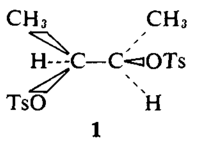
Preparation and Reactivity under SN1 Solvolytic Conditions of Vinyl Tosylates and Brosylates

Sir:

Although sulfonic acid esters have been intensively studied as substrates in solvolytic displacement reactions, little is known of the preparation and reactions of vinyl sulfonates.[1] The possible occurrence or absence of solvolytic reactions proceeding *via* vinyl cation intermediates is of particular interest. We wish to report a simple preparation of cyclic and acyclic vinyl benzenesulfonates and a study of their reactivity in formic acid and 50% aqueous methanol.

The appropriate ditosylate or dibrosylate upon reaction with potassium *t*-butoxide in refluxing *t*-butyl alcohol for 15 min gave the vinyl sulfonate. An example is the formation of 2-buten-2-yl tosylate (**2**) from the ditosylate **1**.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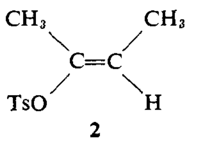
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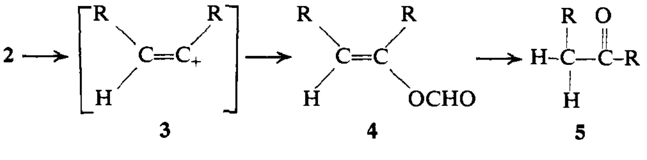
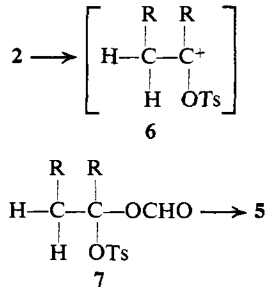
The compounds prepared and their yields and properties are: 1-cyclohexenyl tosylate, 77% (oil), nmr (CCl_4) δ 5.32 (m, 1, -C*H*=COTs-); 1-cyclohexenyl brosylate, 67% (mp 56–57.3°), nmr (CCl_4) δ 5.32 (m, 1, -C*H*=COBs-); *cis*-2-buten-2-yl tosylate, 66% (oil), nmr (CCl_4) δ 5.05 (q, showing allylic coupling, 1, -C*H*=COTs-); and *cis*-2-buten-2-yl brosylate, 55% (mp 46–46.9°), nmr (CCl_4) δ 5.09 (q, showing allylic coupling, 1, -C*H*=COBs-). The vinyl tosylates had uv max (95% C_2H_5OH) 226 mμ (log ϵ 4.15), and the vinyl brosylates had uv max (95% C_2H_5OH) 236 mμ (log ϵ 4.23). The 1-cyclohexenyl derivatives had ir (CCl_4) 1600 (phenyl) and 1678 cm^{-1} (C=C—OTs); and the *cis*-2-buten-2-yl derivatives had ir (CCl_4) 1600 (phenyl) and 1690 cm^{-1} (C=C—OTs).[2]

Reaction of the 1-cyclohexenyl and *cis*-2-buten-2-yl tosylates (0.07 *M*) with formic acid (0.15 *M*) in sodium formate) at 59.8° gave cyclohexanone (92%) and 2-butanone (100%), respectively, as measured by gas chromatography utilizing a base forecolumn.[3] These reactions may be explained either by a solvolysis mechanism (Scheme I) or by an acid addition to the olefinic bond (Scheme II). A solvolysis would involve formation of a vinyl cation (**3**), collapse to a vinyl formate (**4**), and, ultimately, formation of a ketone (**5**).[4] An addition mechanism would involve protonation to give **6**, capture of solvent molecule to give **7**, and further reaction to give ketone **5**.

Scheme I



Scheme II



Distinction between these mechanisms lies in the comparison of the relative reaction rates of the brosylates and tosylates. If solvolysis occurred, one would predict the brosylate rate constant to be three times that of the tosylate.[5] If addition were the mechanism, one would expect the brosylate to react more slowly than the tosylate owing to the *para*-substituent effects of the bromine atom and the methyl group.[3] We found the tosylate rates to be over three times those of the brosylates (see Table I), suggesting that in formic acid addition was the mode of reaction.[6]

Table I. Rates of Addition of Formic Acid to Vinyl Sulfonates at 59.8°

Compound	$k \times 10^7$ sec^{-1}
1-Cyclohexenyl tosylate	12.1
1-Cyclohexenyl brosylate	3.67
cis-2-Buten-2-yl tosylate	10.6
cis-2-Buten-2-yl brosylate	3.07

cis-2-Buten-2-yl tosylate and brosylate (0.02 *M*) were found to be unreactive ($k < 9.0 \times 10^{-8}$ sec^{-1}) in 50% aqueous methanol (0.05 *M* in sodium acetate) at 59.8° for 18 days, a solvent of "ionizing power" similar to that of formic acid.[7] The 2-butyl tosylate rate constant (0.015 *M* tosylate in 50% aqueous meth-

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[1] (a) L. Ruzicka, Pl. A. Plattner, and Furrer, *Helv. Chim. Acta*, **27**, 524 (1944); (b) J. C. Sauer and J. D. C. Wilson, *J. Am. Chem. Soc.*, **77**, 3793 (1955); (c) D. Y. Curtin and Y. G. Hendrickson, *J. Org. Chem.*, **21**, 1260 (1956); (d) A. N. Nesmeyanov, I. F. Lutsenko, R. O. Komutov, and V. A. Dubovitskii, *J. Gen. Chem. USSR*, **29**, 2776 (1959); (e) I. Fleming and J. H. Mason, *Proc. Chem. Soc.*, 245 (1961); (f) I. Fleming and J. H. Mason, *J. Chem. Soc.*, 4771 (1963); (g) *ibid.*, 4778 (1963); (h) J. D. Brown and J. H. Mason, *ibid.*, 1390 (1966); (i) C. L. McIntosh, P. de Mayo, and R. W. Yip, *Tetrahedron Lett.*, 37 (1967); (j) W. M. Jones and F. Miller, *J. Am. Chem. Soc.*, **89**, 1960 (1967); (k) only ref 1i mentions a simple, secondary, aliphatic, vinyl sulfonate. None of these references contains solvolytic data for vinyl sulfonates.

[2] The crystalline brosylates gave satisfactory C and H analyses. The stereochemical assignments, *e.g.*, the presumed formation of the *cis*-tosylate **2**, from the *meso* precursor **1**, are based on our demonstration that *cis*-1,2-cyclohexanediol ditosylate underwent elimination approximately ten times faster than the *trans* isomer to give a vinyl tosylate of higher purity, suggesting *trans* elimination. That the aliphatic tosylates underwent elimination stereospecifically is shown by the formation of different vinyl tosylates from *meso*- and *dl*-2,3-butanediol ditosylates.

[3] P. E. Peterson and G. Allen, *J. Am. Chem. Soc.*, **85**, 3608 (1963).

[4] P. E. Peterson and J. E. Duddey, *ibid.*, **88**, 4990 (1966).

[5] S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and V. G. C. Robinson, *ibid.*, **78**, 328 (1956).

[6] Rates were determined by titration of the sodium formate in aliquots with 0.05 *N* perchloric acid in glacial acetic acid using brom cresol green as an indicator.

[7] E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).

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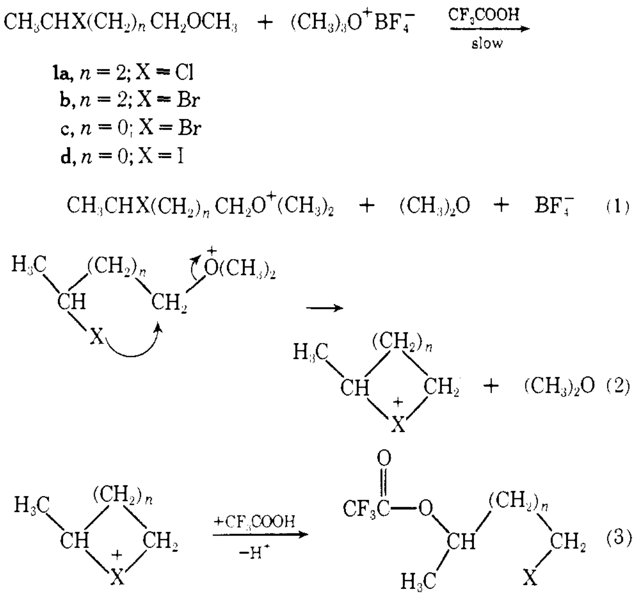
Oxonium Ions in Trifluoroacetic Acid. Quantitative Halogen Shifts in Solvolyses of Halogen-Substituted Trialkyloxonium Ions

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).