

still at δ 9.60 ($J \approx 3.5$ cps). In the case of the protonated benzenesulfonic and toluenesulfonic acids, the $S(OH)_2^+$ peaks at δ 9.66 and 9.60, respectively, are analogously temperature dependent.

Judging by the published data, the sulfonation reaction in SO_2 - FSO_3H - SbF_5 which occurs with the 3-phenyl-2-butanols appears also to be a disturbance in the case of the 1-phenyl-1-*p*-tolyl-2-propanol which was reported⁸ to give a phenonium ion. At least some disturbance from sulfonation is also evident in the published data¹² obtained by Olah for benzene, toluene, and *m*-xylene in various SO_2 - HF - SbF_5 mixtures in the course of studying benzenium ions from protonation of aromatic hydrocarbons.

(12) G. A. Olah, *J. Am. Chem. Soc.*, **87**, 1103 (1965); T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **42**, 502 (1964), have protonated *m*-xylene in FSO_3H - SbF_5 in the absence of SO_2 .

(13) National Institutes of Health Predoctoral Fellow, 1965-1967.

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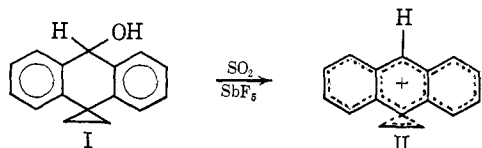
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Received September 2, 1966

Phenonium and Benzylic Cations from 3-Phenyl-2-butanols in FSO_3H - SbF_5 ¹

Sir:

In solvolysis of β -arylalkyl toluenesulfonates, anchimerically assisted ionization (k_A) with formation of an aryl-bridged cation (phenonium ion) predominates substantially over anchimerically unassisted ionization (k_S) for a number of systems in the proper solvent.^{2a-c} For the 2-anthryl-1-ethyl system, the bridged ion II has been observed directly^{2d} by nmr in SO_2 - SbF_5 . In this medium, ion II, generated from the parent alcohol I, is stable for long times at low temperatures. In the case of the 3-phenyl-2-butyl system, a 1:1 mixture of *cis*- and *trans*-phenonium ions VI has been reported by Olah³ to be formed from either the *threo*- or the *erythro*-alcohol III-OH. However, as reported in the previous communication,⁴ phenonium ions are not generated from the alcohols in the SO_2 - FSO_3H - SbF_5 medium because the benzene ring is sulfonated. Here we report attempts to generate and observe the phenonium ions by treating the alcohols in FSO_3H - SbF_5 medium without SO_2 . While phenonium ions have not been observed, our results are informative regarding their formation and behavior.



When either *erythro*- or *threo*-III-OH is extracted from pentane at -78° into an 8:1 FSO_3H - SbF_5 mixture, the initial nmr spectrum at -70° shows no H_3O^+ peak. The aromatic proton signals and also the solvent peak are extremely broad. Both diastereomers

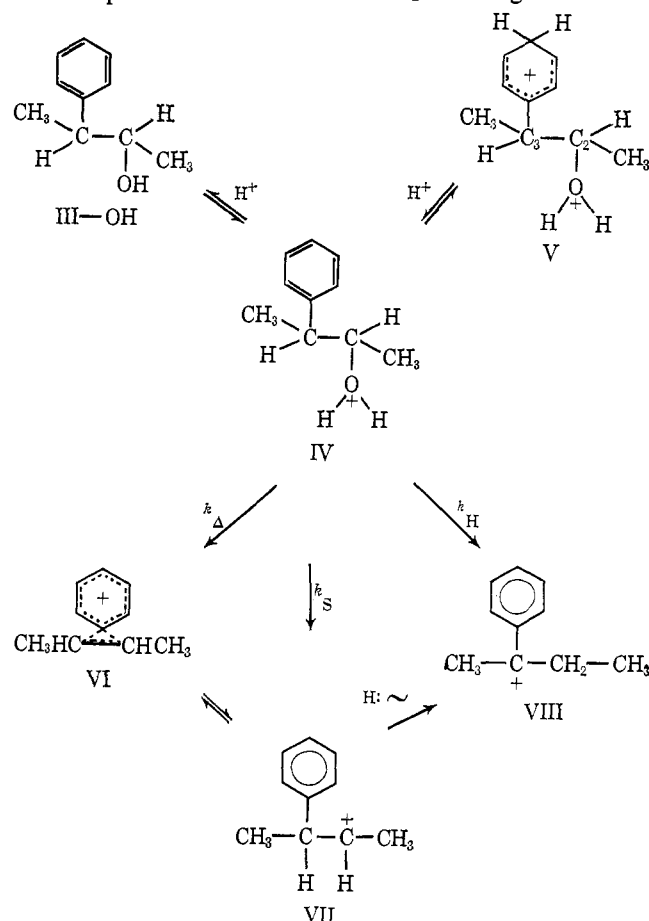
(1) Research sponsored in part by the National Science Foundation.
(2) (a) D. J. Cram, *J. Am. Chem. Soc.*, **86**, 3767 (1964); (b) L. Eberson, J. Petrovich, R. Baird, D. Dyckes, and S. Winstein, *ibid.*, **87**, 3504 (1965); (c) see also earlier papers by D. J. Cram, *et al.*, and S. Winstein, *et al.*; (d) L. Eberson and S. Winstein, *J. Am. Chem. Soc.*, **87**, 3506 (1965).

(3) G. A. Olah and C. U. Pittman, Jr., *ibid.*, **87**, 3509 (1965).

(4) M. Brookhart, F. A. L. Anet, and S. Winstein, *ibid.*, **88**, 5657 (1966).

exhibit one-proton multiplets at δ 5.25⁵ and 3.25 for the C_2 and C_3 protons, respectively. In the *threo*-III-OH case broad peaks⁶ appear at δ 1.67 and 1.28 for the C_1 and C_4 methyls, respectively, while in the *erythro* III-OH solution, the methyl peaks overlap and appear as a broad band at δ 1.40.

With 3-deuterated *erythro*-alcohol (D_1 -III-OH) at -70° , the initial nmr pattern is the same as with the unlabeled alcohol except that the multiplet at δ 3.25 is absent. In the spectrum of 1,1,1,3-tetradeuterated *threo*-alcohol D_4 -III-OH, the δ 3.25 multiplet and the δ 1.67 methyl band are both absent. Probably the species observed initially are diprotonated ions such as V. The extreme breadth of the solvent and aromatic proton signals indicates exchange of the aromatic protons with the solvent. Exchange broadening or masking of the peak by the very broad solvent peak could explain the absence of an OH_2^+ nmr signal.



Both *erythro*- and *threo*-III-OH solutions in FSO_3H - SbF_5 , when warmed to *ca.* -50° , decompose in *ca.* 15-30 min with C-O heterolysis and accumulation of the benzylic ion⁷ VIII. This is evidenced by the appearance in the nmr of a three-proton triplet ($J = 7$ cps) at δ 1.60 assigned to the β -methyl group, a singlet at δ 3.51 for the α -methyl group, a quartet at δ 3.72 (partially overlapping the δ 3.51 singlet) for the two methylene protons, a triplet at δ 7.93 for two aromatic protons, and a multiplet for three aromatic protons at δ 8.63. Further, the solvent peak ($\delta \sim 10.3$) sharpens

(5) All chemical shifts (δ) are in parts per million downfield from TMS using internal CH_2Cl_2 (δ 5.30) as a secondary standard.

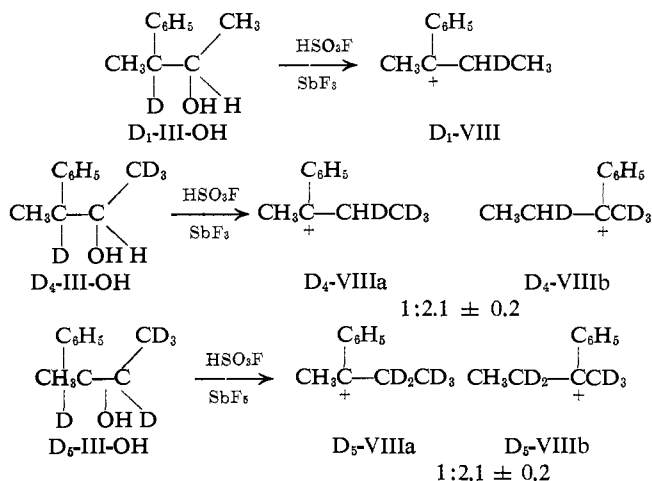
(6) The broadening of these methyl bands is probably, in part, a viscosity broadening.

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

and a sharp singlet for H_3O^+ appears at δ 9.96. The benzylic ion with an identical spectrum was also generated independently in this medium from phenyl-ethylmethylcarbinol.

When *threo*-III-OH in $\text{FSO}_3\text{H-SbF}_5$ at -60° , at different stages of conversion to benzylic ion, was quenched⁸ by addition of this solution through a Dry Ice jacketed syringe to a rapidly stirring solution of SO_2 -6 *N* aqueous KOH (9:1, v/v) at -78° , only mixtures of *threo*-III-OH and phenylmethyl-ethylcarbinol (IX) with ca. 30% recovery were obtained with <1% of the recovered alcohols being *erythro*-III-OH (vpc). When *erythro*-III-OH solutions were quenched in the same way, only mixtures of *erythro*-III-OH and benzylic alcohol IX were obtained with <1% *threo*-III-OH (vpc).

Detailed information on the mechanism of formation of the benzylic ion from 3-phenyl-2-butanol was obtained with deuterated alcohol specimens prepared by conventional methods. The $\text{FSO}_3\text{H-SbF}_5$ solution of *erythro*-D₁-III-OH decomposes at -50° to give D₁-VIII with the β -methyl signal appearing as a clear doublet. When *threo*-D₄-III-OH is extracted into $\text{FSO}_3\text{H-SbF}_5$ from CH_2Cl_2 at -78° it decomposes at -50° to a mixture of D₄-VIIIa and D₄-VIIIb in which the ratio of phenyl-shifted D₄-VIIIb to phenyl-unshifted D₄-VIIIa is ca. 2.1 ± 0.2 . *threo*-D₅-III-OH under the same conditions decomposes to a mixture of D₅-VIIIa and D₅-VIIIb in which the ratio of phenyl-shifted D₅-VIIIb to phenyl-unshifted D₅-VIIIa is again ca. 2.1 ± 0.2 . A methylene proton signal is absent, and the β -methyl signal appears as a clear singlet at δ 1.60. The appearance of the proton signals for the α - and β -methyl groups and the methylene group in the case of the labeled systems, especially the D₅-III-OH, as well as the observed integrations, indicate very little or no extraneous proton exchange or scrambling.



The high degree of phenyl scrambling indicates predominant phenyl participation (k_Δ) in the ionization step to give phenonium ion VI. Hydrogen-assisted ionization (k_H) leading directly to benzylic ion VIII would leave the phenyl group unshifted. Simple ionization (k_s) to give open secondary carbonium ion as a predominant process predicts competing hydrogen and phenyl migration to secondary carbon² and therefore diminished phenyl scrambling. Since phenonium ion accumulation is too small to allow direct nmr ob-

(8) This quenching procedure was suggested to us by Dr. G. A. Olah.

servation, ionization must be slower than conversion of phenonium ion VI to benzylic ion VIII. The rate-determining step must be initial heterolysis of the C-O bond, probably of ROH_2^+ species IV, present in low concentration in equilibrium with the unreactive diprotonated species V.

In order to give benzylic ion VIII, the phenonium ion must open, presumably reversibly, and rotate, presumably also reversibly, to a conformation favorable to hydride shift. A rather complex blend of deuterium isotope effects produces the VIIIb:VIIIa ratio of benzylic ions from D₅-III-OH and D₄-III-OH. With D₅-III-OH there are secondary deuterium isotope effects due to the CD₃ group on the direction of phenonium ion opening and on the deuteride shift in each of the classical ions. If the over-all β -deuterium isotope effect is as large as 1.28 per deuterium, then $(1.28)^3 = 2.1$ and the observed VIIIb:VIIIa ratio is accounted for. With D₄-III-OH there is a secondary β -deuterium isotope effect from the CD₃ group and a secondary α -deuterium isotope effect due to the D atom on the direction of opening. For the hydride shift, besides the secondary isotope effects from a CD₃ group and an α -D, there is a primary isotope effect due to the fact that H migrates in one open ion and D shifts in the other. The additional effects in D₄-III-OH compared to D₅-III-OH tend to cancel, and this cancelation seems to be quite complete, since nearly the same ratio of VIIIb:VIIIa is formed from D₄-III-OH and D₅-III-OH.

In both solvolysis^{2a} of 3-phenyl-2-butyl toluenesulfonate and ionization of the system at hand, k_Δ appears to dominate over k_H and k_s . The solvolyses involve media of considerable nucleophilicity, and the rate constant for conversion to covalent product is too high to permit significant leakage from bridged to open classical ion. In nonnucleophilic $\text{FSO}_3\text{H-SbF}_5$ medium no stable covalent product can be formed, and therefore such leakage does occur and prevents accumulation of enough phenonium ion for direct observation. We presently are investigating ways of generating phenonium ions rapidly at much lower temperatures in the hope that ionization may be sufficiently fast relative to phenonium ion decay to permit direct observation of the bridged ions.

(9) National Institutes of Health Predoctoral Fellow, 1965-1967.

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Radical Anions as Intermediates in Substitution Reactions

Sir:

Evidence for the view that radical anions are intermediates in the carbon alkylation of nitroparaffin salts has recently been presented.¹ We now deal with the alkylation of a β -keto ester anion (I), a reaction which, as will become apparent, is also capable of proceeding as a radical-anion process.

Table I describes the variation in yields of carbon and oxygen alkylation products when the sodium salt of

(1) R. C. Kerber, G. W. Urry, and N. Kornblum, *J. Am. Chem. Soc.*, **86**, 3904 (1964); **87**, 4520 (1965).