Kinetic control tends to favor spiro-VI products, while thermodynamic control gives the IV type. Presumably because of such thermodynamic control, acetolysis of IV-OTs leads entirely to IV-OAc, and we have so far obtained only IV-RCl,[10] m.p. 93–96°, from various treatments of VI-OH with HCl or SOCl₂.

(11) (a) On leave, 1964–1965, from the University of Lund, Sweden, on Sweden–America Foundation and Fulbright travel grants; (b) N.S.F. Postdoctoral Fellow, 1964–1965; (c) N.S.F. Undergraduate Summer Fellow, Yale University, 1962.

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Direct Observation of the Anthrylethyl Bridged Cation[1]

Sir:

Solvolysis and deuterium scrambling studies[2] of I-OTs show that the 9-anthryl group is a better participating group than phenyl. Even in 60% aqueous dioxane under conditions of kinetic control, essentially all of the product is formed through an aryl-bridged cation (II), the product being partly I-OH (15%) but mainly the spiro-III-OH (85%). We now report that II is sufficiently stable for direct observation in SO₂–SbF₅, in which a number of chemically unstable cations have recently become accessible for n.m.r. spectroscopy.[3]
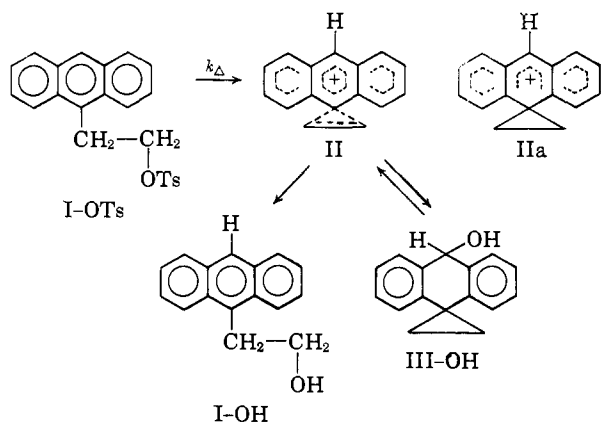
Since we have so far been unable to convert III-OH into a halide (III-Cl or III-F) because of the extreme ease of rearrangement, III-OH was used directly for n.m.r. studies in SO₂–SbF₅. Careful addition of III-OH at −80° to a 2.5 M excess of SbF₅ dissolved in SO₂ gave a brown solution having signals[4] (at −55°) at 3.44 (sharp singlet), 7.73 (triplet), 8.20 (triplet), and 9.64 (sharp singlet) p.p.m. with integrated band areas in the proportions 4:4:4:1. Two other singlets at 10.0 and 8.80 p.p.m. (area ∼1) broadened and finally

(1) (a) Reported in summary at the Japanese-American Seminar in Physical Organic Chemistry, Kyoto, Japan, April 6–10, 1965; (b) research sponsored by the U. S. Army Research Office (Durham).

(2) L. Eberson, J. P. Petrovich, R. Baird, D. Dyckes, and S. Winstein, J. Am. Chem. Soc., 87, 3504 (1965).

(3) (a) G. A. Olah, ibid., 86, 932 (1964); (b) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, ibid., 86, 1360 (1964).

(4) Unless otherwise stated, all n.m.r. band positions are given in p.p.m. downfield from external (CH₃)₄Si.

almost disappeared as the temperature was gradually raised to −15° (the rest of the spectrum remained unchanged). By using III-OD these signals were eliminated from the spectrum, showing their origin from the removed OH group. Positions and assignments of n.m.r. signals in the spiro alcohol III-OD and its solution in SO₂–SbF₅ are summarized in Table I.

Table I. Proton Signals in p.p.m. Downfield from (CH₃)₄Si

ᵃ Me₄Si as internal standard.

By treatment of the carbonium ion solution with excess methanol at −80° there was obtained a 79% yield of crude I-OCH₃, identified by comparison with authentic I-OCH₃, m.p. 69–69.5°, prepared from I-ONa and methyl iodide. This is the product of thermodynamic control as would be expected from the strongly acidic nature of the medium.

The observed n.m.r. spectrum of the carbonium ion obtained from the spiro alcohol III-OH is in excellent agreement with that expected for a symmetrical bridged ion[5] II. The proton in the 10-position of II displays a signal (9.60 p.p.m.) at nearly the same chemical shift as that of the analogous α-proton in the benzhydryl cation[3a] (9.80 p.p.m.), and the aromatic protons in this latter cation are deshielded to approximately the same extent as are those in II. The sharp singlet signal from the "cyclopropane" protons in II is appropriate for a symmetrical structure, and the chemical shift for these protons is very far from that which would be expected for rapidly equilibrating classical ArCH₂CH₂⁺

(5) Attempts to prepare the ion II from derivatives of the I series and SbF₅ failed since I-OH and I-Cl gave σ-complexes with SbF₅. The n.m.r spectra of these solutions were like that of 9-ethylanthracene (I–H) under the same conditions. Unchanged starting materials were recovered almost quantitatively by water quenching of the SO₂–SbF₅ solutions. Anthracene is known to give σ-complexes with strong Lewis acids [W. I. Aalbersberg, G. J. Hoijtink, E. L. Mackor, and W. P. Weijland, J. Chem. Soc., 3055 (1959)]. 2-Phenylethyl fluoride and 2-(α-naphthyl)ethyl fluoride were also investigated but did not give solutions stable enough for n.m.r. measurements.

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 $ArCH_2CH_2^+$ 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 ketone[6] 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 excepted 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 ion[7] 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.

H₃C   CH₃
VI   VII   VIII
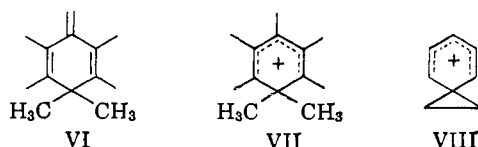
The IIa representation is analogous to the symbol VIII employed for the ethylenephenonium ion by Deno,[8] who describes such ions as "typical cyclopropyl-substituted cyclohexadienyl cations." While Deno discusses elsewhere the now well-known enormous electron-releasing or conjugating effect of the cyclopropyl 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

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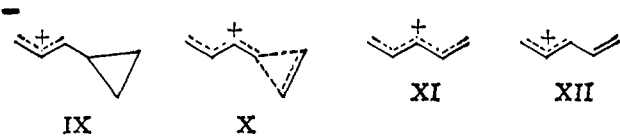
other hand, the pentadienyl cation is formulated as XI and not XII. Considering the relative effects of vinyl

(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.

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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-

I   II
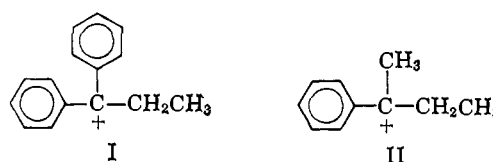
phenylisopropylcarbonium ion was obtained, as were all the other ions reported here, by dissolving the indicated alcohols in $SO_2-SbF_5-FSO_3H$ solutions at $-60°$.
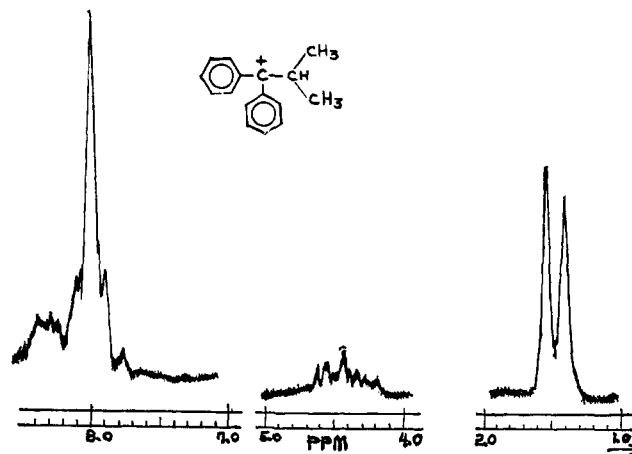
Figure 1.

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).