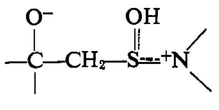

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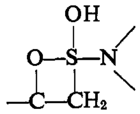


9

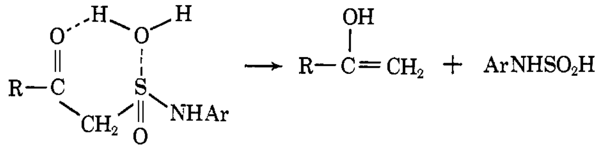
enhancement of basicity of the sulfinyl group by nitrogen. The same effect of nitrogen operates to prevent olefin-forming elimination from O-lithium salts of β-hydroxy sulfinamides. Close similarities between the β-hydroxy sulfinamide and β-hydroxy phosphonamide[7] systems are apparent.

We have also discovered that certain β-hydroxy sulfoxides can be converted to olefins by an elimination of the vicinal hydroxyl and sulfinyl functions. Thus, the β-hydroxy sulfoxide from benzophenone and methylsulfinylcarbanion[8,9] is converted to 1,1-diphenylethylene in 45% yield by heating to *ca.* 160° at 0.3 mm. Furthermore, acid catalysis of this elimination has been noted in the case of the β-hydroxy sulfoxide from benzophenone and phenylsulfinylcarbanion which decomposes with 10% sulfuric acid in 95% ethanol at 25° for 15 hr to give 1,1-diphenylethylene in 65% yield. Olefin formation from β-hydroxy sulfoxides is potentially an extremely important reaction, and this too is being pursued.

The reaction of 2 equiv of the dilithio derivative **2** with esters affords, after addition of water, methyl ketones in good yield. For example, ethyl benzoate,

$$\mathrm{RCOOR'} + 2\,\mathbf{2} \xrightarrow{\mathrm{THF}} \xrightarrow[0^\circ]{\mathrm{H_2O}} \mathrm{RCOCH_3}$$

ethyl cyclohexanecarboxylate, and ethyl pivalate gave acetophenone, acetylcyclohexane, and pinacolone in 89, 84, and 93% yield, respectively. Methyl *n*-alkyl ketones and α,β-unsaturated ketones have also been prepared readily. β-Keto sulfinamides, which are reasonable intermediates in these reactions, are evidently extraordinarily unstable in the presence of water. This is also indicated by the observation that the oxidation of the β-hydroxy sulfinamide **3**, R_1 = C_6H_5, R_2 = H, with manganese dioxide in chloroform at 25° afforded directly acetophenone and not the corresponding β-keto sulfinamide. A number of plausible pathways suggest themselves for the remarkably facile conversion of β-keto sulfinamides to ketones, for example[10]



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(7) E. J. Corey and G. T. Kwiatkowski, *J. Am. Chem. Soc.*, **88**, 5653 (1966).

(8) E. J. Corey and M. Chaykovsky, *ibid.*, **84**, 866 (1962); **87**, 1345 (1965).

(9) E. J. Corey and M. Chaykovsky, *J. Org. Chem.*, **28**, 254 (1963).

(10) This work was supported by the National Institutes of Health.

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Received August 15, 1966

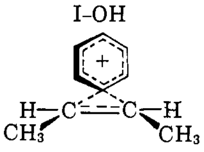
The Behavior of the 3-Phenyl-2-butanols in SO_2–FSO_3H–SbF_5[1]

Sir:

Having recently reported the direct observation of the aryl-bridged anthrylethyl cation,[2] we were very interested in the possibility of observing simpler analogs of this species. In this connection, Olah and Pittman[3] have recently reported the direct observation of phenonium ions from β-arylalcohols in SO_2–FSO_3H–SbF_5 at −60°. In particular, they reported that both *threo-* and *erythro*-3-phenyl-2-butanols (I-OH and II-OH) give an equimolar mixture of *cis-* and *trans*-phenonium ions III and IV in this medium. The spectrum from either alcohol was reported to show methyl doublets at δ 1.37 and 1.68, a methine multiplet assigned to the C_2 and C_3 protons at δ 3–3.5, and a quartet at δ 8.02 and a doublet at δ 9.54 assigned to the aromatic protons. It was reported that the areas were in accord with theory, and quenching of the solution led to a good yield of monomer alcohols and olefins.

threo-$CH_3CH(C_6H_5)CH(OH)CH_3$

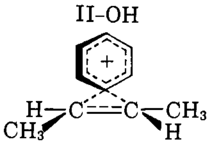
I-OH



III

erythro-$CH_3CH(C_6H_5)CH(OH)CH_3$

II-OH



IV

There are several troublesome features of the report of Olah and Pittman. On mechanistic grounds it was very difficult to understand a lack of stereospecificity in the formation of phenonium ions and yet no accompanying major production of benzylic ion from hydride shift. As regards their reported nmr spectrum, the δ 8.02 signal which appeared as an AB-like quartet seemed more appropriate for the A_2B_2 pattern of a *para*-disubstituted benzene than for a phenonium ion.[4] Our own examination of this system has shown that phenonium ions are not generated from I-OH and II-OH in SO_2–FSO_3H–SbF_5.

In SO_2–FSO_3H–SbF_5 medium, the *threo-* and *erythro*-I-OH and -II-OH do not give rise to identical spectra. When *threo*-I-OH was extracted from pentane into HSO_3F–SbF_5–SO_2 at −78°, the nmr[5,6] at −52° showed five signals at chemical shifts approximately as reported by Olah and Pittman. These were

(1) Research supported in part by the National Science Foundation.

(2) 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) The methyl signals for the assumed *cis-* and *trans*-phenonium ions would be expected to be more complex than those reported: F. A. L. Anet, *Can. J. Chem.*, **39**, 2262 (1961).

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

(6) Viscosity broadening of peaks is observed in some cases, and this depends on the ratio of reagents used. Sharp spectra were obtained with mole ratios of FSO_3H–SbF_5–SO_2–ROH of 1:1:4:0.2 and 6.5:1:5:0.5. Severe viscosity broadening occurred below −45° with 3.5:1:4.5:0.5 mole ratios.

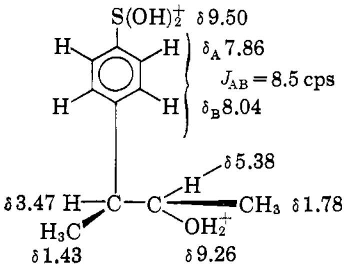
two methyl doublets ($J \simeq 7$ cps for each) at δ 1.43 and 1.78, a broad one-proton methine multiplet at δ 3.47, an AB-like quartet integrating for four protons centered at δ 7.90, and a two-proton doublet at δ 9.26 ($J \simeq 3.5$ cps). In addition,[7] two signals not reported previously,[3] a one-proton methine multiplet at δ 5.38 and a two-proton singlet at δ 9.50, were visible. With *erythro* II-OH as substrate, the same pattern is observed for the AB-like quartet and the two one-proton methine multiplets. However, the two high-field methyl doublets now overlap, with chemical shifts of δ 1.42 and 1.49, and one broad singlet integrating for four protons at δ 9.60 is observed instead of the two distinct two-proton peaks in the *threo* case (δ 9.26 and 9.50).

Clearly the 3-phenyl-2-butanols are not converted to carbonium ions in the SO_2–FSO_3H–SbF_5 medium since an H_3O^+ peak[8] is absent in the nmr spectrum. Such a peak is always observed at *ca.* δ 9.96 when alcohols ionize in this medium. The OH group is clearly protonated but C–O heterolysis has not occurred. In the *threo* case, the two-proton doublet ($J \simeq 3.5$ cps) at δ 9.26 is assigned to the OH_2^+ group while the corresponding signal in the *erythro* case appears at δ 9.60. These chemical shifts and coupling constants are of the same order of magnitude observed for ROH_2^+ species in general in this medium.[8,9] For example,[9] the OH_2^+ quartet ($J \simeq 3.8$ cps) of CH_3-OH_2^+ occurs at δ 9.33.

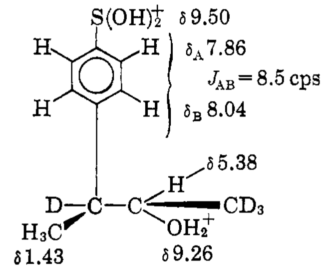
As anticipated, the clean four-proton AB-like quartet for the aromatic protons in the spectra for the *threo*- and *erythro*-alcohols in the SO_2–FSO_3H–SbF_5 medium is indeed due to *para* substitution in the benzene ring, sulfination occurring in this medium (see below). In this strongly acidic medium the sulfinic acid group is protonated, and thus the two proton signals in the nmr spectra at −52° at δ 9.50 for *threo* and δ 9.60 for *erythro* are due to the $S(OH)_2^+$ protons.

Treatment of the 1,1,1,3-tetradeuterated *threo*-alcohol in SO_2–FSO_3H–SbF_5 gives rise to the corresponding diprotonated species whose nmr spectrum is helpful in assigning the methyl doublets and the two methine multiplets in the spectrum of the undeuterated analog.[10] The various assignments are summarized in V, V-D_4, and VI.

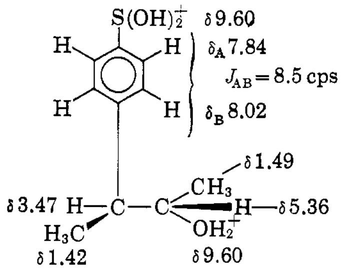
Aromatic sulfination with SO_2 in the presence of Friedel–Crafts catalysts is a known reaction.[11] In the present work, control experiments were performed on benzene and toluene, these compounds being extracted from pentane into SO_2–FSO_3H–SbF_5 at −78°. The nmr spectra observed at −60° were those for protonated benzenesulfinic acid and *p*-toluenesulfinic acid, respectively. For the benzene case, the spectrum showed signals for five aromatic protons centered at δ 8.00 and a two-proton singlet at δ 9.66. The toluene solution exhibited a methyl singlet at δ 2.48, an AB-like quartet for the four aromatic protons centered at δ 7.83, and a two-proton singlet at δ 9.60. That the latter spectrum is that of protonated *p*-toluenesulfinic acid was verified in two ways. First, the identical spectrum was observed for a solution of authentic *p*-toluenesulfinic acid in this medium. Second, from quenching of a solution of toluene in SO_2–FSO_3H–SbF_5 in stirred, dilute aqueous hydrochloric acid at 0°, there was recovered a high yield of *p*-toluenesulfinic acid identified by comparison (melting point, mixture melting point, and infrared spectrum) with an authentic sample.



threo-V



threo-V-D_4



erythro-VI

The behavior of the protonated sulfinic acids in the SO_2–FSO_3H–SbF_5 medium as the temperature is raised is interesting. When the solution of the *threo*-3-phenyl-2-butanol is allowed to warm, no change in the OH_2^+ signal occurs until *ca.* −25°, where fairly general decomposition sets in. Up to this temperature, proton exchange between the OH_2^+ group and solvent is quite slow on the nmr time scale and the OH_2^+ doublet is sharp. On the other hand, proton exchange between the $S(OH)_2^+$ and solvent becomes sufficiently rapid that the $S(OH)_2^+$ signal broadens and then begins to merge with the solvent signal at *ca.* −30°. In the *erythro* case, the behavior is analogous; as the temperature is raised the δ 9.60 four-proton band broadens at the base due to the $S(OH)_2^+$ proton exchange, making visible the sharp OH_2^+ doublet

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(7) In some scattered runs a broad singlet at δ 7.40 of varying area was observed. This singlet slowly decays at −45° and appears to produce the $EtMe(C_6H_5)C^+$ ion.

(8) The H_3O^+ peak in this medium is temperature dependent due to exchange with the solvent. The peak broadens and merges with solvent at *ca.* −35°. The H_3O^+ species has also been reported in BF_3–HF at −70° by C. MacLean and E. L. Mackor, *J. Chem. Phys.*, **34**, 2207 (1961); *Discussions Faraday Soc.*, 34, 165 (1962). These authors have reported the $CH_3CH_2O^+H_2$ species in BF_3–HF at −70° with $J_{OH,CH}$ = 3.4 cps.

(9) M. Brookhart, A. Diaz, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 3135 (1966).

(10) In the spectrum from the 3-deuterated *erythro*-alcohol, the δ 3.47 methine signal is missing and the δ 1.42 methyl signal is a singlet. When 1,1,1,2,3-pentadeuterated *threo*-alcohol is treated in 1:1 FSO_3H–SbF_5 diluted with SO_2, both methine signals at δ 5.38 and δ 3.47, as well as the δ 1.78 methyl signal, are absent.

(11) (a) G. A. Olah, "Friedel–Crafts and Related Reactions," Vol. 1, Interscience Publishers, Inc., New York, N. Y., Chapter 2; (b) E. Knoevenagel and J. Kenner, *Ber.*, 41, 3316 (1908).

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

Judging by the published data, the sulfination 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 reported[3] to give a phenonium ion. At least some disturbance from sulfination is also evident in the published data[12] 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_6 in the absence of SO_2.

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

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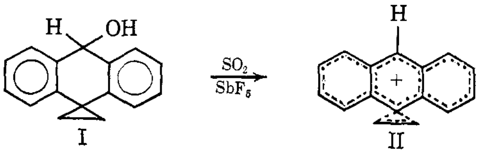
Contribution No. 1995, Department of Chemistry
University of California, Los Angeles, California 90024
Received September 2, 1966

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

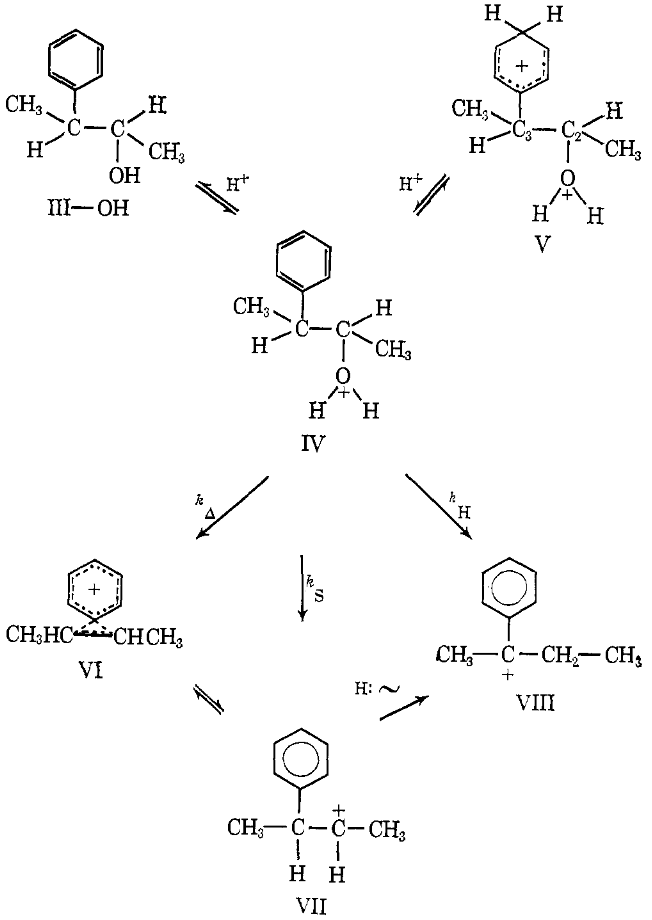
Sir:

In solvolysis of β-arylalkyl toluenesulfonates, anchimerically assisted ionization (k_Δ) 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 Olah[3] 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 sulfinated. 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 exhibit one-proton multiplets at δ 5.25[5] and 3.25 for the C_2 and C_3 protons, respectively. In the *threo*-III-OH case broad peaks[6] 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 ion[7] 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 (δ ~10.3) sharpens

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(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).

(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).