.01 N carbonate-free sodium hydroxide solution to pH 7.50 for the 4-nitrobenzoates and to pH 8.50 for the single acetate studied (See Section III). A Leeds and Northrup direct-reading pH meter was employed. Preliminary titrations using indicators gave poor results.

If a larger ester concentration could have been employed along with a lower acid concentration, the accuracy of the method would have been increased. The quantity of pure materials available and the insolubility of several of the esters in the solvent system chosen were the limiting criteria for the concentration range employed (approximately 0.01 N in ester).

The analyses and melting points of the esters solvolyzed are summarized in Table III below. The rate data are summarized in Tables IV-XII.

TABLE III

Melting Points and Analyses of the Esters Hydrolyzed

	M.p. °C.	Analysis % Calculated C	H	Cl	Found C	H	Cl
I. 4-Nitrobenzoates							
Cinnamyl Alcohol	76.5-77.0	67.84	4.63		67.62	4.72	
Methylstyrylcarbinol	61-65	68.67	5.09		68.84	5.15	
Cyclobutanol (sample obtained from Marc S. Silver)	86.5-87.4	59.72	5.01		59.59	4.98	
cis-3-Phenylcyclobutanol	131-132	68.67	5.09		68.80	5.23	
trans-3-Phenylcyclobutanol	60.7-63.0	68.67	5.09		68.62	5.05	
2-Chloro-3-phenylcyclobut-2-enol	172-173	61.92	3.67	10.75	62.10	3.80	10.71
3-Phenylcyclobut-2-enol	146-149	69.14	4.44		69.05	4.60	
II. Acetate							
1,3-Diphenylcyclobutanol	89.8-90.6	81.17	6.81		81.02	6.93	

TABLE IV

Acid-catalyzed Hydrolysis of Cinnamyl 4-Nitrobenzoate in 80% Acetone-water 0.0960 N in Perchloric Acid at 100.20±0.02°

Kinetic Run 10*

t, hr.	Ml. of 0.01155 N base (corrected) after addition of 24.88 ml. of 0.01910 N base	% Unreacted	$10^2 \times k_1'$, hr.$^{-1}$
0.0	0.000	100.0	
1.0	0.500	91.3	9.10
3.0	1.110	80.7	7.13
4.0	1.010	72.0	8.21
8.25	2.955	48.6	8.74
10.0	3.225	43.9	8.22
15.5	4.390	23.7	9.30
20.5	4.955	13.8	9.66
24.5	5.390	6.26	11.31

Best initial rate constant obtained graphically = $8.26 \pm 0.49 \times 10^{-2}$ hr.$^{-1}$

Kinetic Run 12*

t, hr.	Ml. of 0.01155 N base (corrected) after addition of 24.88 ml. of 0.01910 N base	% Unreacted	$10^2 \times k_1'$, hr.$^{-1}$
0.0	0.000	100.0	
2.0	0.685	88.1	6.34
3.5	1.470	74.4	8.42
6.0	2.190	61.9	7.98
7.75	2.620	54.4	7.84
11.5	3.645	36.6	8.73
15.0	4.520	21.4	10.28
20.08	4.740	17.6	8.66
26.0	5.660	1.57	15.99

Best initial rate obtained graphically = $8.35 \pm 0.49 \times 10^{-2}$hr.$^{-1}$

*Theoretical titer 5.750 ml.; 0.01225 N in ester

TABLE V

Acid-catalyzed Hydrolysis of Methylstyryl Carbinyl 4-Nitrobenzoate in 80% Acetone-water 0.0951 N in Perchloric Acid at 100.20±0.02°

Kinetic Run 16*

t, min.	Ml. of 0.01062 N base (corrected) after addition of 24.88 ml. of 0.01894 N base	% Unreacted
0.0	0.000	100.0
2.5	0.660	87.9
3.0	1.045	80.9
4.0	1.500	72.5
5.0	2.210	59.5
8.17	3.235	40.8
10.0	3.590	34.3
12.5	4.155	24.5
20.0	4.795	12.2
30.0	4.970	9.52
60.0	5.025	7.97
130.0	5.355	6.50

Best initial rate constant obtained graphically = 7.73±0.22 hr.$^{-1}$. Graphically obtained rate constant for a slower reacting minor component = 0.17±0.02 hr.$^{-1}$

*Theoretical titer 5.460 ml.; 0.01163 N in ester.

TABLE VI

Acid-catalyzed Hydrolysis of Cyclobutyl 4-Nitrobenzoate in 80% Acetone-water 0.0960 N in Perchloric Acid at 100.20±0.02°

t, hr.	Ml. of 0.01062 N base (corrected) after addition of 24.88 ml. of 0.01910 N base	% Unreacted	$10^{2} x k_{1}$, hr.$^{-1}$
		Kinetic Run 13*	
0.00	0.000	100.0	
0.25	0.070	98.4	12.3
	0.145	97.0	6.31
2.0	0.395	91.8	4.31
	0.315	93.4	3.38
5.0	0.910	81.0	4.22
	0.850	82.2	3.91
8.0	1.420	70.3	4.40
	1.370	71.4	4.42
11.0	1.670	65.1	3.90
	1.695	64.5	3.97
11.52	1.795	62.5	4.08
14.0	1.990	58.4	3.84
	2.115	55.8	4.17
19.5	2.840	40.7	4.62
	2.655	44.5	4.14
24.5	3.220	32.7	4.56
29.5	3.440	28.1	4.27
	3.800	20.6	5.31

Best initial rate constant obtained graphically = 4.02±0.20 x 10^{-2}hr.$^{-1}$

*Theoretical titer 4.785 ml.; ester 0.01019 N.

TABLE VII

Acid-catalyzed Hydrolysis of cis-3-Phenylcyclobutanyl 4-Nitrobenzoate in 80% Acetone-water 0.0960 N in Perchloric Acid at 100.20±0.02°

t, hr.	Ml. of 0.01155 N base (corrected) after addition of 24.88 ml. of 0.01910 N base	% Unreacted	$10^2 \times k_1'$, hr.$^{-1}$
	Kinetic Run 8*		
0.0	0.000	100.0	
2.0	0.310	93.2	3.54
5.5	0.765	83.1	4.10
9.0	1.065	76.5	2.98
13.0	1.725	61.9	3.68
19.0	2.285	49.6	3.67
25.0	3.075	32.1	4.54
27.0	2.950	34.9	3.90
30.0	3.230	28.7	4.16

Best initial rate constant obtained graphically =

$3.60 \pm 0.38 \times 10^{-2}$ hr.$^{-1}$

Kinetic Run 9*

0.0	0.000	100.0	
2.0	0.360	92.1	4.14
5.0	0.790	82.6	3.83
7.25	0.975	78.5	3.34
10.0	1.430	68.4	3.79
13.5	1.775	60.8	3.68
18.5	2.425	46.5	4.14
22.0	2.685	40.7	4.08
27.5	3.175	29.9	4.39
31.0	3.475	23.4	4.69

Best initial rate constant obtained graphically =

$3.77 \pm 0.14 \times 10^{-2}$ hr.$^{-1}$

*Theoretical titer 4.530 ml.; 0.01049 N in ester.

TABLE VIII

Acid-catalyzed Hydrolysis of trans-3-Phenylcyclobutanyl 4-Nitrobenzoate in 80% Acetone-water 0.0951 N in Perchloric Acid at 100.20±0.02°

t, hr.	Ml. of 0.01062 N base (corrected) after addition of 24.88 ml. of 0.01894 N base	% Unreacted	$10^2 \times k_1'$, hr.$^{-1}$
0.0	0.000	100.0	
3.02	0.255	92.2	2.68
6.02	0.845	74.2	4.94
8.75	1.275	61.1	5.62
12.0	1.580	51.8	4.56
14.0	1.320	59.8	3.67
20.0	1.910	41.8	4.37
23.25	2.150	34.5	4.58

Best initial rate constant obtained graphically = $4.52 \pm 0.63 \times 10^{-2}$ hr.$^{-1}$

*Theoretical titer 3.280 ml.; 0.00698 N in ester.

TABLE IX

Acid-catalyzed Hydrolysis of 3-Phenylcyclobut-2-enyl 4-Nitrobenzoate in 80% Acetone-water 0.0951 N in Perchloric Acid at 100.20±0.02°

t, min.	Ml. of 0.01062 N base (corrected) after addition of 24.88 ml. of 0.01894 N base	% Unreacted
	Kinetic Run 11*	
0.0	0.000	100.0
3.0	0.215	95.4
5.0	0.415	91.2
10.0	0.665	85.8
15.0	0.930	80.2
25.0	1.630	65.3
40.0	2.235	52.8
60.0	2.905	38.1
90.23	3.545	24.5
120.00	3.835	18.3

Best initial rate constant obtained graphically = 0.996±0.026 hr.$^{-1}$

t, min.	Ml. of 0.01062 N base (corrected) after addition of 24.88 ml. of 0.01894 N base	% Unreacted
	Kinetic Run 14**	
0.0	0.000	100.0
3.0	0.185	96.1
10.0	0.655	86.1
20.0	1.280	72.8
35.0	2.020	57.1
50.0	2.620	44.3
70.0	3.240	31.1
90.0	3.575	24.0
120.0	3.975	15.5
180.0	4.380	6.91

Best initial rate constant obtained graphically = 0.986±0.012 hr.$^{-1}$

*Theoretical titer 4.695 ml.; 0.01000 N in ester.
**Theoretical titer 4.705 ml.; 0.01002 N in ester.

TABLE X

Acid-catalyzed Hydrolysis of 2-Chloro-3-phenylcyclobut-2-enyl 4-Nitrobenzoate in 80% Acetone-water 0.0960 N in Perchloric Acid at 100.20±0.02°

t, hr.	Infinity titer of sample in ml.	Ml. of 0.01155 N base (corrected) after addition of 24.88 ml. of 0.01962 N base	% Unreacted	10^2 xk_1', hr.$^{-1}$
		Kinetic Run 4		
0.0		0.000	100.0	
2.5	5.595	0.510	90.9	3.81
5.0	5.725	1.035	81.9	3.99
10.5	6.470	2.150	66.8	3.84
13.0	5.365	2.355	56.1	4.44
16.0	5.340	2.380	55.5	3.69
23,0	5.805	3.385	41.7	3.80
32.5	5.585	4.470	20.0	4.96
Average value of rate constant* = 3.93±0.19 x 10^{-2}hr.$^{-1}$				
		Kinetic Run 6**		
0.0		0.000	100.0	
2.5	5.940	0.570	90.5	4.03
4.5	6.005	0.845	85.9	3.37
10.0	5.885	1.955	68.0	4.03
13.0	5.950	1.970	66.9	3.09
18.0	6.330	2.975	53.0	3.52
23.5	5.910	3.295	44.2	3.47
28.0	6.715	4.745	29.3	4.38
36.5	5.780	4.765	17.6	4.76

Average value of rate constant* = 3.59±0.30 x 10^{-2}hr.$^{-1}$

*In each case the last point was not included in the average, and in Run 6 the 28.0 hr. point was not included in the average.

**Titration with 0.01155 N base after addition of 24.88 ml. of 0.01910 N base.

TABLE XI

Acid-catalyzed Hydrolysis in the Material Believed to be 1,3-Diphenylcyclobutyl Acetate in 80% Acetone-water 0.0951 N in Perchloric Acid at 100.20±0.02°

t, min.	Ml. of 0.01062 N base (corrected) after addition of 24.88 ml. of 0.01894 N base	% Unreacted
		Kinetic Run 15*
0.0	0.000	100.0
2.5	1.650	67.7
3.5	2.575	49.7
4.0	3.020	41.0
5.0	3.440	32.8
10.0	4.655	8.99
17.5	4.925	3.72
120.0	4.985	2.54

Best initial rate constant obtained graphically = 18.7±0.7 $hr.^{-1}$

*Theoretical titer 5.115 ml.; 0.01089 N in ester.

TABLE XII

Preliminary Study of the Uncatalyzed Solvolysis of 3-Phenylcyclobut-2-enyl 4-Nitrobenzoate in 80% Acetone-water at 100.20±0.02°

Kinetic Run 18*

t, hr.	Ml. of 0.01062 N base	% Unreacted	$10^2 \times k_1$, hr.$^{-1}$
0.0	0.000	100.0	
5.5	0.450	88.9	2.14
18.25	1.140	71.89	1.81
42.25	1.995	50.8	1.60
64.42	2.515	38.0	1.50

Best initial rate constant obtained graphically = $2.63 \pm 0.13 \times 10^{-2}$ hr.$^{-1}$

*Theoretical titer 4.055 ml.; 0.00863 N in ester.

PART II

CALCULATION OF THE DELOCALIZATION ENERGIES OF SOME SMALL-RING SYSTEMS EMPLOYING THE SIMPLE MOLECULAR ORBITAL TREATMENT

INTRODUCTION

The molecular orbital (M.O.) and valence bond (V.B.) treatments are the two quantum mechanical methods most often used to obtain approximate ideas of the electronic structures of complex molecules. Application of either method leads to a secular determinant (eigenvalue matrix). In the V.B. treatment, the secular determinants are very large even for only moderately complicated molecules, and the eigenvalue λ usually appears both off and on the main diagonal of the determinants. Diagonalization is not always possible. The M.O. method always gives secular determinants with λ only on the principal diagonal. This type of eigenvalue matrix is much easier to solve than the former situation. Also, for a given system, the M.O. method generally yields a much smaller secular determinant than does the corresponding V.B. treatment. For the above reasons and because of its simplicity, the molecular orbital method treatment is the most widely employed of the two methods. In the present research, the simple molecular orbital method (LCAO) was used in a theoretical survey of a number of conjugated small-ring compounds.

DISCUSSION

A previous study of the application of the simple molecular orbital method (LCAO) to many small-ring hydrocarbons and free radicals was made by Roberts, Streitwieser and Regan (58). One purpose of this work was "a search for new cyclic conjugated systems, particularly derivatives of cyclobutadiene, which might be predicted on the theoretical grounds to be reasonably stable." The present survey is an extension of this work to more complex systems with which numerical computations would have been difficult without the aid of a high-speed digital computer, in this case the Datatron 204 (59).

All of the calculations were carried out by the simple molecular orbital method (LCAO) (60, 61, 62, 63) with neglect of resonance integrals between non-adjacent atoms and of non-orthogonality of atomic orbitals on different atoms. Group theory procedures were employed to factor the secular determinants where possible (62). The results obtained are regarded as only essentially qualitative because of the known limitations of the LCAO method (64). For each system the delocalization energy (DE) and a ΔDE value in units of β (about -20 kcal/mole) are given. Originally it was intended to calculate also the bond orders and the "free-valence" indices for each system. However, although the Datatron routine for the solution of the eigenvalue problem also yields for each eigenvalue the magnitude of all its eigenvectors, these are given only to an arbitrary basis. In order to calculate the properties mentioned above, each set of vectors must be re-normalized to unity. This process is cumbersome to perform by hand and a Datatron sub-routine was written to perform this computation, but limitation of time prohibited its use to finish computation of the bond-orders and the "free valences." A description of the use of this sub-routine is given in the Appendix below.

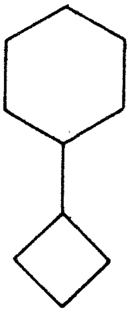
For each compound for which the simple molecular orbital theory predicts a triplet ground state, a "T" is placed after the DE value in the figures on the following pages. In some of the figures only the carbon framework is shown, each corner representing a carbon atom. In the other cases a valence bond structure is drawn for identification.

Compounds I-XXII are cyclobutadiene derivatives of various types. Cyclobutadiene itself is predicted to have zero DE and an unstable triplet ground state (58,65,66). So far all attempts to prepare cyclobutadiene itself have failed. It has been stated that the apparent instability of the substance cannot be wholly due to angular strain, since cyclopropene which should have comparable or greater strain is known. However, the apparent instability might be due to the triplet ground state (65). Jahn and Teller (67) have proved that orbital degeneracy such as gives a lowest triplet state and molecular stability are simultaneously incompatible except for linear molecules. This means that a square molecule in a triplet state would have at least one normal mode of vibration with a negative restoring force and hence be unstable. Consequently cyclobutadiene with its square arrangement might well possess an intrinsic "decomposition coordinate" which would cause it to undergo, for all practical purposes, instantaneous decomposition. Coulson and Moffitt (65) have discussed the magnitude of the strain energy in cyclobutadiene using the bent-bond and pairing approximations. Using a variational procedure, they arrived at a figure of about 0.8 electron volt (18 kcal.) of strain energy per C-H for cyclobutadiene or a total strain energy of about 72 kcal. By the method described in Section 4, Part 1 (26) an estimate of about 67 kcal. was obtained. These latter figures are significantly higher than the estimate of 45 kcal. made by Roberts (2). Comparisons of several other strain energy calculations show that all of the theoretical treatments so far conceived predict strain energies greater than those observed from heats of combustion studies for cyclobutane (20-50% too high) and cyclopropane (400% too high) (26). Roberts' estimate of 45 kcal./mole for cyclobutadiene thus seems quite reasonable.

Craig (68) has discussed the validity of application of the simple molecular orbital treatment to calculation of the properties of cyclobutadienes and other pseudo-aromatic compounds where neglect of configuration interaction is likely to be particularly important. He has concluded that many of these compounds should not act like ordinary aromatic compounds, but should show considerable bond fixation with unequal bond distances and considerable tendencies toward polymerization. Recently it has been believed that cyclobutadiene derivatives have been formed as reaction intermediates when a 3,4-dihalocyclobutene or mono- and dihalobenzocyclobutenes are treated with an active metal or base (69). If cyclobutadiene systems are produced, they are indeed reactive and either add to themselves or to a diene in high yields.

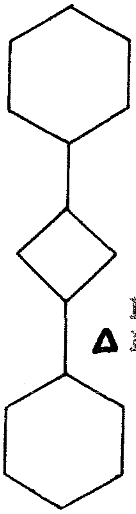
Previously it has been shown that various substituted (mostly vinyl) cyclobutadienes without fused rings are predicted to have moderate DE's but to possess triplet ground states (58). In the present work, the effect of phenyl substitution on the predicted delocalization energy imparted to the cyclobutadiene ring is shown by compounds I-VII. The ΔDE given in the figures is calculated in the following manner: from the total DE of the system the portion of the DE assumed to be characteristic of the isolated substituents is subtracted. As an example, for

I



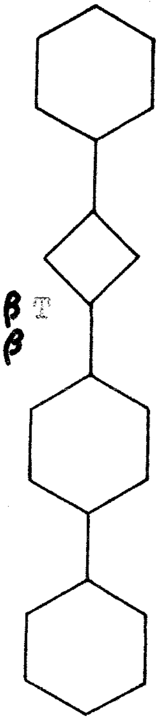
DE 2.5273 β T
Δ DE 0.5273 β

II



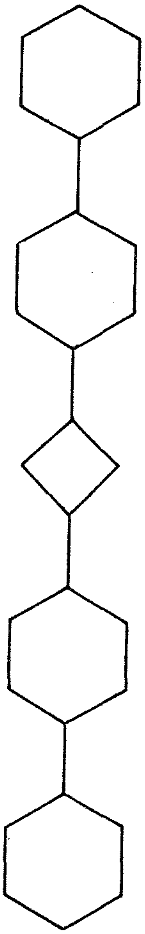
DE 5.0196 β T
Δ DE 1.0196 β

III



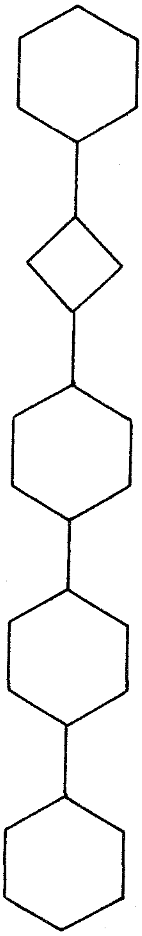
DE 7.4212 β T
Δ DE 1.0702 β

IV



DE 9.8240 β T
Δ DE 1.1220 β

V



DE 9.8140 β T
Δ DE (1.042 β ?)(71)

Fig. 12

III, the total DE is 7.4212 β. The DE for an isolated benzene ring is 2.0000 β and that for an isolated biphenyl system is 4.3510 β. Subtraction of these figures from the DE gives a ΔDE of 1.0702 β for the extra delocalization energy of the cyclobutadienyl ring with the substituents. In all the systems the ΔDE's were calculated in an analogous manner.

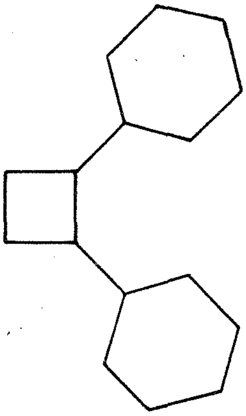
Substitution of one phenyl group on cyclobutadiene as in I gives a ΔDE of 0.5273 β while two phenyl groups in the 1,3-relation as in II give a ΔDE of 1.0196 β and in the 1,2-relation as in VI gives a ΔDE of 1.0588 β. The ΔDE's calculated here are slightly less than the ΔDE's calculated for vinyl substituents (58), and this might be because one should use slightly different carbon-carbon exchange integrals for polyenes than for aromatic systems. In the present work these integrals were all taken equal to β. There is some evidence bearing on this question (70) which suggests that a slightly smaller exchange integral should be used for polyenes. As is seen for II-V and VII, increasing the complexity of the phenyl substitution (either 1,3- or 1,2-) on the cyclobutadiene ring only increases the DE about 0.1 β. For all these compounds a triplet ground state is predicted (see the discussion above).

The difference between the DE of II and VI predicted by molecular orbital theory can be predicted qualitatively from simple valence bond theory since any ionic valence bond structures of II involving double bonds between the four- and six-membered rings should not be as stable as those that can be written for VI. For an ionic structure of VI it is possible for one of the charges to be in the phenyl ring and the opposite charge in the other phenyl ring. Thus there are correspondingly more valence bond structures which can be written for VI. A similar example of this effect is predicted for the cases of vinyl substituents (58).

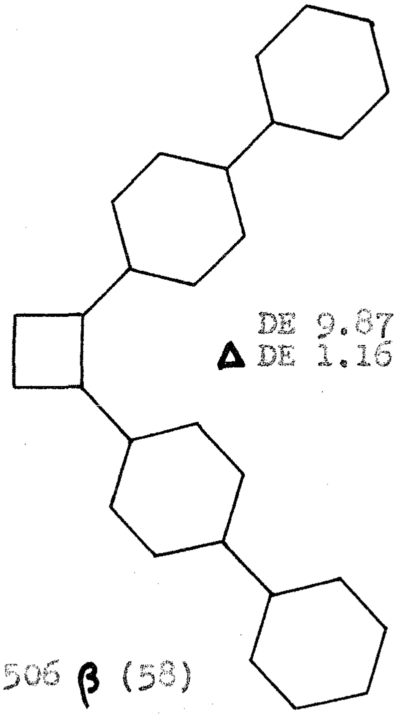
Several other types of substitution on the cyclobutadiene ring have not been explored by molecular orbital theory. Calculations on phenyl substituents in the 1,2,3- and 1,2,3,4-positions might give some interesting results. Strong electron donating and attracting groups in the phenyl rings of a 1,3- or 1,2-disubstituted cyclobutadiene might produce an electronic push-pull effect that would be evidenced by a very large increase in DE. Preliminary calculations were started in the present study taking a 4-amino and 4'-nitro group as the phenyl substituents, but none of the eigenvalue problems for these cases were solved.

VI

DE 5.0588 β T
Δ DE 1.0588 β

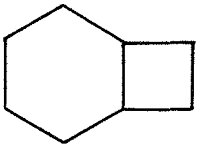


VII



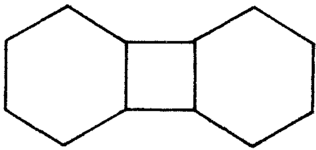
DE 9.8718 β T
Δ DE 1.1698 β

DE 2.3812 β (58)

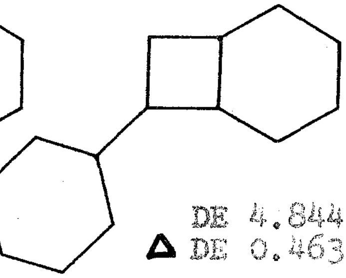


VIII

DE 4.506 β (58)

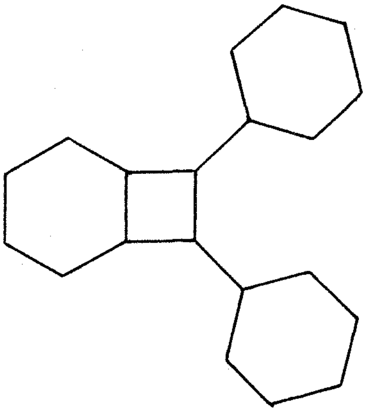


IX



DE 4.8448 β
Δ DE 0.4636 β

X



DE 7.3230 β
Δ DE 0.9418 β

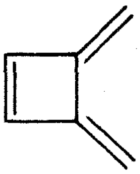
XI

Fig. 13

Systems VIII-XI are benzocyclobutadiene derivatives for which a triplet ground state is not predicted. As was mentioned above, VIII has been liberated in the reaction of an active metal with 1,2-dihalobenzcyclobutene or base on a 1-halobenzocyclobutene, and it has been found to be a very reactive species. IX is a stable compound and has been known for some time (72). A number of similar compounds are known (73). X and XI are two compounds on which no synthetic studies have been launched. X shows an increase of DE over VIII of 0.4636β and XI of 0.9418β. Since VIII is known now as an unstable intermediate, a moderate increase of DE of the benzocyclobutadiene system might allow one or the other of X and XI to be isolated. This prediction awaits experimental verification.

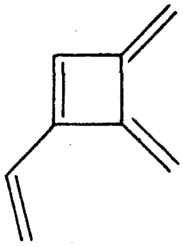
XII-XIX are cyclobutadiene derivatives for which a triplet ground state is not predicted. In all the compounds containing oxygen one must make allowances for the electronegativity at each heteroatom. The Coulomb integral for oxygen in a C=O bond was taken in this work as $\alpha + 2\beta$, and the C=O resonance integral as $\sqrt{2}\beta$ (27). XII-XV are diexomethylenecyclobutenes for which various synthetic pathways have been suggested (30). XV has been isolated recently by Blomquist and Meinwald (74). It will be interesting to compare the predictions of the simple molecular orbital theory with electron diffraction, X-ray, microwave, or thermochemical studies made on this substance.

XII



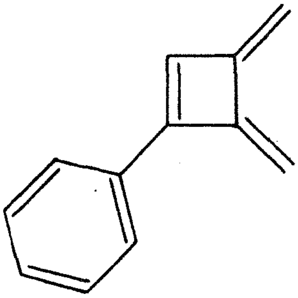
DE 1.2078 β

XIII



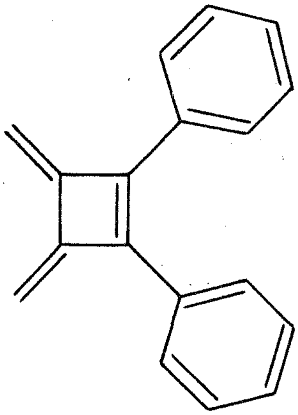
DE 1.6932 β
Δ DE 0.4854 β

XIV



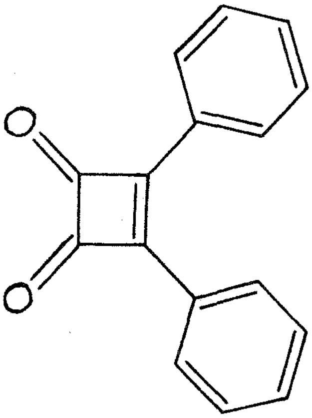
DE 3.4724 β
Δ DE 0.2646 β

XV



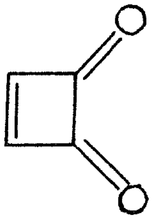
DE 6.0884 β
Δ DE 0.8806 β

XVI



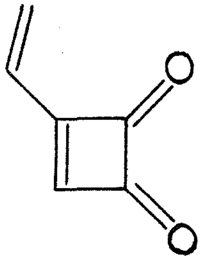
DE 6.0266 β
Δ DE 0.7891 β

XVII



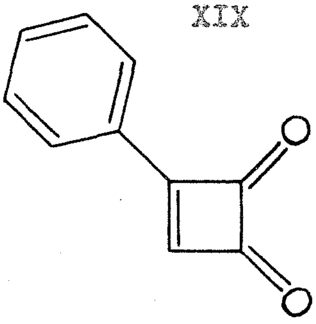
DE 1.2375 β

XVIII



DE 1.7368 β
Δ DE 0.4993 β

XIX

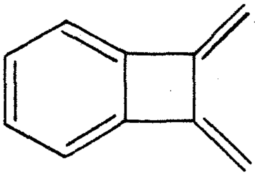


DE 3.6816 β
Δ DE 0.4441 β

Fig. 14

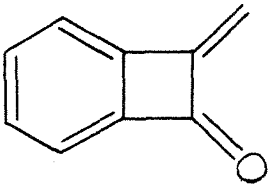
The compounds XVI-XIX are cyclobutadienoquinones (11). The stability of the cyclobutadienoquinone system has been demonstrated by the fact that both XVIII (6) and XIX (11) have been isolated as stable yellow, crystalline solids. Preliminary attempts to prepare XVII and XVI were unsuccessful (30, 92). A number of interesting derivatives of XIX have been prepared and studied (2,11). Preliminary heats of combustion indicate that the total angle strain energy of XIX exceeds the total resonance energy by 6 kcal. (2). Phenylcyclobutadienoquinone and cyclobutadiene are expected to have the same formal degree of angle strain and, as stated previously, Roberts has estimated this to be about 45 kcal. On this basis XIX would have a resonance energy on the order of 30-40 kcal./mole. This is very large, and Roberts has attributed this to the fact that a cyclic system with four π-electrons would be stabilized by electron-attracting groups which by electron withdrawal could reduce the effective number of electrons in the ring below the unfavorable number of four (2). Comparison of XII and XVI-XIX would seem to bear this out. Smutny and Roberts have predicted that the quinones of the unknown cyclic hydrocarbons "pentalene" and "heptalene" might be considerably more stable than the parent hydrocarbons (2, 11,18).

XX



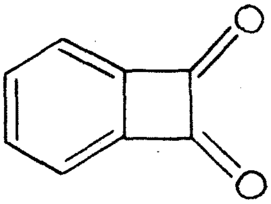
DE 3.1524 β

XXI



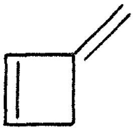
DE 3.1713 β

XXII



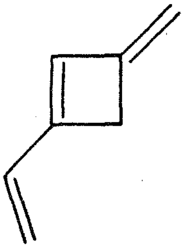
DE 3.1266 β

XXIII



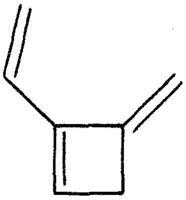
DE 0.4722 β
(same as butadiene)

XXIV



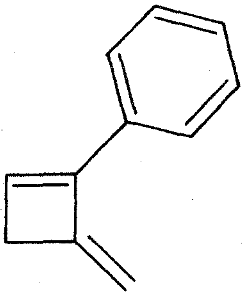
DE 0.9878 β
(same as hexatriene)
Δ DE 0.5156 β

XXV



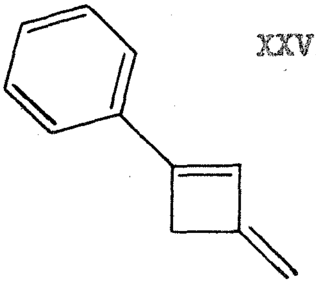
DE 0.8990 β
(same as 2-ethenyl-butadiene)
Δ DE 0.4268 β

XXVI



DE 2.8572 β
Δ DE 0.3850 β

XXVII



DE 2.9322 β
Δ DE 0.4600 β

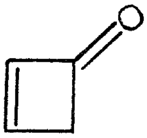
Fig. 15

Substitution of a vinyl group on XVII is seen to increase DE more than a phenyl group in XIX. It is not known whether this effect is real or due, as mentioned above, to different resonance integrals being required for both polyene and aromatic systems. Heats of combustion might settle this point. Addition of two phenyl groups (XVI) is seen to give a substantial increase in stabilization of XVII. The X-ray diffraction studies of the crystal structure of XIX (85) have been completed and that of 1-cyclohexenylcyclobutadieneoquinone (78) is being worked out. It will be interesting to compare the results with the bond orders computed from the results of the present work. Inclusion of 1,3-interaction of the p-orbitals on the 1- and 3-positions in XVI-XIX should increase the calculated DE considerably. Smutny, as was mentioned previously, found for XVII that this effect was astonishingly great (see XXXIV). He employed a 1,3-overlap integral of 0.5 β and found that the DE was increased from 1.2375β to 1.9863β, an increase of about 15 kcal./mole.

XX-XXII are benzocyclobutadiene derivatives for which very nearly the same DE is predicted whether there is *exo*-methylene or carbonyl substitution. These substances are not predicted to have triplet ground states. XXII has been isolated by Cava and Napier (75) and found to be quite stable. Thus the prediction of Smutny and Roberts (2,10,18) concerning the stability of the quinones of unknown cyclic hydrocarbons has been verified in another case.

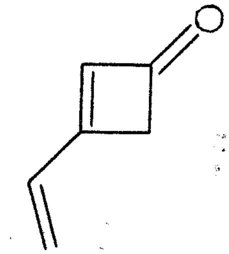
XXIII-XXXII are a number of substances whose structures, without consideration of 1,3-interaction, would have the same electronic energy as the corresponding open-chain compounds. Smutny, as mentioned previously (18), has done a number of calculations employing 1,3-interactions. For XXVIII, assuming reasonable geometry to obtain a 1,3-resonance integral of 0.5β, he found that DE increased significantly from 0.4927β to 0.8694β or about 7.5 kcal./mole. A number of very stable halogen-substituted derivatives of XXXII were prepared in the present and previous work. XXXII is discussed in Part I, Section 1, and has proved to be somewhat unstable. The heat of combustion of XXXII has been measured, but the results have not been published (30). An X-ray diffraction study on XXXII has been started (78). A derivative of XXXI is known (86), and several stable derivatives of XXIX have been synthesized (6). No derivatives of XXX or the parent compound XXVIII are known. Hydrocarbon XXIII has been synthesized and found to be unstable (76,77). Material believed to be XXVII has also been synthesized in very small yields (77). No derivatives of XXIV, XXV, or XXVI are known. In compounds XXIV-XXVII and XXIX-XXXII, the effect of through-conjugation versus cross-conjugation as predicted by the

XXVIII



DE 0.4927β (18)

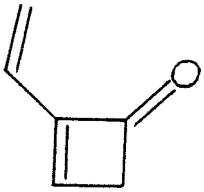
XXIX



DE 1.0265 β

Δ DE 0.5338 β

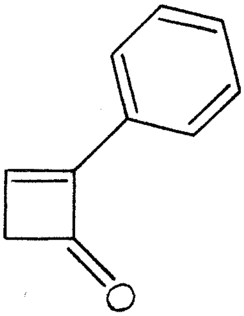
XXX



DE 0.9155 β

Δ DE 0.4228 β

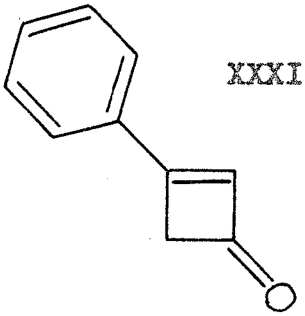
XXXI



DE 2.8747 β

Δ DE 0.3820 β

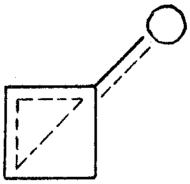
XXXII



DE 2.9665 β

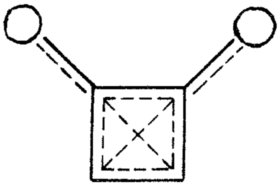
Δ DE 0.4738 β

XXXIII



H_{13}	DE	Δ DE
0.2 β	0.6277 β (18)	0.1350 β
0.5 β	0.8694 β (18)	0.3972 β

XXXIV



$H_{13} = H_{24} = 0.5\ \beta$

DE 1.9863 β (18)

Δ DE 0.7488 β

Fig. 16

simple LCAO-MO method is shown. The through-conjugated isomers are predicted to be more stable by about 0.1β. There is some ultraviolet data in the literature in support of this prediction (79).

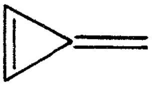
XXXV-XXXVIII are possible fulvene-like compounds which are predicted to have considerable DE and singlet ground states. So far there is no experimental evidence on any systems of this type.

XXXIX-XLII are unknown cyclopropenones and are predicted to have substantial DE values. For XII, the introduction of two oxygen atoms to give XVII only increases the predicted DE about 0.03β, while introduction of an oxygen into XXXV to give XL increases DE by 0.40β. This is a drastic change, and suggests that appropriately substituted derivatives of the unknown cyclopropenone might be prepared (93).

The cyclopropenyl cation (XLII) has been predicted to have a delocalization energy of 2.00β (58). This is extraordinarily large and suggests that perhaps XLIII might be isolable as a stable salt and that the halides and ester derivatives of XLIII should be extremely reactive in solvolytic reactions. The effect of phenyl substitution on the DE of XLIII is shown in the systems XLIV-XLVI for the cation, radical and anion. The increase in DE of the cation XLIII on introduction of one phenyl group is about 0.4β. Two phenyl groups increase the DE by 0.7β, and three phenyl groups by 1.2β. All these calculations were made

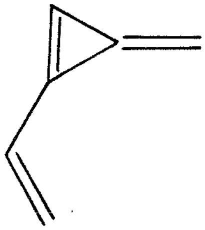
XXXV

DE 0.9624 β (58)



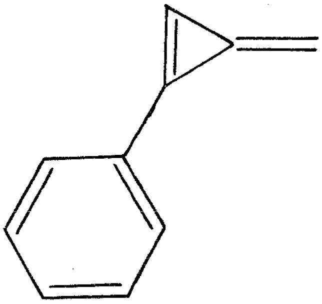
XXXVI

DE 1.4160 β
Δ DE 0.4536 β



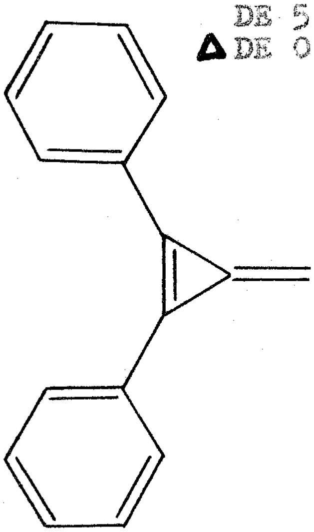
XXXVII

DE 3.3690 β
Δ DE 0.4066 β

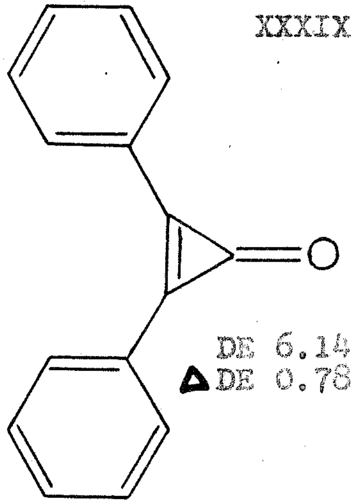


XXXVIII

DE 5.7920 β
Δ DE 0.8296 β

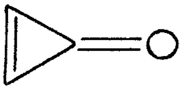


XXXIX



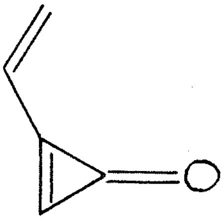
DE 6.1499 β
Δ DE 0.7858 β

XL



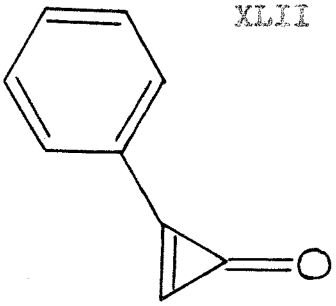
DE 1.3641 β (18)

XLI



DE 1.7915 β
Δ DE 0.4372 β

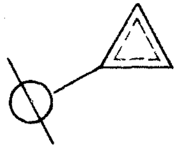
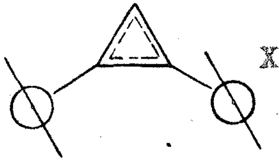
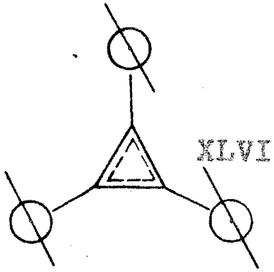
XLII



DE 3.7497 β
Δ DE 0.3854 β

Fig. 17

Fig. 18. Results of Simple Molecular Orbital (LCAO) Calculations on Some Cyclopropene Derivatives

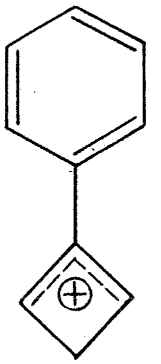
	 XLIII	 XLIV	 XLV	 XLVI
Cation	2.0000 β	4.3860 β	6.7016 β	9.1872 β
	DE-DE of Ø's	2.3860 β	2.7016 β	3.1872 β
	DE imparted to 3-membered ring	0.3860 β	0.7016 β	1.1872 β
Radical	1.0000 β	3.7934 β	6.1973 β	8.6829 β
	DE-DE of Ø's	1.7934 β	2.1973 β	2.6829 β
	DE imparted to 3-membered ring	0.7934 β	1.1973 β	1.6829 β
Anion	0.0000 β	3.2000 β	5.6930 β	8.1786 β*
	DE- DE of Ø's	1.2000 β	1.6930 β	2.1786 β
	DE imparted to 3-membered ring	1.2000 β	1.6930 β	2.1786 β

*triplet ground state

on the reasonable assumption of planar configuration of the rings. Recently, Breslow succeeded in preparing several stable salts of XLVI (80). Not only the cation of XLVI is predicted to have substantial DE, but the radical and anion are also predicted to have substantial DE's. For the latter, however, a triplet ground state is predicted. All the forms of XLIV and XLV are predicted to have substantial electron delocalization energies.

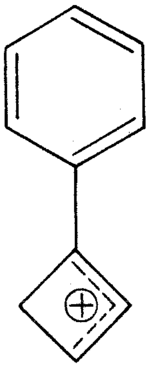
Systems XLVII-LIV represent carbonium ions which are of interest for various reasons. In XLVII-L the effect of cross-conjugation (XLVII and XLIX) versus through-conjugation (XLIII and L) is seen. For vinyl substitution, the through-conjugated system is more stable by 0.24β, and for the phenyl derivatives, by 0.20β. Again the vinyl substituent appears to impart more stabilization to a conjugated system than a phenyl ring. LI-LIV have been discussed previously in Part I, Sections 1 and 5. These systems give some indication of the effect of the inclusion of 1,3-interaction on the predicted DE's for the cyclic carbonium ions.

XLVII



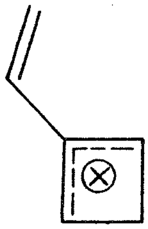
DE 3.1888 β
Δ DE 0.3604 β

XLVIII



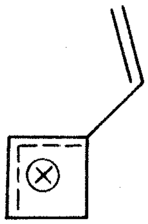
DE 3.3848 β
Δ DE 0.5564 β

XLIX



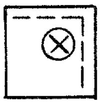
DE 1.2264 β
Δ DE 0.3980 β

L



DE 1.4641 β
Δ DE 0.6357 β

LI

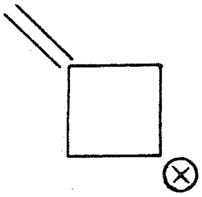


DE 0.8284 β

LII

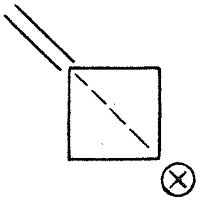
H_{13}	DE	Δ DE
0.2 β	1.0356 β	0.2072 β
0.5 β	1.3734 β	0.5450 β

LIII



DE 0.000

LIV



H_{13}	DE
0.2 β	0.038 β
0.5 β	0.152 β

Fig. 19

Appendix

The evaluation of the secular determinants resulting from the molecular orbital treatments made in the present work were carried out with the aid of a Datatron digital computer model 204 (59). The Datatron 204 is a general purpose, internally programmed, decimal, electronic computer with magnetic drum storage. A complete description of the operation and capabilities of the Datatron 204 is given by Datatron Bulletins 3021, 3022, 3024, 3027, 3028 and 3030c, available from the ElectroData Division of The Burroughs Corporation (59).

The program employed to solve the secular determinants in the present work was written by John Christopher and Hannah Fox of ElectroData (81). It is capable of finding all the eigenvalues and all the real eigenvectors of an arbitrary, real matrix up to order 20x20. The method of solution is in two parts. First the characteristic polynomial of the matrix is computed according to a modified Lanczos method (82), and the eigenvalues are obtained from the roots of this equation. The eigenvectors are then subsequently computed to an arbitrary basis from these roots. The use of this program is very well described in a Datatron Applied Mathematics Bulletin (82). The results are accurate to at least four decimal places, and the time required for complete solution of a 20x20 matrix is about 15-20 minutes.

For the computation of bond order and "free valence" indices from the results obtained as above it is necessary to renormalize all the eigenvectors to unity (63,83), since the sets of calculated eigenvectors are each to an arbitrary basis. This computation would be quite time consuming for most of the systems studied in the present work. To perform this simple but tedious mathematical operation, a short Datatron subroutine for matrices up to order 20x20 was written which can be fitted onto the eigenvalue routine described above or used separately to obtain the normalized vectors. A description of its use and its Datatron code is described below. This subroutine has not been checked in its present form, but before several minor changes were made and its relative storage address was changed, it was successfully tested by itself on several 6x6 cases.

The master eigenvalue program takes up cells 0020 through 1330 for the code proper and locations 1340 through 3239 for storage of initial data, intermediate results, and the final results. The normalization subroutine takes up 180 locations in memory from cell 3240 through 3389, and it uses cells 3600 through 3999 for storage of the final results. Thus there are still 210 cells left in main storage. The subroutine has its own sum check read into the 7000 loop which determines whether its read-in is correct or incorrect. After correct read-in of a correctly punched tape, the computer will stop with the command 08 0000 in the C-register and 0000 00 0000 in the A-register. If the read-in is not correct, the computer will stop with the command 08 5555 in the C-register, and the A-register will contain the difference between the true sum and the sum of the program just read in. In this event, the tape, if correctly punched, should be read in again.

If several sets of vectors of the same dimension have been computed to an arbitrary basis and one wishes to normalize them to unity, the subroutine can be used for this purpose by itself. The dimension of the sets of vectors or size of the secular determinant from which they were obtained, denoted as $\underline{n}$ is scaled as $\underline{n} \times 10^{-10}$ and loaded into cell 0810; this is the same location for $\underline{n}$ that is used by the master eigenvalue routine. The number of sets of vectors of dimension $\underline{n}$ that are to be normalized is denoted as $\underline{k}$, and $(\underline{k}-1) \times 10^{-10}$ is loaded into cell 1122. The first vector is loaded into 2400, 2401, ..., 2400 + $(\underline{n}-1)$; the second vector into 2420, 2421, ..., 2420 + $(\underline{n}-1)$; and the $\underline{k}$th vector into 2400 + 20 $(\underline{k}-1)$, ..., 2420 + 20 $(\underline{k}-1)$ $(\underline{n}-1)$. All the components of the vectors must be in floating point form and in the correct order. The location of the vectors is the same as that employed by the master eigenvalue program for storage of the final eigenvectors it computes. The program is entered with a CUB 3241. The output can be recorded either by flexiwriter or high-speed punch. The program prints out "Normalized Vectors" and then follows this with the sets of normalized vectors, each set separated by two spaces. The sets of normalized vectors are stored in cells 3600-3999; the first in 3600, 3601, ..., 3600 + (n-1); the kth in 3600 + 20 (k-1), ..., 3600 + 20 (k-1) + (n-1). The computer then stops.

In molecular orbital calculations secular determinants are often factorable by group theory, and thus the molecular wave functions will contain certain normalization factors that must be applied to each normalized eigenvector of a set to give the correct coefficient to be used in further computation. A set of floating point unit coefficients are stored in cells 3370-3389. If some factorization has been applied one can enter the correct factor in floating point form in the correct component of this unit vector. The program will start with the nth component of the unity normalized vector and divide it by the nth normalization factor; next the (n-1)th component is divided by the (n-1)th factor and so on. The limits of k and n are twenty because of the limit of a 20 word block in the high-speed loop employed in Datatron 204.

If one has a set of k eigenvalues from an n x n matrix (where n = 20) it is possible to calculate both the arbitrary normalized and unity normalized eigenvectors. The master eigenvalue routine and the normalization routine are fed in. The number n and the matrix in floating point form are fed in as described for the eigenvalue routine (81). The number ($\underline{k}$-1) x 10^{-10} is placed in cell 1122 and the eigenvalues in floating point form are entered in $\underline{k}$ consecutive locations beginning at cell 1500. The break-point is set to 4, and the eigenvalue program is begun by CU 3240, but the print-out of the matrix may be suppressed if desired (81). The computer will set up a so-called "matrix dictionary" which is used later and then stop. The computer is cleared, the break-point set to off, and the program re-entered by CUB 1095. The computer proceeds to use the stored eigenvalues to compute sets of arbitrarily normalized eigenvectors, and after completing this operation the computer proceeds to normalize each set of vectors to unity as described in the last paragraph. The print-out of the arbitrarily normalized vectors can be suppressed (81) if desired.

Finally one can start with an $\underline{n}$ x $\underline{n}$ matrix and enter the master eigenvalue program with a CU 3240 and compute the characteristic polynomial, the eigenvalues, the arbitrarily normalized eigenvectors, and the unit normalized vectors in one step. The only additional pieces of information besides the matrix and its size which must be put into the computer are any normalization factors due to factorization of the matrix by group theory.

The following pages contain the Datatron code described above for the normalization to unity of a set of arbitrarily normalized vectors.

Datatron Code Sheet

Datatron 205 Subroutine to be Used with Code 2.42.025 for the Normalization of a Set of Eigenvectors to Unity

Numerical Code				Cell	Instruction			
S	Spare	Ord.	Address	No.	S	Order	Address	Comments
4	0000	00	3240					
0	0000	31	0795	3240		CUBR	0795	To main eigenvalue routine
0	0000	64	1122	3241		CAD	1122	Bring up <u>k</u>-1
0	0000	02	3279	3242		STC	3279	Store <u>k</u>-1 in 3279
0	0000	30	3244	3243		CUB	3244	
0	0000	07	0500	3244		PTWF		Print Format "Normalize Vectors"
0	0000	07	0500	3245		PTWF		
0	0000	07	0500	3246		PTWF		
0	0000	64	7261	3247		CAD	7261	
0	0000	03	8410	3248		PWT		
0	0000	64	7260	3249		CAD	7260	
0	0000	03	8410	3250		PWT		
0	0000	64	7259	3251		CAD	7259	
0	0000	03	8410	3252		PWT		
0	0000	64	7258	3253		CAD	7258	
0	0000	03	8410	3254		PWT		
0	0000	64	7257	3255		CAD	7257	
0	0000	30	3262	3256		CUB	3262	
0	2232	05	0000	3257				
0	6462	23	7521	3258				
0	6463	34	3053	3259				

Numerical Code				Cell No.	Instruction			Comments
S	Spare	Ord.	Address		S	Order	Address	
0	7320	36	7057	3260				
0	3074	27	7521	3261				
0	0000	72	7278	3262		SB	7278	Zero 5000 loop
0	0000	22	7264	3263		DB	7264	
1	0000	02	5000	3264	1	STC	5000	
1	0000	02	5000	3265	1	STC	5000	
0	0000	22	7265	3266		DB	7265	
0	0000	74	3279	3267		AD	3279	k-1
0	0000	74	7277	3268		AD	7277	k
0	0000	12	3276	3269		ST	3276	Store k
0	0000	75	7277	3270		SU	7277	k-1
0	0000	60	7278	3271		M	7278	(k-1)20 in R
0	0000	14	0010	3272		SL		(k-1)20 in A
0	0000	12	3279	3273		ST	3279	
0	0000	74	3284	3274		AD	3284	0 0000 36 2400 + (k-1)20 in A
0	0000	30	3280	3275		CUB	3280	
0	0000	00	0000	3276				k stored here
0	0000	00	0001	3277				
0	0000	00	0020	3278				
0	0000	00	0000	3279				k-1 stored here
0	0000	02	7284	3280		STC	7284	0 0000 36 2400 + (k-1)20 to 7284
0	0000	74	7287	3281		AD	7287	
0	0000	75	7291	3282		SU	7291	1 0000 66 6400 + (k-1)20 in A

Numerical Code				Cell	Instruction			
S	Spare	Ord.	Address	No.	S	Order	Address	Comments
0	0000	02	7287	3283		STC	7287	
0	0000	36	2400	3284		BT6	2400	Block vectors to 6400 loop
0	0000	72	0810	3285		SB	0810	Set B to n
0	0000	22	7287	3286		DB	7287	
1	0000	66	6400	3287	1	CADA	6400	Transfer vectors as absolute values to 4000 loop
1	0000	12	4000	3288	1	ST	4000	
0	0000	22	7287	3289		DB	7287	
0	0000	30	3292	3290		CUB	3292	
0	0000	00	0000	3291				
0	0000	72	0810	3292		SB	0810	Set B to n
0	0000	22	7294	3293		DB	7294	
1	0000	64	4000	3294	1	CAD	4000	Find magnitude of largest vector and store in 5000
0	0000	12	5000	3295		ST	5000	
0	0000	22	7298	3296		DB	7298	
0	0000	30	3303	3297		CUB	3303	
1	0000	81	4000	3298	1	FSU	4000	
0	0000	73	7297	3299		OSGD	7297	
0	0000	28	7294	3300		CC	7294	
0	0000	64	5000	3301		CAD	5000	
0	0000	22	7298	3302		DB	7298	
0	0000	64	7308	3303		CAD	7308	1 0000 64 6400 in A
0	0000	74	3279	3304		AD	3279	1 0000 64 6400 + (k-1)20 in A

Numerical Code				Cell	Instruction			Comments
S	Spare	Ord.	Address	No.	S	Order	Address	
0	0000	12	7308	3305		ST	7308	
0	0000	72	0810	3306		SB	0810	
0	0000	22	7308	3307		DB	7308	
1	0000	64	6400	3308	1	CAD	6400	
0	0000	83	5000	3309		FDIV	5000	Find c_1/c_{max}
1	0000	12	4000	3310	1	ST	4000	
1	0000	82	4000	3311	1	FM	4000	Form $(c_1/c_{max})^2$
0	0000	02	5001	3312		STC	5001	
0	0000	64	5002	3313		CAD	5002	Sum of $(c_1/c_{max})^2$ in 5002
0	0000	80	5001	3314		FAD	5001	
0	0000	12	5002	3315		ST	5002	
0	0000	22	7308	3316		DB	7308	
0	0000	30	3318	3317		CUB	3318	
0	0000	60	7337	3318		M	7337	Find square root
0	0000	74	7336	3319		AD	7336	sum of $(c_1/c_{max})^2$
0	0000	14	0002	3320		SL		
0	0000	06	0000	3321		UA		
0	0000	14	0018	3322		SL		
0	0000	02	7335	3323		STC	7335	
0	0000	64	5002	3324		CAD	5002	
0	0000	83	7335	3325		FDIV	7335	
0	0000	81	7335	3326		FSU	7335	
0	0000	82	7334	3327		FM	7334	
0	0000	80	7335	3328		FAD	7335	

Numerical Code				Cell	Instruction			
S	Spare	Ord.	Address	No.	S	Order	Address	Comments
0	0000	81	7335	3329		FSU	7335	
0	0000	15	3338	3330		NOR	3338	
0	0000	80	7335	3331		FAD	7335	
0	0000	02	7324	3332		STC	7324	
0	0000	20	7324	3333		CU	7324	
0	5050	00	0000	3334				
0	0000	00	0000	3335				
0	2550	00	0000	3336				
0	5000	00	0000	3337				
0	0000	64	7335	3338		CAD	7335	Square root of sum $(c_i/c_{max})^2$ in $\underline{A}$
0	0000	30	3340	3339		CUB	3340	
0	0000	02	5003	3340		STC	5003	
0	0000	72	0810	3341		SB	0810	
0	0000	22	7343	3342		DB	7343	
0	0000	36	3370	3343		BT6	3370	Block normalization factors to 6000 loop
1	0000	64	4000	3344	1	CAD	4000	c_i/c_{max} divided by square root of sum of $(c_i/c_{max})^2$ and normalization factors; result stored in 6000 loop over normalization factors
0	0000	83	5003	3345		FDIV	5003	
1	0000	02	6000	3346	1	STC	6000	
1	0000	02	6000	3347	1	STC	6000	
0	0000	22	7344	3348		DB	7344	
0	0000	72	0810	3349		SB	0810	
0	0000	22	7333	3350		DB	7333	Print the normalized vectors
0	0000	07	0500	3351		PTWT		
0	0000	07	0500	3352		PTWT		

Numerical Code				Cell	Instruction			
S	Spare	Ord.	Address	No.	S	Order	Address	Comments
0	0000	07	0500	3353		PTWT		
1	0000	64	6000	3354		CAD	6000	
0	0000	03	8510	3355		PTW		
0	0000	22	7352	3356		DB	7352	
0	0000	64	3299	3357		CAD	3299	(k-1)20
0	0000	74	3361	3358		AD	3361	0 0000 26 3600 + (k-1)20
0	0000	30	3360	3359		CUB	3360	
0	0000	02	7361	3360		STC	7361	Answers to main storage
0	0000	26	3600	3361		BF6	3600	
0	0000	64	3276	3362		CAD	3276	
0	0000	75	7369	3363		SU	7369	
0	0000	04	7366	3364		CNZ	7366	
0	0000	08	0000	3365		STOP		
0	0000	75	7369	3366		SU	7369	
0	0000	02	3279	3367		STC	3279	
0	0000	30	3262	3368		CUB	3262	Compute second set of normalized vectors
0	0000	00	0001	3369				
0	5110	00	0000	3370				Set of unit normalization factors
0	5110	00	0000	3371				
0	5110	00	0000	3372				
0	5110	00	0000	3373				
0	5110	00	0000	3374				
0	5110	00	0000	3375				
0	5110	00	0000	3376				

Numerical Code				Cell	Instruction			
S	Spare	Ord.	Address	No.	S	Order	Address	Comments
0	5110	00	0000	3377				
0	5110	00	0000	3378				
0	5110	00	0000	3379				
0	5110	00	0000	3380				
0	5110	00	0000	3381				
0	5110	00	0000	3382				
0	5110	00	0000	3383				
0	5110	00	0000	3384				
0	5110	00	0000	3385				
0	5110	00	0000	3386				
0	5110	00	0000	3387				
0	5110	00	0000	3388				
0	5110	00	0000	3389				
4	0000	00	7000					
0	0000	72	7014	7000		SB	7014	Sum check
0	0000	64	7005	7001		CAD	7005	
0	0000	75	7014	7002		SU	7014	
0	0000	02	7005	7003		STC	7005	
1	0000	64	3240	7004		CAD	3240	
0	0000	74	7015	7005		AD	7015	
0	0000	28	7008	7006		CC	7008	
0	0000	12	7015	7007		ST	7015	
0	0000	22	7005	7008		DB	7005	

Numerical Code				Cell No.	Instruction			Comments
S	Spare	Ord.	Address		S	Order	Address	
0	0000	75	7016	7009		SU	7016	
0	0000	04	7013	7010		CNZ	7013	
0	0000	08	0000	7011		STOP	0000	
0	0000	08	5555	7012		STOP	5555	
0	0000	00	0149	7013				
0	0000	00	0000	7014				
0	0398	34	2602	7015				

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90. The proton NMR spectrum of trimethylene oxide has been reported, and this molecule is an $A_2X_2A_2$ system to a first approximation. The X_2 region of the spectrum shows evidence of fourteen lines, and this complexity is certainly due to the relatively small ratio of chemical shift difference of the A and X groups and the spin-spin coupling constants. However, from the general form of the X_2 region it can be inferred that perhaps the X_2 region in XXIV should be a quintet. See H. Primas, K. Frei and Hs. H. Gunthard, Helv. Chim. Acta, 41, 35-38 (1958).

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Propositions

1. Recently it has been reported that perchloryl fluoride ($FClO_3$) reacts readily with certain aromatic compounds in the presence of aluminum chloride to give perchloryl derivatives (1). Perchlorylbenzene in alkaline solution is hydrolyzed rapidly to phenol and chlorate ion (1). The perchlorylation of ferrocene might be feasible because of the apparent stability of perchloryl fluoride in oxidative reactions (2). Subsequent displacement reactions on perchlorylferrocene by nucleophilic reagents such as hydroxide ion or *t*-butoxide ion might give hydroxyferrocene or *t*-butylferrocenyl ether.

2. Simple molecular orbital calculations predict that 1-phenylbenzocyclobutadiene should have substantial delocalization energy and a singlet ground state (3). Two possible syntheses for this molecule are proposed. One approach would start with the coupling of the Grignard reagent of 1-bromobenzocyclobutene (4) with cyclohexanone to give 1-cyclohexylbenzocyclobuten-1-ol. Aromatization of the cyclohexyl ring might give 1-phenylbenzocyclobutene. Introduction of an additional double bond to give the desired product could be attempted by a number of standard procedures. The second synthetic approach would depend on the synthesis of benzocyclobuten-1-ol (an unknown compound) from 1-bromobenzocyclobutene via standard procedures. Oxidation of the alcohol to

benzocyclobutenone (an unknown compound) followed by coupling of the ketone with phenylmagnesium bromide might yield 1-phenylbenzocyclobuten-1-ol. Elimination of the elements of water from this molecule could be attempted by a number of standard methods and might yield the desired product.

3. The acid hydrolysis of magnesium boride (Mg_3B_2) gives boron hydrides, but on hydrolysis with water alone it yields a number of oxygenated compounds classified as the borohydrates. Under certain conditions, two minor components, having the empirical formula $H_6B_2O_2$, are formed (5). It has been suggested that the structures of these compounds have boron-boron double bonds and that these compounds are *cis-trans* isomers, but this explanation does not seem tenable in light of recent structure determinations of other boron systems (6). One of the isomers loses two hydrogen atoms to give $H_4B_2O_2$, while the other loses four hydrogen atoms to give $H_2B_2O_2$. It is proposed that useful information concerning the structures of all these compounds might be gained by NMR and deuterium exchange studies.

4. Many different chemical and physical properties have been employed as measures of the strain in carbocyclic ring systems. It is proposed that the oxidation-reduction potentials of the quinones of the benzocarbocyclenes might provide another means for measuring ring strain.

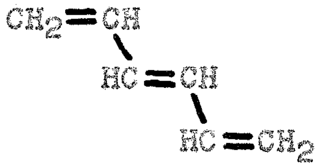
5. The dehydration of alcohols by phosphorus oxychloride in pyridine has been widely employed in organic synthesis. In many cases mixtures of isomers result. A study designed to demonstrate the importance of steric and electric effects in determination of the products from this reaction is proposed. The influence of the nature of the tertiary amine employed in the reaction should also be investigated.

6. The pK_A's of ferrocenylamine, aniline, p-ferrocenylaniline, m- ferrocenylaniline, and p-phenylaniline have been reported as 8.81, 10.14, 9.66, 9.85, and 10.89 in 80% ethanol at 20°, respectively (7). The weakly basic properties of aniline relative to an aliphatic amine are attributed to the resonance forms involving the electron pair on nitrogen, and such a mesomeric effect is probably responsible for the basic strength of ferrocenylamine. The pK_A's of p-phenylaniline, p- and m-ferrocenylaniline suggest that the sum of the mesomeric and polar effects of the ferrocenyl system is opposite in direction to that of the phenyl system. To enable a clear identification of the inductive properties of the ferrocenyl system, it is proposed that the determination of the pK_A's of ferrocenylmethyl-, 2-ferrocenylethyl-, and 3-ferrocenylpropylamine and of the corresponding acids be carried out.

7. It is proposed that the heat of hydrogenation of vinylferrocene (8) should give a direct measure of the mesomeric properties of the ferrocenyl system.

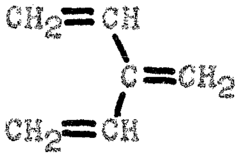
8. Simple molecular orbital calculations predict that in a π-electron system the through-conjugated isomer (I) should have a larger π-electron delocalozation energy (DE) than the cross-conjugated isomer (II) (3,9):

I



DE 0.988 β (9)

II

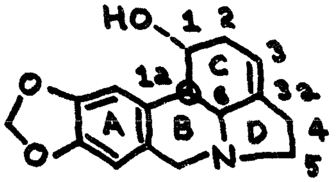


DE 0.899 β (9)

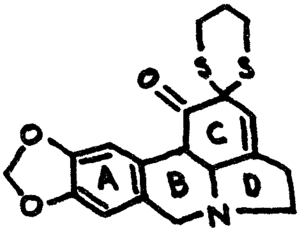
In order to provide experimental evidence for this energy difference it is proposed that heat of hydrogenation and/or combustion studies and solvolysis rate studies on suitable derivatives be carried out on conjugated systems of these two types.

9. Huisgen and König (10) have recently employed intramolecular benzyne addition reactions to close ring systems containing nitrogen in the case of 2-(3-chlorophenyl-ethyl and 3-(3-chlorophenyl)propyl N-methylamines which gave five- and six-membered rings, respectively. It is proposed that the same reaction with a 3-bromobenzylamine might yield a benzo-1-azacyclobutene derivative.

10. Wildman and coworkers have reported the isolation and characterization of a number of the amaryllidaceae alkaloids, among them caranine (11), a $C_{16}H_{17}NO_3$ base having the following structure:



A synthesis of this molecule is proposed which begins by the coupling of the intact ring A to 1,4-cyclohexanedione via the Grignard of 4-bromo-1,2-methylenedioxybenzene to give rings A and C. Dehydration of this alcohol would be followed by introduction of the propane 1,3-dithio blocking group, via the hydroxymethylene group, at the 2-position. Alkylation with chloroacetic ester at the 3a-position would provide a functional side chain for the construction of ring D. At this point the ketone at the 3-position must be reduced, and the resulting alcohol must be esterified. Next a ketone group at the 1-position and a 1a-6 double bond have to be introduced. The key step here could be the formation of the 1,1a-diol. Saponification followed by dehydration to give the 3-3a double bond would transform the C-ring into a cyclohexadieneone system. By the Arndt-Eistert and Curtius sequence the primary amine could be introduced in the side chain, and cyclization in the presende of formaldehyde might give the ABCD-ring system:

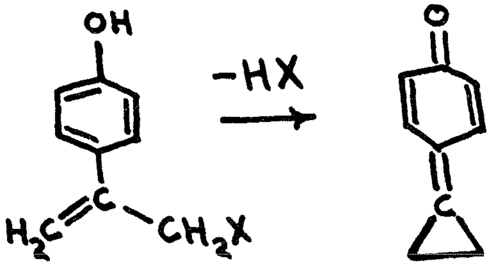


Removal of the dithioketal group and reduction of the ketone to an alcohol complete the synthesis. Caranine has only three centers of asymmetry. Two of these are closely related and should be in the correct relation in the final product. The synthetic product should thus be dl-caranine.

11. Lithium exists in nature as two stable isotopes, one of atomic mass 6.017121 (abundance 7.52%) and the other of atomic mass 7.018223 (abundance 92.47%) (12). It is proposed that electrolytic transference and conductance experiments be carried out with each of the separate isotopes (or enriched preparations) in order to determine the magnitude of the isotope effect on these properties and ion mobilities in aqueous solutions.

12. A study of the solvolysis and displacement reactions of β-(p-hydroxyphenyl)allyl halides is proposed which would explore the possibility of ring closure via an intramolecular

displacement to give a three-membered ring, an <u>exo</u>-methylenecyclopropane derivative:



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