

showed no peak at 309 $m\mu$, but showed a strong band at *ca.* 270 $m\mu$. The solution was dissolved in water and extracted with methylene chloride. The methylene chloride layer was washed with sodium bicarbonate solution, dried over magnesium sulfate, and evaporated to give 3.0 g. of yellow fluid. Distillation gave 2.5 g. (0.0142 mole, 83%) of 2,6-dimethyl-4-(1-methyl)allylphenol (**17**), b.p. 84–86° (0.35 mm.), n_D^{25} 1.5265.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.8; H, 9.09. Found: C, 81.5; H, 9.17.

B. **16** (1.0 g., 0.0569 mole) was shaken in 10 ml. of 6 *M* sulfuric acid for 15 min. The mixture was extracted with methylene chloride and the methylene chloride layer was washed with sodium bicarbonate solution, dried over magnesium sulfate, and evaporated to give 0.60 g. of **17**, identical in infrared and n.m.r. spectra and v.p.c. retention time (11.6 min. on a 6-ft., 10% diethylene glycol succinate on Gas Chrom Z column at 220°) with the product of procedure A.

Thermal Rearrangement of 16. **16** (3.0 g., 0.0170 mole) was heated to 105°, and maintained at that temperature for 1 hr. Distillation of the product gave 2.5 g. (0.0142 mole, 83%) of **17**, b.p. 82–88° (0.4 mm.), n_D^{25} 1.5261, identical with the product of the acid-catalyzed rearrangements.

Reaction of 4-trans-2-Butenyl-2,4-dimethylcyclohexadien-1-one (15) with Acid. *A.* **15** (0.30 g., 0.0017 mole) was dissolved in a solution of 20 ml. of glacial acetic acid and 0.2 ml. of concentrated sulfuric acid. After standing for 30 min., the mixture was worked up as described for **16**, to give 0.3 g. of colorless liquid. The infrared spectrum showed no carbonyl peak. V.p.c. analysis (6-ft., 2% SE30 silicone gum column at 150°) showed the presence of two peaks, retention times 6.0 and 11.9 min., in the area ratio of 2.0:1.0. The components were isolated by v.p.c. The major

component was shown by its n.m.r. and infrared spectra and v.p.c. retention times to be 2-(1-methylallyl)-4,6-dimethylphenol.¹⁸ The minor product crystallized in waxy, white needles, m.p. 57–59°. Its n.m.r. spectrum indicated it to be 3-(*trans*-2-butenyl)-4,6-dimethylphenol (**18**).

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.8; H, 9.09. Found: C, 81.5; H, 9.17.

B. A mixture of 0.1 g. of **15** and 0.5 g. of thiophenol was reacted with acid and worked up as described in procedure A. V.p.c. analysis of the product showed the ratio of the two phenols to be 2.0:1.0. No 2-butenyl phenyl thioether could be detected.

Reaction of 4-Allyl-2,4-dimethylcyclohexa-2,5-dienone (11) with Acid. To an ice-cooled solution of 0.2 ml. of concentrated sulfuric acid in 20 ml. of glacial acetic acid was added 3.0 g. of **11** (0.0185 mole). After standing in ice for 15 min., the mixture was worked up as usual to give 3.0 g. of yellow fluid. V.p.c. analysis on a 6-ft., 20% diethylene glycol column at 225° showed the presence of two components in the ratio of 1.5:1.0. Chromatography on Florisil gave, on elution with methylene chloride, 1.4 g. (0.00865 mole, 47%) of the major component, which was found to have infrared and n.m.r. spectra identical with those of 2-allyl-4,6-dimethylphenol.¹⁹ Elution with chloroform gave 1.0 g. of a mixture containing approximately equal amounts of the two products. The minor product was isolated by v.p.c. as a colorless oil, n_D^{25} 1.5315. Its n.m.r. spectrum indicated that it was 3-allyl-4,6-dimethylphenol.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.5; H, 8.64. Found: C, 81.4; H, 9.03.

(18) Q. R. Bartz, R. F. Miller, and R. Adams, *J. Am. Chem. Soc.*, **57**, 371 (1935).

(19) L. Claisen and E. Tietze, *Ann.*, **449**, 81 (1926).

Carbonium Ions. XX. Acid-Catalyzed Cleavage Reactions

N. C. Deno and Edward Sacher

Contribution from the College of Science, The Pennsylvania State University, University Park, Pennsylvania. Received July 16, 1965

The xanthylium cation, but not the less stable triphenylmethyl cation, is ejected from protonated primary, secondary, and tertiary alcohols and protonated ketones in 10–50% H_2SO_4 at 25°. This effect of the xanthylium cation, formally insulated from the functional group by a saturated carbon, shows that in the transition state the positive charge is delocalized throughout the xanthylium system, the forming olefin, and the leaving H_2O .

Introduction

The acid-catalyzed polymerization of olefins is one of the classic reactions of synthetic organic chemistry. Although the reaction is well known to be reversible,¹ examples where the products of reversal are dominant

(1) For a study demonstrating this reversibility, see J. E. Hofmann and A. Schriesheim, *J. Am. Chem. Soc.*, **84**, 953, 957 (1962).

are relatively rare. The most complete study of this latter type is that of Whitmore and Stahly,² who studied the fragmentation of alcohols and 1,3-diols. The successful examples were confined to tertiary alcohols, even for the 1,3-diols,^{2,3} which left the impression that fragmentation was possible only *via* relatively stable carbonium ions, specifically *t*-alkyl cations in the cases cited (of course, the reactant must be constituted so that it can eject a stable carbonium ion, the *t*-butyl in the cases cited, but this aspect of the reaction is not under discussion). A single example of cleavage of a ketone, the formation of 3-methyl-2-butanone from

(2) F. C. Whitmore and E. E. Stahly, *ibid.*, **55**, 4153 (1933); **67**, 2158 (1945); *Chem. Eng. News*, **26**, 668 (1948).

(3) A. N. Slovjanzov, *J. Russ. Phys. Chem. Soc.*, **39**, 140 (1907); *Chem. Abstr.*, **1**, 2077 (1907); A. Kalishev, *J. Russ. Phys. Chem. Soc.*, **46**, 428 (1914); *Chem. Abstr.*, **8**, 3186 (1914); L. S. Schmerling, B. S. Friedman, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **62**, 2446 (1940).

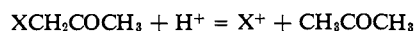
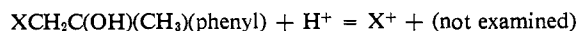
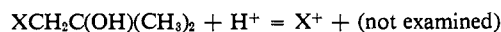
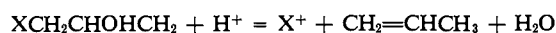
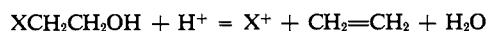
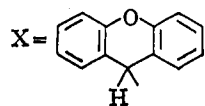
3,3,4,4-tetramethyl-2-pentanone in 96% H₂SO₄,⁴ followed the pattern in that the intermediate protonated ketone can be considered as a relatively stable hydroxy carbonium ion.

The objective of this work was to determine if fragmentation could be achieved with protonated primary alcohols, secondary alcohols, and carboxylic acids. It was thought that the reaction might proceed if an unusually stable carbonium were expelled and for this purpose the xanthy cation, half-formed from 9-xanthenol in 11% H₂SO₄,⁵ was chosen.

The work was completed in 1960.⁶ Before publication, Grob's extensive studies began appearing on fragmentations accompanying solvolysis of γ -aminoalkyl chlorides, tosylates, etc.⁷ Since these can be regarded as the expulsion of the very stable amino carbonium ion, the point was demonstrated. The results reported herein are thus an elaboration of this theme.

Discussion

The following reactions were all observed to take place quantitatively in 40–70% aqueous sulfuric acid. The appearance of the xanthy cation (X⁺) was monitored using the absorption at 375 m μ . The formation of ethylene, propene, and acetone were independently demonstrated.



A series of triphenylmethyl derivatives analogous to the xanthy compounds completely failed to eject (C₆H₅)₃C⁺, which would have been instantly detected in even minute concentration by its visible spectrum. This was true throughout the range 0–96% H₂SO₄. The series included RCH₂CH₂OH,⁸ RCH₂C(OH)(CH₃)₂, RCH₂COCH₃,⁹ RCH₂COOH,¹⁰ and RCH₂COOCH₃,¹¹ where R stands for the triphenylmethyl group. Even at 100° in 75 and 96% H₂SO₄, RCH₂C(OH)(CH₃)₂ failed to produce R⁺ (though the alcohol probably disappeared by cyclization). These results are most significant because they show that in the transition state for cleavage, much of the positive charge can be delocalized into the carbonium ion being ejected. Only in this way can the xanthy cation, which is much more stable relative to its alcohol than the triphenylmethyl cation, so drastically influence and in-

(4) H. D. Zook, W. E. Smith, and J. L. Greene, *J. Am. Chem. Soc.*, **79**, 4436 (1957).

(5) N. Deno, J. J. Jaruzelski, and A. Schriesheim, *ibid.*, **77**, 3044 (1955).

(6) Ph.D. Thesis of Edward Sacher, the Pennsylvania State University, 1960.

(7) C. A. Grob and co-workers, *Helv. Chim. Acta*, **45**, 1119, 1672, 1823, 2539 (1962); **46**, 936, 1190, 2646 (1963); *Gazz. chim. ital.*, **92**, 902 (1962).

(8) W. D. McPhee and E. G. Lindstrom, *J. Am. Chem. Soc.*, **65**, 2177 (1945).

(9) R. L. Garner and L. Hellerman, *ibid.*, **68**, 823 (1946).

(10) L. Hellerman, *ibid.*, **49**, 1737 (1927).

(11) S. M. McElvain and L. R. Morris, *ibid.*, **74**, 2657 (1952).

crease the rate of reaction. The transition state for cleavage is pictured as X--CH₂=CH₂--OH₂⁺ with the positive charge distributed throughout the system.

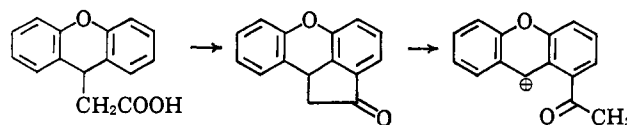
The reverse reaction must proceed through the same transition state which means that the xanthy cation attacks the olefin with simultaneous addition of water. An entirely analogous mechanism has been advanced for the addition of H₂O (hydration) to olefins.¹²

It must be this synchronous nature of some alkylations which rationalizes the formation of primary alkyl derivatives from *t*-alkyl derivatives such as in the formation of 3,3-dimethyl-1-chlorobutane from *t*-butyl chloride plus ethylene.¹³ In this reaction, the energy barrier that would have arisen if there had been a primary carbonium intermediate is presumably alleviated by bonding of Cl⁻ to ethylene concomitant with attack by *t*-C₄H₉⁺.

The rates of the xanthy cation cleavages were studied as a function of the concentration of sulfuric acid. Values of $d \log k/d(\% \text{H}_2\text{SO}_4)$ were close to values of $-dH_R/d(\% \text{H}_2\text{SO}_4)$.⁶ This parallel is interpreted to mean that the positive charge in the transition state is delocalized extensively so that specific hydrogen bonding to H₂O is eliminated.¹⁴ It is evident that this is identical with the conclusion made earlier.

The rate constants were first order in the reactant. Representative values of $\log k$ (k in sec.⁻¹) at 25° in 45% H₂SO₄ were -3.00 for 2-xanthyethanol, -2.80 for 3-xanthy-2-methyl-2-propanol, and -4.2 for xanthyacetone. A value of $\log k$ of -1.9 was found for 3-xanthy-2-phenyl-2-propanol in 20% H₂SO₄.

Treatment of 9-xanthyacetic acid with 85% H₃PO₄ led to the production of 1-acetyl-9-xanthy cation. Drowning of the acid solution in ice and water produced 1-acetyl-9-xanthenol. In 75–96% H₂SO₄ this reaction was accompanied by sulfonation.



The cleavage reactions were extended to aliphatic unsaturated alcohols. Both 2,2,3-trimethyl-3-buten-1-ol¹⁵ and 2,3,3,4-tetramethyl-4-penten-2-ol quantitatively cleaved to acetone in 15% H₂SO₄ at 25°. The rate of appearance of acetone and the yield were



estimated by conversion to the 2,4-dinitrophenylhydrazone. These cleavages can be regarded as ejections of the relatively stable 2-hydroxy-2-propyl cation and thus relate to cleavage of xanthy cation and amino carbonium ions.

3,3,4-Trimethyl-4-penten-2-one¹⁶ and 2,2,3-trimethyl-3-butenic acid¹⁷ failed to produce acetone in the range 0–73% H₂SO₄ at 25°.

(12) W. M. Schubert, B. Lamm, and J. R. Keefe, *ibid.*, **86**, 4727 (1964); N. Deno, F. A. Kish, and H. J. Peterson, *ibid.*, **87**, 2157 (1965).

(13) L. Schmerling, *ibid.*, **67**, 1153 (1945).

(14) N. Deno, *Surv. Progr. Chem.*, **2**, 169 (1964).

(15) A. Courtot, *Bull. soc. chim. France*, [3] **35**, 302 (1906).

(16) J. Cologne and K. Mostafavi, *ibid.*, [5] **6**, 353 (1939).

(17) J. Cologne and P. Dumont, *ibid.*, [5] **14**, 45 (1947); C. G. Overberger and M. B. Berenbaum, *J. Am. Chem. Soc.*, **74**, 3295 (1952).

Experimental Section

9-Xanthylacetic Acid. This acid was prepared as described by Ziegler.¹⁸ This alkylation of malonic acid by xanthenol is viewed as alkylation of the enol or enolate form of malonic acid by xanthyl cation which is produced in small equilibrium amounts by direct ionization of 9-xanthenol to xanthyl cation.

Addition of traces of 9-xanthylacetic acid (dissolved in acetic acid) to 96% H_2SO_4 produced an absorption band at 380 $\text{m}\mu$. Extinction coefficients at several representative wave lengths were 3600 (350), 6100 (360), 8400 (370), 13300 (380), and 6100 (390 $\text{m}\mu$). Although this is similar to the spectrum of the xanthyl cation,¹⁹ it is not identical leading to the suspicion that a substituted xanthyl cation had been formed. The following work identifies this ion as a sulfonated 1-acetyl-9-xanthyl cation. Its spectrum in 50 and 96% H_2SO_4 is identical showing that the cation is still completely formed in 50% acid as would be expected from its structure.

A solution of 2 g. of 9-xanthylacetic acid in 50 ml. of 85% H_3PO_4 was prepared. After 30 min., the solution was poured onto ice and ether extracted. A crystalline solid, 1.8 g. (90% yield based on its identification as 1-acetyl-9-xanthenol), m.p. 151.5–152.5°, was isolated. The infrared spectrum indicated the presence of both carbonyl group and xanthyl ring.

Anal. Calcd. for $\text{C}_{15}\text{H}_{12}\text{O}_3$: C, 75.0; H, 5.0. Found: C, 74.3; H, 5.2.

The ketonic nature of the product was substantiated by preparation of a 2,4-dinitrophenylhydrazone, m.p. 168° dec., and an oxime, m.p. 153°.

The 1-acetyl-9-xanthenol was oxidized with CrO_3 in acetic acid to produce an 85% yield of a product, m.p. 175–176°, which is presumed to be 1-acetyl-9-xanthone. Treatment of this product with Cl_2 in aqueous NaOH gave mainly unchanged starting material, but 8% was converted to an acid, m.p. 228–231°. This is the melting point reported for 9-xanthone-1-carboxylic acid²⁰ and is thus identified.

9-Xanthylacetone. Ethyl acetoacetate was alkylated with 9-xanthenol by the method reported.²¹ The yield of material, m.p. 75–78°, was 77%. Several recrystallizations from alkanes were required to raise the melting point to 87–89°.

The keto ester was hydrolyzed by refluxing 10 g. of the keto ester in 100 ml. of ethanol with 40 ml. of 5% aqueous NaOH . Acidification produced 9-xanthylacetone, long needles, 93% yield, m.p. 94°. Ten recrystallizations from alkanes were required to raise the melting point to 101–103°.²¹ A 2,4-dinitrophenylhydrazone was prepared which melted at 146–147°. It is very soluble in ethanol.

A solution of 1 g. of the ketone, 50 ml. of acetic acid, and 50 ml. of 96% H_2SO_4 was allowed to stand for 20 min. An excess of a solution of 2,4-dinitrophenylhydrazine in 50% H_2SO_4 was added. The yield of the dinitrophenylhydrazone of acetone was 70% after correcting for the slight solubility of the solid in the system. The other product of cleavage, xanthyl cation,

(18) K. Ziegler, *Ann.*, **434**, 60 (1923).

(19) N. Deno and W. L. Evans, *J. Am. Chem. Soc.*, **79**, 5804 (1957). For spectra of substituted xanthyl cations, see N. Deno, P. Groves, and G. Saines, *ibid.*, **81**, 5790 (1959).

(20) O. Kruber, *Ber.*, **70B**, 1556 (1937).

(21) R. Fosse, *Bull. soc. chim. France*, [3] **35**, 1011 (1906).

was identified by its characteristic ultraviolet absorption spectrum.

2-(9-Xanthyl)ethanol. 9-Xanthylacetic acid was converted to the ethyl ester as reported.¹⁸ Reduction with LiAlH_4 in ether gave a 64% yield of pure white crystals, m.p. 56.5–57°, after recrystallization from alkanes.

Anal. Calcd. for $\text{C}_{15}\text{H}_{14}\text{O}_2$: C, 79.6; H, 6.2. Found: C, 79.5; H, 6.2.

A solution of 0.235 g. of the alcohol in 50 ml. of acetic acid was treated with 200 ml. of 70% H_2SO_4 in a closed system. Nitrogen gas was introduced and the exit gas led through two scrubbing towers in series. These contained Br_2 in acetic acid. After 1 hr., 500 ml. of gas had passed through the reaction vessel. At this point, KI was added to the acetic acid solutions of bromine and the solutions were titrated with aqueous $\text{Na}_2\text{S}_2\text{O}_3$. This is a standard procedure for analyzing gases for ethylene.²² The yield of ethylene was 93.6%. A run using half the amount of alcohol gave a 90.4% yield of ethylene. The other product of the cleavage, xanthyl cation, was identified by spectrum.

1-(9-Xanthyl)-2-propanol. 9-Xanthylacetone was reduced with LiAlH_4 in ether. Distillation gave an oil, b.p. 217–220° (12 mm.), 38% yield, which partially solidified to a waxy solid, m.p. 59–61.5°. Unexplicably, efforts to recrystallize this product were unsuccessful and the analysis reflects the impure condition of the product.

Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_2$: C, 80.0; H, 6.7. Found: C, 78.5, 79.0, 79.3; H, 6.8, 7.0, 6.5.

The 1-(9-xanthyl)-2-propanol was cleaved in acid to produce xanthyl cation (100%) and propene (88%). The procedure used to determine propene was identical with that used to determine the ethylene produced from 2-(9-xanthyl)ethanol.

1-(9-Xanthyl)-2-methyl-2-propanol. Addition of ethyl 9-xanthylacetate to an excess of CH_3MgI produced the tertiary alcohol, m.p. 83–84°,²³ in 79% yield. Only the xanthyl cation was measured as a product of cleavage in acid.

1-(9-Xanthyl)-2-phenyl-2-propanol. Addition of $\text{C}_6\text{H}_5\text{MgBr}$ to 9-xanthylacetone produced the tertiary alcohol, m.p. 102–103°, in 40% yield. Starting material and solvent were removed by steam distillation and the residue recrystallized from alkanes.

Anal. Calcd. for $\text{C}_{22}\text{H}_{20}\text{O}_2$: C, 83.5; H, 6.4. Found: C, 82.7; H, 6.5.

Only the xanthyl cation was measured as a product of cleavage in acid.

4,4,4-Triphenyl-2-methyl-2-butanol. Excess CH_3MgI in ether was treated with 3,3,3-triphenylpropionyl chloride.²⁴ The product, after recrystallization twice from alkanes and once from methanol, melted at 116–119°, 62% yield.

Anal. Calcd. for $\text{C}_{23}\text{H}_{24}\text{O}$: C, 87.3; H, 7.6. Found: C, 87.0; H, 7.9.

2,3,3,4-Tetramethyl-4-penten-2-ol. Ethyl 2,2,3-trimethyl-3-butenolate¹⁷ was treated with excess CH_3MgI

(22) S. A. Miller and F. H. Pearman, *Analyst*, **75**, 492 (1950).

(23) S. Agaki and T. Iwashige, *J. Pharm. Soc. Japan*, **74**, 608 (1954); *Chem. Abstr.*, **48**, 10742 (1954).

(24) L. Hellerman, *J. Am. Chem. Soc.*, **49**, 1737 (1927).

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

Charles U. Pittman, Jr., and George A. Olah^{1b}

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

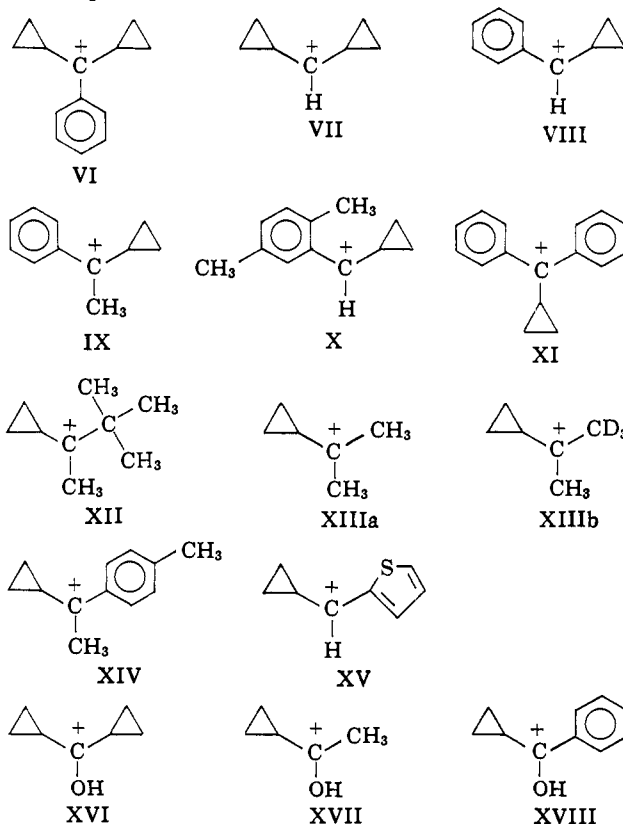
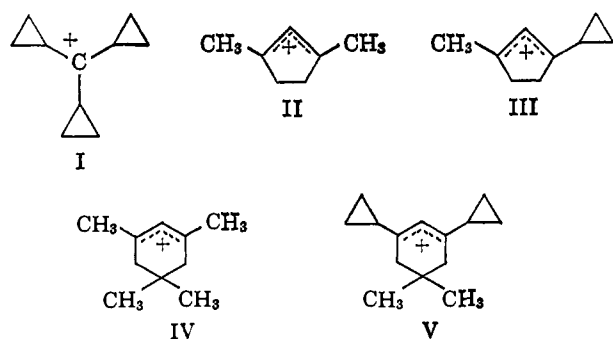
An extended study² of the direct observation of a series of cyclopropyl carbonium ions including mono- and dicyclopropyl ions was carried out. The orientation of the cyclopropyl ring next to a positive carbon atom is elucidated. A series of protonated cyclopropyl ketones were also investigated. These 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 $\text{CF}_3\text{CO}_2\text{H}$, and in $\text{CH}_2\text{Cl}_2\text{-AlCl}_3$ 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 comparisons⁵ 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.