anol 0.018 M in sodium acetate) was found to be $k = 1.7 \times 10^{-3}$ sec^{-1} at 59.8°.[8] From these data, in combination with the assumption of a factor of 3 for converting tosylate rates to brosylate rates, the relative rate of carbonium ion formation by solvolysis from sp^3-hybridized carbon compared to sp^2-hybridized carbon is found to be greater than 5.7×10^4. This difference in reactivity may be attributed to the high energy of vinyl cations, although the addition of trifluoroacetic acid to alkynes *via* a vinyl cationic transition state occurs almost as rapidly as the comparable reactions of alkenes, or to the resonance stabilization of vinyl sulfonates which would be lost upon solvolysis.[9,10]

(8) Rates were determined by titration of the sodium acetate in aliquots with aqueous 0.05 N hydrochloric acid using Mallinckrodt IndicatAR pH 3–4 as an indicator.

(9) P. E. Peterson and J. E. Duddey, *J. Am. Chem. Soc.*, **85**, 2865 (1963); *cf.* ref 4.

(10) *Cf.* J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p 148, for a comparable discussion of the reactivity of vinyl halides.

(11) The award of a National Science Foundation Graduate Traineeship (1966 to present) is gratefully acknowledged by J. M. I.

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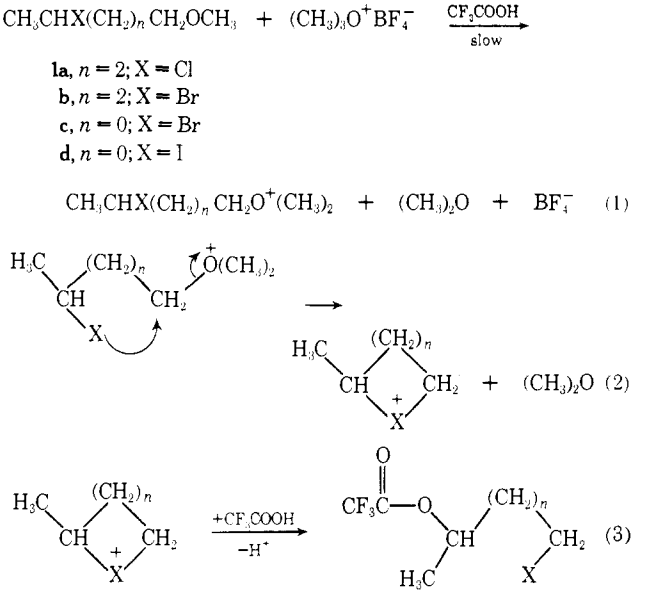
Oxonium Ions in Trifluoroacetic Acid. Quantitative Halogen Shifts in Solvolyses of Halogen-Substituted Trialkyloxonium Ions

Sir:

Examples of 1,5-halogen shifts and quantitative 1,4-halogen shifts arising *via* halonium ions have been reported in solvolyses of primary *p*-nitrobenzenesulfonates.[1] Methanol quenching of halonium ions generated in antimony pentafluoride–sulfur dioxide resulted in formation of 1,2-halogen-shifted ethers in high yield.[2] Inconvenience, expense, or sluggishness of rate limit the synthetic application of these halogen-shift reactions. We now report a new reaction in which halogenated ethers cleanly undergo halogen shifts. Our new procedure complements other methods and offers considerable synthetic utility.

We have found that trimethyloxonium fluoroborate is rapidly solvolyzed in acetic and formic acids. However, the salt is sufficiently stable in trifluoroacetic acid to allow alkylation of an added halogen-containing methyl ether to occur. The transient, halogen-substituted trialkyloxonium ion which resulted did, in suitable cases, undergo an intramolecular displacement of dimethyl ether by halogen. The resulting halonium or halonium ion like transition state collapsed only in an "SN1 manner" with solvent to form halogen-shifted products, as illustrated in Scheme I. The postulated SN1-like ring openings are those expected by analogy with known openings of five-membered-[1] and three-membered-ring (*vide infra*) halonium ions in trifluoroacetic acid. It is to be noted that dimethyl ether derived from oxonium ions serves as the leaving group in these solvolytic reactions. The comparison of the properties of this leaving group with those of the more common ones (halide, tosylate, etc.) is in itself of interest.

Scheme I. Mechanism for Halogen Shift Involving a Trialkyloxonium Ion Intermediate



The mechanism shown in Scheme I is suggested by our preliminary observation, based on nmr measurements, of second-order kinetics (first order in trimethyloxonium ion and in ether). No haloalkyldimethyloxonium ion was observable (by nmr) in cases where halogen participated. However, when methyl propyl or ethyl propyl ether was allowed to react with trimethyl- or triethyloxonium fluoroborates, second-order formation of mixed oxonium ions was indicated by nmr spectroscopy early in the reaction. These ions were observable by nmr because they underwent further reaction (forming predominantly isopropyl trifluoroacetate) less readily than oxonium ions which were capable of halogen participation.

A molar equivalent of concentrated sulfuric acid caused 1,4-chlorine shift with 4-chloro-1-methoxypentane (**1a**) in trifluoroacetic acid, but the rate relative to trimethyloxonium ion promoted reaction was about 0.01. It is improbable that fluoroboric acid produced in the slow trifluoroacetolysis of trimethyloxonium fluoroborate (eq 4) was initiating the observed halogen

$$CF_3COOH + (CH_3)_3O^+BF_4^- \longrightarrow HBF_4 + CH_3O_2CCF_3 + (CH_3)_2O \quad (4)$$

shift reactions. The H_0 value for the solvent in the sulfuric acid promoted reaction (1.6 M sulfuric acid in trifluoroacetic acid) is more negative than −7.59.[3] The pK_a for dimethyl ether (54.4% aqueous sulfuric acid) is −3.83.[4] Thus, although the acidity of fluoroboric acid in trifluoroacetic acid is unknown, ethers are probably not protonated to any further extent by minute quantities of fluoroboric acid than by 1.6 M sulfuric acid. It follows that the rate of the alkylation–halogen shift sequence was too great to be ascribed to acid catalysis.

All isolated products were identified by infrared and nmr spectra and by gas chromatography. In the case

(1) P. E. Peterson and J. F. Coffey, *Tetrahedron Lett.*, 3131 (1968).
(2) G. A. Olah and J. M. Bollinger, *J. Am. Chem. Soc.*, **90**, 947 (1968).
(3) H_0 for 0.763 mol of H_2SO_4/1000 g of CF_3COOH (≈1.2 M) is −7.59: C. Dallinga and G. Ter Maten, *Rec Trav. Chim.*, **79**, 737 (1960).
(4) E. M. Arnett and C. Y. Wu, *J. Am. Chem. Soc.*, **84**, 1680, (1962).

of 4-bromo-1-methoxypentane (**1b**) 10.0 g of the ether yielded 13.14 g (89.6%) of distilled 5-bromo-2-pentyl trifluoroacetate. That the product was free of the isomeric (nonhalogen shifted) 4-bromo-1-pentyl trifluoroacetate was demonstrated by capillary column gas chromatography on DC-550, which gave excellent separation, showing 99.97 ± 0.03% isomeric purity. 2-Bromo-1-methoxypropane (**1c**) and 4-chloro-1-methoxypentane (**1a**) yielded 1-bromo-2-propyl trifluoroacetate (98.5 ± 1.5% isomeric purity) and 5-chloro-2-pentyl trifluoroacetate, respectively. 2-Chloro-1-methoxypropane (**1**, $n = 0$; X = Cl) has not yet been subjected to the reaction, but the corresponding three-membered chloronium ion has been generated by trifluoroacetolysis of 2-chloropropyl *p*-nitrobenzenesulfonate, which yielded 1-chloro-2-propyl trifluoroacetate, 99 ± 1% free of the product of "normal" solvolysis.

The reaction of 2-iodo-1-methoxypropane (**1d**), followed by nmr, proceeded with iodine shift, exhibiting formation of a methyl doublet at δ 1.50 at the expense of the original doublet at δ 1.88. The expected sextet at δ 4.9–5.5 appeared simultaneously.

3-Chloro-1-methoxybutane (**1**, $n = 1$; X = Cl) and 3-bromo-1-methoxybutane (**1**, $n = 1$; X = Br) did not undergo 1,3-halogen shifts with trimethyloxonium fluoroborate in trifluoroacetic acid. Following commonly expressed ideas pertaining to ring formation, we postulate that favorable entropy effects cannot compensate for strain in the formation of four-membered-ring halonium ions, in contrast with the balance of effects which results in relatively rapid three-membered-ring formation.

Dimethyl ether is at least moderately better than *p*-nitrobenzenesulfonate as a leaving group. Trimethyl- and triethyloxonium fluoroborates solvolyzed about 25 and 3 times as fast, respectively, as did ethyl *p*-nitrobenzenesulfonate.[5] Departure of dimethyl ether was not rate determining, yet the over-all reaction of 4-chloro-1-methoxypentane (**1a**) (0.8 *M* trimethyloxonium fluoroborate, 0.43 *M* **1a**) to form 5-chloro-2-pentyl trifluoroacetate occurred three times faster than trifluoroacetolysis of 4-chloro-1-pentyl *p*-nitrobenzenesulfonate[1] to give the same product.

(5) Ethyl *p*-nitrobenzenesulfonate was studied in our group by Mr. Joseph Coffey. Ethyl tosylate has been trifluoroacetolyzed by J. E. Nordlander and W. G. Deadman, *J. Am. Chem. Soc.*, **90**, 1590 (1968).

(6) NDEA predoctoral fellow, 1966 to present.

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Molecular Structure of Bisdethiodi(methylthio)acetylaranotin Including Absolute Configuration

Sir:

In the attempt to determine those metabolites responsible for the antiviral activity of the fungus *Arachniotus aureus* (Eidam) Schroeter, several new molecular species were isolated. These include the three similar substances aranotin, acetylaranotin, and bisdethiodi(methylthio)acetylaranotin (BDA). Structures have recently been proposed for these molecules without any steric assignments.[1] This communication will report the complete structure of BDA including the absolute configuration. The structures of aranotin and acetylaranotin follow from the relationships among these molecules.[1]

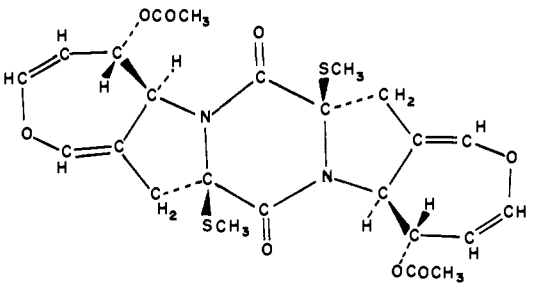

Figure 1. Conventional chemical representation of the stereochemistry of BDA.

Crystals of BDA ($C_{24}H_{26}O_8N_2S_2$) are monoclinic in space group $P2_1$. There are two molecules in the unit cell which has parameters $a = 14.53$ Å, $b = 12.41$ Å, $c = 6.85$ Å, and $\beta = 94.3°$. The data were collected about the *a* and *c* axes employing Cu Kα radiation with the use of a manually operated Buerger diffractometer. Bijvoet anomalous scattering pairs were collected for approximately one-half of the *a* axis. The data from the two axes were correlated after the usual corrections had been made for Lorentz and polarization factors. The structure was solved with the aid of a three-dimensional Fourier map whose terms were weighted by the method of Sim[2] and whose phases were taken to be determined solely by the positions of the two sulfur atoms in the asymmetric unit, the locations of which having been determined by the interpretation of a sharpened three-dimensional Patterson function. A three-dimensional minimum function superposition based on the sulfur positions and using a sharpened Patterson map was also calculated. Those peaks which the Sim-weighted Fourier and the superposition function shared in common and whose distances and angles relative to neighboring peaks were chemically reasonable where used as the starting point of successive Fourier analysis which eventually let to the solution of the structure. The absolute configuration was determined by comparing the calculated and observed signs of $I_{hKl} = I_{hKl} - I_{h\bar{K}\bar{l}}$[3] for all reflections on the first three levels of *a* for which $\Delta I/|F_o|^2 > 0.20$. The value of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ is 0.108 for 1434 observed reflections.

The molecular structure, stereochemistry, and absolute configuration are given in Figures 1 and 2. It will be noted that the previously proposed structure by Nagarajan, *et al.*,[1] is indeed correct. It should also be noted that the absolute configuration of BDA and thus of aranotin and acetylaranotin is identical with that of gliotoxin and sporidesmin[4] and that the steric conformations of those groups which both aranotin and gliotoxin share are identical.

Although BDA possesses a molecular twofold axis of symmetry, this symmetry element is not used by the

(1) R. Nagarajan, L. L. Huckstep, D. H. Lively, D. C. DeLong, M. M. Marsh, and N. Neuss, *J. Amer. Chem. Soc.*, **90**, 2980 (1968).

(2) G. A. Sim, *Acta Cryst.*, **12**, 813 (1959).

(3) J. M. Bijvoet, A. F. Peerdeman, and A. J. van Bommel, *Nature*, **168**, 271 (1951).

(4) J. Fridrichsons and A. M. Mathieson, *Acta Cryst.*, **23**, 439 (1967).