in ether. The product, b.p. 68–72° (23 mm.), was isolated in 62% yield after hydrolysis. Its identity was confirmed by hydrating to the known diol (2,3,3,4-tetramethyl-2,4-pentanediol).[3] This was accomplished in 20% yield by shaking for 3 days in 6% aqueous sulfuric acid at 25°.

In preparing an authentic sample of the diol for comparison by treatment of ethyl 2,2-dimethyl-3-ketobutanoate with excess CH_3MgI,[3] it was found that the ether solvent had to be replaced by benzene before addition of the ester, and then the yield of diol, b.p. 89–90° (4 mm.), m.p. 75–76°, was only 10%.

Stable Carbonium Ions. XVII.[1a] Cyclopropyl Carbonium Ions and Protonated Cyclopropyl Ketones

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Contribution from the Eastern Research Laboratory,
The Dow Chemical Company, Wayland, Massachusetts. Received June 28, 1965

An extended study[2] of the direct observation of a series of cyclopropyl carbonium ions including mono- and dicyclopropyl ions was carried out. The orientation of the cyclopropyl ring next to a positive carbon atom is elucidated. A series of protonated cyclopropyl ketones were also investigated. These serve as models to compare with the cyclopropyl carbonium ions.

Introduction

N. C. Deno, et al.,[3] observed the tricyclopropyl carbonium ion (I) on dissolving tricyclopropylcarbinol in concentrated sulfuric acid. Surprisingly, its p.m.r. spectrum in H_2SO_4 at room temperature was a single band at −2.26 p.p.m. The same single band was observed in CF_3CO_2H, and in CH_2Cl_2–$AlCl_3$ at −25°.

This ion exhibited surprising stability. It had a pK value of −2.34 and was half-formed (cation concentration equal to alcohol concentration) in 22% H_2SO_4 whereas the triphenylmethyl cation was half-formed in 50% H_2SO_4.[4] Other examples of the stabilizing effect of a cyclopropyl ring on a carbonium ion are the comparisons[5] of the half-protonation acidity of the

1,3-dimethylcyclopentenyl cation (II, 35% H_2SO_4) compared with the 1-cyclopropyl-3-methylcyclopentenyl cation (III, 11% H_2SO_4) and of 1,3,5,5-tetramethylcyclohexenyl cation (IV, 50% H_2SO_4) with the 1,3-dicyclopropyl-5,5-dimethylcyclohexenyl cation (V, 1.8% H_2SO_4). Despite the stabilizing effect of the cyclopropyl ring on a carbonium ion, mono- and dicyclopropyl carbonium ions were never observed. All attempts in H_2SO_4 or oleum systems resulted in exothermic reactions leading to unidentifiable acid-soluble products.
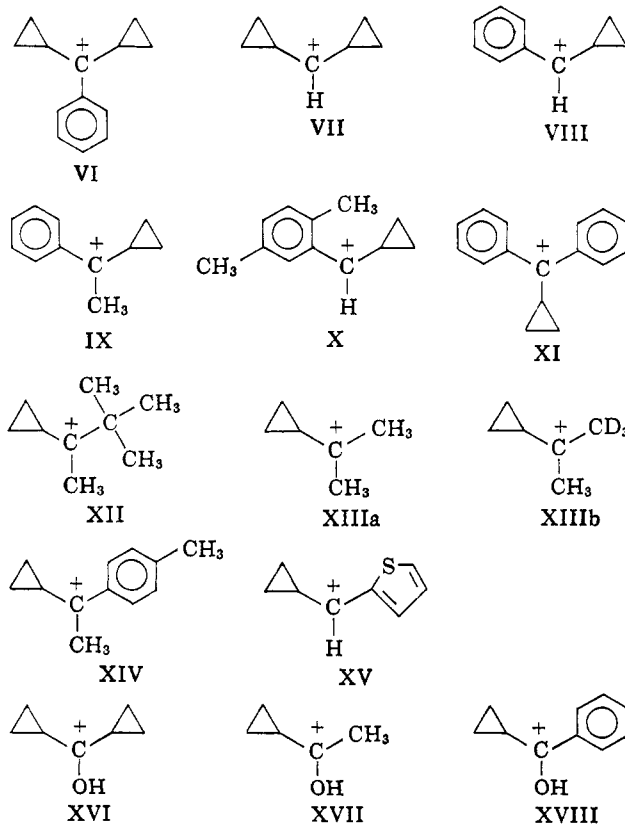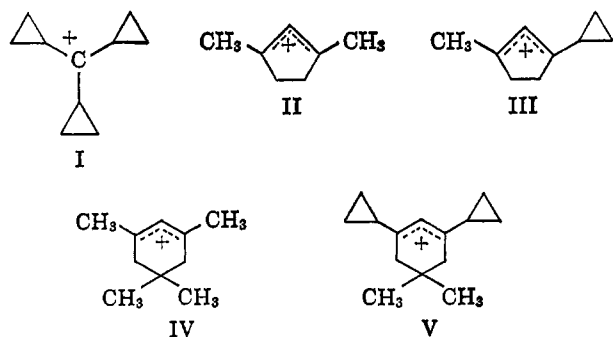
(1) (a) Part XVI: G. A. Olah and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **87**, 3509 (1965); (b) to whom inquiries should be addressed at the Department of Chemistry, Western Reserve University, Cleveland, Ohio 44106.

(2) Charles U. Pittman, Jr., and George A. Olah, *ibid.*, **87**, 2998 (1965).

(3) N. Deno, H. G. Richey, Jr., J. S. Liu, J. D. Hodge, J. J. Houser, and M. J. Wisotsky, *ibid.*, **84**, 2016 (1962).

(4) N. C. Deno, A. Schriesheim, and J. J. Jaruzelski, *ibid.*, **77**, 3044 (1955).
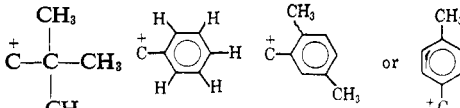
(5) Ph.D. Thesis of J. S. Liu, The Pennsylvania State University,

Results and Discussion

Carbonium ions VI–XVIII have been directly observed by n.m.r. spectroscopy. Both the cyclopropyl

1963. N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *J. Am. Chem. Soc.*, to be published.

Table I. P.m.r. Shifts of Cyclopropyl Carbonium Ions (at $-60°$, in FSO_3H–SbF_5–SO_2 Solution, p.p.m. from External TMS)

Carbonium ion	α^a	β^a	C⁺H	⁺C—CH₃	CH₃C⁺CH₃	aromatic	p-CH₃
Dicyclopropylphenyl	−3.00 to −3.30	−2.85 to −2.45				−7.55 to −8.10	
Dicyclopropyl	−2.92 to −3.45	−2.35 to −2.74	−8.14				
Cyclopropylphenyl	−2.86 to −3.28	−2.33 to −2.62	b			−7.15 to −8.42	
Cyclopropylphenyl-methyl	−3.56 to −3.90	−2.82 to −2.98		−2.52		−7.34 to −8.27	
Cyclopropyl-2,5-di-methylphenyl	−2.96 to −3.32	−2.40 to −2.86	b			−7.3 to −8.20	−2.04 and −2.33
Cyclopropylphenyl	−3.40 to −3.95	−2.35 to −2.74				−7.30 to −7.85	
Cyclopropylmethyl-*t*-butyl	−3.17 to −3.56	−2.30 to −2.90		−2.40	−1.10		
Cyclopropyldimethyl	−3.44 to −3.95				−3.14 *cis* −2.60 *trans*		
Tricyclopropyl	Singlet, −2.14						
Cyclopropyl-*p*-tolyl-methyl	−3.37 to −3.88	−2.52 to −2.75		−2.47		−7.23 to −8.25 A₂B₂ quartet	−2.25
Cyclopropylthienyl	−2.80 to −3.37	−2.20 to −2.70	c				d

a These bands have complex splitting patterns. *b* In the phenyl hydrogen region. *c* In with the thiophene hydrogens. *d* Thiophene hydrogens have complex splitting pattern from −7.85 to −8.95 p.p.m.

carbonium ions VI–XVI and the protonated cyclopropyl ketones XVI–XVIII were generated by adding the corresponding alcohols and ketones to FSO_3H–SO_2–SbF_5 at $-78°$ with vigorous stirring. This method has been previously described.[6] The n.m.r. spectra were then taken at low temperature. Cyclopropyl ketones were also dissolved into 96% H_2SO_4 at room temperature and quantitatively protonated.

In all the cyclopropyl carbonium ions except I the α- and β-hydrogens on the cyclopropyl rings were resolved and the characteristic splittings were observed. The integrated areas were in accord with structure in ev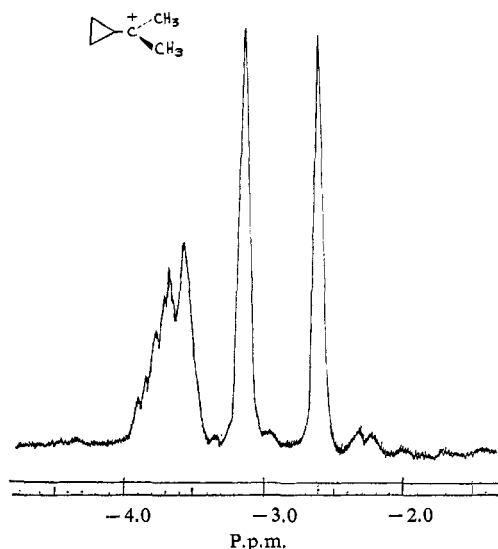ery case. Ions VI–XV were all stable at $-65°$ with the exception of ion XII which slowly decayed over a 30-min. period at $-65°$. All ions VI–XV were destroyed on raising the temperature to $-25°$. The products from warming XII to room temperature were a mixture of cyclopentenyl cations.[7] This as-

Figure 1. Spectrum in SO_2–$SOClF$–SbF_5 at $-75°$.

Figure 2. Spectrum in SO_2–SbF_5–FSO_3H at $-70°$.

(6) G. A. Olah, M. B. Comisarow, C. A. Cupas, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, 87, 2997 (1965).

(7) N. C. Deno, H. G. Richey, N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *ibid.*, 85, 2991 (1963).
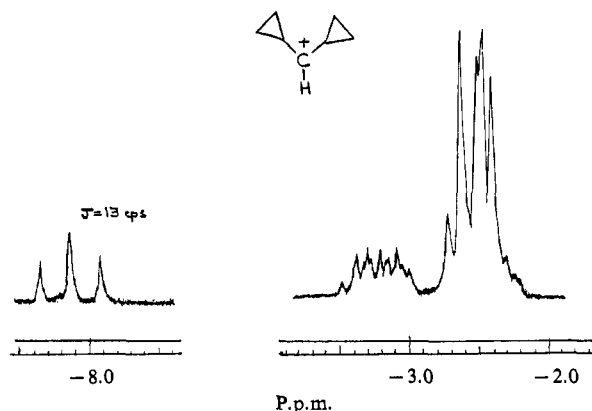
Figure 3. Spectrum in SO_2-FSO_3H-SbF_5 at $-60°$.

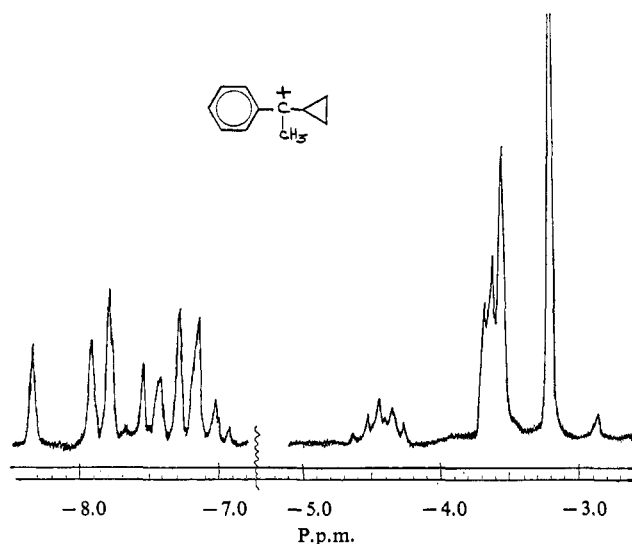Figure 4. Spectrum in SO_2-SbF_5-FSO_3H at $-60°$.

Figure 5. Spectrum in SO_2-SbF_5-HSO_3F at $-60°$.

Figure 6. Spectrum in SO_2-SbF_5-FSO_3H at $-65°$.
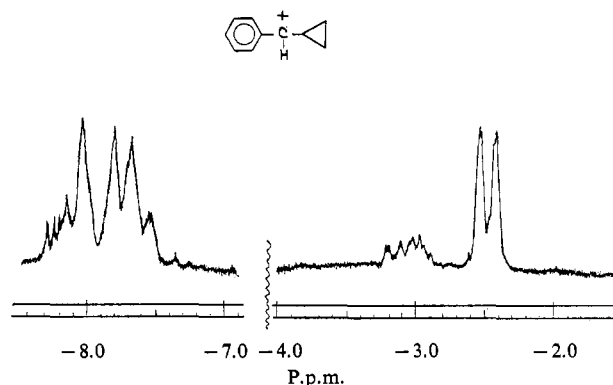
Figure 7. Spectrum in SO_2-SbF_5-FSO_3H at $-60°$.
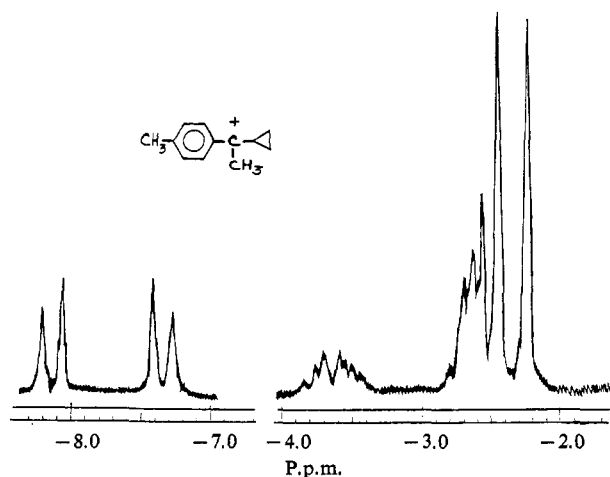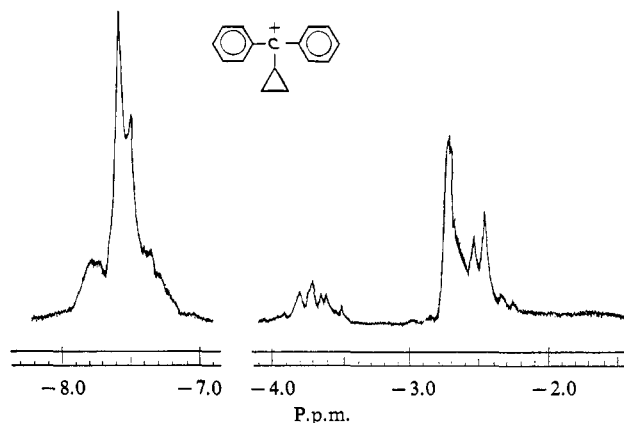

Figure 8. Spectrum in SO_2SbF_5-FSO_3H at $-60°$.

signment followed directly from the n.m.r. spectrum of the products of decomposition which is shown in Figure 13. The n.m.r. spectra of cyclopentenyl cations and cyclopentenyl cation mixtures are well known.[7,8] Figures 1–20 exemplify the resolution and quality of

the p.m.r. spectra obtained. Table I contains the p.m.r. band positions and assignments of ions VI–XV and Table III contains the p.m.r. data for the protonated cyclopropyl ketones XVI–XVIII. Each of the cyclopropyl ketones studied was recovered from drowning 96% H_2SO_4 solutions of XVI, XVII, and XVIII into 15% aqueous NaOH in yields of 78, 70, and 83%, respectively.

The p.m.r. spectrum of the dimethylcyclopropyl carbonium ion XIII is especially noteworthy. The methyl groups are not equivalent, but separated by 0.54 p.p.m. This demonstrates the cyclopropyl ring lies in a plane which is perpendicular to the plane of the $\overset{+}{C}(CH_3)_2$ system and does not rotate. Thus, the plane

(8) Ph.D. Thesis of C. U. Pittman, Jr., The Pennsylvania State University, 1964.

Figure 9. Spectrum in $SO_2-SbF_5-FSO_3H$ at $-60°$.
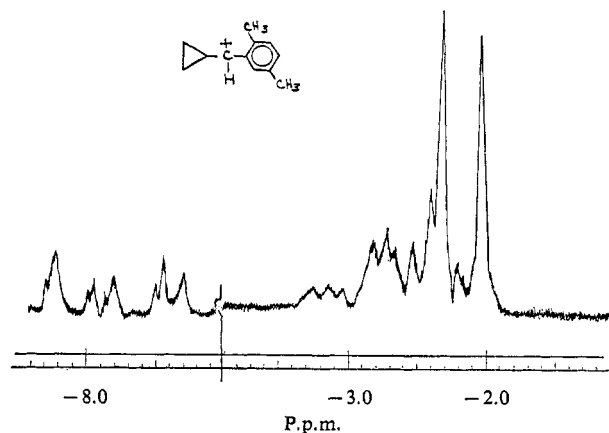

Figure 10. Spectrum in $SbF_5-SO_2-FSO_3H$ at $-65°$.

Figure 11. Spectrum in $SO_2-SbF_5-FSO_3H$ at $-65°$.

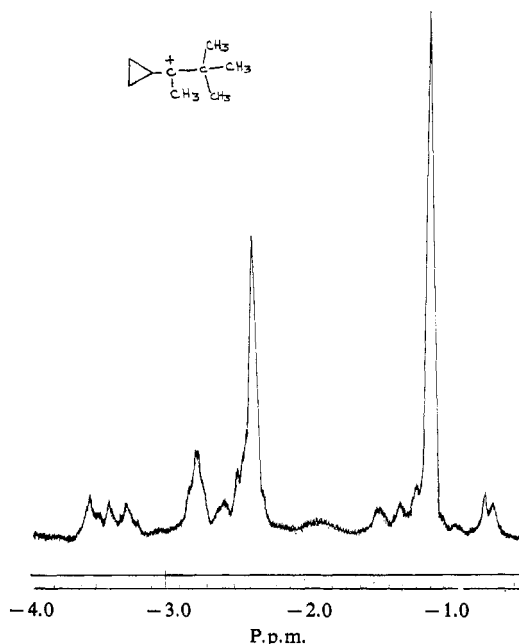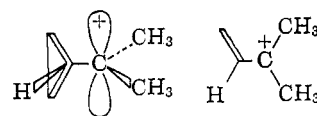of the cyclopropyl ring would be parallel to the axis of the vacant p-orbital. In this orientation the cyclopropyl ring now lies *cis* to one methyl group and *trans*

Figure 12. Spectrum in $SO_2-SbF_5-FSO_3H$ at $+20°$.

Figure 13. Spectrum in $SO_2-SbF_5-FSO_3H$ at $-65°$.

to the other. This orientation may be called the "bisected" form.

The steric configuration of the dimethylcyclopropyl

carbonium ion is shown above. Models show clearly that the *cis* methyl now lies in the face of the cyclopropyl ring. In this orientation the *cis* methyl group will experience the diamagnetic anisotropy of the cyclopropane ring; thus it will be found at higher field than the *trans* methyl group. It is known in several cases that this diamagnetic anisotropy causes such geometrically positioned hydrogens to be shifted upfield from 0.3 to 0.5 p.p.m. in uncharged systems.[9, 10] This is in agreement with the 0.54-p.p.m. difference we observed. 1,1,1-Trideuterio-2-cyclopropyl-2-propanol was prepared, and the p.m.r. spectrum (Figure 2) of the corresponding carbonium ion XIIIb was found to be identical with that of ion XIIIa (Figure 1) except that the two methyl bands at -3.14 and -2.60 p.p.m. were

(9) S. Forsen and T. Norin, *Tetrahedron Letters*, No. 39, 2845 (1964).
(10) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3218 (1963).
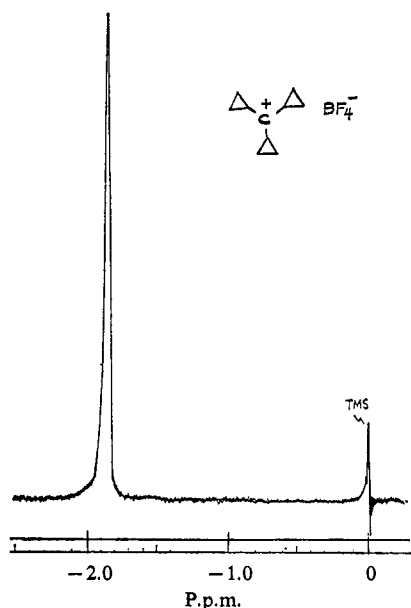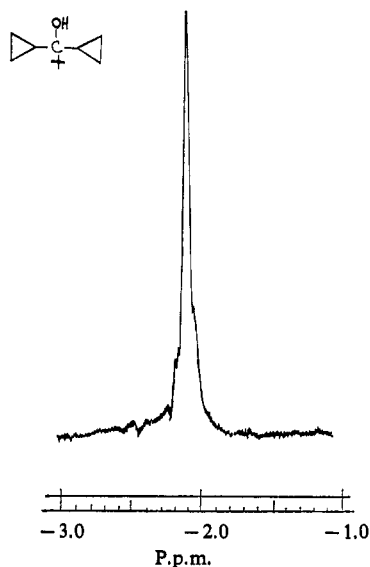
Figure 14. Spectrum in SO₂ at −65°.

Figure 15. Spectrum in 96% H₂SO₄ at 40°.

Figure 16. Spectrum in FSO₃H–SO₂–SbF₅ at −60°.
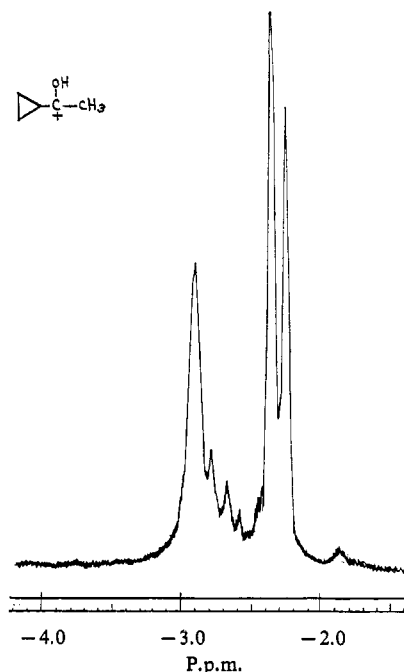
Figure 17. Spectrum in FSO₃H–SO₂–SbF₅ at −60°.

only one-half as intense as in XIIIa. This is what would be expected, since in the alcohol the cyclopropyl group can rotate about its bond to the central carbon. Thus, there is an equal probability that carbonium ion will be formed with the CD₃ group *cis* or *trans*.

No rotation of the cyclopropyl ring was observed in p.m.r. studies of ion XIII on warming to −35°. Fast cyclopropyl rotation would cause coalescence of the two methyl bands into a single band. Between −35 and −30° the ion was rapidly destroyed, and on destruction no coalescence of the methyl bands was observed. Instead the two bands decayed separately. Thus, no exact value of the barrier to rotation of the cyclopropyl about the cyclopropyl-C̈ bond could be obtained, although a coalescence temperature higher than −35° would indicate a barrier of at least 8–10 kcal./mole.

Evidence for delocalized orbitals in the cyclopropyl ring has been reported from ultraviolet,[11,12] infrared,[13] n.m.r.,[8,13] and theoretical[14,15] studies. The cyclopropyl ring's "banana bond" type geometry contrasts sharply with the π-orbitals of benzene which lie above and below the plane of the benzene ring. Thus, it is not surprising that the cyclopropyl ring can be perpendicular to the plane of the C̈(CH₃)₂ system in order to give maximum orbital overlap with the vacant p-orbital, instead of being coplanar as with the benzene ring.

The large downfield shifts of the α- and β-hydrogens of ions VI–XV demonstrate a large amount of charge delocalization into the cyclopropyl ring. The p.m.r.

(11) R. H. Eastman, *J. Am. Chem. Soc.*, **76**, 4115, 4118 (1954); **77**, 6645 (1955).
(12) E. M. Kosower and M. Oto, *Proc. Chem. Soc.*, 25 (1962).
(13) A. P. Cross, *J. Am. Chem. Soc.*, **84**, 3206 (1962); D. H. Williams and N. S. Bhacca, *ibid.*, **85**, 2861 (1963); K. B. Wiberg and B. J. Nist, *ibid.*, **83**, 1226 (1961).
(14) A. S. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).
(15) C. A. Coulson and W. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

Table II. P.m.r. Shifts of Cyclopropyl Alcohols (in SO_2 Solution, p.p.m. from External TMS at $-60°$)

Carbinol	▷— α	β	C—H	C—CH₃	OH	t-Butyl H	Phenyl H	Methyl on phenyl
Dicyclopropylphenyl	−0.52 to −1.03	+0.15 to −0.30			−2.40		−7.16 to −7.64	
Dicyclopropyl	−0.13 to −0.66	+0.43 to 0.00	Triplet broadened at −1.73		−1.89			
Cyclopropylphenyl	−0.42 to −0.88	+0.28 to −0.23	−2.77		−2.57		−6.94	
Cyclopropylphenyl-methyl	−0.44 to −0.91	+0.41 to +0.02		−0.77	−2.38		−6.73 to −7.21	
Cyclopropyl-2,5-di-methylphenyl	−0.20 to −0.65	+0.50 to +0.09	−3.50		−2.92		−6.51 to −6.82	−1.55 to −1.59
Cyclopropyldiphenyl	−0.75 to −1.3	+0.42 −0.07			−2.21		−6.77 to −7.16	
Cyclopropylmethyl-t-butyl	−0.17 to −0.53	+0.52 to +0.22		−0.35	−1.57	−0.32		
Cyclopropyldimethyl	−0.23 to −0.65	+0.44 +0.04		−0.67	−2.17			
Tricyclopropyl	Broad rounded band centered at −0.12				−2.05			
Cyclopropyl-p-tolyl-methyl	−0.44 to −0.90	+0.30 to +0.03		−0.79	−2.13		Quartet, J = 8, centered at −6.79	−1.72
Cyclopropylthienyl	−0.51 to −0.92	+0.23 to −0.22	Rounded doublet at −4.4		−4.28		−7.43 to −9.95[a]	

a Thienyl hydrogens.

band position of the carbonium ions in Table I can be compared with the band positions of their corresponding alcohols in SO_2 given in Table II. Generally, in cyclopropyl carbonium ions both α- and β-hydrogens
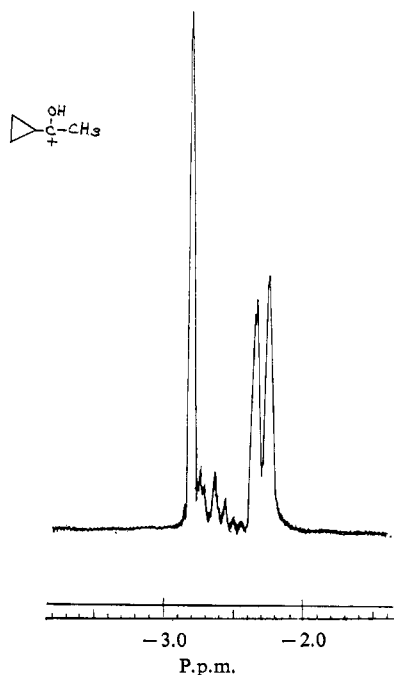

Figure 18. Spectrum in 96% H_2SO_4 at $+40°$.

are shifted about 3 p.p.m. downfield from their positions in the precursor alcohols.

In the dicyclopropyl carbonium ion (VII, Figure 3) the hydrogen on the central, charged carbon atom appears as a sharp triplet at −8.14 p.p.m. with $J =$

13 c.p.s. This sharp symmetrical triplet shows that both α-hydrogens in VII are equivalent and that no coupling to the β-hydrogens is found. Since it is now established that the plane of the cyclopropyl ring will exist parallel to the axis of the vacant p-orbital and that the two α-hydrogens in II are equivalent, it would seem only two structures for the ion are possible. We favor a over b as shown below. Models

top views
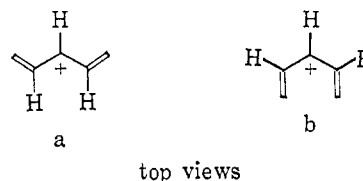
indicate that b would be quite sterically hindered, and the coupling constant of 13 c.p.s. would favor the hydrogens being "*trans.*" It is interesting to compare the position of the hydrogen at the central charged carbon atom in VII with the corresponding hydrogens in the isopropyl cation[16] (in neat SbF_5, −13.5 p.p.m.) and the benzyhydryl cation[17] (in SO_2–SbF_5, −9.8 p.p.m.). The value of −8.14 p.p.m. for C̈–H in ion VII indicates that the cyclopropyl rings probably delocalized more charge than the phenyl rings in the benzhydryl cation. However, since the diamagnetic anisotropy and ring current effects cannot be clearly separated from electron withdrawal effects only this qualitative observation can be made.

The cyclopropylthienyl carbonium ion XV (Figure 11) is interesting in that the thiophene ring remains intact and unprotonated on dissolving in SO_2–

(16) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. Mc-Intyre, and I. J. Bastien, *J. Am. Chem. Soc.*, 86, 1360 (1964).
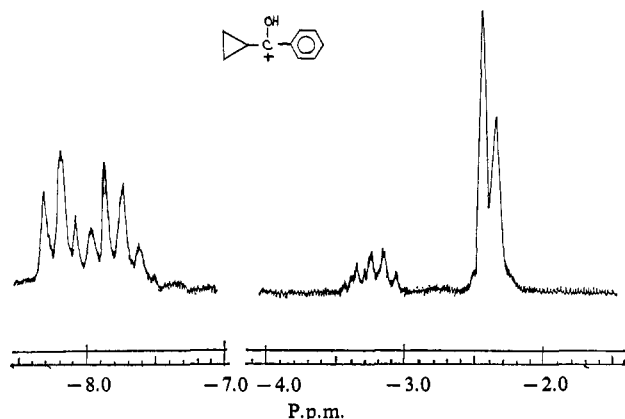(17) G. A. Olah, *ibid.*, 86, 952 (1964).

Figure 19. Spectrum in 96% H_2SO_4 at $+40°$.

Figure 20. Spectrum in $FSO_3H-SO_2-SbF_5$ at $-60°$.

SbF_5-FSO_3H at low temperatures. The ionization of the OH occurs and the resulting positive charge on ion XV protects the thiophene ring from further reactions.

The instability of the cyclopropylmethyl-*t*-butyl carbonium ion XII is not surprising considering the steric bulk of the *t*-butyl group and the inability of the *t*-butyl group to donate electrons toward the positive central carbon atom by hyperconjugation. The p.m.r. spectrum at $-65°$ (Figure 12) shows only one *t*-butyl band and one methyl band. Thus, the ion exists with either the cyclopropyl group *cis* or *trans* to the *t*-butyl group but not in both configurations. If the *t*-butyl group could possibly exist *cis* to the cyclopropyl ring then there is no apparent reason why it could not also exist *trans;* thus two methyl p.m.r. bands would be expected. For this reason we feel that the *t*-butyl group must be only *trans* to the cyclopropyl ring as shown below. This view is supported by models which predict severe steric interactions
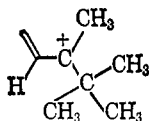
between the *t*-butyl and the cyclopropyl groups if they exist *cis*.

In view of our observation that in a whole series of investigated cyclopropyl carbonium ions the α- and β-cyclopropyl protons were well resolved, we reinvestigated the finding that in the tricyclopropyl carbonium ion the α- and β-protons coincide giving one sharp band.[3] Figures 13 and 14 show the p.m.r. spectrum of tricyclopropylcarbinol in $FSO_3H-SbF_5-SO_2$ at $65°$ and that of isolated stable tricyclopropylcarbonium tetrafluroborate dissolved in SO_2 at $-65°$. In both spectra only a single sharp band occurs. Thus we confirm Deno's findings even in an aprotic solvent at $-65°$. We feel, however, that the coincidence of the α- and β-protons is not due entirely to a conjugative effect which shifts the more distant β-protons as far downfield as the α-protons, but, instead, is due to an anisotropy effect of the cyclopropyl rings in the ion.[9,10] This interpretation is further suggested by the observation that the α- and β-hydrogens are only poorly resolved in tricyclopropylcarbinol in SO_2 at $-60°$. In ion I, each alpha proton lies in the face of another cyclo-
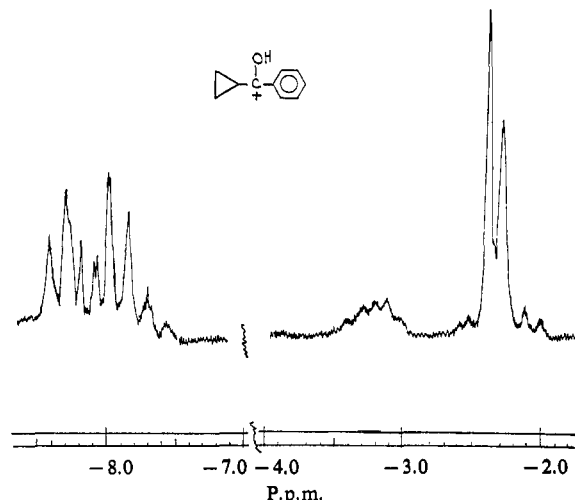
propyl ring. In this orientation it will experience the diamagnetic anisotropy effect of the cyclopropane ring; thus it will be found at a higher field than expected and can coincide with the less deshielded β-hydrogens. Based on models, the equivalence of the α-hydrogens, and the elucidated geometry of the cyclopropyl ring in ion XIII we favor the bisected orientation in ion I.

The top view of the proposed geometry for the tricyclopropyl carbonium ion is shown below.
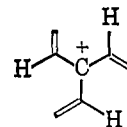
The ultraviolet spectrum of the dimethylcyclopropylcarbonium ion in FSO_3H-SbF_5 at $-60°$ exhibits a single absorption maximum at 289 mμ (ϵ 10,800). The close resemblance to the ultraviolet spectra of allylic carbonium ions[18,19] demonstrates the frequently cited double-bond character of the cyclopropyl ring. This character appears to be strongly enhanced when the cyclopropyl ring is located adjacent to a vacant p-orbital. The reported ultraviolet absorption of the tricyclopropylcarbonium ion in sulfuric acid solution is at 270 mμ (ϵ 22,000).[3] Thus, increasing the number of cyclopropyl groups located adjacent to the vacant p-orbital does not shift the wave length of the absorption maximum (in marked contrast to the adding of double bonds causing a marked shift of the absorption maximum of allylic cations to longer wave lengths[20,21]), only enhances the intensity.

Protonated ketones can be generally used as models for carbonium ions.[18] Therefore we extended our investigations to the protonation of some cyclopropyl ketones in our acidic solvent systems.[22]

(18) N. C. Deno, *Chem. Eng. News*, **42**, 88 (1964).
(19) J. Hodge, Ph.D. Thesis, The Pennsylvania State University, 1963.
(20) N. C. Deno and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **86**, 1871 (1964).
(21) N. C. Deno, C. U. Pittman, Jr., and J. O. Turner, *ibid.*, **87**, 2153 (1965).
(22) Protonated dicyclopropyl ketone was reported by N. C. Deno, "Progress in Physical Organic Chemistry," Vol. 2, S. Cohen, A. Streitwieser, and R. Taft, Ed., John Wiley and Sons, Inc., New York, N. Y., 1964, p. 182.
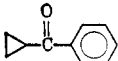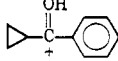
Table III. P.m.r. Shifts of Cyclopropyl Ketones and Protonated Cyclopropyl Ketones[a]

| Species	α-H	β-H	CH₃	C₆H₅ H
(structure) In CCl₄[b]	−1.77 to −2.14	−0.70 to −1.00		
(structure) In 96% H₂SO₄[c]		−2.12		
In SO₂–SbF₅–FSO₃H[b]	Multiplet −3.30 to −3.95 centered −3.60	Very broadened doublet at at −1.98		
(structure) In CCl₄[b]	−1.69 to −2.05	−0.68 to −0.91	−2.17	
(structure) In 96% H₂SO₄[c]	Multiplet −2.54 to −2.85 centered at −2.63	Broadened doublet centered at −2.30, J = 5 c.p.s.	−2.81	
In SO₂–SbF₅–FSO₃H	Multiplet centered at −2.76	Broadened doublet centered at −2.30	−2.90	
(structure) In CCl₄[b]	−2.36 to −2.78	−0.85 to −1.15		−7.26 to −8.03
(structure) In 96% H₂SO₄[a]	Multiplet −2.95 to −3.40 centered at −3.19	Broadened doublet centered at −2.38, J = 6 c.p.s.		−7.60 to −8.30
In SO₂–SbF₄–FSO₃H[c]	Multiplet −3.00 to −3.40 centered at −3.21	Broadened doublet at −2.38, J = 6 c.p.s.		−7.60 to −8.34

[a] In p.p.m. [b] Relative to TMS internal. [c] Relative to TMS in CHCl₃ external.

In all of the protonated cyclopropyl ketones XVI–XVIII studied, the α- and β-hydrogens were resolved with the exception of protonated dicyclopropyl ketone (XVI) in 96% H₂SO₄ (Figure 14). However, the α- and β-hydrogens of XVI were resolved in SO₂–SbF₅–FSO₃H at −60° (Figure 15). Rapid exchange of the α-hydrogens of XVI with the sulfuric acid solvent could explain the lack of resolving the α-hydrogen band, but this has not been demonstrated. This would seem unlikely in view of the resolution of the α-hydrogen (showing it is not exchanging rapidly with solvent) of protonated cyclopropylmethyl ketone XVII in 96% H₂SO₄ solutions. No simple explanation of the spectrum of XIII in 96% H₂SO₄ is apparent.

The large, downfield shifts of the α- and β-hydrogens in the protonated ketones relative to the unprotonated ketones is illustrated in Table III. This shows a large amount of charge delocalization into the cyclopropyl rings in the protonated ketones. In all cases the β-hydrogens in protonated ketones move downfield from 1 to 1.5 p.p.m. whereas in ion XV delocalization into the phenyl ring causes only a 0.3 p.p.m. downfield shift of the phenyl hydrogens. However, since the phenyl ring has an aromatic ring current and six carbons over which to delocalize the positive charge,

the downfield shifts of the cyclopropyl β-hydrogens relative to the phenyl hydrogens cannot be used as a quantitative measure of the amount of charge delocalization.

Representative pairs of comparisons of protonated ketones to carbonium ions are the following.
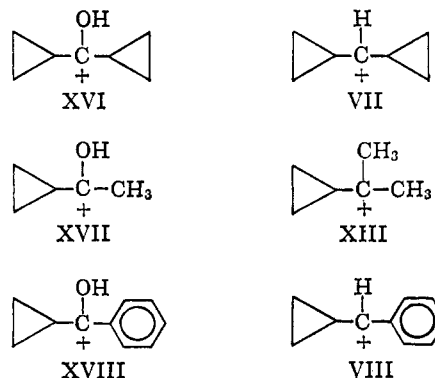
In each of these pairs the deshielding effects are greater in the carbonium ion than in the protonated ketone, indicating a greater charge density on the carbonium ion's central carbon atom. Thus, in protonated ketones

the resonance hybrid **1b** makes a significant contribution to the ion.

$$^+C{-}OH \longleftrightarrow C{=}\overset{+}{O}{-}H$$
$$\textbf{1a} \qquad\qquad \textbf{1b}$$
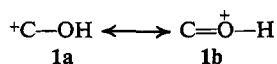
Experimental Section

The spectra of the cyclopropyl alcohols (ketones) in liquid SO_2 were taken by condensing SO_2 directly in the n.m.r. tube containing about 5 to 15% of the alcohol or ketone. The tubes were then immediately sealed to prevent any moisture from entering the system. In several cases the SO_2 solutions became quite viscous or solid at $-60°$; thus it was necessary to take the spectra at higher temperatures. However, it was shown that the chemical shifts were relatively insensitive to temperature changes with the exception of the OH hydrogen band. This is illustrated in Table IV. Also illus-

Table IV. N.m.r. Shifts of Dimethylcyclopropylcarbinol as a Function of Temperature[a]

Protons	CCl_4, $+40°$	SO_2, $+40°$	SO_2, $0°$	SO_2, $-20°$	SO_2, $-40°$
$(CH_3)_2$	-1.14	-0.65	-0.63	-0.66	-0.65
α-H	-0.82	-0.46	-0.46	-0.46	-0.46
β-H	-0.33	$+0.12$	$+0.13$	$+0.11$	$+0.12$
OH	-2.19	-1.45	-1.78	-2.17	-2.39

[a] Positions are given in p.p.m.

trated is the upfield shift found going from CCl_4 to SO_2 as a solvent which was true in all cases. Thus when viscosity broadening prevented sharp SO_2 spectra from being obtained at $-60°$ the samples were warmed to $-30°$ and their spectra were recorded.

The spectra of cyclopropyl alcohols and ketones in SO_2-SbF_5-FSO_3H were taken by dissolving an approximately equal weight of SbF_5 into FSO_3H. This was then cooled to $-20°$, and SO_2 as diluent was added and cooled to $-78°$. Then with rapid stirring and exclusion of moisture, SO_2 solutions of the alcohols and ketones were added to the acid systems.

A Varian Associates Model A56-60 n.m.r. spectrometer with a variable temperature probe was used for all spectra. The field resolution was brought to a maximum using a methanol sample at the temperature at which the particular spectrum was to be run, and the spectrum was run immediately thereafter.

We are grateful to Professor N. C. Deno for a sample of tricyclopropylcarbinol and dicyclopropylphenylcarbinol. The following compounds were obtained from the Aldrich Chemical Co., Milwaukee, Wis.: cyclopropylmethyl-p-tolylcarbinol; dicyclopropyl ketone; cyclopropyl phenyl ketone; cyclopropyl methyl ketone; cyclopropyl-2,5-dimethylphenylcarbinol; cyclopropylphenylcarbinol; dicyclopropylcarbinol; cyclopropylmethylphenylcarbinol; cyclopropyldiphenylcarbinol; cyclopropyl-2-thienylcarbinol; and cyclopropylmethylcarbinol.

Dimethylcyclopropylcarbinol. Thirty grams of cyclopropyl methyl ketone was added to 285 ml. (1.35 mole excess) of a 1.7 M methyllithium solution in diethyl ether (Foote Mineral Co.). After dropwise addition was completed, the solution was stirred for 4 hr. at room temperature and then hydrolyzed with excess distilled water. The layers were separated and the ether layer was washed with water and dried over anhydrous magnesium sulfate. Aspiration was followed by distillation through a 6-in. Vigreux column to give an 89% yield of the cyclopropyldimethylcarbinol boiling at $119{-}120°$ (1 atm.).[23] The n.m.r. spectrum of the alcohol in CCl_4 using TMS as internal standard was in agreement with structure, exhibiting peaks at -0.21, -0.23, and -0.33 p.p.m. for the β-hydrogens on the cyclopropyl ring, a multiplet from -0.62 to -0.97 p.p.m. for the α-hydrogens, a singlet at -1.14 p.p.m. for the methyls, and a singlet at -2.18 for the OH hydrogen. The areas were 4.1: 1.0:6.0:0.9, respectively. The infrared spectrum exhibited a broad OH band at 3360 cm.$^{-1}$ and no carbonyl band.

3,3-Dimethyl-2-cyclopropyl-2-butanol. Lithium sand was made by the usual technique of heating and shaking lithium in Nujol. Four grams of lithium sand was suspended in ether under a N_2 atmosphere. Cyclopropyl bromide (Aldrich Chemical Co., 16 g.) was added dropwise to the lithium at $0°$. Next, 0.08 mole of pinacolone (Aldrich Chemical Co.) was added to the solution still kept at $0°$, and after addition of the ketone was complete, the solution was warmed to room temperature. The reaction mixture was hydrolyzed with distilled water after removing the excess lithium. The ether layer was washed with water, dried over anhydrous $MgSO_4$, and aspirated. The crude alcohol was distilled to give a 71% yield of 3,3-dimethyl-2-cyclopropyl-2-butanol boiling at $68{-}70°$ (20 mm.). The n.m.r. spectrum in CCl_4-TMS exhibited bands for β-hydrogens -0.22, -0.35, and -0.42 p.p.m., α-hydrogen multiplet -0.72 to -1.10 p.p.m., t-butyl hydrogens -0.97 p.p.m., methyl hydrogens -1.03 p.p.m., and the OH did not resolve. The areas were $4:1^{24}:9.2:3.1$, respectively.

The infrared spectrum exhibited an OH band at 3500 with a shoulder at 3610 cm.$^{-1}$.

1,1,1-Trideuterio-2-cyclopropyl-2-propanol. To 7 g. of magnesium metal in diethyl ether, an ether solution of 17 g. of trideuteriomethyl bromide (Merck Sharp and Dohme) was added dropwise with vigorous stirring. The reaction mixture was held between -5 and $0°$. After the addition was completed, the reaction mixture was kept at $0°$ for 1 hr. followed by warming to room temperature for 1 hr. Fourteen grams of cyclopropyl methyl ketone was then added dropwise and after the addition was completed the reaction mixture was refluxed for 3 hr. Hydrolysis was accomplished with saturated aqueous ammonium chloride solution and the ether layer was worked up in the usual way. Careful distillation through an 8-in. Vigreaux column followed by redistillation gave 12 g. of product boiling from 118 to $121°$. However, n.m.r. analysis indicated the presence of about 20% ketone in the product. This was largely removed by treatment with saturated aqueous $NaHSO_3$ solution and further distillation. The n.m.r. spectrum of the alcohol in CCl_4 using TMS as an internal standard at $+40°$ was identical with the n.m.r. of the undeuterated alcohol except that the area of the methyl band at -1.14 p.p.m. integrated for three

(23) G. Churdoglu and S. Van Walle, *Bull. soc. chim. Belges,* **66,** 612 (1957), reported 123° (760 mm.).

(24) Buried under t-butyl and methyl band.

hydrogens instead of six. The infrared spectrum gave an OH band at 3360, C–D bands at 2235, 2150, and 2060, and a noticeable carbonyl band at 1645 cm.$^{-1}$. The purity was sufficiently good for our n.m.r. studies. Further attempts to remove the last traces of ketone by treatment with hydroxylamine in ethanolic OH solution resulted in degration of the alcohol.

Tricyclopropylcarbinol. Lithium sand was prepared by melting 4 g. of lithium in hot Nujol and shaking vigorously. As soon as the sand had formed, the Nujol was cooled rapidly and the sand was separated by diluting the Nujol with ether and filtering through a glass plug. The sand was ether washed and then suspended in 200 ml. of dry ether in a three-neck, round-bottom flask under N_2 atmosphere. Cyclopropyl bromide (Aldrich), 25 g., was added dropwise at 0° with vigorous stirring. After the addition was completed another hour was allowed for completion of the reaction at 0°. Then 16.5 g. of dicyclopropyl ketone was added dropwise followed by an additional 3 hr. of reaction at 0° and 28 hr. at room temperature. Hydrolysis was completed with an excess of distilled water and the ether layer was separated, washed, and dried over anhydrous $MgSO_4$. The ether was aspirated and (14.1 g. of) the title alcohol was obtained on vacuum distillation through a jacketed, 8-in. Vigreux column with a boiling range of 87 to 88.5° (10 mm.) (lit.[25] b.p. 88.5° at 10 mm.).

Preparation of Tricyclopropylcarbonium Tetrafluoroborate. Twelve grams of tricyclopropylcarbinol was dissolved into 300 ml. of propionic anhydride. The solution was then cooled to between 15 and 20° while a 1.1 mole excess of 50% aqueous HBF_4 was added in small aliquots. Crystallization occurs, and the BF_4^- salt was obtained in 21% yield.

(25) H. Hart and P. A. Law, *J. Am. Chem. Soc.*, 81, 320 (1959).

Approaches to "Push–Pull" Stabilized Cyclobutadienes[1]

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Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. Received June 10, 1965

It is predicted that cyclobutadienes substituted by conjugated electron-donor and electron-acceptor groups will be stabilized. In approaches to such systems several nitrodimethylaminocyclobutenes have been prepared. However, dehydrohalogenations under mild conditions which should generate the nitrodimethylaminocyclobutadienes lead chiefly to tarry products. Dehydrobromination to produce a tetrasubstituted cyclobutadiene with its dimethylamino group conjugated with both nitro and benzoyl groups similarly leads chiefly to tarry products. Studies on a push–pull substituted cyclobutenone show that enolization to the cyclobutadiene is slow compared with hydrolysis of the compound. A number of cyclobutene rearrangements have been encountered, including an unusual ring-chain tautomeric equilibrium.

Introduction

Overwhelming evidence is available that the cyclobutadiene system is kinetically and thermodynamically unstable.[2a] This is reflected in the properties not only of the parent substance, but also of a variety of derivatives. Thus even tetraphenylcyclobutadiene, an extensively conjugated and rather hindered compound, dimerizes on generation.[2b] Theoretical explanations for such instability are available.[3]

However, some stable cyclobutadiene derivatives have been prepared. One class of such derivatives, complexes of cyclobutadienes with transition metals, is of considerable interest, but bears little electronic resemblance to cyclobutadiene itself.[4] Another sort of derivative is exemplified by biphenylene (A) and the recently prepared[5] naphthalene derivative (B). In
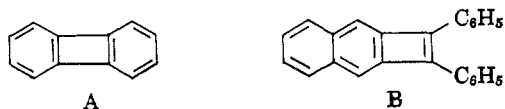
these cases the system is stable because the structures drawn are not the sole, or even the principal, resonance forms. In other resonance forms it becomes apparent that A and B may also be considered to be derivatives of the rather stable[6] dimethylenecyclobutane system.

The same principle, that a compound may be stable if a cyclobutadiene structure is only one of the important resonance forms, is the valence-bond explanation of the postulated[7] "push–pull" effect. Simple molecular orbital calculations[7] show that cyclobutadienes substituted with conjugated electron-donor and electron-acceptor groups should have considerable resonance energy. Furthermore, the degeneracy of

(2) (a) For a review of some of the evidence, *cf.* A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 261; (b) H. H. Freedman, *J. Am. Chem. Soc.*, 83, 2195 (1961); R. C. Cookson and D. W. Jones, *J. Chem. Soc.*, 1881 (1965).

(3) *E. g.*, M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, 87, 685 (1965), and many earlier calculations.

(4) H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.*, 1969 (1956); R. Criegee and G. Schröder, *Ann.*, 623, 1 (1959); H. H. Freedman, *J. Am. Chem. Soc.*, 83, 2194 (1961); P. M. Maitlis and M. L. Games, *ibid.*, 85, 1887 (1963).

(5) M. P. Cava, B. Hwang, and J. P. van Meter, *ibid.*, 85, 4032 (1963).

(6) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *ibid.*, 74, 4579 (1952).

(7) S. L. Manatt and J. D. Roberts, *J. Org. Chem.*, 24, 1336 (1959), and our own calculations.