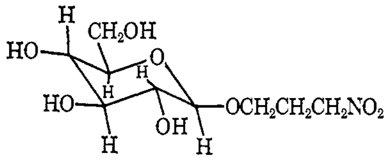

I

3-nitro-1-propanol (which would correspond to a toxic dose of the original plant material) caused death with symptoms identical with those of *A. miser* poisoning.[6] Miserotoxin was rapidly metabolized to 3-nitro-1-propanol in livestock rumen fluid.[7]

Miserotoxin is a new addition to the small number of known aliphatic nitro compounds and is most closely related to the endecaphyllins,[8] which are glucose derivatives of 3-nitropropanoic acid (hiptagenic acid) and are constituents of *Indigofera* (Leguminosae) species. We did not find 3-nitropropanoic acid or any of its derivatives in *A. miser*, although the structural closeness to miserotoxin and 3-nitro-1-propanol might indicate a similar biogenesis.[9]

[6] M. C. Williams, K. R. Van Kampen, and F. A. Norris, *Am. J. Vet. Res.*, in press.

[7] M. C. Williams, F. A. Norris, and K. R. Van Kampen, *ibid.*, in press.

[8] A. Cooke, *Arch. Biochem. Biophys.*, **55**, 114 (1955); R. A. Finnegan and W. H. Mueller, *J. Pharm. Sci.*, **54**, 1136 (1965); R. A. Finnegan and R. A. Stephani, *ibid.*, **57**, 353 (1968).

[9] P. D. Shaw and J. A. McCloskey, *Biochemistry*, **6**, 247 (1967); P. D. Shaw, *ibid.*, **6**, 2253 (1967).

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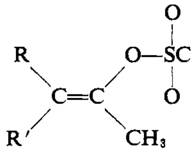
Preparation and Solvolysis of Vinyl Trifluoromethanesulfonates. I. Evidence for Simple Alkylvinyl Cation Intermediates

Sir:

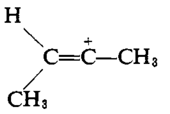
Few vinyl cations have been generated by direct solvolysis of suitable vinyl precursors, and in each known case either an aromatic ring,[1] a neighboring double bond,[2] or a cyclopropyl ring[3] was attached to the carbon bearing the leaving group, resulting in delocalization and special stabilization of the cation observed. We wish to report the preparation and solvolysis of vinyl trifluoromethanesulfonates (triflates) and present evidence for a simple alkylvinyl cation intermediate.

Recently, Peterson and Indelicato reported the first preparation and investigation of cyclic and acyclic alkylvinyl arenesulfonates.[4] However, both the cyclohexenyl and the *cis*-2-buten-2-yl sulfonates were found to react in formic acid *via* an addition–elimination mechanism rather than unimolecular ionization and vinyl cations. Furthermore, the *cis*-2-buten-2-yl tosylate and brosylate were found to be unreactive in 50% aqueous methanol at 59.8° for 18 days. It therefore seems that even such excellent leaving groups as a tosylate and brosylate are unreactive when attached to a trigonal carbon substituted with only alkyl groups. Yet there is no reason to believe that simple alkylvinyl cations are inherently unstable; gas-phase data indicate that the heat of formation of $CH_3CH{=}CH^+$ is in between those of methyl and ethyl cations.[5] Since trifluoromethanesulfonates are known to be at least 10^4–10^5 more reactive[6] under solvolytic conditions than the corresponding arenesulfonates, we undertook an investigation of the preparation and reactivity of the alkylvinyl triflates.

Addition of an equimolar amount of trifluoromethanesulfonic acid to methylacetylene at −78° and subsequent warming to room temperature in a sealed tube afforded, upon distillation, isopropenyl triflate (**1**): 60–80% (bp 25–27° (12 mm)), nmr (CCl_4) δ 2.03 (s, 3, CH_3), 4.88 (m, 1), 5.00 (d, 1). Addition to allene gave the identical product. Addition[7] to dimethylacetylene gave a two-component product (bp 36–37° (12 mm)) in a 65:35 ratio, which was readily separated by preparative gas chromatography (5 ft × 0.25 in., 15% FFAP, 40°) into the *trans* isomer **2** [nmr (CCl_4) δ 1.31 (doublet of quartet, 3, CH_3), 1.66 (broad quintet, 3, CH_3), 4.98 (quartet of quartet, 1, H)] and the *cis* isomer **3** [nmr (CCl_4) δ 1.22 (doublet of quartet, 3, CH_3), 1.68 (multiplet, 3, CH_3), 5.27 (quartet, 1, H)], respectively.[8]



1, R = R′ = H
2, R = CH_3; R′ = H
3, R = H; R′ = CH_3



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The rates[9] of solvolyses of vinyl triflates **1** through **3** are summarized in Table I. Compound **2** in 80% aqueous ethanol at 76° gave 98 ± 3% dimethylacetylene as the only product, measured by gas chromatography utilizing an internal standard; the *cis* isomer **3** at 100° gave 58% dimethylacetylene, 33% 2-butanone, and

[1] C. A. Grob and G. Cseh, *Helv. Chim. Acta*, **47**, 194 (1964); G. Cappozzi, G. Melloni, G. Modena, and M. Piscitelli, *Tetrahedron Letters*, 4039 (1968); L. L. Miller and D. A. Kaufman, *J. Am. Chem. Soc.*, **90**, 7282 (1968).

[2] C. A. Grob and R. Spaar, *Tetrahedron Letters*, 1439 (1969).

[3] S. A. Sherrod and R. G. Bergman, *J. Am. Chem. Soc.*, **91**, 2115 (1969); M. Hanack and T. Bässler, *ibid.*, **91**, 2117 (1969).

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

[5] J. L. Franklin, "Carbonium Ions," Vol. I, G. A. Olah and P. von R. Schleyer, Ed., Interscience Publishers, New York, N. Y., 1968, pp 85–88.

[6] (a) A. Streitwieser, Jr., C. L. Wilkins, and E. Kiehlmann, *J. Am. Chem. Soc.*, **90**, 1598 (1968); (b) P. von R. Schleyer, T. M. Su, and W. Sliwinski, *ibid.*, in press.

[7] In analogy to similar electrophilic additions to triple bonds (R. C. Fahey, in "Topics in Stereochemistry," Vol. 3, E. Eliel and N. L. Allinger, Ed., Interscience Publishers, New York, N. Y., 1968), this reaction probably proceeds *via* vinyl cations, although this has not yet been investigated.

[8] Stereochemistry was assigned on the basis of chemical shifts and coupling constants. In the *trans* isomer **2**, the vicinal coupling is J = 7.4 Hz and the long-range coupling between the two methyl groups is J = 1.6 Hz and between the hydrogen and methyl is J = 1.1 Hz: in the *cis* isomer **3**, the values are J = 7.6 Hz, J = 1.3 Hz, and $J \leq 1$ Hz, respectively. See S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964), and G. P. Newsoroff and S. Sternhell, *Tetrahedron Letters*, 6117 (1968), for long-range allylic coupling in substituted ethylenes.

[9] Rates were determined in duplicate or triplicate either conductometrically or by titration with NaOH using phenolphthalein as an indicator. In all cases good first-order rates were observed for more than 90% reaction.

Table I. Rates of Reaction of Vinyl Triflates in 80% Aqueous Ethanol

Compd	Temp, °C	k, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
1	25.0^a	9.45×10^{-8}	24.7	−7.7
	50.0^a	2.59×10^{-6}		
	76.1	$(4.95 \pm 0.28) \times 10^{-5}$		
	100.1	$(5.26 \pm 0.25) \times 10^{-4}$		
1^b	25.0^a	6.81×10^{-7}	24.9	−3.3
	50.2	$(1.95 \pm 0.05) \times 10^{-5}$		
	76.1	$(3.72 \pm 0.25) \times 10^{-4}$		
1^c	50.2	$(9.64 \pm 1.0) \times 10^{-5}$		
2	25.0^a	1.49×10^{-6}	23.8	−5.3
	50.2	$(3.72 \pm 0.05) \times 10^{-5}$		
	76.1	$(6.29 \pm 0.20) \times 10^{-4}$		
3	25.0^a	3.67×10^{-8}	25.3	−7.7
	76.2	$(2.25 \pm 0.08) \times 10^{-5}$		
	100.1	$(2.48 \pm 0.08) \times 10^{-4}$		

^{a} Extrapolated. ^{b} 50% aqueous ethanol. ^{c} NaOH (1.1 equiv) added.

9% methylallene. This product ratio for the *cis* isomer **3** did not change in the presence of a base, such as pyridine, added prior to reaction.[10]

In principle alkylvinyl triflates under solvolytic conditions could undergo reaction according to four possible mechanisms: (a) nucleophilic attack at sulfur with cleavage of the S–O bond, (b) an addition–elimination sequence similar to that observed by Peterson[4] for the arenesulfonates in formic acid, (c) a unimolecular SN1 type ionization to a vinyl cation, and (d) a concerted elimination.

Mechanism a is not expected, for nucleophilic attack on sulfur in sulfates is unlikely, and is further ruled out by the extreme unreactivity of phenyl triflates.[6b,11] Mechanism b is ruled out by the improbability of protonation in neutral aqueous media as well as the absence of ketone as product in the *trans* isomer **2**.

A close examination of the data reveals a mechanism that is a delicate balance between a concerted elimination and a unimolecular ionization involving a vinyl cation. In the *trans*-dimethyl isomer **2**, the only product of reaction is acetylene, while the *cis* isomer **3** also gives methylallene and 2-butanone as product. Although the olefinic products could arise from either concerted elimination or rate-determining formation of a vinyl cation followed by subsequent loss of proton, the ketone must arise from solvent capture of an incipient vinyl cation **4**. The solvolysis rates of isopropenyl triflate (**1**) in 80 and 50% aqueous ethanol correspond to $m = 0.52$, a value comparable to that observed in the solvolysis of simple secondary alkyl systems, such as $m = 0.40$ for isopropyl brosylate.[12] The 37-fold rate acceleration observed in the presence of NaOH, although small, points toward a concerted elimination. Furthermore, the rate of the *trans* isomer **2** is 40 times that of the *cis* isomer **3**, suggesting that the former, which is in a geometrically favorable conformation for concerted elimination, reacts by such a pathway, whereas the *cis* isomer in a geometrically unfavorable configuration undergoes reaction *via* unimolecular ionization and a vinyl cation intermediate. As a test of this hypothesis we prepared the deuterio-*trans* (**2**, R′ = D) and deuterio-*cis* (**3**, R = D) compounds and measured the deuterium isotope effects.[13] $k_H/k_D = 2.09$ was observed for the *trans* isomer **2** in 80% aqueous ethanol at 76°, whereas the value obtained for the *cis* isomer **3** was $k_H/k_D = 1.20$ at 100°. The value of $k_H/k_D = 2.09$ for the *trans* isomer is more consistent with a primary deuterium isotope effect indicative of bond breaking in the transition state and mechanism d, whereas that of the *cis* isomer, $k_H/k_D = 1.20$, is more like a normal β-deuterium isotope effect and more consistent with a simple alkylvinyl cation intermediate.[14]

In summary, we think that, on the basis of the observed products and their invariance in the presence of base, the relative rates, and the deuterium isotope effects, solvolysis of *cis*-2-buten-2-yl triflate (**3**) proceeds through a disubstituted carbonium ion **4**, and represents the first example of a simple alkyl-substituted vinyl cation.

Further mechanistic studies on these and other vinyl triflates are under investigation and will be reported in future papers.

Acknowledgments. The authors are grateful to Professor Paul von R. Schleyer for many stimulating discussions and helpful suggestions, and partial support through National Science Foundation Grant GP 9233. We are indebted to Dr. R. L. Hansen of the Minnesota Mining and Manufacturing Co. for samples of the barium salt of trifluoromethanesulfonic acid.

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(10) Products were identified by comparison of retention times with authentic samples and were found to be essentially stable under the reaction conditions, with only methylallene undergoing isomerization to the acetylene, but only to the extent of 5–10%.

(11) Private communication, A. Streitwieser, Jr.

(12) (a) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948); (b) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(13) The deuterio compounds were prepared in the usual manner from CF_3SO_3D. Both low-voltage mass spectrometric analysis as well as nmr indicate 68 ± 3% deuterium incorporation. In numerous attempts under a variety of conditions it proved to be impossible to obtain more than 70% deuteration due to scrambling during addition. The isotope effects reported are extrapolated to 100% deuteration.

(14) There are no values in the literature for the β-deuterium isotope effect on the solvolysis of vinyl derivatives. However, a β-deuterium isotope effect in the acid-catalyzed electrophilic addition of H_2O to $C_6H_5C{\equiv}CD$ involving a vinyl cation is consistent with our value (see D. S. Noyce and M. D. Schiavelli, *J. Am. Chem. Soc.*, **90**, 1023 (1968)).

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Mediation of a Primary Kinetic Isotope Effect by Asymmetric Induction

Sir:

Reduction of isopropyl phenyl ketone with a Grignard reagent from (*R*)-(−)-3-phenylbutyl chloride gives a 25% enantiomeric excess of (*R*)-(+)-isopropylphenylcarbinol. This reduction has been described in terms of the symmetry principles involved.[1] We have subsequently found that reduction of *t*-butyl phenyl ketone with this Grignard reagent yields an 8% enantiomeric excess of (*R*)-(+)-*t*-butylphenylcarbinol (**4**). Deuterium-labeling experiments with the latter system have revealed some of the mechanistic details of this reaction. Most striking is the observation that the C-3 chiral cen-

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(1) J. D. Morrison, D. L. Black, and R. W. Ridgway, *Tetrahedron Lett.*, 985 (1968).