

Carbonium Ions. XIX. The Intense Conjugation in Cyclopropyl Carbonium Ions¹

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The cyclopropyl ring intensely conjugates with carbonium ions and stabilizes them to a degree greater than phenyl substituents. This effect manifests itself in the thermodynamic stabilities, the ultraviolet spectra, restricted rotation about single bonds, n.m.r. band positions, the totally reversed chemical reactivity of the cyclopropyl rings, and stabilities of ions in the gas phase.

It has been known for some time that cyclopropane rings have the ability to conjugate with adjacent π -orbitals. In a moment of insight, Kohler and Conant stated in 1917, "A cyclopropane ring, in which all of the carbons are nominally saturated, and a carbonyl group in the proper position can form a conjugated system, which is identical in properties with that found in many ethylenic compounds."²

The above conclusion was based on chemical reactivity, but the physical properties measured in succeeding years have only reinforced the validity of Kohler and Conant's insight. Noteworthy is the absorption spectrum of phenylcyclopropane which lies intermediate between that of benzene and styrene.³ The many other effects have been reviewed.⁴

The conjugation between cyclopropyl rings and π -orbitals reaches its greatest intensity in the cyclopropyl carbonium ions and the measurement of their physical properties would appear to be the area of choice for studying such conjugation. To this end this work was directed.

Already, an appreciation of the stability of cyclopropyl carbonium ions has been gained from solvolysis studies.^{5,6} In particular Hart and co-workers showed that successive replacement of isopropyl by cyclopropyl groups led to large increases in the solvolysis rate and by nearly constant increments in $\log k$ per cyclopropyl group introduced.⁶

This paper reports direct observations on cyclopropyl carbonium ions, some of which appeared in preliminary form in two reviews.^{7,8}

Structure of the Cyclopropyl Carbonium Ions. The structure of such ions has been largely settled by the work of Pittman and Olah,⁹ who showed that the two methyl groups in the 2-cyclopropyl-2-propyl cation were not equivalent. This result is most compatible with the

"bisected" structure⁷ in which the trigonal plane of the carbonium carbon bisects the cyclopropyl ring.

This structure had already been strongly indicated by the discovery that the closely related cyclopropanecarboxaldehyde exists in a *cis* and a *trans* isomer,¹⁰ both of which have the bisected conformation. The bisected structure had also been indicated from ultraviolet studies on cyclopropyl ketones¹¹ and their protonated derivatives (work of Richey quoted in ref. 7).

On the basis of isotopic scrambling experiments, Roberts has championed a "bicyclobutonium" structure for the cyclopropylmethyl cation.¹² This structure can be characterized geometrically by placement of one of the two β -carbons in the plane of the trigonal carbonium ion with the result that the two β -carbons are nonequivalent. We have already pointed out that such experiments are not a sound basis for structure assignments because of the inability of distinguishing scrambling due to rapid rearrangement from that due to equivalent carbons in an unstable intermediate.⁷ Despite this objection, Roberts' structure is in accord with the direct observations if it be assumed that rapid oscillation occurs between the two equivalent Roberts' structures with the bisected structure as the symmetrical midpoint. Experiments are in progress to settle this question.

Hart's result⁶ is regarded as strong evidence that the mode of conjugation in mono-, di-, and tricyclopropyl carbonium ions is the same. Thus the bisected structure is accepted for the tricyclopropylmethyl cation¹³ and several dicyclopropylalkyl cations.^{9,14}

Thermodynamic Stabilities. A dramatic result is the greater stabilization of carbonium ions by cyclopropyl substituents than by phenyl. This is true either for direct attachment to the carbonium center as in R_3C^+ structures or attachment to the terminal carbons of allyl cation systems.

The change in concentration of tricyclopropylmethyl cation with per cent H_2SO_4 was measured and the data are presented in Table I. Three facts suggest that the equilibrium is between cation and alcohol rather than cation and olefin. (1) The shift in equilibrium with acid concentration fits eq. 1, in which H_R values were

$$H_R = pK_{R^+} + \log C_{ROH}/C_{R^+} \quad (1)$$

obtained from measurements on the equilibrium be-

(1) This paper is largely drawn from the Ph.D. Thesis of J. S. Liu, The Pennsylvania State University, 1963.

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(3) M. T. Rogers, *ibid.*, **69**, 2544 (1947).

(4) M. Y. Lukina, *Russ. Chem. Rev.* (English Transl.), 419 (1962).

(5) C. G. Bergstrom and S. Siegel, *J. Am. Chem. Soc.*, **74**, 145, 254 (1952).

(6) H. Hart and P. A. Law, *ibid.*, **84**, 2462 (1962); H. Hart and J. M. Sandri, *ibid.*, **81**, 320 (1959).

(7) N. Deno, *Progr. Phys. Org. Chem.*, **2**, 129 (1964).

(8) N. Deno, *Chem. Eng. News*, **42**, 88 (1964).

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(11) E. M. Kosower, *Proc. Chem. Soc.*, 25 (1962).

(12) J. D. Roberts, *et al.*, *J. Am. Chem. Soc.*, **81**, 4390 (1951); **83**, 2719, 3671 (1961); *Tetrahedron*, **11**, 171 (1960).

(13) N. Deno, H. G. Richey, Jr., J. S. Liu, J. D. Hodge, J. J. Houser, and M. J. Wisotsky, *J. Am. Chem. Soc.*, **84**, 2016 (1962).

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Table I. Position of the Tricyclopropylmethanol-Tricyclopropylmethyl Cation Equilibria as a Function of Per Cent H₂SO₄ at 3.0°

H ₂ SO ₄ , %	Log (R ⁺ /ROH)	H _R ^a	pK _R ^{+b}
32.0	1.005	-3.50	-2.50
30.0	0.892	-3.25	-2.36
25.0	0.240	-2.55	-2.31
20.0	-0.414	-1.92	-2.33
15.0	-0.925	-1.32	-2.24
12.0	-1.160	-1.00	-2.30
		Best value	-2.31

^a E. M. Arnett and R. D. Bushick, *J. Am. Chem. Soc.*, **86**, 1564 (1964). ^b From eq. 1.

tween triarylmethyl cations and triarylmethanols.¹⁵ (2) The tricyclopropylmethyl cation does not exchange hydrogen for deuterium in 96% D₂SO₄ as shown by the constant height of the n.m.r. band relative to a standard. (3) The alcohol, tricyclopropylmethanol, is quantitatively recovered on rapid dispersal drowning in aqueous alkali, and the n.m.r. spectrum of the recovered alcohol shows no trace of olefin.

The fit of the data with eq. 1 is interpreted to mean that the positive charge in the tricyclopropylmethyl cation is delocalized to an extent comparable with that in the triphenylmethyl cation with the result that specific bondings to solvent are much reduced.¹⁶ This interpretation is supported by its great stability, half-formed in 22% H₂SO₄ (pK = -2.34 by eq. 1). In contrast, the triphenylmethyl cation requires 50% H₂SO₄ for its half-formation from triphenylmethanol (pK = -6.63).¹⁵

This superiority of cyclopropyl over phenyl extends to the cyclohexenyl and cyclopentenyl cations as shown in Table II.

Ultraviolet Spectra. The λ_{max} 270 mμ (ε 22,000) for the tricyclopropylmethyl cation is amazingly intense and finds no counterpart in simple alkyl cations. For example, measurements on the *t*-butyl cation showed only a weak maximum at ~300 mμ (ε <500)¹⁷ and we suspect that this absorption is due to cyclopentenyl cations formed at the moment of mixing.⁷

The intensity of absorption in the tricyclopropylmethyl cation can only come about because of a conjugated system in which large changes in dipole moment and charge distribution occur during the transition. This conjugative effect of cyclopropyl groups extends to allyl cations as indicated by the shifts of λ_{max} to longer wave lengths with increasing cyclopropyl substitution (at the terminal carbons of the allylic system), Table II.

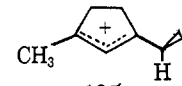
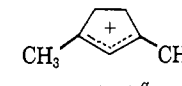
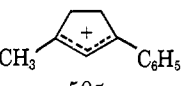
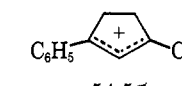
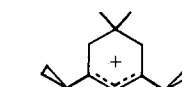

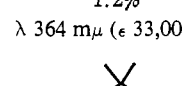
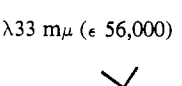
A number of molecular orbital descriptions can be devised for this conjugation involving varying values for the overlap integral between the carbonium carbon and the α- and β-carbons of the cyclopropyl rings. It is anticipated that work in progress on the electronic spectra of a variety of cyclopropyl carbonium ions will lead to a choice between these various MO descriptions.

(15) N. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955).

(16) N. Deno, *Sur. Progr. Chem.*, **2**, 155 (1965).

(17) G. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Am. Chem. Soc.*, **86**, 1360 (1964).

Table II. Per Cent H₂SO₄ at Which Cation Is Half-Formed from Diene and/or Alcohol

	
12%	35% ^a
λ 309 mμ, (ε 28,000)	λ 275 mμ (ε 11,000)
	
50%	54.5%
λ 378 mμ (ε 23,500)	λ 446 mμ (ε 17,400)
	
1.2%	
λ 364 mμ (ε 33,000)	λ 33 mμ (ε 56,000)
	
50% ^a	52% ^a
λ 314 mμ (ε 9100)	λ 411 mμ (ε 44,800)

^a N. Deno, J. Bollinger, N. Friedman, K. Hafer, J. D. Hodge, and J. J. Houser, *J. Am. Chem. Soc.*, **85**, 2998 (1963).

N.m.r. Spectra. A positive charge on an atom adjacent to a cyclopropyl ring exhibits two dramatically different effects. When the effect is strictly inductive, as in the cyclopropylammonium ion (Table III), the α-hydrogen in the cyclopropyl ring is shifted downfield by about 2 p.p.m., whereas the β-hydrogens are much less affected and are shifted about 0.5 p.p.m. downfield.

In the cyclopropyl carbonium ions, a conjugative effect has been added which delocalizes charge more effectively into the β-carbons relative to the closer α-carbons. The combination of inductive and conjugative effects is to shift both α- and β-hydrogens about 2 p.p.m. downfield as shown in several examples in Table III.

Intermediate cases are encountered. Exemplary is the 9-cyclopropyl-9-xanthyl cation. In this ion, the xanthyl cation, itself, is so stable¹⁵ that relatively less charge is delocalized into the cyclopropyl ring. The β-hydrogens are not moved as much downfield and the spectrum approaches that of the cyclopropylammonium ion in respect to the n.m.r. band positions of the cyclopropyl hydrogens (Table III).

The single band of the tricyclopropylmethyl cation has aroused some speculation. However, all signs point to this result as due to simple coincidence of the α-hydrogens and both *cis* and *trans* β-hydrogens. The single band appears at -2.26 p.p.m. in the following media: 96% H₂SO₄ at 25°, CF₃COOH at -25°, 25% SO₃ in H₂SO₄ at 25°, CH₂Cl₂-AlCl₃ at -25°, and FSO₃H-SO₂ at -65°. The measurements at low temperature fail to reveal any splitting and thus suggest that the single band is not a result of rapid equilibrations.¹⁸ This conclusion was further sup-

(18) Communication from C. U. Pittman, Jr., and G. Olah, Dow Chemical Co.

Table III. N.m.r. Band Positions of Cyclopropyl Carbonium Ions^a

Cation	Band positions ^b		
	α -H	β -H	Other H
2-Cyclopropyl-2-propyl ^e	(3.4 to	4.0)	2.60, 3.14
Dicyclopropylmethyl ^{e,d}	2.9-3.5	2.3-2.8	8.24 ^e
1,1-Dicyclopropylethyl ^d	3.00	2.56, 2.66	2.28 ^e
Tricyclopropylmethyl	2.26	2.26	
2,2,3,3-Tetramethyltricyclopropylmethyl	(2.3 to	2.48)	<i>f</i>
1-Cyclopropyl-3,5,5-trimethylcyclohexenyl	(2.3 to	2.7(?))	<i>gem</i> -Dimethyl 0.98, H on C-2 7.32, CH ₃ on C-3 2.44, H on C-4 and -6 2.3-2.7?
1-Cyclopropyl-3-methylcyclopentenyl	(2.2 to	2.6)	H on C-2 7.23, CH ₃ on C-3 2.73, H on C-4 and -5 3.29
1,3-Dicyclopropyl-5,5-dimethylcyclohexenyl	2.4	1.97 ^e 2.01 ^e	<i>g</i>
9-Cyclopropyl-9-xanthy ^l	2.96	1.38 ^e 1.96 ^e	<i>h</i>
Cyclopropylammonium ⁱ	2.93 ^e	0.93 ^e	

^a Showing the effect of decreasing cyclopropyl conjugation. The solvent for entry 1 was SbF₅-FSO₃H at -70°, for entries 2 and 3 it was FSO₃H at -50°, for entries 4-6 it was CF₃COOH at -25°, and for entries 7-10 it was 96% H₂SO₄ at 25°. ^b In p.p.m. downfield from (CH₃)₄Si. ^c Reference 12. ^d Reference 14. ^e Multiplet. ^f See Figure 1. ^g See Figure 2. ^h See Figure 3. ⁱ The band positions are close to those of the free amine in CCl₄ (tetramethylsilane standard), which are 2.25 for the α -H and 0.25 for β -H.

ported by quantitative recovery of α,α' -dideuterio-tricyclopropylmethanol from the cation showing that no exchange occurs between α - and β -hydrogens. The quantitative recovery was easily demonstrated by showing that the n.m.r. spectrum of the CCl₄ extract from rapid dispersal drowning of the cation (in 10% aqueous NaOH) was identical with that of the dideuterated alcohol used to produce the cation.

The single band at -2.26 p.p.m. includes all 15 H's in the ion, since the ratio of the area of this band to the methyl band in equimolar acetophene was 14.5:3.0.

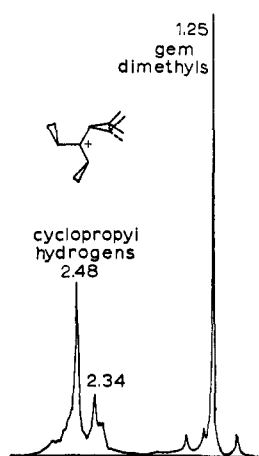


Figure 1. N.m.r. spectrum of the 2,2,3,3-tetramethyltricyclopropylmethyl cation in CF₃COOH at -25°.

The constancy of the band position at -2.26 p.p.m. in different solvent systems is evidence that the positive charge is highly delocalized in the tricyclopropylmethyl cation. Three of the n.m.r. spectra of Table III are illustrated in Figures 1-3.

Chemical Reactivity. Cyclopropane rings are usually characterized by their sensitivity to acids.

For the simplest example, cyclopropane, addition of the gas to 96% H₂SO₄ produces a solution exhibiting only the n.m.r. spectrum of 1-propyl hydrogen sulfate, the product of simple ring opening. An adjacent positive charge does protect the ring and the cyclopropylammonium ion is stable in 96% H₂SO₄. As the

positive charge is moved away from the ring, the sensitivity to acid returns. For example, cyclopropylmethylammonium ion is immediately ring opened in 96% H₂SO₄ and has a half-life of about 3 hr. in 76% H₂SO₄ at 25°.

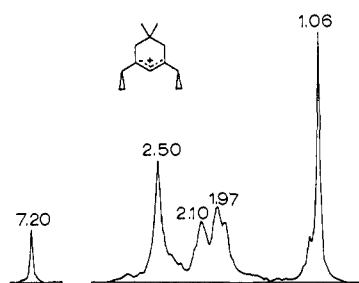


Figure 2. N.m.r. spectrum of the 1,3-dicyclopropyl-5,5-dimethylcyclohexenyl cation in 96% H₂SO₄ at 25°.

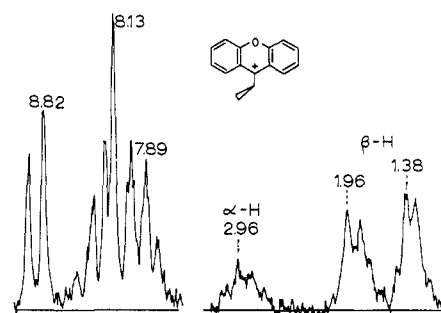


Figure 3. N.m.r. spectrum of the 9-cyclopropyl-9-xanthy cation in 96% H₂SO₄ at 25°.

In the cyclopropyl carbonium ions, the chemistry of cyclopropyl rings is dramatically reversed. The sensitivity to acids has been lost and has been replaced by a sensitivity to nucleophilic bases. Of course all carbonium ions are sensitive to bases, but we are not speaking of a simple conversion of the carbonium ion to an alcohol or olefin, but rather of attack by H₂O on a β -carbon with ring opening. The rate of this reaction for the tricyclopropylmethyl cation can be followed by the decrease in the absorption at 270 m μ . The rate is first order in the tricyclopropylmethyl cation concen-

tration from 13 to 77% H₂SO₄. The rate was also found to be first order in the activity of water throughout this range, but more particularly in 50–77% H₂SO₄ where the activity of water undergoes a change from 0.350 to 0.0118 and the kinetic test was definitive. The over-all rate law is

$$-dC_{R^+}/dt = k_2 C_{R^+} a_{H_2O} \quad (2)$$

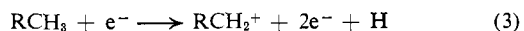
The half-life of the tricyclopropylmethyl cation at 3.0° was 13 sec. from 15 to 30% H₂SO₄. At 25°, it ranged from 15 sec. in 42% H₂SO₄ to 1.36 × 10³ sec. in 77% H₂SO₄.

The initial product of ring opening is presumably 4,4-dicyclopropyl-3-buten-1-ol. A derivative of this alcohol, 1,1-dicyclopropyltetrahydrofuran, was isolated in small amounts and identified solely from n.m.r. and infrared spectra.¹³ With the appearance of the work of Hart and Law,⁶ work on this reaction was discontinued.

The tricyclopropylmethyl cation is less stable in 20% SO₃-80% H₂SO₄ than in 96% H₂SO₄. Although the products have not been studied, the reaction is most probably a new mode of decomposition and not that represented by eq. 2.

Other cyclopropyl carbonium ions show this sensitivity to ring opening by bases. The half-life of 1,3-dicyclopropyl-5,5-dimethylcyclohexenyl cation is 50 sec. in 16% H₂SO₄, 30 sec. in 5.7% acid, and 22 sec. in 1.8% acid, all at 3.0°. From 16 to 1.8% H₂SO₄, the activity of water varies by only 10% so that the rate increase is primarily a salt effect. Despite this complexity, the decomposition is certainly not acid catalyzed. In fact the salt effect is in the expected direction for a rate-determining attack of water on the cation since by this mechanism the charge would be more dispersed in the transition state than in the reactant cation.

Gas Phase Stabilities. The stabilizing effect of various substituents on CH₃⁺ in the gas phase has been determined by measuring the appearance potentials for reaction 3.¹⁹ Relative to zero for R = H, R = CH₃



was 36 kcal./mole (−1.58 e.v.),²⁰ R = phenyl was 55 kcal./mole, and R = cyclopropyl was 58 kcal./mole.

Thus the superiority of cyclopropyl over phenyl in stabilizing carbonium ions is also found in the gas phase. Actually the superiority may be 5–10 kcal. greater than indicated by the above direct appearance potentials. It is known that the product from C₆H₅CH₃ is the cycloheptatrienyl cation, C₇H₇⁺, not C₆H₅CH₂⁺.²¹ Insofar as the ejection of H· is synchronized with the rearrangement of C₆H₅CH₂⁺ to C₇H₇⁺, the appearance potential is lowered below that required for the hypothetical formation of C₆H₅CH₂⁺. The value of 55 kcal./mole is thus too high.

Stable Salts. Adding tricyclopropylmethanol to a solution of HBF₄ in trifluoroacetic acid–trifluoroacetic

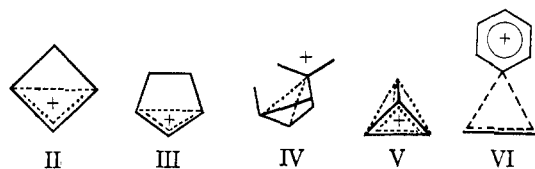
(19) R. W. Taft, R. H. Martin, and F. W. Lampe, *J. Am. Chem. Soc.*, **87**, 2490 (1965); R. H. Martin, Ph.D. Thesis, Pennsylvania State University, 1965.

(20) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press Inc., New York, N. Y., 1957.

(21) F. Meyer and A. G. Harrison, *J. Am. Chem. Soc.*, **86**, 4757 (1964); H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963.

anhydride at 0° produced a white, free-flowing, crystalline solid. The n.m.r. spectrum of this salt in 96% H₂SO₄ gave only the single −2.26-p.p.m. band of tricyclopropylmethyl cation and the n.m.r. spectrum in a KBr pellet showed the same bands as a solution of the cation in 96% H₂SO₄.¹³ Unfortunately, a C, H, and F analysis indicated the anion to have the average formula BF₃(OH)[−]. The main interest in such a salt would be for X-ray diffraction analysis, and the group at Dow Chemical Co. is studying its preparation with this objective.

Structural Formulas. We have taken a conservative position in drawing the structural formulas of carbonium ions.^{7,8} Carbon–carbon σ-bonds of 80–100 kcal./mole energy have been represented by single lines. π-Bonds of about 1β for the overlap integral have been represented by a dashed line. Now, it would have been possible to represent weaker π-bondings of say 0 to 0.3β by dashed lines in which case the cyclobutenyl and cyclopentenyl cations would have become II and III and cyclopropyl carbonium ions something perhaps like IV or V. It is our opinion that such representations cause confusion.



Recently, we have been criticized for not using VI as the representation for certain cyclopropyl carbonium ions.²² Structure VI connotes weakened bonds between the α- and β-carbons as well as an unusually strong bond (C=C) between β-carbons. The evidence does not support such implications.

Relation of Direct Observations to Solvolysis Studies. For cations such as triphenylmethyl and tricyclopropylmethyl, which exhibit extensive internal conjugation, specific interaction is reduced and the physical properties are insensitive to solvent.¹⁶ For the *t*-butyl cation in basic solvents such as H₂O, we can expect the positive charge to be delocalized into solvent by hydrogen bonding. This leaking of charge to solvent will be much reduced in strong acids so that spectra and other physical properties will be solvent sensitive.

These considerations lead to the conclusion that if an internally conjugated (nonclassical) form of the norbornyl cation exists, it is more likely to exist in strongly acidic media where more demand is made on the ion to delocalize charge internally.

Experimental Section

Electronic (Ultraviolet) Spectra. These were recorded on either a Cary 15 or Beckmann DU spectrophotometer. For kinetic experiments, thermospacers were used to hold the sample at 25.0 ± 0.1° or 3.0°.

Infrared Spectra. The infrared spectra of nearly every intermediate was recorded. These appear in the thesis of J. S. L.¹ In all cases they were in satisfactory agreement with the assigned structure.

N.m.r. Spectra. These were measured on a Varian A-60 instrument. The sample temperature was about

(22) L. Ebersson and S. Winstein, submitted for publication.

35°. Again, spectra were measured for nearly every intermediate and these appear in the thesis of J. S. L.¹ Reference is made to these spectra only in the cases where there was some added difficulty in identifying a compound.

1-Cyclopropyl-3-methyl-2-cyclopenten-1-ol. The cyclization of 2,5-hexanedione produces 3-methyl-2-cyclopentenone.²³ Although the product distilled over a narrow range, 57–60° (8 mm.), the n.m.r. spectrum showed that the product was only 50% of the desired ketone. This crude ketone was used in this and the following two syntheses.

Cyclopropyllithium was prepared from chlorocyclopropane²⁴ and lithium as reported.²⁵ The crude 3-methyl-2-cyclopenten-1-one was added to an excess of cyclopropyllithium and the substituted cyclopentenol, b.p. 48–50° (4 mm.), was isolated after hydrolysis with water. The product formed two layers on standing for 1 day presumably due to dehydration. Since it was inconvenient to get an immediate analysis, the identification rests upon the n.m.r. spectrum of the derived cation (Table III) and the n.m.r. spectrum of the freshly prepared 1-cyclopropyl-3-methyl-2-cyclopenten-1-ol. The latter showed a band at –4.8 p.p.m. for the vinylic H on C-2, a sharp spire at –1.5 for the CH₃ at C-3, a complex band system from –1.6 to –2.2 for the four hydrogens on C-4 and C-5, a complex band system at –0.1 to –0.3 for the β-hydrogens, and a multiplet from –0.7 to –1.0 due to the α-hydrogen. Both band positions and band areas supported the identification.

1,3-Dimethylcyclopentadiene. The product from excess CH₃MgI and crude 3-methyl-2-cyclopentenone was hydrolyzed with 5% aqueous HCl to produce an 88% yield, b.p. 87–89°.²⁶ An ethanolic solution of the diene mixture exhibited λ_{max} 252 mμ (log ε 3.44).

1-Phenyl-3-methylcyclopentadiene. The product from excess C₆H₅MgBr and crude 3-methyl-2-cyclopentenone was hydrolyzed with 5% aqueous HCl to produce a 56% yield, b.p. 95–96° (2 mm.),²⁷ m.p. 55–58° (lit.²⁷ 57–62°). The diene proved to be sensitive to air and the crystals turned to a gum in 1-hr. exposure.

1,3-Diphenylcyclopentadiene. 1-Phenyl-1,4-pentanedione was prepared from the condensation of levulinoyl chloride²⁸ and benzene catalyzed by AlCl₃. The product, b.p. 110–113° (1 mm.),²⁷ was obtained in 25% yield. It was cyclized by refluxing in 2% aqueous NaOH for 15 min. to produce 3-phenyl-2-cyclopentenone, m.p. 82.5–84°, in 30% yield.²⁹ Treatment with excess C₆H₅MgBr produced 1,3-diphenylcyclopentadiene, m.p. 155–156.5°,³⁰ in 18% yield. A solution of the diene in ethanol–acetic acid exhibited λ_{max} 250 mμ (log ε 4.08).

1,3-Dicyclopropyl-5,5-dimethylcyclohexadiene. 5,5-Dimethyl-1,3-cyclohexanedione (dimedon) was con-

verted to its mono-enol ether, 5,5-dimethyl-3-ethoxy-2-cyclohexen-1-one.³¹ The enol ether (22.0 g., 0.13 mole) was added to 0.30 mole of cyclopropyllithium in ether. The n.m.r. spectrum of the product (after hydrolysis) indicated it to be a mixture of the title compound and 5,5-dimethyl-3-cyclopropyl-2-cyclohexen-1-one. It is evident that this latter compound arises from direct attack of RLi on the keto group whereas the former arises from 1,4-addition of RLi, loss of ethoxide anion, and addition of a second mole of RLi.

The mixture was retreated with excess RLi to produce (after hydrolysis) 10.5 g., 43%, b.p. 78–80° (2 mm.), of the diene. The infrared spectrum showed the complete absence of –OH and C=O bands. The identification was supported by the n.m.r. spectrum which showed a single sharp band at –1.77 (the *gem*-dimethyl at C-5), broad absorption from –0.7 to –1.2 (the β-hydrogens of the cyclopropyl rings), and a poorly resolved narrow multiplet at –3.37 p.p.m. (the vinyl hydrogens).

Anal. Calcd. for C₁₄H₂₀: C, 89.3; H, 10.7. Found: C, 89.0; H, 10.6.

The n.m.r. spectrum of the derived cation (Table III) also supports the identification.

1-Cyclopropyl-3,5,5-trimethyl-2-cyclohexen-1-ol. Addition of 3,5,5-trimethyl-2-cyclohexen-1-one (isophorone) to 1 equiv. of cyclopropyllithium followed by hydrolysis gave the product, b.p. 79–80° (6 mm.), in 37% yield. The infrared spectrum showed bands characteristic of OH and C=C and the n.m.r. spectrum showed the vinyl hydrogen at –5.22, the *gem*-dimethyl at –0.98, and the CH₃ on C-1 at –1.70 p.p.m. as well as the other requisite features.

Anal. Calcd. for C₁₂H₂₀O: C, 79.9; H, 11.2. Found: C, 79.6; H, 11.3.

9-Cyclopropyl-9-xanthenol. 9-Xanthenone was added to an excess of cyclopropyllithium in ether. After hydrolysis and two recrystallizations from cyclohexane–benzene, the product was obtained in 55% yield as yellow crystals, m.p. 96–97°.

Anal. Calcd. for C₁₆H₁₄O₂: C, 80.6; H, 5.9. Found: C, 80.3; H, 6.3.

2,2,3,3-Tetramethyltricyclopropylmethanol. This alcohol was prepared by two methods. The better method proceeded *via* ethyl 2,2,3,3-tetramethylcyclopropanecarboxylate. This was prepared by mixing 70 g. of 2,3-dimethyl-2-butene, 1 g. of ethyl diazoacetate, and 1 g. of CuCl₂. The end of the induction period was signaled by evolution of N₂. A total of 35 g. of ethyl diazoacetate was then added at a rate sufficient to produce smooth N₂ evolution. The product was obtained in 52% yield, b.p. 107–110° (60 mm.). The product has previously been obtained in 26% yield by a related procedure.³² The ethyl 2,2,3,3-tetramethylcyclopropanecarboxylate was added to an excess of cyclopropyllithium in ether at 0–5°. After 1 hr. at 25° followed by hydrolysis, the 2,2,3,3-tetramethyltricyclopropylmethanol was isolated in 57% yield, b.p. 76–77° (2 mm.).

Anal. Calcd. for C₁₄H₂₄O: C, 80.7; H, 11.6. Found: C, 81.1; H, 11.9.

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The second method of preparation proceeded *via* 1-chloro-2,2,3,3-tetramethylcyclopropane. This compound has been prepared in 67% yield from chlorocarbene and 2,3-dimethyl-2-butene.³³ In our hands, the yield was 43%.

The chlorotetramethylcyclopropane was converted to the lithium derivative in a manner identical with the preparation of cyclopropyllithium. This lithium derivative was treated with an excess of dicyclopropyl ketone. By this method, 2,2,3,3-tetramethyltricyclopropylmethanol was prepared in a 24% yield based on the chlorotetramethylcyclopropane.

2,3-cis-Dimethyltricyclopropylmethanol. The lithium derivative of 1-chloro-2,3-*cis*-dimethylcyclopropane³² was prepared in the same manner as cyclopropyllithium. Treatment with excess dicyclopropyl ketone produced (after hydrolysis) the title alcohol in 50% yield based on the chloride, b.p. 72–74° (3.5 mm.).

Anal. Calcd. for C₁₂H₂₀O: C, 79.9; H, 11.2. Found: C, 79.8; H, 11.7.

Attempts to observe the carbonium ion derived from this alcohol failed at 25°. In view of recent work,^{12,14} it would probably be easily observable at –50°.

α,α'-Dideuteriotricyclopropylmethanol. 1,7-Dichloro-4-heptanone was prepared as described.³⁴ A

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mixture of 66 g. of the ketone, 80 g. of D₂O, and 10 g. of PCl₅ was heated and stirred for 20 hr. at 40–50°. The organic layer was separated and washed with water and aqueous Na₂CO₃. The n.m.r. spectrum indicated that the α-hydrogens were 86% deuterated. The process was repeated to increase the deuteration to 93%.

A mixture of 150 ml. of 20% aqueous NaOH and 40 g. of 3,3,5,5-tetradeuterio-1,7-dichloro-4-heptanone was refluxed for 30 min. with vigorous stirring. An additional 100 ml. of water was added and the ketone was separated by steam distillation. Despite this treatment, little deuterium was lost. After ether extraction and Na₂SO₄ drying, dicyclopropyl ketone was obtained in 86% yield and it was 75% deuterated as calculated from n.m.r. band areas.

The addition of α,α'-dideuteriodicyclopropyl ketone to excess cyclopropyllithium produced α,α'-dideuteriotricyclopropylmethanol. The n.m.r. spectrum showed the expected reduction of the band areas of the α-hydrogen to about 50% of their normal value.

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Nucleophilic Displacements on Three-Membered Rings

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Two routes to monochloroaziridines have been discovered and the stereochemistry of these compounds has been determined by spectroscopic methods. The chemistry of these monohaloaziridines has been investigated and found to have little analogy with similar cyclopropyl systems. The chloro group is easily displaced from these monochloroaziridines and the displacement products are formed with inversion of stereochemistry. These displacements constitute the first facile displacements on three-membered rings of any kind. Evidence is presented for the intermediacy of the aziridinyl cation, and the reasons for its stereospecific attack are discussed.

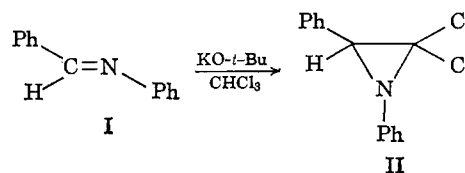
Introduction

Displacements of leaving groups from carbocyclic three-membered rings are notoriously difficult. This difficulty has been ascribed to various factors including the relatively high electronegativity of cyclopropyl carbon atoms and the introduction of "I" strain in the developing transition state.² Furthermore, exothermic

generation of cationic centers on three-membered rings leads to noncyclic products except in those cases where steric constraint inhibits ring opening.³ This paper deals with the dramatic enhancement in reactivity caused by the presence of a nitrogen atom in a three-membered ring and the accompanying facile displacements on these heterocyclic compounds without loss of ring integrity. The particular systems in which these results have been observed are the monochloroaziridines.

Synthesis and Stereochemistry

Dichloroaziridines are readily available from the addition of dichlorocarbene to Schiff bases.⁴ Prior



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