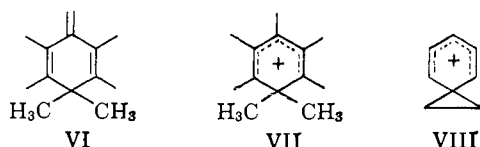


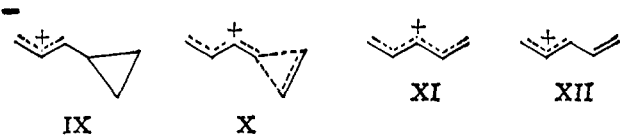
ions. For the latter, one would expect the average signal from the α - and β -protons to appear at least 8.5 p.p.m. downfield from TMS, judging by the 13.5 p.p.m. α -proton signal in the isopropyl cation^{3b} and 4.5 p.p.m. signal for the methylene protons in the *t*-amyl cation.^{3b} Thus, the signal for the "cyclopropane" protons is at least 5 p.p.m. away from the value corresponding to equilibrating classical $\text{ArCH}_2\text{CH}_2^+$ cations. Another powerful argument against this type of ion is the absence of isomerization to a benzyl-type cation by means of 1,2-H shift.

It was of some interest to examine the analogous hydroxycarbonium ion V from protonation of the known spiro ketone⁶ IV, so the n.m.r. spectrum of IV was examined in concentrated H_2SO_4 , from which solvent it could be recovered in 93% yield by quenching with water. The n.m.r. spectrum summarized in Table I is in good agreement with what would be expected for an ion depicted as V.

The extensive deshielding of the cyclopropane protons on conversion of III-OH to the carbonium ion II is quite interesting, and it is instructive to compare this effect with the deshielding of the *gem*-methyl groups in the conversion of the parent hydrocarbon VI to the heptamethylbenzenonium ion⁷ VII. While the "cyclopropane" protons in II are deshielded by more than 2 p.p.m. relative to III-OH, the similarly located *gem*-methyl group protons are deshielded by only 0.7 p.p.m. in the conversion of VI to VII. It is evident that extensive delocalization of the positive charge into the cyclopropane methylene groups occurs in the conversion of III-OH to II. On this basis II is a better representation of the bridged ion than is IIa which does not indicate the extensive involvement of the cyclopropane ring in the carbonium ion system.



The IIa representation is analogous to the symbol VIII employed for the ethylenephonium ion by Deno,⁸ who describes such ions as "typical cyclopropyl-substituted cyclohexadienyl cations." While Deno discusses elsewhere the now well-known enormous electron-releasing or conjugating effect of the cyclopropyl group in cations, he uniformly omits any indication of this electron delocalization in his representations. For instance, a cyclopropyl-substituted allyl cation is represented by IX and not X. On the



other hand, the pentadienyl cation is formulated as XI and not XII. Considering the relative effects of vinyl

(6) A. Mustafa and M. K. Hilmy, *J. Chem. Soc.*, 1434 (1952).
 (7) W. von E. Doering, *et al.*, *Tetrahedron*, **4**, 178 (1958).
 (8) N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 150 (1964).

and cyclopropyl groups in cations, it seems to us inconsistent to indicate explicitly the delocalization from a vinyl but not a cyclopropyl group.

(9) On leave, 1964–1965, from the University of Lund, Sweden, on Sweden–America Foundation and Fulbright travel grants.

Lennart Ebersson,⁹ S. Winstein

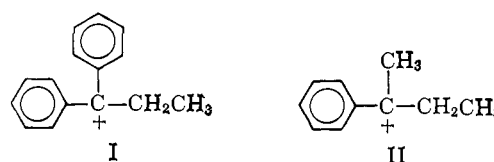
Contribution No. 1827, Department of Chemistry
 University of California, Los Angeles, California 90024

Received May 18, 1965

Carbonium Ions. XV.¹ Observation of "Classical" Phenylethyl Cations

Sir:

We wish to report the observation of a number of stable phenylethyl cations (I–VIII, see Figures 1–5) using the method we developed previously.² The diphenylethylcarbonium ion (I) and the phenylmethylethylcarbonium ion (II) were reported by us earlier.² The di-



phenylisopropylcarbonium ion was obtained, as were all the other ions reported here, by dissolving the indicated alcohols in SO_2 - SbF_5 - FSO_3H solutions at -60° .

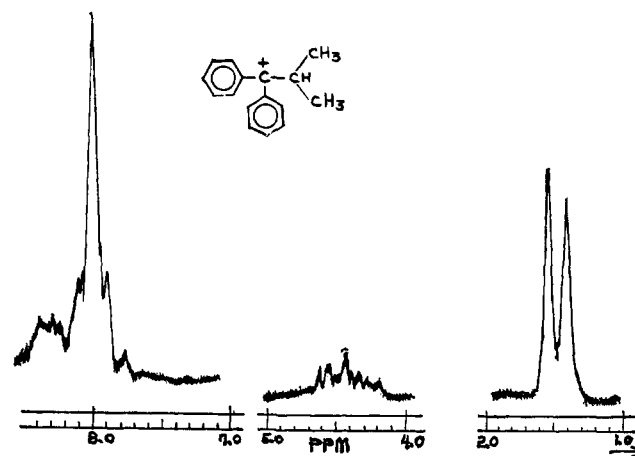


Figure 1.

The diphenylisopropylcarbonium ion (III, Figure 1), the phenylisopropylcarbonium ion (IV, Figure 2), and the diphenylbenzylcarbonium ion (V, Figure 3)

(1) C. U. Pittman, Jr., and G. A. Olah, *J. Am. Chem. Soc.*, **87**, 2998 (1965).

(2) G. A. Olah, M. B. Comisarow, C. A. Cupas, and C. U. Pittman, Jr., *ibid.*, **87**, 2997 (1965).

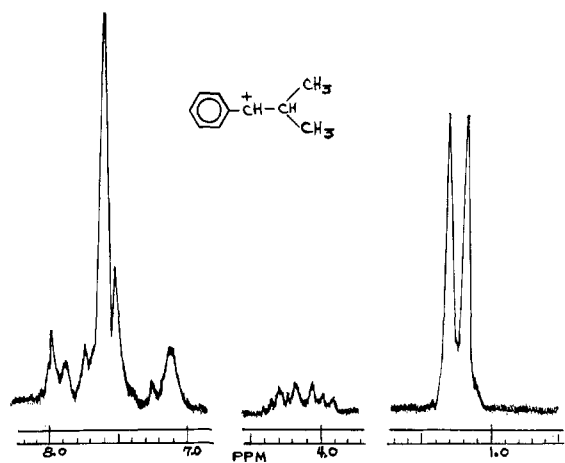


Figure 2.

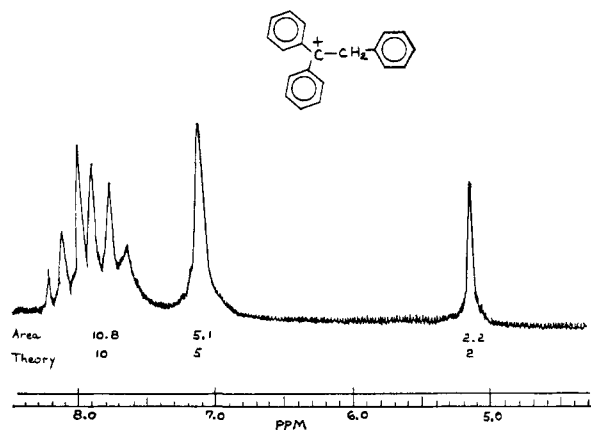


Figure 3.

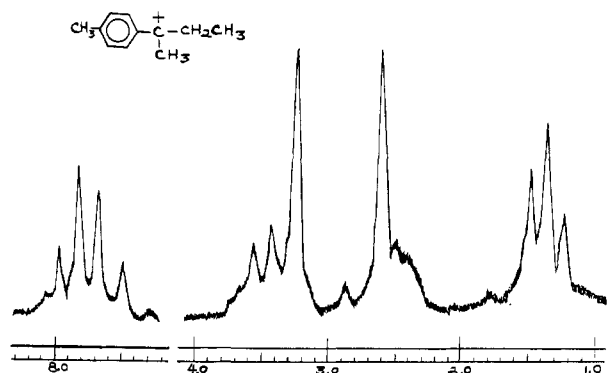


Figure 4.

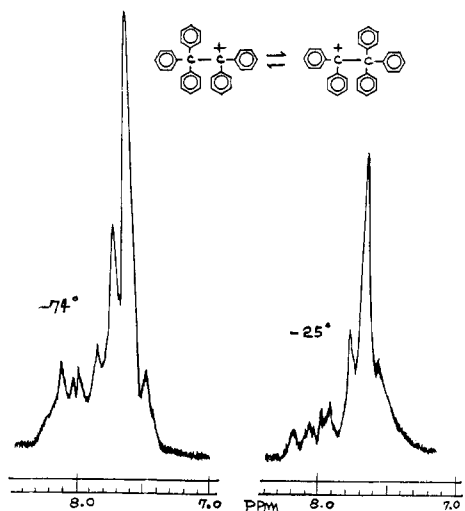
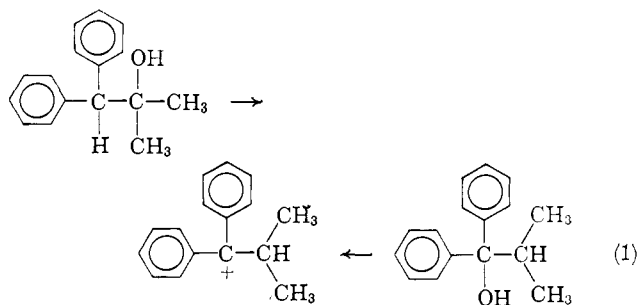


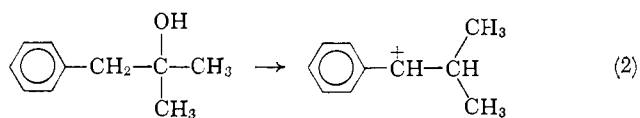
Figure 5.

could be formed from their corresponding β -alcohols as shown in eq. 1-3. Initial ionization of the OH must be followed by a 1-2-hydride shift in each case. The formation of ion VI from 1,2-triphenyl-1-deuterio-1-ethanol³ is especially interesting.

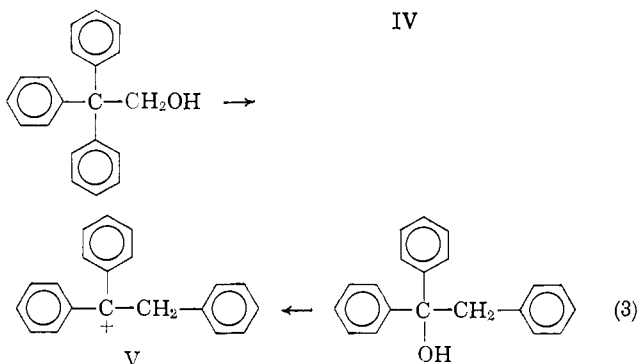
The benzyl hydrogen band at -5.12 p.p.m. has a relative area of two in V (Figure 3), but only one in VI,



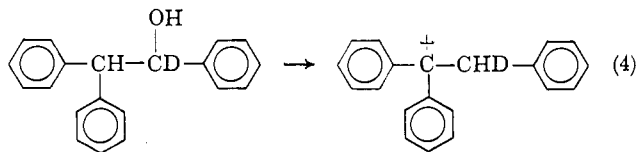
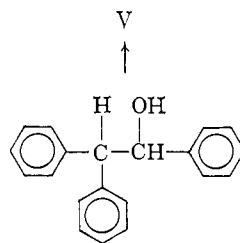
III



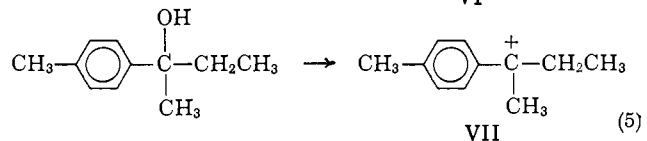
IV



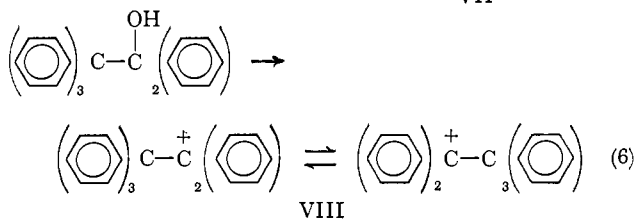
(3)



VI



(5)



VIII

(3) We are grateful to Dr. C. J. Collins for a sample of this material as well as that of 1,2-triphenyl-1-ethanol.

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.

G. A. Olah, C. U. Pittman, Jr.

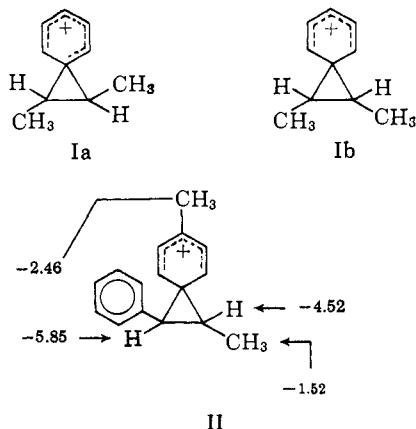
Contribution from the Eastern Research Laboratory
Dow Chemical Company, Wayland, Massachusetts

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,

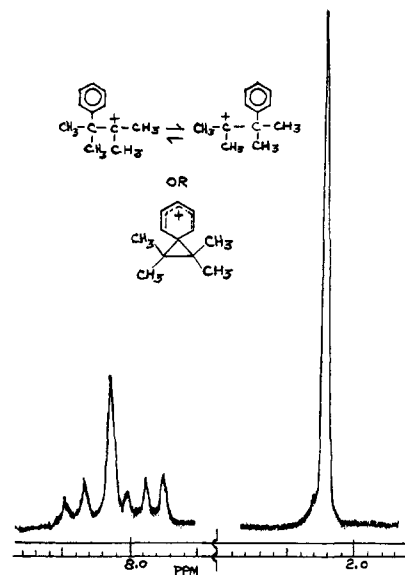


Figure 1.

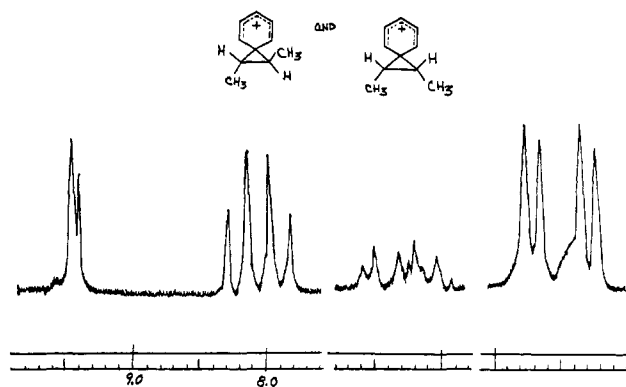


Figure 2.

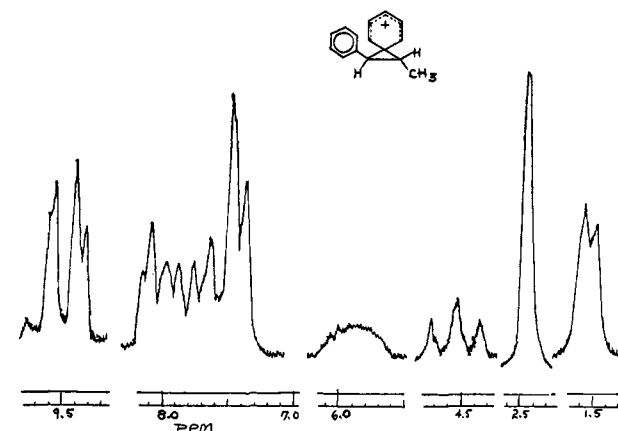


Figure 3.

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).