

showing the deuterium has not exchanged with solvent protons. In both ions III and IV the hydrogen α to the positive charge in the isopropyl group is split by 6 hydrogens. This is split out and not well resolved. Its position in III and VI is between -4 and -4.5 p.p.m. This is in good agreement with the methylene quartet of II which appears at ~ -3.9 p.p.m.

In the spectrum of the pentaphenylethyl cation (VIII, Figure 5), the phenyls appear equivalent, indicating rapid equilibration. That this region contains 25 hydrogens was demonstrated by calibration with a known amount of tetramethylammonium chloride. The equilibration at low temperature is not unexpected considering the crowding of the phenyl groups. However, no evidence of a bridged ion was found.

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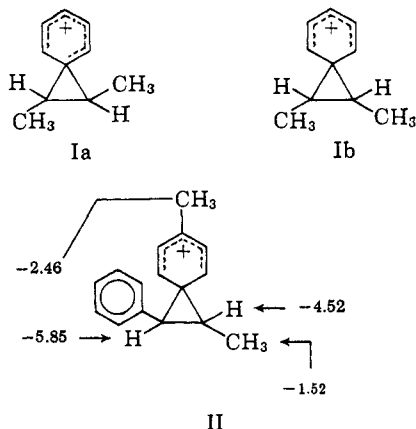
Contribution from the Eastern Research Laboratory
Dow Chemical Company, Wayland, Massachusetts

Received April 22, 1965

Carbonium Ions. XVI.¹ Observation of Bridged Phenonium Ions

Sir:

Considerable interest has been centered on the question of the existence of bridged phenonium ions.^{2,3} Recently a critical re-examination of the importance of phenonium ions in the solvolysis of symmetrically substituted β -phenylethyl derivatives suggested rapidly equilibrating classical ions instead of bridged structures.³ We report here strong evidence for the existence of the bridged phenonium ions I and II in $\text{SO}_2\text{-SbF}_5\text{-FSO}_3\text{H}$



systems at -60° . We also report observations on an ion which could be either a bridged ion III or the equilibrating ion IV.

When 2,3-dimethyl-3-phenylbutanol-2,2-phenyl-3,3-dimethylbutanol-2' or a mixture of the two alcohols is dissolved into $\text{SO}_2\text{-SbF}_5\text{-FSO}_3\text{H}$ at -60° the same carbonium ion (III or IV) is obtained.⁴ The p.m.r.

(1) G. A. Olah and C. U. Pittman, Jr., *J. Am. Chem. Soc.* **87**, 3507 (1965).

(2) D. J. Cram, *ibid.*, **71**, 386, 3875 (1949). For a summary of phenonium ions as discrete intermediates, see D. J. Cram, *ibid.*, **86**, 3767 (1964).

(3) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *ibid.*, **87**, 2137 (1965).

(4) Initial ionization of 2-phenyl-3,3-dimethylbutanol-2 would give the unstable phenylmethyl-*t*-butylcarbonium ion. The steric interaction of the *t*-butyl group with the phenyl ring prevents coplanarity,

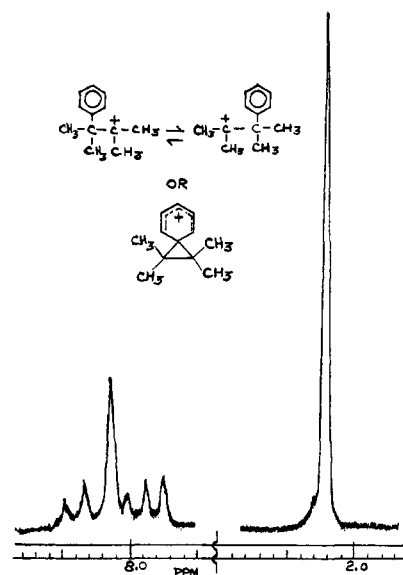


Figure 1.

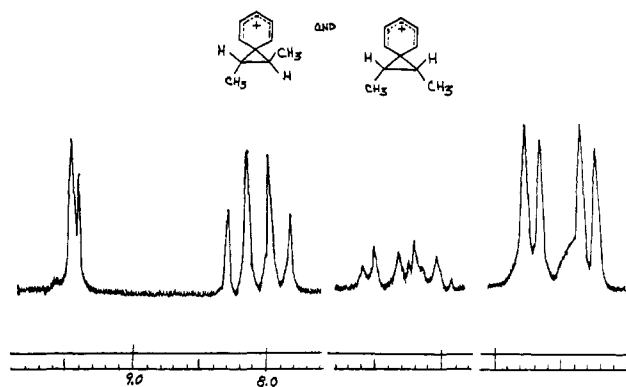


Figure 2.

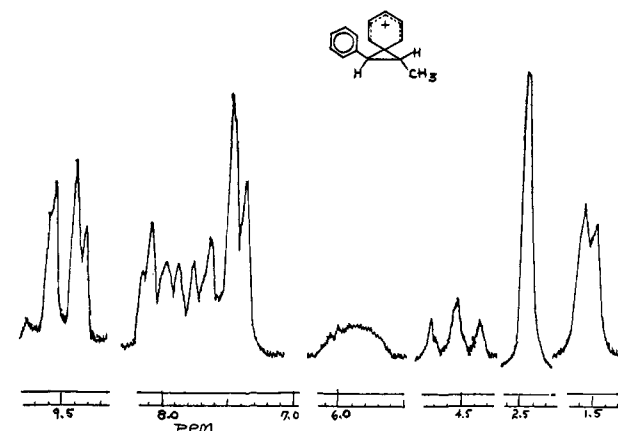
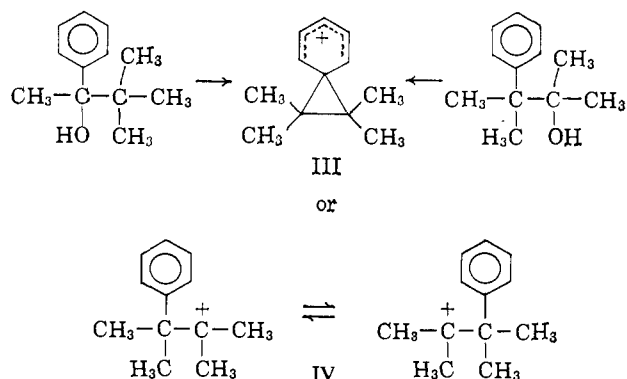


Figure 3.

spectrum (Figure 1) shows all four methyl groups are equivalent, and this held true down to -120° in $\text{SO}_2\text{F}_2\text{-SbF}_5\text{-FSO}_3\text{H}$. The positions of the methyls at -2.20 p.p.m. is in poor agreement with the predicted value of -3.31 p.p.m. for structure IV.⁵ The

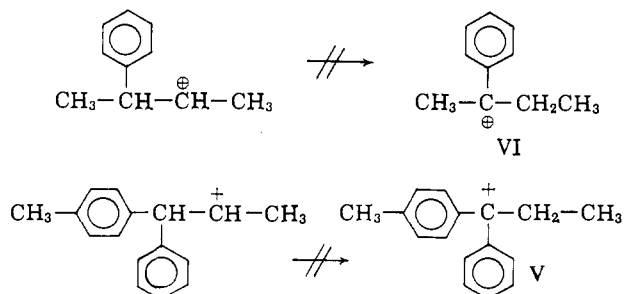
thus hindering overlap of the vacant p-orbital and the ring. Though the methylethylphenylcarbonium ion can be observed even in $\text{H}_2\text{SO}_4\text{-SO}_3$ systems, the phenylmethyl-*t*-butylcarbonium ion has never been observed even in our systems.

(5) If it were IV the band position should be the average of the methyls in the *t*-butyl cation (-4.35) and the methyl in the *t*-pentyl cation (-2.27).



lack of resolution of the methyl band at -120° seems to favor structure III, but a clear choice between III and IV is not possible.

The ionization of *erythro*- and *threo*-3-phenyl-2-butanols at -60° gave the n.m.r. spectrum in Figure 2, showing two methyl doublets at -1.37 and -1.68 p.p.m. These doublets are attributed to the methyls in ions Ia and Ib in an equimolar mixture. The hydrogens on the cyclopropane ring are found between -3.0 and -3.50 p.p.m. This agrees exactly with the -3.44 p.p.m. band for the cyclopropane hydrogens Winstein and Ebersson found in the anthrylethyl-bridged ion.⁶ The ring hydrogens exhibit bands centered at -8.02 p.p.m. (quadruplet) and -9.54 p.p.m. (doublet) and do not resemble the spectra of any other known aryl-carbonium ion. However, this region is similar to the spectra of protonated benzene and toluenes previously observed, which should provide the ideal model for comparison,⁷ and to the -9.60 value of the hydrogen on the 10-position of the anthrylethyl-bridged ion.^{6,8} Drowning the solution of I gave a good yield of monomer alcohols and olefins, demonstrating a polymer ion was not being observed. 1-*p*-Methylphenyl-1-phenyl-2-propanol in our system gave the spectrum shown in Figure 3 (the assignments are shown in structure II). This is obviously not the spectrum of V, as the spectrum in Figure 2 is not that of VI. Both V and VI were expected to be formed *via* 1,2-hydride shifts if the corresponding classical carbonium ions would be more stable in our solvent system than the bridged phenonium ions.



In all spectra the areas were in accord with theory. The results reported here should not be extrapolated to previous stereochemical and kinetic solvolyses studies since in our highly acidic and ionizing solvent a shift from possible equilibrating ions, in more basic solvents, to static bridged ions would be favored.

(6) L. Ebersson and S. Winstein, *J. Am. Chem. Soc.*, **87**, 3506 (1965).

(7) G. A. Olah, *ibid.*, **87**, 1103 (1965).

(8) Although interpretation of the ring proton in I is not easy (it is an A_2B_2C system further complicated, being a mixture of Ia and Ib with nonidentical *ortho* protons), the experimentally observed spectra is consistent with one of the many allowed patterns.

Acknowledgment. We are grateful to Professor H. C. Brown for samples of *erythro*- and *threo*-3-phenyl-2-butanols and to Dr. C. J. Collins for a sample of 3-phenyl-3-*p*-tolyl-2-butanol.

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Introduction of an Angular Methyl Group by Decarboxylative Cyclopropane Ring Opening¹

Sir:

We wish to report a novel decarboxylative cyclopropane ring opening with formation of an angular methyl group which we encountered while studying the carboxylic acid III-COOH. This acid, needed in the course of another investigation,² was obtained from Birch reduction of 4-hydrindacenecarboxylic acid³ (I), m.p. $232-233^\circ$, to II-COOH,⁴ m.p. $156-158^\circ$, conversion of II-COOH to its methyl ester⁴ II-COOME, m.p. $40-41^\circ$, with diazomethane, and then the Simmons-Smith reaction⁵ on II-COOME. Saponification of the crude product and recrystallization led to pure III-COOH,⁴ m.p. 185° dec., in 45% over-all yield from II-COOME. Although a careful search for another bis adduct has not yet been made, it is clear that the Simmons-Smith reaction with II-COOME is at least moderately stereospecific.

In its n.m.r. spectrum (CCl_4) III-COOH showed a singlet at τ 7.13 for the α -proton, a singlet at τ 9.71 for 4 cyclopropane protons, and an AB quartet (partly hidden under the remaining methylene signals) for the C-8 methylene protons, with $J_{AB} = 14$ c.p.s., τ_A 7.69, and τ_B 8.29. As regards stereochemistry, the acid III-COOH is judged to be the all-*cis* form. The most direct evidence for the *cis* relationship between the two cyclopropane methylenes is the conversion of the acid to the parent *cis* hydrocarbon III-H by methods not involving opening of the cyclopropane rings.² That the carboxyl group in III-COOH is *cis* to the cyclopropane methylene group is indicated by physical and chemical considerations. The singlet signal for the cyclopropane protons in III-COOH, due to essentially identical chemical shifts for the "inside" and "outside" protons, is ascribed to the presence of the *cis*-carboxyl group which has a differential effect on the "inside" relative to the "outside" protons. By contrast, the cyclopropane methylene signal appears as an AB quartet in the *cis* hydrocarbon III-H and other derivatives, as well as the *trans* hydrocarbon.² The tendency toward stereospecificity in the Simmons-Smith reaction on II-COOME also speaks for the all-*cis* configuration for III-COOH since the preferred *cis* relationship between the cyclopropane rings may be ascribed to a directing effect of the COOME group akin to the *cis*-directing

(1) Reported in outline at the Annual Meeting of the Japanese Chemical Society, Osaka, Japan, April 4, 1965.

(2) L. Birladeanu and T. Hanafusa, unpublished work.

(3) R. T. Arnold and E. Rondstedt, *J. Am. Chem. Soc.*, **67**, 1265 (1945).

(4) The indicated compounds gave satisfactory carbon and hydrogen analyses.

(5) (a) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959); (b) S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235 (1961); P. Radlick and S. Winstein, *ibid.*, **86**, 1866 (1964); W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963).