tions often coincide with those from the uncatalyzed Diels–Alder reaction, mechanistically the two reactions may be largely unrelated,[13] the catalyzed version being more reasonably classifiable as a vinylogous variant of the Friedel–Crafts acylation of olefins.

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(13) For leading references to discussions of the mechanism of the normal Diels–Alder reaction, see ref 12.

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Vinylic Cations from Solvolysis. III. Solvolysis of Triarylvinyl Arylsulfonates in Aqueous Acetone

Sir:

Evidence for intermediate vinyl cations in solvolysis of vinyl sulfonates and halides activated by aryl group,[1] cyclopropyl ring,[2] double bond,[3] and alkyl groups[1k,4] is increasing. The possibility of sulfur–oxygen cleavage was discussed for vinyl triflates,[11] although attack of base on sulfur occurs with phenyl[5] and vinyl tosylates.[6] We now report the reactivity of several trianisylvinyl arylsulfonates and relevant solvent effects, which give additional evidence for vinyl-cationic transition states *via* carbon–oxygen cleavage.

Trianisylvinyl arylsulfonates were prepared by the reaction of trianisylvinyl bromide with silver arylsulfonates in dry acetonitrile.[7] Their solvolysis rate at 0.002–0.008 M concentrations in 70% acetone (containing 0.004–0.02 M 2,6-lutidine) was followed conductometrically (Table I). For all compounds $\Delta H^{\neq} = 25$–27 kcal/mol and $\Delta S^{\neq} = -5$ to -1 eu, and the product is 1,2,2-trianisylethanone.[8] For trianisylvinyl bromide, $k_1 = 2.52 \times 10^{-6}$ sec^{-1} at 75° (extrapolated value), $\Delta H^{\neq} = 26$ kcal/mol, $\Delta S^{\neq} = -10$ eu. A 4.2- and a 5.7-fold increase in the lutidine concentration caused a 13 and 8% decrease in k_1 for the tosylate and for the bromide, respectively. From Table I Hammett's ρ at 75° for changes in the leaving group is 1.67 (correlation coefficient 0.997).[9] Triphenylvinyl tosylate is 830-fold less reactive than 1-anisyl-2,2-diphenylvinyl tosylate at 120°.

Table I. Rates of Solvolysis of Triarylvinyl Arylsulfonates[a]

Ar$^{1\,b}$	Ar$^{2\,b}$	X	$10^5 k_1$, sec^{-1}
An	Ph	*p*-Me	2.72 ± 0.08
An	An	*p*-MeO	4.95 ± 0.18
An	An	*p*-Me	8.10 ± 0.60
An	An	H	14.1 ± 0.70
An	An	*p*-Br	35.5 ± 1.7
An[c]	An	*p*-NO_2	335.0 ± 11.2[d]
An[e]	An	*o*-NO_2	678.0 ± 10.0[d,f]

[a] $Ar_2^2C{=}C(Ar^1)OSO_2C_6H_4X$ in 70% acetone at 75°; [RX] = 0.008 M, [lutidine] = 1.6–1.7 × 10^{-2} M. [b] An = anisyl. [c] [RX] = 0.002 M, [lutidine] = 0.004 M. [d] Extrapolated from data in 90% acetone, assuming m = 0.41 as found for the tosylate (Table II). [e] [RX] = 0.005 M, [lutidine] = 0.02 M. [f] Extrapolated from data at lower temperatures.

In the solvolysis of trianisylvinyl tosylate in aqueous acetone k_1 increases with the water content (Table II) and a plot of log k *vs.* Grunwald–Winstein's Y[10] is linear, m = 0.41 (correlation coefficient 0.997). Solvolysis of 0.02 M tosylate in 70% acetone in the presence of 0.38 M Bu_4NBr gave over 95% of trianisylvinyl bromide.

Table II. Rates of Solvolysis of Trianisylvinyl Tosylate in Acetone–Water Mixtures at 75°[a]

Solvent, v/v	Y[b]	$10^5 k_1$, sec^{-1}
90% acetone	−1.86	1.23 ± 0.07
80% acetone	−0.67	4.43 ± 0.20
70% acetone	0.13	8.10 ± 0.60
60% acetone	0.80	15.1 ± 0.60

[a] [ROTs] = 0.008 M, [lutidine] = 0.016 M. [b] From ref 10b.

A rate-determining electrophilic "addition–elimination" of a proton from the water to the double bond (transition state **1**) is rejected since it requires a negative ρ value for substitution in the leaving group.[11] Attack on sulfur by hydroxide ion, formed by the reaction of lutidine with water, should be sensitive to the lutidine concentration and be slower on increasing the dielectric constant,[12] contrary to what was found. However, an O–S cleavage by water (transition state **2**) will show the same substituent and solvent effects as the rate-determining C–O cleavage (transition state **3**), since **2** is dipolar. The inertness of phenyl tosylate toward water,[5] the tosylate–bromide exchange, the lower reactivity of the β,β-diphenyl compared to the β,β-dianisyl derivative as found for the corresponding bromides,[1j,13] and the much higher reactivity of the α-anisyl compared to the α-phenyl group are compatible only with the vinyl-cationic transition state **3**.[14]

(1) (a) C. A. Grob and G. Cseh, *Helv. Chim. Acta*, **47**, 194 (1964); (b) C. A. Grob, J. Csapilla, and G. Cseh, *ibid.*, **47**, 1590 (1964); (c) G. Modena and U. Tonellato, *Chem. Commun.*, 1363 (1968); (d) G. Modena, U. Tonellato, and F. Naso, *ibid.*, 1676 (1968); (e) G. Capozzi, G. Melloni, G. Modena, and M. Piscitelli, *Tetrahedron Lett.*, 4039 (1968); (f) Z. Rappoport, A. Gal, and Y. Apeloig, *Israel J. Chem. Proc.*, 16p (1968); (g) S. J. Huang and M. V. Lessard, *J. Amer. Chem. Soc.*, **90**, 2432 (1968); (i) W. M. Jones and D. D. Maness, *ibid.*, **91**, 4134 (1969); (j) Z. Rappoport and A. Gal, *ibid.*, **91**, 5246 (1969); (k) P. E. Peterson and J. M. Indelicato, *ibid.*, **91**, 6194 (1969); (l) Z. Rappoport and Y. Apeloig, *ibid.*, **91**, 6734 (1969); *Israel J. Chem. Proc.*, **7**, 34p (1969).

(2) (a) S. A. Sherrod and R. G. Bergman, *J. Amer. Chem. Soc.*, **91**, 2115 (1969); (b) M. Hanack and T. Bassler, *ibid.*, **91**, 2117 (1969); (c) D. R. Kelsey and R. G. Bergman, *ibid.*, **92**, 228 (1970).

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

(4) P. J. Stang and R. Summerville, *J. Amer. Chem. Soc.*, **91**, 2117 (1969).

(5) C. A. Bunton and Y. H. Frei, *J. Chem. Soc.*, 1872 (1951).

(6) N. Frydman, R. Bixon, M. Sprecher, and Y. Mazur, *Chem. Commun.*, 1044 (1969).

(7) All new compounds reported here gave satisfactory analyses and showed spectral properties in agreement with the assigned structures.

(8) The compound was obtained only as an oil. See footnote 20 of ref 1j on this point.

(9) σ values given by H. H. Jaffé (*Chem. Rev.*, **53**, 191 (1951)) were used.

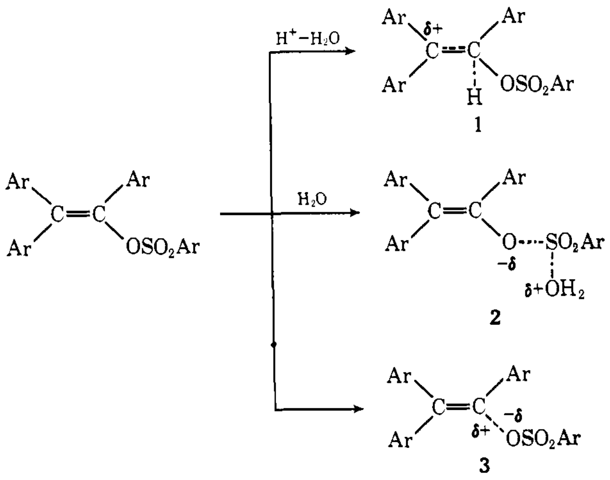
(10) (a) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 846 (1948); (b) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

(11) P. E. Peterson and J. M. Indelicato (*ibid.*, **90**, 6516 (1968)) used a similar argument to show that in formic acid several vinyl arylsulfonates solvolyze by the electrophilic addition–elimination route.

(12) K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1963, p 388.

(13) Z. Rappoport and A. Gal, unpublished results. The threefold rate difference between the β,β-dianisyl and the β,β-diphenyl derivatives points also to the absence of β-anisyl participation.

(14) A referee suggested that enough protons may be formed by the dissociation of the lutidinium ion, so that the addition–elimination forming the $AnCX^+$–$CHAn_2$ cation contributes to the reaction. This is in contradiction to several of the criteria discussed above. Moreover,



The m value is low for an S$_N$1 process and this may be due to the presence of the α-anisyl group[1j,16] or to considerable solvent participation in **3**.[17] The most likely explanation is, however, severe hindrance to solvation of **3**, since one lobe of the incipient cationic p orbital is directed toward the highly crowded *cis*-stilbene unit while the other lobe is shielded by the leaving group and the *cis* group.[18] It is interesting that the k_{OTs}/k_{Br} ratio of 32 is higher than those assigned to S$_N$2 processes,[19] but is still low compared to ratios in substrates reacting by the S$_N$1 mechanism, excluding neophyl and *p*-methoxyneophyl systems. Whether this is due to solvent participation, to "early" transition state for the tosylate, to reduced solvation, or to different electron donation by the leaving groups to the reaction center is not yet known.

Further studies in this and related systems are in progress and will be soon reported.

at 50% reaction of, *e.g.*, 0.008 M [RX] and 0.016 M [lutidine], $[H^+] \sim 5.8 \times 10^{-6}$ M (using $pK_{BH^+} = 5.77$ in 50% ethanol). At this acid concentration the pseudo-first-order rate coefficient for the addition of H_3O^+ to *p*-amino-α-bromostyrene in water at 50° is *ca.* 10^{-9} sec^{-1}.[15] The extrapolated (by the mY relationship) k_1 value in water at 50° for the solvolysis of trianisylvinyl brosylate is *ca.* 3×10^{-4} sec^{-1}, *i.e.*, five orders of magnitude faster, without taking into account that bromine stabilizes a positive charge better than brosylate. Since according to the addition–elimination mechanism the *p*-aminophenyl derivative should be *more* reactive than the anisyl derivative, the addition–elimination route is unimportant under our conditions.

(15) W. M. Schubert and G. W. Barfknecht, *J. Amer. Chem. Soc.*, **92**, 207 (1970).

(16) S. Winstein and R. Heck, *ibid.*, **78**, 4801 (1956).

(17) Neither solvent nor β-aryl participation is reflected in the stereochemistry of the solvolysis of triarylvinyl halides in acetic acid or in 80% ethanol.[11]

(18) The steric hindrance to solvation is lower in α-halostyrenes, and indeed α-bromostyrene[1a] and α-bromo-*p*-methoxystyrene show higher m values.[13] We want to emphasize that in an electrophilic solvent (*e.g.*, acetic acid), where solvation of the leaving group is important, the hindrance to solvation by the *cis*-aryl group is small and higher m values are expected.

(19) H. M. R. Hoffmann, *J. Chem. Soc.*, 6753, 6762 (1965).

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Transmetallations Involving Mercury(II) Salts. A Convenient Anti-Markovnikov Alkene Hydrobromination Procedure

Sir:

Although there has been considerable effort devoted toward investigations of the chemistry of organoboranes, there are relatively few known reactions which can efficiently functionalize all three boron-bound groups under mild conditions. Examples include certain oxidations[1] and carbonylations[2] of organoboranes and their reactions with silver oxide[3] and carboxylic acids.[4]

We should like to report herein that the reaction of primary trialkylboranes with certain mercury(II) salts results in a facile transmetallation and produces the corresponding primary alkyl mercury salts in excellent yield and under mild conditions.

$$R_3B + HgX_2 \longrightarrow RHgX + BX_3$$

Our research efforts in this direction were prompted by attempts to develop a convenient method for the *anti*-Markovnikov hydrohalogenation of olefins. While iodine has been shown to react with primary trialkylboranes in the presence of sodium hydroxide to cleave up to two of the boron-bound groups,[5] all other direct[6] and indirect[7] halogenations of trialkylboranes investigated to date have proven to be exceedingly inefficient. The successful transmetallation procedure involving mercury(II) salts, which is described below, provides the means of halogenating all three of the boron-bound groups

$$RCH{=}CH_2B \xrightarrow[THF]{BH_3} (RCH_2CH_2)_3B \xrightarrow{Hg(OAc)_2} RCH_2CH_2HgOAc$$

$$RCH_2CH_2HgOAc \xrightarrow{Br_2} RCH_2CH_2Br$$

When a THF solution of primary trialkylborane, obtained from the hydroboration of 1-alkene, was refluxed with 3 mol equiv of mercuric acetate, primary alkyl mercuric acetate was produced. The reaction can be followed by observing the disappearance of the insoluble mercuric acetate. The alkylmercuric acetate can be isolated at this stage by removal of the solvent and dissolution of the product mixture in refluxing pentane, resulting in the crystallization of the alkylmercuric acetate upon cooling. In the case of tri-*n*-hexylborane, a 73% yield of *n*-hexylmercuric acetate, mp 49–50° (lit.[8] mp 50°), is produced. While transmetallations involving organoboranes and compounds of mercury (*e.g.*, mercuric oxide) have been reported previously,[9] the yields of the dialkylmercurials produced suggest the transfer of only one or, at best, two of the alkyl groups from boron.

The alkylmercuric salts can be conveniently brominated[10] *in situ* to afford primary alkyl bromides in 71–86% yield. The results derived from similar studies of a number of organoboranes are summarized in Table I. From these results, it is clear that primary trialkylboranes give good yields of primary alkyl bromides in this one-flask sequence of reactions. Secondary trialkyl-

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(2) H. C. Brown, *Accounts Chem. Res.*, **2**, 65 (1969).

(3) H. C. Brown and C. H. Snyder, *J. Amer. Chem. Soc.*, **83**, 1001 (1961).

(4) H. C. Brown and K. Murray, *ibid.*, **81**, 4108 (1959).

(5) H. C. Brown, M. W. Rathke, and M. M. Rogić, *ibid.*, **90**, 5038 (1968).

(6) (a) J. R. Johnson, H. R. Snyder, and M. G. VanCampen, Jr., *ibid.*, **60**, 115 (1938); (b) L. H. Long and D. Dollimore, *J. Chem. Soc.*, 3902, 3906 (1953).

(7) J. Sharefkin and H. Banks, *J. Org. Chem.*, **30**, 4314 (1965).

(8) K. H. Slotta and K. R. Jacobi, *J. Prakt. Chem.*, **120**, 249 (1929).

(9) J. Honeycutt and J. Riddle, *J. Amer. Chem. Soc.*, **81**, 2593 (1959).

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