Vinyl Cations. The Solvolysis of Vinyl Sulfonates[1]

Sir:

Recently evidence has appeared which implicates vinyl cationic transition states in the solvolytic reactions of vinyl compounds in which the potential cationic center is conjugated with a benzene ring,[2] a double bond,[3] or a cyclopropyl ring.[4] Earlier we reported that simple aliphatic and alicyclic sulfonates failed to react in 50% aqueous methanol at 59.8°.[5] We now report the reactivity of these sulfonates, and also of 1-phenyl-1-ethenyl tosylate, in this solvent at 130.0°. This study complements the very recent work of Stang and Summerville on the reactivity of vinyl trifluoromethanesulfonates.[6]

The rates of reaction for the vinyl sulfonates (0.02–0.002 *M*) and for 2-butyl tosylate (0.02–0.01 *M*) in 50% aqueous methanol (0.025–0.0025 *M* and 0.025–0.0125 *M*, respectively, in sodium acetate) are given in Table I, and some products of reaction are given in Table II. The tenfold rate increase for the *trans*- over the *cis*-2-buten-2-yl tosylate is analogous to rate effects observed in Stang and Summerville's study where the β-deuterium isotope effect suggested predominantly transcoplanar E2-type elimination, with the solvent as the base, for the *trans* case (Scheme I) and increased vinyl cationic character in the reaction of the *cis* isomer (Scheme II).[7] In our study the increase in 2-butanone formation from *cis*-2-buten-2-yl tosylate, compared to that from the *trans* isomer, is consistent with an analogous change in mechanism. 2-Butyne as well as ethynylbenzene were shown not to form ketones under the reaction conditions. Presently, however, we are unable to exclude the possibility of the formation of 1,2-butadiene and its subsequent hydration to form 2-butanone.

Table I. Rates of Reaction of Sulfonates in 50% Aqueous Methanol at 130.0°

Compound[a]	$k \times 10^6$, sec^{-1}
cis-2-Buten-2-yl brosylate[b]	2.71
cis-2-Buten-2-yl tosylate[b]	0.71
trans-2-Buten-2-yl tosylate[b,c]	7.10
1-Cyclohexenyl brosylate[b]	≤0.01[d]
1-Phenyl-1-ethenyl tosylate[e]	174[f]
2-Butyl tosylate[g]	810,000[h]

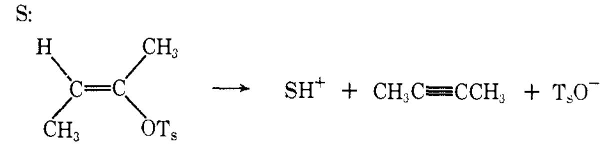
[a] Method of preparation, yields, and physical constants for vinyl sulfonates can be found in ref 5 except as noted. [b] Data were determined by titration of the sodium acetate in aliquots with aqueous 0.05 *N* hydrochloric acid using Mallinckrodt IndicatAR pH 3–4 as an indicator. The rate was found to be independent of changes in the sodium acetate concentration in the range 0.025–0.039 *M* for the reaction of the (0.02 *M*) *trans* isomer. [c] Prepared by the method given in ref 5, 65% yield, mp 32.8–34.4°, nmr (CCl_4) δ 4.94 (q, 1, showing allylic coupling, $-CH{=}COTs-$). [d] This compound appeared to be unreactive after 425 hr at 130.0°. [e] Prepared by the method given in ref 5, 55% yield, mp 48.0–50.5°, nmr (CCl_4) δ 5.02 and 5.27 (2 d, 2, $J_{H-H} = 2.7$ Hz, $C_6H_5COTs{=}CH_2$). Rate measured by a combination of titration and uv methods. [f] Calculated from *k* values 2.46×10^{-6}, 1.58×10^{-5}, and 3.67×10^{-5} measured at 80.0, 100.0, and 110.0°, respectively; $E_a = 24.2$ kcal/mole. [g] Rates were determined by ultraviolet spectroscopy of samples quenched in 2-propanol. [h] Calculated from *k* values 1.67×10^{-6}, 9.21×10^{-5}, and 8.96×10^{-4} measured at 0.0, 30.0, and 50.0°, respectively; $E_a = 22.7$ kcal/mole.

Table II. Products of the Reaction of Vinyl Sulfonates in 50% Aqueous Methanol[a]

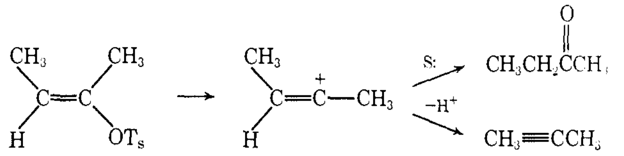
Vinyl sulfonate	Ethynylbenzene, %	Acetophenone, %	2-Butyne, %	2-Butanone,[b] %
trans-2-Buten-2-yl tosylate			95	5
cis-2-Buten-2-yl brosylate			72	28
1-Phenyl-1-ethenyl tosylate	37	63		

[a] Relative yields based on gas chromatography of a carbon tetrachloride extract of a 0.02 *M* solution of vinyl sulfonate reacted for one half-life. Measured total yields were 72, 82, and 113%, respectively, for the *trans*, *cis*, and phenylethenyl tosylates. [b] Based on gas chromatography of the aqueous methanol layer after a carbon tetrachloride extraction of a 0.02 *M* solution of vinyl sulfonate reacted for one half-life.

Scheme I



Scheme II



If we accept as a working hypothesis the cationic nature of the transition states involved, three new points of theoretical importance emerge from our data. Based on data for *cis*-2-buten-2-yl tosylate and 2-butyl tosylate, the relative rate of carbonium ion formation by solvolysis from sp^3-hybridized carbon, compared to sp^2-hybridized carbon, is found to be $0.81/(0.71 \times 10^{-6}) = 1.1 \times 10^6$. This value may be compared with the estimate of Jones and Maness of 10^6 from the solvolysis of triphenylvinyl fluorosulfonate.[2g] Second, the ratio of the solvolysis rate of 1-phenyl-1-ethenyl tosylate to that of *cis*-2-buten-2-yl tosylate is $174 \times 10^{-6}/(0.71 \times 10^{-6}) = 245$, whereas the ratio of the solvolysis rate of

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(3) C. A. Grob and R. Spaar, *Tetrahedron Lett.*, 1439 (1969).

(4) (a) S. A. Sherrod and R. G. Bergman, *J. Am. Chem. Soc.*, **91**, 2115 (1969); (b) M. Hanack and T. Bassler, *ibid.*, **91**, 2117 (1969).

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

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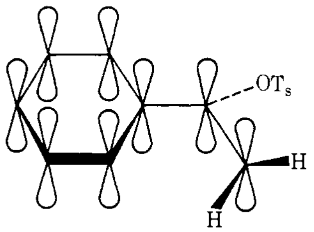
(7) For *trans*-2-buten-2-yl tosylate, the vicinal coupling is $J = 6.9$ Hz, the homoallylic coupling between the two methyl groups is $J = 1.3$–1.6 Hz, and that between the vinyl hydrogen and methyl is $J \sim 1.0$ Hz; for the *cis* isomer the values are $J = 7.2$ Hz, $J = 1.0$–1.2 Hz, and $J \sim 1.0$ Hz, respectively. The trends in *J* follow those of the triflates,[6] but the trends in chemical shifts do not. In view of the similarity of *J* values in *cis*- and *trans*-vinyl tosylates, the presumption of preferred *trans* elimination in their preparation and in the solvolysis of the *trans* isomer provides the best basis for the assignment of stereochemistry.

1-chloro-1-phenylethane to that of 2-chloropropane is 5000.[8] Accordingly the ability of a phenyl ring to stabilize a vinyl cation is shown to be less than that for a saturated cation. This result may be in part a consequence of the breaking of the conjugation of the vinyl p orbitals with those of the benzene ring in going from the ground state **1** to the transition state **2**. Grob has suggested the operation of similar effects in the solvolysis of bromides corresponding to **1** and of allylic vinyl bromides.[2,3]



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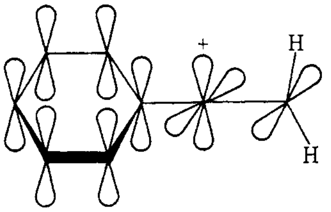

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Finally, from the ratio of the solvolysis rates of *cis*-2-buten-2-yl brosylate and cyclohexenyl brosylate (≥ 270) the predicted[9] preference for a linear over a bent vinyl cation is demonstrated. The absence of reactivity in 1-cyclohexenyl brosylate is analogous to that in phenyl tosylate[10a] and triflate.[10b] The phenyl data suggest that a *cis*-2-buten-2-yl to 1-cyclohexenyl rate ratio may be higher than the minimum of ~270 observed in our study, where no measurable reaction of 1-cyclohexenyl brosylate was observed.

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(8) Derived from the ratio of rates of *t*-butyl chloride and 1-chloro-1-phenylethane solvolyses at 50°, 80% aqueous ethanol, ~1, and isopropyl bromide and *t*-butyl bromide at 55°, 80% aqueous ethanol, ≃ 5000: A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1963, pp 43 and 44.

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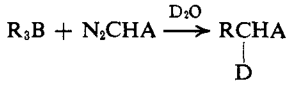
The Reaction of Organoboranes with Diazo Esters and Diazo Ketones in the Presence of Deuterium Oxide. A New Synthesis of α-Deuterio- and α,α-Dideuterio Esters and Ketones

Sir:

The facile alkylation of functionally substituted diazoalkanes with trialkylboranes (available from olefins *via* hydroboration[1]) affords a convenient synthesis of homologated nitriles,[2] esters,[2] ketones,[3] and diketones[4] (1) where A = CN, $COOC_2H_5$, $COCH_3$, COC_6H_5, and $CO(CH_2)_nCOCHN_2$, $n = 2, 3$.

$$R_3B + N_2CHA \xrightarrow{-N_2} \xrightarrow{\text{hydrolysis}} RCH_2A \qquad (1)$$

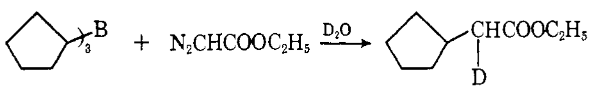
The observation that the intermediate functionalized organoborane underwent rapid cleavage by water[2] suggested the possibility[5] of specific deuterium incorporation by employing deuterium oxide as the hydrolytic medium. We wish to report that diazo esters and diazo ketones, such as ethyl diazoacetate, diazoacetone, and diazoacetophenone, react with organoboranes in the presence of deuterium oxide to produce high yields of site-specific monodeuterated esters and ketones with high isotopic purity (2). Consequently, this development provides a simple procedure for the synthesis of homologated monodeuterated derivatives unencumbered by the usual problems (polydeuteration, self-condensation) encountered in typical acid- or base-catalyzed exchange processes.[6]



$$R_3B + N_2CHA \xrightarrow{D_2O} R\underset{\underset{\displaystyle D}{|}}{C}HA \qquad (2)$$

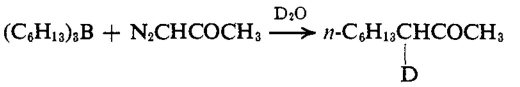
A = $COOC_2H_5$, $COCH_3$, COC_6H_5

Tricyclopentylborane, in the presence of deuterium oxide, reacts with ethyl diazoacetate to produce a 97% yield of ethyl α-d_1-cyclopentylacetate with virtually quantitative incorporation of one deuterium atom (3).



(3)

The synthesis of a methylene-monodeuterated ketone is exemplified by the conversion of trihexylborane to 2-nonanone-3-d_1 in 99% yield (4).



$$(C_6H_{13})_3B + N_2CHCOCH_3 \xrightarrow{D_2O} n\text{-}C_6H_{13}\underset{\underset{\displaystyle D}{|}}{C}HCOCH_3 \qquad (4)$$

Dideuterio derivatives may also be prepared by a simple extension of this methodology. Diazoacetone-d_1 and deuteriodiazoacetic ester are readily available

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(5) It should be emphasized that the mechanism suggested[2] has been employed purely as a working hypothesis, and has proven helpful in designing new experiments. However, our main efforts have been directed at the practical synthetic aspects of this reaction, and the suggested mechanism should not be regarded as firmly established.

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