Compound **1** was converted to *erythro*-3,3-dimethylbutyl-1,2-d_2 *p*-bromobenzenesulfonate (J = 8.6 Hz), and thence to **2** by reaction with Na[Fe(CO)$_2$C$_5$H$_5$]. The nmr spectrum of the C*H*DC*H*D region of **2** consisted of a *single* AB quartet centered at δ 1.38, with $\Delta\nu$ = 0.122 ppm and J = 4.4 Hz (Figure 1); the infrared spectrum of **2** in the carbonyl stretching region consisted of bands at 2005 and 1955 cm^{-1}. An independent analysis of the nmr spectrum of **2**-d_0 established that the *threo* and *erythro* diastereomers of **2** are characterized by vicinal coupling constants $J_{erythro}$ = 13.1 and J_{threo} = 4.5 Hz. Thus, transformation of **1** to **2** takes place with *inversion* of configuration.[6] Within the limits of detection of our experiment, no (<5%) *erythro* diastereomer is produced in this reaction.

It is worthwhile pointing out that this stereochemical result is of considerable interest in its own right. It provides the first direct evidence that nucleophilic displacement on an alkyl carbon atom by a metalate anion proceeds with inversion of configuration at carbon.[7] Further, the observation that no detectable loss in stereochemistry was observed in **2** on standing for >12 hr at 30° provides an indication of the configurational stability to be expected for this class of carbon–transition metal σ bonds.

Reaction of **2** with triphenylphosphine in THF followed by unexceptional work-up gave **3** as a yellow solid, mp 143° dec. The deuterium-decoupled nmr spectrum of the compound consists of two, equally intense, AX patterns arising from the two pairs of diastereomers represented by **3a** and **3b**.[8] The -C*H*D-CO- resonances of **3** occurred at δ 2.72 and 2.46; both patterns were characterized by the same vicinal coupling constant, J = 4.4 Hz (Figure 1). The infrared spectrum of **3** in the carbonyl stretching region consisted of bands at 1925 and 1615 cm^{-1}. *Anal.* Calcd for C$_{31}$H$_{33}$O$_2$FeP: C, 71.00; H, 6.34. Found: C, 70.55; H, 6.43. Comparison of the observed coupling constant with those estimated for the *threo* (J = 4.2 Hz) and *erythro* (J = 12.5 Hz) diastereomers of **3** from analysis of the ABXY spectrum of **3**-d_0 establishes that conversion of the alkyl–iron bond of **2** to the corresponding carbon–carbon bond of **3** has taken place with complete (>95%) *retention* of configuration.

Related studies of the stereochemistry of other reactions occurring at carbon–transition metal σ bonds will be reported later.

Acknowledgment. We gratefully acknowledge the experimental assistance of Dr. J. Fleming and Mr. J. Simms.

---

[6] A similar technique has been used to determine the stereochemistry of solvolysis of 2-phenylethyl tosylate: R. J. Jablonski and E. I. Snyder, *Tetrahedron Letters*, 1103 (1968); see also R. G. Weiss and E. I. Snyder, *Chem. Commun.*, 1358 (1968).

[7] For recent discussions of the nucleophilic reactivity of metal atoms toward saturated carbon, see R. E. Dessy, R. L. Pohl, and R. B. King, *J. Amer. Chem. Soc.*, 88, 5121 (1966); J. P. Birk, J. Halpern, and A. L. Pickard, *ibid.*, 90, 4491 (1968); J. P. Collman, *Accounts Chem. Res.*, 1, 136 (1968).

[8] A related proton diastereotropism due to chirality at iron has been observed for C$_6$H$_5$CH$_2$Fe(CO)(PPh$_3$)(C$_5$H$_5$): J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, **91**, 1550 (1969).

[9] National Institutes of Health Predoctoral Fellow, 1967–1969.

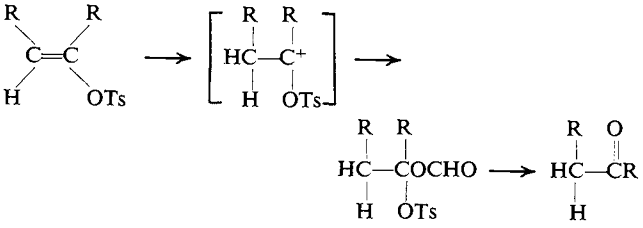
George M. Whitesides, David J. Boschetto[9]
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received April 16, 1969

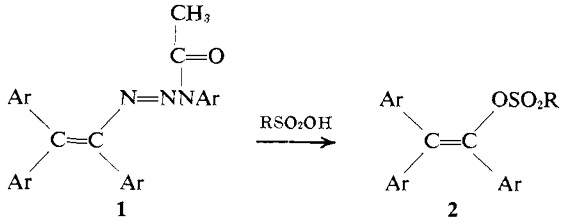
Solvolysis of Sulfonic Acid Esters of Triphenylvinyl Alcohol by a Heterolytic Mechanism

Sir:

Although vinyl cations have finally become acceptable members of the "reactive intermediate" community,[1] their generation by heterolytic cleavage of a group attached directly to a double bond has been limited to vinyl diazonium ions[2,3] and vinyl halides.[4-6] To date, one mechanistic study of the solvolysis of vinyl sulfonic acid esters[7,8] has been reported. Although the reaction led to products that could be explained by a simple SN1 mechanism, the authors very elegantly showed that their products arose by an addition–elimination path.



At this time, we would like to present preliminary evidence for a simple heterolytic cleavage mechanism for the solvolysis of the following vinyl sulfonates: triphenylvinyl fluorosulfonate, triphenylvinyl trifluoromethanesulfonate, and triphenylvinyl tosylate.



Ar = C$_6$H$_5$

a, R = F
b, R = CF$_3$
c, R = *p*-tolyl

All sulfonates were synthesized by allowing the acyltriazene **1**[9,10] to react with the appropriate sulfonic acid[11] in methylene chloride at −50°.

---

[1] H. G. Richey and J. M. Richey in "Carbonium Ions," Vol. II, G. A. Olah and P. von R. Schleyer, Ed., Interscience Publishers, New York, N. Y., in press. The authors express appreciation to Professor Richey for furnishing us with a preprint of his manuscript.

[2] M. S. Newman and A. E. Weinberg, *J. Am. Chem. Soc.*, 78, 4654 (1956); M. S. Newman and A. Kutner, *ibid.*, 73, 4199 (1951); D. Y. Curtin, J. A. Kampmeier, and B. R. O'Connor, *ibid.*, 87, 863 (1965); D. Y. Curtin, J. A. Kampmeier, and M. L. Farmer, *ibid.*, 87, 874 (1965); A. C. Day and M. C. Whiting, *J. Chem. Soc.*, *B*, 991 (1967).

[3] W. M. Jones and F. W. Miller, *J. Am. Chem. Soc.*, 89, 1960 (1967).

[4] C. A. Grob and G. Cseh, *Helv. Chim. Acta*, 47, 194 (1964).

[5] L. L. Miller and D. A. Kaufman, *J. Am. Chem. Soc.*, 90, 7282 (1968).

[6] S. J. Huang and M. V. Lessard, *ibid.*, 90, 2432 (1968).

[7] P. E. Peterson and J. M. Indelicato, *ibid.*, 90, 6515 (1968).

[8] Very recently, G. Capozzi, G. Melloni, G. Medona, and M. Piscitelli (*Tetrahedron Letters*, 4039 (1968)) have reported that 1,2-diaryl-2-arylmercaptovinyl 2,4,6-trinitrobenzenesulfonates undergo reactions suggestive of a vinyl cation mechanism. If these reactions do involve heterolysis of the sulfonate from a vinyl carbon, their rates when compared with those reported in this note would point to substantial participation of the neighboring sulfur.

[9] Synthesized by acylating the triazene[3] with acetyl chloride.

[10] All new compounds reported in this note showed satisfactory analyses and spectral properties agreed with structure assignments.

[11] Conversion of the acyltriazene to the sulfonic acid ester most certainly also involves formation of a vinyl cation as evidenced by the observation that the 2,2-di-*p*-tolyl-substituted triarylvinyltriazene gives rearranged products when treated with fluorosulfuric acid.

The fluorosulfonate **2a**[12] was selected for initial study because fluorosulfuric acid is one of the strongest known pure acids[14] and as a result the fluorosulfonate ion would be expected to be a very effective leaving group. That this is actually the case was apparent when it was found that triphenylvinyl fluorosulfonate undergoes acetolysis to triphenylvinyl acetate[15] at room temperature (25°, half-life 33 hr).

Rate studies led to specific rate constants and activation parameters which are recorded in Table I. In all reactions the rates were cleanly first order. Changes in sodium acetate concentration showed only small effects on the rate, thus excluding either an SN2 substitution reaction by acetate or an acetate addition–elimination reaction. A change from proteated to deuterated solvent also showed essentially no effect on the rate. The absence of a solvent isotope effect can be taken as strong evidence[16] against the addition mechanism that was demonstrated by Peterson and Indelicato[7] for the solvolysis of 1-cyclohexenyl and *cis*-2-buten-2-yl tosylates. Support for this conclusion is found in the facts that the acetolysis of triphenylvinyl tosylate is about 10^4 slower than that of the fluorosulfonate.

Table I. Rate Constants and Activation Parameters for Acetolysis of Vinyl Sulfonates at 150.8°

Compd	k, sec^{-1}	k_{rel}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
2a	0.699^{a-d}	13,500	23.3	−6.5
2b	2.16^{a-c}	41,700	24.3	−2.0
2c	$5.18 \times 10^{-5\ e,f}$	1	25.7	−20.3

[a] Extrapolated from rate data obtained at lower temperatures. [b] Acetolysis kinetics followed by uv. [c] About 10^{-4} *M* in ester. Buffered with approximately 25 *M* excess of sodium acetate. [d] The acetolysis of this compound was also followed titrimetrically. The rate constant was identical with that obtained by the uv method. [e] Acetolysis kinetics followed titrimetrically. [f] About 0.005 *M* in ester. Buffered with slight molar excess of sodium acetate.

While this work was under way Streitwieser, Wilkens, and Kiehlmann[17] reported a study of the acetolysis of ethyl trifluoromethanesulfonate (triflate). It was found that the triflate undergoes solvolysis some 30,000 times faster than the tosylate. Inasmuch as fluorosulfuric acid and trifluoromethanesulfuric acid have both been submitted as candidates for the strongest known pure acid,[14,18] we felt that it would be interesting to compare the rates of solvolysis of the vinyl fluorosulfonate with the corresponding vinyl triflate.[19] Acetolysis occurred 3.1 times (150.8°) faster than the fluorosulfonate, thus indicating that the trifluoromethanesulfonate ion is a slightly better leaving group (in this system) than the fluorosulfonate ion.[20]

Acetolysis of triphenylvinyl tosylate was also examined. Although the rate of the reaction was over 10^4 slower than the corresponding fluorosulfonate or triflate a change from proteated to deuterated solvent once again showed essentially no effect on the rate and as a result we must conclude that this reaction also proceeds by a simple heterolysis mechanism.

Finally, it is interesting to attempt to compare the rate of ionization of the unsaturated system with a suitable aliphatic sulfonate. For a model, we have selected the tosylate of 1,2,2,2-tetraphenylethanol. Although solvolysis of this material has not been reported, a solvolysis rate constant of at least 10^{-3} at 25° can be extrapolated from known systems[21] with fair confidence.[22] Extrapolation of the rate of acetolysis of triphenylvinyl fluorosulfonate to 25° gives a rate constant of about 10^{-5}. Assuming an acceleration of the fluorosulfonate relative to the tosylate of at least 10^4 gives a difference of 10^6 between the vinyl and the saturated sulfonates.[23] Although numerous assumptions are included in this game with numbers, it certainly points up the fact that bonding a sulfonic acid ester to a carbon–carbon double bond dramatically reduces its tendency to ionize. The probable reasons for this have been amply discussed elsewhere.[5,7]

Acknowledgment. The authors gratefully acknowledge support for this work received from the Petroleum Research Fund administered by the American Chemical Society.

---

(12) To the best of our knowledge, the synthesis of only one other vinyl fluorosulfonate has been reported.[13]

(13) M. A. Belaventsev, G. A. Sokol'skiy, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2461 (1967); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 2344 (1967).

(14) R. J. Gillespie, *Accounts Chem. Res.*, **1**, 202 (1968).

(15) The triphenylvinyl fluorosulfonate and the triphenylvinyl triflate gave essentially quantitative yields of triphenylvinyl acetate from their acetolysis. The triphenylvinyl tosylate gave a 39% yield of the corresponding acetate.

(16) For lead references on solvent isotope effects on similar systems see D. S. Noyce and R. M. Pollack, *J. Am. Chem. Soc.*, **91**, 119 (1969).

(17) A. Streitwieser, Jr., C. L. Wilkins, and E. Kiehlmann, *ibid.*, **90**, 1598 (1968).

(18) T. Gramstad, *Tideskr. Kjemi, Bergvesen Met.*, **19**, 62 (1959). R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 4228 (1954); E. S. Lane, *Talanta*, **8**, 849 (1961); R. E. Banks and R. N. Haszeldine in "The Chemistry of Organic Sulfur Compounds," Vol. II, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press, New York, N. Y., 1966, Chapter 6.

(19) The authors express their appreciation to Minnesota Mining for furnishing us with a sample of trifluoromethanesulfuric acid which was used for this synthesis.

(20) An ionization mechanism (in contrast to an addition–elimination mechanism) is further supported by the observation that solvolysis of the vinyl triflate goes 1.6 times faster in 98% aqueous ethanol than in acetic acid. Grunwald and Winstein *Y* values (E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, 70, 846 (1948)) predict similar "ionizing power" for these two solvents. Similar rates would not be expected for the addition–elimination mechanism.[7] By varying the water content, an "*m*" value of 0.56 was obtained. The predominant product in all cases was triphenylvinyl ethyl ether.

(21) H. C. Brown, R. Bernheimer, and K. J. Morgan, *J. Am. Chem. Soc.*, **87**, 1280 (1965); S. Winstein and H. Marshall, *ibid.*, **74**, 1120 (1952); S. Winstein and B. K. Morse, *ibid.*, **74**, 1133 (1952).

(22) This includes an approximate steric acceleration from the three β-phenyls of 400. Miller and Kaufman[5] report no steric acceleration (in fact, small retardation) from the two β-phenyl groups in the ionization of α-phenylvinyl halides. This surprising difference between the saturated and unsaturated systems is presently under investigation for the sulfonic acid ester systems. If no steric acceleration is found, then our model is obviously a poor one.

(23) Peterson and Indelicato[7] estimate a minimum rate difference of 5.7×10^4.

W. M. Jones, D. D. Maness
Department of Chemistry, University of Florida
Gainesville, Florida 32601

Received May 9, 1969

The Reactions of Bivalent Sulfur Compounds–Copper(II) Complexes

Sir:

In this communication, the reactions of the bivalent sulfur compounds, such as benzaldehydediethylmercaptal (**1a**), benzophenone diethyl mercaptole (**1b**), and