

# Solvolysis of Aryl-Substituted Vinyl Sulfonates by a Heterolytic Mechanism<sup>1</sup>

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**Abstract:** A number of triphenylvinyl sulfonates have been synthesized by the reaction of the acyltriazenes **2** with sulfonic acids. 1-Phenylvinyl fluorosulfonate has been synthesized by the addition of fluorosulfuric acid to phenylacetylene. The solvolyses of these sulfonic acid esters have been studied. Both product and kinetic evidence point to a simple S<sub>N</sub>1 ionization mechanism. The following have been eliminated as possible reaction mechanisms: (1) S<sub>N</sub>2 nucleophilic substitution by acetate ion; (2) acetate addition-elimination; (3) slow proton addition to the double bond with subsequent elimination (and rearrangement); and (4) nucleophilic attack on the sulfur of the sulfonate moiety. An "m" value of 0.56 was determined for the triphenylvinyl triflate by a Grunwald-Winstein relationship. The effect of solvent nucleophilicity on the ionization was shown to be small. The β-deuterium isotope effect was found to be  $k_H/k_D = 1.45 \pm 0.04$ . This value agrees quite well with secondary isotope effects for saturated systems involving cationic intermediates. The effect of β-phenyl substitution appears to be small, probably as a result of compensating effects. The resistance of substituted ethylenes to undergo S<sub>N</sub>1 solvolyses is discussed.

By analogy to saturated systems, the solvolysis of sulfonic acid esters of vinyl alcohols should furnish useful information about heterolyses from trigonal carbon.<sup>2,3</sup> At the inception of this work no mechanistic studies on the nucleophilic substitution of vinyl sulfonic acid esters had been reported. As of this writing, several such reports have appeared. These include reactions that have been clearly shown to go by an addition-elimination mechanism<sup>11</sup> (eq 1), ionizations that probably involve extensive intramolecular assistance<sup>12</sup> (eq 2), and ionizations for which participation is less likely (eq 3).<sup>13</sup>

At this time, we would like to present a full account of the synthesis and solvolysis of sulfonic acid esters **1a, b, c, d, and e**. Solvolyses of **1f** and **1g** have been reported by Stang and Summerville.<sup>13b</sup> Solvolyses of **1h** have been studied by Peterson and Indelicato.<sup>13c</sup>

(1) Taken from the Ph.D. Dissertation of D. D. Maness, University of Florida, 1969.

(2) For an excellent review, see H. G. Richey and J. M. Richey in "Carbonium Ions," Vol. II, G. A. Olah and P. von R. Schleyer, Ed., Interscience, New York, N. Y., in press. The authors express appreciation to Professor Richey for furnishing a preprint of his manuscript.

(3) Other reactions that occur by heterolysis at trigonal carbon include decomposition of vinyl diazonium ions<sup>4,5</sup> and substitutions on vinyl halides.<sup>6-10</sup>

(4) W. M. Jones and F. W. Miller, *J. Amer. Chem. Soc.*, **89**, 1960 (1967).

(5) M. S. Newman and A. E. Weinberg, *ibid.*, **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).

(6) C. A. Grob and G. Cseh, *Helv. Chim. Acta*, **47**, 194 (1964); C. A. Grob, J. Csapilla, and G. Cseh, *ibid.*, **47**, 1590 (1964); C. A. Grob and R. Spaar, *Tetrahedron Lett.*, 1439 (1968).

(7) L. L. Miller and D. A. Kaufman, *ibid.*, **90**, 7283-6515 (1968) (1968).

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

(9) M. Hanack and T. Bassler, *ibid.*, **91**, 2115 (1969).

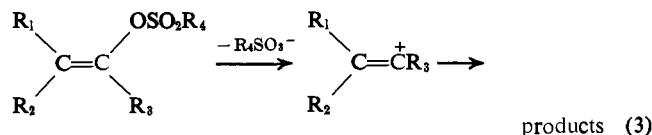
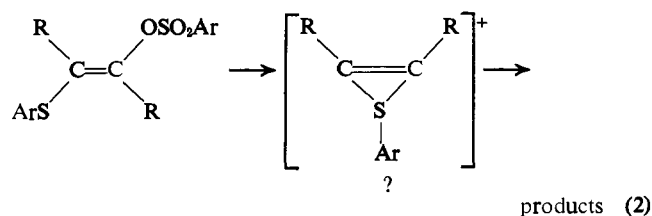
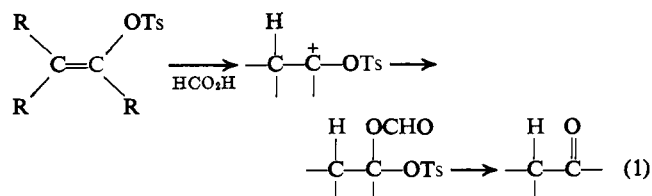
(10) (a) S. A. Sherrod and R. G. Bergman, *ibid.*, **91**, 2115 (1969);

(b) Z. Rappoport and A. Gal, *ibid.*, **91**, 5246 (1969).

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

(12) G. Capozzi, G. Melloni, G. Modena, and M. Piscitelli, *Tetrahedron Lett.*, 4039 (1968); G. Modena and U. Tonellato, *Chem. Commun.*, 1676 (1968); G. Modena, U. Tonellato, and F. Naso, *ibid.*, 1363 (1968).

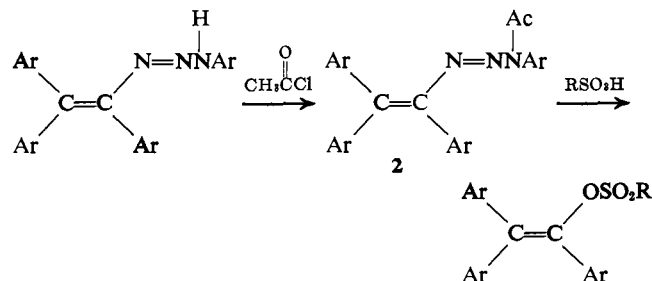
(13) (a) W. M. Jones and D. D. Maness, *J. Amer. Chem. Soc.*, **91**, 4314 (1969); (b) P. J. Stang and R. Summerville, *ibid.*, **91**, 4600 (1969); (c) P. E. Peterson and J. M. Indelicato, *ibid.*, in press. We are indebted to the authors for furnishing us with a preprint of their work.



**1a**, R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = C<sub>6</sub>H<sub>5</sub>; R<sub>4</sub> = F  
**b**, R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = C<sub>6</sub>H<sub>5</sub>; R<sub>4</sub> = CF<sub>3</sub>  
**c**, R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = C<sub>6</sub>H<sub>5</sub>; R<sub>4</sub> = *p*-tolyl  
**d**, R<sub>1</sub> = R<sub>2</sub> = H; R<sub>3</sub> = C<sub>6</sub>H<sub>5</sub>; R<sub>4</sub> = F  
**e**, R<sub>1</sub>, R<sub>2</sub> = H, D; R<sub>3</sub> = C<sub>6</sub>H<sub>5</sub>; R<sub>4</sub> = F  
**f**, R<sub>1</sub> = R<sub>2</sub> = H; R<sub>3</sub> = CH<sub>3</sub>; R<sub>4</sub> = CF<sub>3</sub>  
**g**, R<sub>1</sub>, R<sub>2</sub> = H, CH<sub>3</sub>; R<sub>3</sub> = CH<sub>3</sub>; R<sub>4</sub> = CF<sub>3</sub>  
**h**, R<sub>1</sub>, R<sub>2</sub> = H, alkyl; R<sub>3</sub> = C<sub>6</sub>H<sub>5</sub> or alkyl;  
 R = *p*-tolyl or *p*-C<sub>6</sub>H<sub>4</sub>Br

## Results

The triphenylvinyl sulfonates (**1a, b, c**) were synthesized from the acylated triphenylvinyltriazenes<sup>14</sup> **2**.



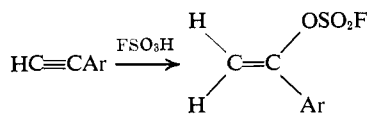
(14) Conversion of the acyltriazenes to the sulfonic acid ester most certainly also involves formation of a vinyl cation as evidenced by the

Table I. Rate Constants and Activation Parameters for Solvolyses of Vinyl Sulfonates<sup>a</sup>

Compd	Solvolysis medium	T, °C	10 <sup>4</sup> k, sec <sup>-1</sup>	H <sup>‡</sup> , kcal/mol <sup>†</sup>	S <sup>‡</sup> , eu <sup>‡</sup>	k <sub>rel</sub> <sup>b</sup>
1a <sup>d-f</sup>	AcOH	74.9	16.4	22.6 ± 0.2	-6.5 ± 0.7	42,000
	AcOH	67.0	7.64			
	AcOH with 2.5 × 10 <sup>-3</sup> M NaOAc	58.5	3.04			
	AcOH with 5.0 × 10 <sup>-3</sup> M NaOAc	58.6	3.14			
	AcOH	67.5	8.40			
	AcOD	67.5	8.05			
1b <sup>d,e</sup>	AcOH	25.0	0.0582 <sup>c</sup>	23.6 ± 0.8	-2.0 ± 2.3	81,000
	AcOH	72.2	29.8			
	AcOH	67.6	19.7			
	AcOH	59.4	7.66			
1b <sup>d,i</sup>	AcOH	25.0	0.112 <sup>c</sup>	23.8 ± 0.1	-20.5 ± 0.2	1
	EtOH	49.9	3.07			
	98% EtOH-H <sub>2</sub> O <sup>j,k</sup>	49.9	4.25			
	95% EtOH-H <sub>2</sub> O	49.9	7.25			
1c <sup>g,h</sup>	90% EtOH-H <sub>2</sub> O	49.9	16.4	23.8 ± 0.1	-20.5 ± 0.2	1
	AcOH	160.2	0.984			
	AcOD	160.2	1.06			
	AcOH	150.8	0.518			
	AcOH	139.0	0.213			
1d <sup>g,h</sup>	AcOH	25.0	1.38 × 10 <sup>-6c</sup>	25.4 ± 0.8	-0.42 ± 2.4	
	AcOH	71.8	5.62			
	AcOH	66.6	2.99			
	AcOH	61.5	1.69			
	AcOH	25.0	0.0145 <sup>c</sup>			

<sup>a</sup> In a prior communication<sup>13a</sup> the  $E_a$  for compounds 1a-c were given under the heading  $H^\ddagger$ . <sup>b</sup> Relative rates are reported for 25°. <sup>c</sup> The rate constants at this temperature were extrapolated from a knowledge of the activation parameters. <sup>d</sup> Solvolysis kinetics followed by uv. <sup>e</sup> About 10<sup>-4</sup> M in ester. Buffered with approximately 25 molar excess of sodium acetate. <sup>f</sup> The acetolysis of this compound was also followed titrimetrically. The rate constant was identical with that obtained by the uv method. <sup>g</sup> Acetolysis kinetics followed titrimetrically. <sup>h</sup> About 0.005 M in ester. Buffered with slight molar excess of sodium acetate. <sup>i</sup> About 6 × 10<sup>-5</sup> M in ester. Buffered with approximately 25 molar excess of sodium acetate. <sup>j</sup> 98% EtOH-H<sub>2</sub>O is 98 ml of absolute ethanol and 2 ml of water. <sup>k</sup> Gave essentially a quantitative yield of triphenylvinyl ethyl ether. Addition of small amounts of water resulted in an appropriate yield of the expected ketone (e.g., an 80% aqueous ethanol solution resulted in the production of 79% ethyl ether and 21% ketone). <sup>†</sup> The listed uncertainties are calculated from a least-squares analysis of the Arrhenius plot only.

Both spectral data and elemental analyses support the proposed structures. Attempts to synthesize 1-phenylvinyl fluorosulfonate (1d) failed at the triazene stage. Synthesis was finally achieved by addition of fluorosulfuric acid to phenylacetylene.<sup>15</sup> Although instability of this vinyl fluorosulfonate precluded



analysis, the following spectral data leave no doubt about the structure.

From the ir and nmr spectra (see Experimental Section) there is no question but that this is a phenylvinyl fluorosulfonate, but due to a lack of availability of appropriate model compounds we did not feel that the vinyl coupling constant ( $J = 3.5$  Hz) was definitive for the  $\alpha$ -phenyl structure. To obtain additional information, fluorosulfuric acid was added to phenylacetylene-*d*. The nmr spectrum of the product showed an aromatic multiplet centered at  $\tau$  2.65, a vinyl singlet at 4.45, and a vinyl doublet ( $J = 1.0$  Hz) centered at 4.63 with a relative area ratio of aromatic to vinyl of 5.6:1. The pattern of the vinyl region can only be

observed that the 2,2-di-*p*-tolyl-substituted triarylvinyltriazene gives rearranged products when treated with fluorosulfuric acid.

(15) (a) Addition of the acid in the absence of added tripropylammonium fluorosulfonate resulted in a small yield (ca. 5%) of  $\alpha$ -chlorostyrene. For a similar chloride abstraction from methylene chloride, see E. H. White, H. P. Tiware, and M. J. Todd, *J. Amer. Chem. Soc.*, **90**, 4734 (1968). This observation and the work of Noyce and Schiavelli<sup>15b</sup> support the intermediacy of a vinyl cation in this synthesis; (b) D. S. Noyce and M. D. Schiavelli, *J. Amer. Chem. Soc.*, **90**, 1023 (1968).

explained by  $\alpha$  substitution since the  $\beta$  isomer (*cis* or *trans*) would require collapse of the vinyl region to a singlet. The residual coupling ( $J = 1.0$  Hz) presumably arises from long-range coupling of a vinyl proton with either an *o*-phenyl proton or, as a referee suggested, the fluorine.

The assigned structure is further supported by treating the fluorosulfonate as a simple acid ester and calculating the expected vinyl hydrogen resonances by the method of Tobey.<sup>16</sup> Although the absolute position should differ from the calculated (due to a lack of appropriate models), the calculated relative positions of the vinyl protons should approximate the true value. The actual chemical shift between vinyl protons (0.18 ppm) is only consistent with  $\alpha$  substitution (calcd  $\Delta = 0.18$  ppm). The calculated separations for the two  $\beta$  isomers are 1.27 and 1.55 ppm for the *cis* and *trans*, respectively.

Acetolyses of 1a-e were carried out in dry acetic acid buffered with sodium acetate. After warming the solution to reaction temperature, the disappearance of the sulfonate was followed either titrimetrically or spectrophotometrically. The kinetics were cleanly first order (followed for at least three half-lives) and gave specific rate constants which are reported in Table I along with activation parameters.

Table II gives products obtained under the conditions in Table I.

Solvolyses of the triphenylvinyl sulfonic acid esters were also studied in deuterated acetic acid as well as

(16) S. W. Tobey, *J. Org. Chem.*, **34**, 1281 (1969).

**Table II.** Solvolysis Product Yields of Vinyl Sulfonates

Compd	Product	% yield
<b>1a</b>	Triphenylvinyl acetate	96 <sup>a</sup>
<b>1b</b>	Triphenylvinyl acetate	99 <sup>a</sup>
<b>1b</b>	Triphenylvinyl ethyl ether	100 <sup>b</sup>
<b>1c</b> (139.0°)	Triphenylvinyl acetate	48 <sup>a,c</sup>
<b>1c</b> (150.8°)	Triphenylvinyl acetate	42 <sup>a,c</sup>
<b>1c</b> (160.2°)	Triphenylvinyl acetate	39 <sup>a,c</sup>
<b>1d</b>	1-Phenylvinyl acetate	87 <sup>a</sup>

<sup>a</sup> Acetolysis. <sup>b</sup> Ethanolysis. In absolute ethanol. <sup>c</sup> The low acetate yields were paralleled by a corresponding low yield of titratable tosylate ion. Triphenylvinyl acetate is stable to reaction conditions.

mixtures of alcohol and water. The kinetic results are recorded in Table I and products are given in Table II.

For  $\beta$ -deuterium isotope studies, 1-phenyl-2-*d*-vinyl fluorosulfonate was synthesized by adding fluorosulfuric acid to phenylacetylene-*d*. From the nmr (discussed previously) the product consisted of a mixture of the *cis*- and *trans*-labeled compounds in about equal amounts. From four different runs,  $k_H/k_D$  was found to equal  $1.45 \pm 0.04$ .

### Discussion

In addition to a simple  $S_N1$  heterolysis there are at least four mechanistically distinguishable pathways that could give the products observed from the above solvolyses (vinyl acetate, ether, etc.). These possibilities include (1)  $S_N2$  substitution; (2) acetate addition followed by sulfonate elimination; (3) an acid addition-elimination mechanism corresponding to eq 1; and (4) nucleophilic attack on the sulfonate sulfur.

The first two possibilities can be readily dispensed with by the single observation that the rate of solvolysis is independent of sodium acetate concentration. Either mechanism should require a kinetic expression that is first order in the nucleophile. Both the magnitude and the direction of the  $\beta$ -deuterium isotope effect further support this conclusion.

The third possibility—an acid addition mechanism similar to that proposed by Peterson and Indelicato<sup>11</sup> (eq 1)—could also explain the solvolysis products. This possibility was attractive not only because of the work of Peterson and Indelicato but also because the literature is abundant with precedents for slow proton addition to multiple bonds. However, both theoretical considerations<sup>17</sup> and experimental data<sup>18</sup> predict that a mechanism in which the slow step is proton addition should show a large solvent isotope effect (up to about 7).<sup>19a</sup> From the results given in Table I, it is clear that the ratio  $k_{SOH}:k_{SOD}$  for both the fluorosulfonate and the tosylate is close to unity. The absence of a solvent isotope effect can be taken as strong evidence against the mechanism (eq 1) that was shown by Peterson and Indelicato for the solvolysis of cyclohexenyl and *cis*-2-buten-2-yl tosylates. It is particularly interesting that solvolysis of the triphenylvinyl tosylate shows no isotope effect since the large negative entropy of

(17) C. A. Bunton and V. J. Shiner, *J. Amer. Chem. Soc.*, **83**, 3214 (1961).

(18) For lead references, see D. S. Noyce and R. M. Pollack, *ibid.*, **91**, 120 (1969), and ref 15b.

(19) (a) The maximum kinetic solvent isotope effect expected for a slow proton addition in an acetic acid system may be calculated from the O-H and O-D stretching vibrations;<sup>19b</sup> (b) W. Weltner, Jr., *J. Amer. Chem. Soc.*, **77**, 3941 (1955).

activation is not only reminiscent of those obtained by Noyce and Schiavelli<sup>15b</sup> for acid additions to acetylenes but also because the entropy of activation seems to be so far out of line with that of other systems.<sup>20</sup> At the present time, we have no explanation for this.<sup>23</sup>

Further evidence against an acid addition mechanism is afforded by the results of the solvolysis of triphenylvinyl triflate in ethanol-water mixtures. Grunwald and Winstein Y values predict that 98% aqueous ethanol should possess an ionizing power similar to that of acetic acid.<sup>24</sup> A comparison of the rates of solvolysis of the vinyl triflate (**1b**) in these solvents gives a rate ratio of 1.6. Similar rates would not be expected for the addition-elimination mechanism.<sup>10a</sup> The ratio  $k_{EtOH}/k_{AcOH}$  can also be taken as a measure of the effect of solvent nucleophilicity on the ionization process.<sup>25</sup> The small value obtained in this system compares well with that obtained from the solvolysis of aryl sulfonates of saturated secondary alcohols<sup>25</sup> which are only slightly dependent on nucleophilicity. An “*m*” value of 0.56 was determined from a plot of the kinetic data listed in Table I for the triphenylvinyl triflate (**1b**). This value is reminiscent of the “*m*” value obtained for saturated secondary sulfonates<sup>25</sup> and is also very similar to that recently reported by Stang and Summerville<sup>13a</sup> for the heterolytic cleavage of isopropenyl triflate (**1f**) ( $m = 0.52$ ). All of these facts point to a rather normal solvolytic ionization in these systems with a substantial degree of positive charge on the vinyl carbon in the transition state.

To explain the vinyl acetate product by an initial nucleophilic attack on the sulfur atom, acylation of the ketone or its enol would be required.<sup>26</sup> Thus, attack on sulfur, the fourth possibility, was readily excluded by the observation that acetolysis of triphenylvinyl fluorosulfonate in the presence of  $\alpha,\alpha$ -ditolylacetophenone produced only triphenylvinyl acetate. No crossover acetate was observed. This conclusion is further supported by the inertness of aryl triflate to typical solvolysis conditions.<sup>13b</sup>

Positive support for an  $S_N1$  heterolytic cleavage is found in the observed  $\beta$ -deuterium isotope effect ( $k_H/k_D = 1.45$ ).<sup>27</sup> This value is in excellent agreement with secondary isotope effects reported in both saturated and unsaturated systems. For example, Shiner and

(20) The large negative entropy is particularly interesting since both Streitwieser<sup>21</sup> and Schleyer<sup>22</sup> have found that in saturated systems the principal factor contributing to the difference in the rates of solvolyses of triflates and tosylates results from activation energy differences rather than activation entropy differences. This disparity between saturated and unsaturated systems is also suggested by the data available for the 1-phenylvinyl fluorosulfonate and tosylate<sup>13c</sup> although this is uncertain since the solvents used for the two systems are different.

(21) A. Streitwieser, Jr., C. L. Wilkins, and E. Kiehlmann, *J. Amer. Chem. Soc.*, **90**, 1598 (1967).

(22) T. M. Su, W. Sliwinski, and P. von R. Schleyer, *ibid.*, **91**, 5386 (1969). We are indebted to the authors for furnishing us with a preprint of their work.

(23) The difference in rates of solvolyses of the tosylate and the triflate further argues against an acid addition mechanism in which proton addition is the slow step.<sup>11</sup>

(24) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 846 (1948).

(25) A. Streitwieser, Jr., “Solvolytic Displacement Reactions,” McGraw-Hill, New York, N. Y., 1962.

(26) S. Oae, T. Kukumoto, and R. Kiritani, *Bull. Chem. Soc. Jap.*, **36**, 346 (1963); S. Oae, *ibid.*, **38**, 765 (1965); and D. R. Christman and S. Oae, *Chem. Ind. (London)*, 1251 (1959).

(27) (a) The absence of an isotope effect in the acid-promoted hydration of styrene and styrene- $\beta,\beta$ -*d*<sub>2</sub><sup>27b</sup> further argues against the possibility of an acid addition mechanism in this system; (b) W. M. Schubert and B. Lamm, *J. Amer. Chem. Soc.*, **88**, 120 (1966).

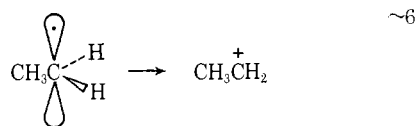
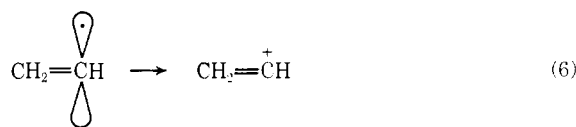
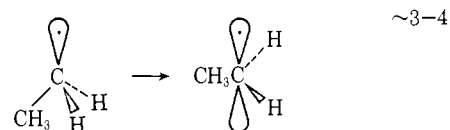
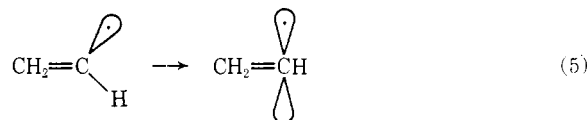
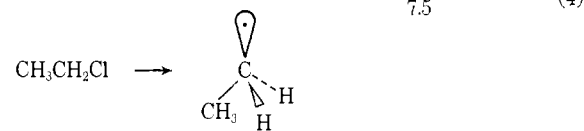
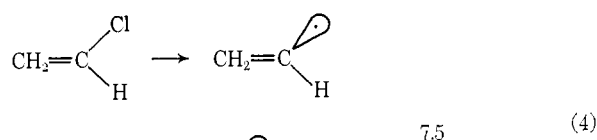
Jewett<sup>28</sup> report a  $\beta$ -deuterium isotope effect of 1.44 for the solvolysis of *cis*-4-*t*-butylcyclohexylbrosylate-*trans*-2-*d* which has a dihedral angle of 180° between the deuterated position and the developing p orbital. Noyce and Schiavelli<sup>15b</sup> estimate values of 1.50 and 1.44 for the  $\beta$ -deuterium isotope effect in the acid-catalyzed hydration of phenylacetylene and *p*-methoxyphenylacetylene, respectively. Finally, Stang and Summerville give a  $\beta$ -deuterium isotope effect of 1.20 for the solvolysis of *cis*-2-buten-2-yl triflate.<sup>29</sup>

By comparing the rates of solvolysis of 1-phenylvinyl fluorosulfonate with triphenylvinyl fluorosulfonate it is seen that substitution of two  $\beta$ -phenyl rings increases the rate of ionization (at 25°) by a factor of only 4. Miller and Kaufman<sup>7</sup> observed a similar effect (actual retardation to about 0.3) for the corresponding bromides. In view of the dramatic acceleration arising from  $\beta$ -phenyl substitution in aliphatic systems<sup>30</sup> (presumably resulting from relief of strain) and since there would certainly be strain relief upon ionization of the triphenylvinyl system, we must agree with Miller and Kaufman that there must be a rather powerful countereffect (probably steric hindrance to solvation) that fortuitously just about cancels strain relief. The low value for  $k_{\text{EtOH}}/k_{\text{AcOH}}$  (1.6) for **1b** supports the idea of relatively little solvent involvement at the substrate carbon during the ionization from the triarylvinylium systems.

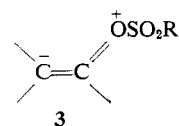
From our work as well as that of many others, substituted ethylenes undergo solvolyses several powers of ten slower<sup>31</sup> than their saturated counterparts. Factors leading to this sluggishness have been speculated upon<sup>32</sup> and have been recently discussed in particular detail by Miller and Kaufman.<sup>7</sup> Using vinyl and ethyl chlorides as models (because necessary information is not available for other systems) we would like to carry the general approach of Miller and Kaufman<sup>7</sup> one step further by dissecting the saturated and unsaturated hypothetical gas-phase ionizations according to eq 4–6.

As has been pointed out by Miller and Kaufman,<sup>7</sup> the energy difference between the first steps (from bond dissociation energies) should yield information about the importance of resonance of the nonbonded pair with the double bond. The small differences between saturated and unsaturated halides (*e.g.*, 2.5 kcal for the chloride)<sup>33</sup> led them to conclude that resonance is not very important. Although the data available to Miller and Kaufman for the chloride have recently been revised (to 7.5 kcal)<sup>34</sup> the difference is no larger than cases (*e.g.*, alkyl substituted)<sup>34</sup> without nonbonded electrons and we are therefore inclined to agree that

energy  
difference, kcal



resonance is unimportant. This conclusion is supported by our observation that the triflate:tosylate rate ratio for the triphenylvinyl system (*ca.* 10<sup>4.9</sup>) is in the same range as a number of saturated systems (10<sup>4.3–10<sup>5.3</sup></sup>).<sup>22</sup> Since resonance form **3** should contribute more to the vinyl tosylate than the triflate, a major contribution from resonance of the nonbonded pair should increase the triflate:tosylate ratio.



Assuming resonance of the nonbonded pair to be unimportant, the difference in energy required to convert the vinyl and saturated chlorides into linear and planar radicals (total of steps 4 and 5) should yield information about the effect of removing the leaving group from different energy orbitals (*sp*<sup>2</sup> *vs.* *sp*<sup>3</sup>) balanced by rehybridization of the bonding electrons on the reacting carbon<sup>35</sup> (possibly modified by eclipsing effects). This should be as valid as the theoretical conclusions of Hinze and Jaffé<sup>36</sup> that the ionization potential of an electron from the “p” orbital of a trigonal carbon is the same as that of an electron from the “p” orbital of a digonal carbon. In other words, steps 4 plus 5 should essentially isolate the effects of resonance and hybridization (including changes) at the

(28) V. J. Shiner and J. G. Jewett, *J. Amer. Chem. Soc.*, **86**, 945 (1964).

(29) The difference between the deuterium isotope effect reported by Stang and Summerville and the values that we found is surprising since the similarity in “*m*” values for the two systems suggests that the degree of ionization in the transition state is similar.

(30) H. C. Brown, R. Bernheimer, and K. J. Morgan, *J. Amer. Chem. Soc.*, **87**, 1280 (1965).

(31) Using various models, rate differences of 10<sup>4</sup>–10<sup>10</sup> have been estimated.<sup>2,10b,11,13a,13c</sup> From the work reported in this paper one of the models<sup>13a</sup> is obviously poor; for MO treatments of the vinyl cation, see R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. von R. Schleyer, *ibid.*, **91**, 3350 (1969), and references therein.

(32) For lead references, see ref 2 and 7.

(33) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

(34) S. W. Benson, “Thermochemical Kinetics,” Wiley, New York, N. Y., 1968, p 215.

(35) Rehybridization would favor solvolysis in the vinyl system since more energy is gained by rehybridizing two *sp*<sup>2</sup> orbitals to *sp* than three *sp*<sup>3</sup> to *sp*<sup>2</sup>.<sup>36,37</sup>

(36) J. Hinze and H. H. Jaffé, *J. Amer. Chem. Soc.*, **84**, 540 (1962).

(37) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **11**, 96 (1960).

reaction terminus. Although this total energy difference is not known with accuracy it probably does not exceed 10–12 kcal (for the chloride) since the bent vinyl radical is probably not more than 3–4 kcal lower energy than the linear form<sup>39–41</sup> and the planar and pyramidal saturated radicals are about the same energy.

Finally, a comparison of the total energy of all three steps should give a measure of resonance effects, rehybridization effects, and “other” electronic effects. From the “best” values available for heats of formation,<sup>42</sup> the total energy for the gas-phase ionization of vinyl chloride is about 17 kcal greater than that for ethyl chloride.<sup>43</sup>

Thus, from this analysis, resonance of the nonbonded pair does not contribute much to the slow ionization, the energy of the orbital from which ionization takes place—even when compensated by the energy gain resulting from rehybridization—makes a major contribution to electronic factors that retard the reaction and, finally, “other” effects may also make a substantial contribution (up to one-third for the chloride). These additional effects can be looked on as any factors that make it more difficult to remove an electron from the linear vinyl radical than from the planar ethyl radical. Possible contributors include differences in hyperconjugation (two  $sp^2$  bonded hydrogens *vs.* three  $sp^3$ ), differences in the electronegativity of  $CH_2$  and  $CH_3$  (basically, the difference in the electronegativity of the orbital originating at the  $CH_2$  or  $CH_3$  and contributing to the  $\sigma$  bond between carbons), and differences in the ability of two electrons in a  $\sigma$  bond (bonded hydrogens) and two electrons in an orthogonal double bond to stabilize a carbonium ion. At this time, we have no basis for evaluating the relative importance of these factors.

Finally, in a solvolytic reaction, hindrance to back-side solvation of the developing carbonium ion may make a real contribution to the solvolytic sluggishness of vinyl systems.<sup>7</sup> The strongest argument for this as an important effect rests on molecular models which show a very unfavorable steric situation for back-side

(38) Although the esr spectrum of vinyl radical has been measured and the rate of equilibration between the two bent forms determined,<sup>39</sup> the mechanism apparently involves tunneling and, as a result, only a minimum energy of 2 kcal could be assigned to the energy required to form the linear species. Recent calculations on the propenyl radical<sup>40</sup> support the conclusion that the energy difference between bent and linear radicals does not exceed a few kilocalories but the actual value has not, to our knowledge, been measured. The reason that the difference between vinyl and alkyl is so small probably rests on the fact that considerably more energy is gained by rehybridizing two  $sp^2$  orbitals to  $sp$  than three  $sp^3$  to  $sp^2$ .<sup>36,37</sup>

(39) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(40) R. M. Kopchik and J. A. Kampmeier, *J. Amer. Chem. Soc.*, **90**, 6733 (1968).

(41) For a good discussion on the problems associated with arriving at a maximum for this difference, see G. D. Sargent and M. W. Browne, *ibid.*, **89**, 2788 (1967).

(42) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, “Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions,” National Bureau of Standards Circular 26, U. S. Government Printing Office, Washington, D. C., 1969.

(43) Miller and Kaufman<sup>7</sup> point out a difference in ionization potentials between vinyl and ethyl radicals of 0.7 eV (16.1 kcal). Using the reported ionization potential of vinyl radical (9.45 eV) the heat of formation of vinyl cation is calculated to be 283 kcal/mol—some 14 kcal higher than the “best” value. This rather large difference apparently arises from the methods used to determine these values (electron impact for ionization potential, photoionization for appearance potentials). In the present discussion, the heats of formation used for both vinyl and ethyl cations were calculated from appearance potentials which were determined by photoionization.

solvation of the vinyl carbon from which the leaving group departs (*e.g.*, examine  $\alpha$ -phenylvinyl). Unfortunately, this is only a model of the ground state and it is difficult to extrapolate to a transition state. More experimental work is needed to test the honesty of the molecular models.

## Experimental Section

**General.** Melting points were taken in a Thomas Hoover capillary melting point apparatus. Melting points and boiling points are uncorrected. A Beckman Model IR10 was used to obtain the infrared spectra. Nuclear magnetic resonance spectra were obtained on a Varian A-60 high-resolution spectrometer. Chemical shifts are given as parts per million from tetramethylsilane. Ultraviolet spectra were recorded on a Cary 15 spectrophotometer. The Hitachi Perkin-Elmer RMU-6E mass spectrometer was used to record mass spectra. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

**Triphenylethylene.** Triphenylethylene was prepared by the method of Adkins and Zartman.<sup>44</sup> The product, mp 68°, was obtained in 61% yield (lit.<sup>44</sup> mp 68–69°).

**Bromotriphenylethylene.** Bromotriphenylethylene was prepared according to the procedure of Koelsch.<sup>45</sup> After recrystallization from ethanol, the yield was 87% of a white solid, mp 114–115.5° (lit.<sup>45</sup> mp 114–115.5°).

**Phenyl Azide.** The method of Lindsay and Allen<sup>46</sup> was used to prepare the azide from phenyl hydrazine. The distillation of the pale yellow oil was performed at pressures below 1 mm. At these pressures the azide distilled at room temperature and was collected in a Dry Ice–acetone trap (72% yield).

**1-(Triphenylvinyl)-3-phenyl-1-triazene.** The procedure of Miller<sup>47</sup> was used to convert the bromide to the triazene. A dry three-necked, 500-ml flask was fitted with a reflux condenser and a septum-covered dropping funnel. This apparatus was flamed under a stream of dry nitrogen and charged with 1.9456 g (0.08 mol) of magnesium turnings, 26.792 g (0.08 mol) of bromotriphenylethylene, an iodine crystal, and a magnetic stirring bar. Dry ether (200 ml) was syringed into the dropping funnel. Sufficient ether was rapidly added to the reaction vessel to effect solution of the bromide. The remaining ether was added after the reaction had begun. Consumption of the magnesium typically was complete after 24 hr at room temperature, at which time 9.520 g (0.08 mol) of phenyl azide in 100 ml of dry ether was added dropwise to the grey solution. Upon addition of the azide the solution underwent a color change from yellow to deep red. After stirring at room temperature for 3 hr, hydrolysis was effected by addition of 100 ml of an ammonium chloride–ammonia stock solution at 0°. (The stock solution consisted of 10 g of ammonium chloride, 33 ml of ammonium hydroxide, and sufficient distilled water to make 100 ml total volume.) A yellow precipitate formed which slowly dissolved in the ether layer. The ether layer was dried over magnesium sulfate and evaporated under a stream of dry nitrogen. The resulting dark red oil was refrigerated after addition of 50 ml of pentane, and after several days a yellow solid was formed. The yellow triazene was filtered, powdered, washed with small amounts of cold pentane, and dried under vacuum. The resulting yellow powder, mp 101–103° with gas evolution, was obtained in 59% yield (17.80 g) (lit.<sup>47</sup> mp 102–103°). The triazene was refrigerated under nitrogen and was stable indefinitely under these conditions.

**1-(Triphenylvinyl)-3-acetyl-3-phenyl-1-triazene.** 1-(Triphenylvinyl)-3-phenyl-1-triazene, 4.75 g (0.01 mol), is dissolved in 100 ml of dry  $CCl_4$  in a three-necked flask fitted with a reflux condenser and rubber septums. The reaction vessel is surrounded with an ice bath. *Via* syringes, 1.727 g (0.022 mol) of acetyl chloride and 2.230 g (0.022 mol) of dry triethylamine are introduced simultaneously through the rubber septums. The reaction color changes from bright yellow to a pale yellow, and a solid (triethylammonium chloride) precipitates. The reaction is maintained at 0° for 1 hr, and then is stirred overnight at room temperature. The  $CCl_4$  solution is washed three times with 100-ml portions of distilled water, dried over magnesium sulfate, and then evaporated on a rotary

(44) H. Adkins and W. Zartman, “Organic Syntheses,” Coll. Vol. II, Wiley, New York, N. Y., 1943, p 606.

(45) C. F. Koelsch, *J. Amer. Chem. Soc.*, **54**, 2045 (1932).

(46) R. O. Lindsay and C. R. H. Allen, “Organic Syntheses,” Coll. Vol. III, Wiley, New York, N. Y., 1955, p 710.

(47) F. W. Miller, Ph.D. Dissertation, University of Florida, 1966.

evaporator. The resulting crude, light yellow solid is crystallized from methylene chloride-pentane solvent system (77% yield). The triazene, mp 134.5–135.5° with decomposition and gas evolution, may be stored at room temperature indefinitely without decomposition.

The infrared spectrum (KBr) exhibited peaks at 3.58, 5.94 (carbonyl), 6.34, 6.71, 6.84, 6.90, 7.32, 7.45, 8.41, 8.70, 8.98, 9.11, 9.29, 9.70, 9.84, 9.91, 10.5, 10.8, 11.6, 12.5, 12.9, 13.1 (doublet), 14.2, 14.5, 15.3, 16.4, 17.3, 18.4, 19.7, 21.9, and 24.4  $\mu$ . The ultraviolet spectrum in  $\text{CCl}_4$  showed an absorption maximum at 333  $m\mu$  ( $\log \epsilon = 4.176$ ). The nmr spectrum in  $\text{CCl}_4$  showed a phenyl multiplet centered at  $\tau$  2.88 and a methyl singlet at 7.88 with relative area ratios of 20.3:3. The mass spectrum showed *m/e* peaks at 420 (molecular ion), 390, 348, 270, 256, 166, 135, 118, 77 (parent peak), and 43.

*Anal.* Calcd for  $\text{C}_{25}\text{H}_{23}\text{N}_3\text{O}$ : C, 80.57; H, 5.51. Found: C, 80.40; H, 5.62.

**Triphenylvinyl Fluorosulfonate.** A 1-l., three-necked flask is fitted with a low-temperature thermometer, a dropping funnel, and a drying tube. This apparatus is charged with 400 ml of dry methylene chloride, 2.87 ml (0.05 mol) of fluorosulfuric acid, and a magnetic stirring bar. All additions to the reaction vessel are made while nitrogen is sweeping the apparatus. The reaction mixture is cooled with a Dry Ice-acetone bath. 1-(Triphenylvinyl)-3-acetyl-3-phenyl-1-triazene, 4.170 g (0.01 mol), dissolved in a minimum amount of dry methylene chloride is added dropwise. A purple reaction mixture is immediately obtained, and gas evolution is noted. The reaction is allowed to proceed at this temperature for 1 hr, after which the reaction had become grey in color. The mixture was allowed to warm up, and when the temperature reached  $-27^\circ$ , methanol was added to decompose the excess fluorosulfuric acid. After addition of the methanol, the reaction mixture was poured onto ice, washed well with water, and dried over magnesium sulfate. Upon removal of the methylene chloride on a rotary evaporator, a crude white solid remained, consisting of triphenylvinyl fluorosulfonate and acetanilide. Rapid passage of this mixture through a short silica gel column using pentane as the eluent gave good separation of the two components. (Some degradation of the fluorosulfonate occurs on the column.) The fluorosulfonate is eluted from the column in the initial fractions and upon solvent removal is obtained as a white solid in 71% yield, mp 108–109° dec. The fluorosulfonate may be further purified by crystallization from a methylene chloride-pentane solvent system and may be stored for several months to a year under refrigeration without significant decomposition.

The infrared spectrum (KBr) exhibited peaks at 3.27, 3.30, 3.34, 5.14, 5.34, 5.52, 6.05, 6.28, 6.36, 6.73, 6.96 (sulfonyl stretch for fluorosulfonate),<sup>48</sup> 7.18 (shoulder), 7.58, 8.16 (sulfonyl stretch for fluorosulfonate), 8.48, 8.62, 9.31, 9.66, 10.0, 10.5, 10.8, 10.9, 11.5, 11.7, 11.8, 12.4, 12.8, 13.1, 14.2, 15.4, 15.7, 15.9, 16.2, 16.8, 18.0, 18.5, and 21.6  $\mu$ . The ultraviolet spectrum obtained in acetic acid showed an absorption maximum at 277  $m\mu$  ( $\log \epsilon = 4.042$ ). The nmr spectrum of the fluorosulfonate in  $\text{CDCl}_3$  showed two aromatic multiplets. One was centered at  $\tau$  2.67 and the other at 2.91. The relative area ratio was 2.15:1. The mass spectrum showed *m/e* peaks at 355 (molecular ion), 272 (parent peak), 256, 244, 166, 135, 93, and 77.

*Anal.* Calcd for  $\text{C}_{20}\text{H}_{15}\text{SO}_3\text{F}$ : C, 67.70; H, 4.23. Found: C, 67.91; H, 4.29.

**Triphenylvinyl Trifluoromethanesulfonate.** The method described for the preparation of triphenylvinyl fluorosulfonate was used to synthesize this trifluoromethanesulfonate (triflate) using trifluoromethanesulfuric acid instead of fluorosulfuric acid. The product obtained was a white solid (47%), mp 83.5–84° dec.

The infrared spectrum (KBr) gave absorption peaks at 3.28, 3.33, 6.10, 6.28, 6.37, 6.70, 6.92, 7.06 (sulfonyl stretch for trifluoromethanesulfonate), 8.14 and 8.26 (sulfonyl stretch), 8.63, 8.83, 9.29, 9.64, 10.1, 10.7, 10.8, 11.6, 12.1, 13.0, 14.2, 14.4, 14.8, 15.5, 16.3, 17.3, 17.9, 19.2, 20.0, and 21.5  $\mu$ . The ultraviolet spectrum of the triflate in acetic acid exhibited an absorption maximum at 267  $m\mu$  ( $\log \epsilon = 4.011$ ). The nmr spectrum of the triflate in  $\text{CCl}_4$  showed an aromatic multiplet centered at  $\tau$  2.62 and one centered at 2.94. The mass spectrum showed *m/e* peaks at 404 (molecular ion), 272, 256, 244, 266, 77, and 69 (parent peak).

*Anal.* Calcd for  $\text{C}_{21}\text{H}_{15}\text{SO}_3\text{F}_3$ : C, 62.37; H, 3.74; S, 7.93. Found: C, 62.19; H, 3.87; S, 8.02.

**Triphenylvinyl Tosylate.** A modification of the procedure for the synthesis of triphenylvinyl fluorosulfonate was used to prepare

this tosylate. The appropriate triazene was allowed to react for 1 hr with *p*-toluenesulfonic acid monohydrate at  $10^\circ$ . The acetanilide was conveniently removed by washing the crude solid several times with hot (*ca.* 60°) water. Crystallization of the tosylate from petroleum ether (bp 65–110°) afforded a 47% yield of a white solid, mp 169° (lit.<sup>47</sup> mp 153°). Because of this difference in the melting points and because of the different methods of preparation, the tosylate was fully characterized.

The infrared spectrum (KBr) exhibited peaks at 3.30 (multiplet), 6.10, 6.28, 6.40, 6.74, 6.94, 7.13, 7.35, 7.76, 7.98, 8.40–8.66 (multiplet characteristic of tosylates), 9.11, 9.32, 9.57, 9.86, 10.6, 11.0, 12.3, 12.8, 13.1 (doublet), 14.1, 15.0, 15.8, 15.9, 16.2, 16.4, 17.2, 17.9, 18.4, and 21.5  $\mu$ . The nmr spectrum of the tosylate in  $\text{CCl}_4$  showed an aromatic multiplet centered at  $\tau$  2.91 and a methyl singlet at 7.73 with a relative area ratio of 21.3:3. The ultraviolet spectrum taken in acetic acid showed an absorption maximum at 274  $m\mu$  ( $\log \epsilon = 4.096$ ).

*Anal.* Calcd for  $\text{C}_{27}\text{H}_{25}\text{SO}_3$ : C, 76.03; H, 5.20; S, 7.52. Found: C, 76.27; H, 5.37; S, 7.65.

**1-Phenylvinyl Fluorosulfonate.** A 300-ml, three-necked flask was swept with nitrogen. This flask was fitted with a drying tube and sealed with rubber septums. Dry methylene chloride, 100 ml, a magnetic stirring bar, and fluorosulfuric acid, 2.87 ml (0.050 mol), were introduced into the reaction vessel. Tripropylamine, 1.90 ml (0.010 mol), in 20 ml of methylene chloride and dried over magnesium sulfate, was added *via* a syringe. The reaction mixture was now cooled with a Dry Ice-acetone bath. Freshly distilled phenylacetylene, 2.20 ml (0.01 mol), dissolved in 10 ml of methylene chloride and dried over magnesium sulfate, was added *via* a syringe. The reaction was stirred at *ca.*  $-78^\circ$  for 5 hr. The reaction mixture was poured onto an iced, saturated sodium acetate solution. The methylene chloride layer was washed three times with 100-ml portions of saturated sodium acetate solution, dried over magnesium sulfate, and evaporated under a stream of nitrogen. Unreacted phenylacetylene, as indicated by an infrared spectrum on the pale yellow oil, was removed under a stream of nitrogen. The yellow liquid was passed through a low activity grade silica gel column using pentane as the eluent. The initial fractions contained the yellow fluorosulfonate (46% yield). Because of the instability of this compound, further purification was not feasible, but it could be stored in a freezer under a nitrogen atmosphere for several weeks without significant decomposition.

The infrared spectrum (neat) exhibited peaks at 3.30, 6.09, 6.36, 6.74, 6.94 (sulfonyl stretch), 8.02, 8.24 (sulfonyl stretch), 8.45, 9.25, 9.38, 9.78, 10.0, 10.42, 11.2, 11.9, 12.5, 13.0, and 14.2  $\mu$ . The ultraviolet spectrum of the fluorosulfonate in acetic acid showed an absorption maximum at 266  $m\mu$  ( $\log \epsilon = 3.653$ ). The nmr spectrum taken in  $\text{CCl}_4$  showed an aromatic multiplet centered at  $\tau$  2.66, a vinyl doublet centered at 4.45 ( $J_{AB} = 3.5$  Hz), and a vinyl doublet of doublets centered at  $\tau$  4.63 ( $J_{AB} = 3.5$  Hz,  $J_{AC} = 1.0$  Hz) with relative area ratios of 5.45:1.05:1.0. The mass spectrum taken at 20 eV showed *m/e* peaks at 202 (molecular ion), 119, 102 (parent peak), and 77.

**1-Phenylvinyl-2-*d*<sub>1</sub> Fluorosulfonate.** A modification of the procedure used to prepare 1-phenylvinyl fluorosulfonate was employed to synthesize this fluorosulfonate. Fluorosulfuric acid was added to ethynyl-*d*-benzene prepared according to the method of Noyce.<sup>151</sup> (Analysis by nmr showed the ethynyl benzene to be *ca.* 99% mono-deuterated.)

The light yellow oil was obtained in 41% yield. The infrared spectrum (neat) was essentially identical with that of 1-phenylvinyl fluorosulfonate. An additional peak appeared at 4.16  $\mu$  which could be assigned to C-D stretch. The nmr spectrum taken in  $\text{CCl}_4$  showed an aromatic multiplet centered at  $\tau$  2.65, a vinyl singlet at  $\tau$  4.45, and a vinyl doublet centered at  $\tau$  4.63 with a relative area ratio of aromatic to vinyl of 5.6:1.

**Triphenylvinyl Acetate.** Triphenylvinyl acetate was prepared according to the method of Barnes.<sup>49</sup> The resulting colorless solid was crystallized from petroleum ether (bp 65–110°) to give pure acetate, mp 104–105° (lit.<sup>49</sup> mp 104°).

**Triphenylvinyl Ethyl Ether.** In a 100-ml round-bottomed flask 1-(triphenylvinyl)-3-acetyl-3-phenyl-1-triazene, 0.417 g (0.001 mol), is dissolved in 50 ml of absolute ethanol. Concentrated sulfuric acid, 1 ml (*ca.* 0.01 mol), is added, and the reaction mixture is allowed to stir for 1 hr. The mixture is diluted with an equal volume of concentrated sodium bicarbonate solution and extracted with ether. The ether is removed on a rotary evaporator, and the crude solid is washed several times with hot (*ca.* 60°) water to remove the

(48) R. G. Pews, *Can. J. Chem.*, **47**, 1260 (1969).

(49) R. P. Barnes, *et al.*, *J. Org. Chem.*, **8**, 153 (1943).

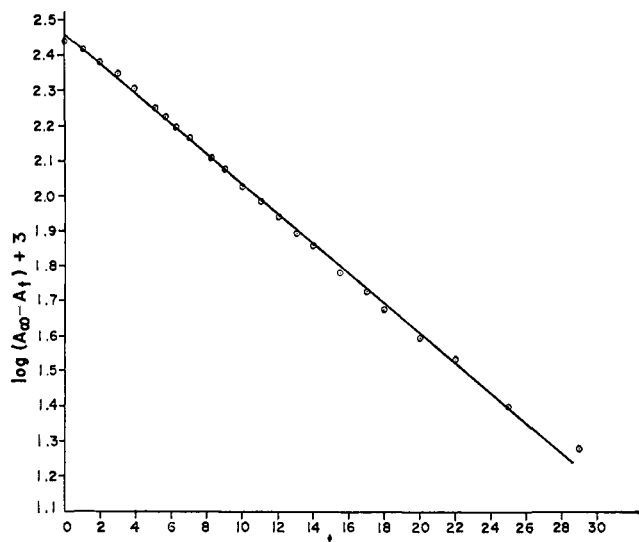


Figure 1. Acetolysis of triphenylethenyl fluorosulfonate at 74.9°.

acetanilide. The triphenylvinyl ethyl ether is crystallized from petroleum ether (bp 65–110°). The pale yellow solid, mp 116–117°, is obtained in 65% yield (lit.<sup>60</sup> mp 117–119°).

**$\alpha,\alpha$ -Diphenylacetophenone.** This ketone was prepared by modifying the procedure given for the synthesis of triphenylvinyl ethyl ether. Reaction of the same material in 50 ml of aqueous acetone (50%) afforded a white solid (72% yield), mp 135–136.5° (lit.<sup>60b</sup> mp 136–136.5°).

**$\alpha$ -Chlorostyrene.**  $\alpha$ -Chlorostyrene was prepared according to the method of Dufraisse and Viel.<sup>61</sup> A clear liquid (35% yield) was obtained, bp 67–71° (10 mm) (lit.<sup>61</sup> bp 199° (760 mm)).

**1-Phenylvinyl Acetate.** 1-Phenylvinyl acetate was prepared in 52% yield from isopropenyl acetate and acetophenone by using the method of Noyce and Pollack.<sup>18</sup> The product was purified by distillation, bp 86–89° (3 mm) (lit.<sup>18</sup> bp 92–95° (4.5 mm)).

**Acetolysis of Triphenylvinyl Fluorosulfonate in the Presence of Added  $\alpha,\alpha$ -Ditolylacetophenone.** Triphenylvinyl fluorosulfonate, 0.03811 g (0.0001075 mol), and  $\alpha,\alpha$ -ditolylacetophenone, 0.07742 g (0.000258 mol), were dissolved in a minimum of acetic acid along with 0.02741 g of sodium acetate. The reaction mixture was heated to 75–80° and maintained at that temperature for 1 hr. After cooling, the acetic acid was removed under vacuum, and the resulting white solid was taken up in acetone and analyzed by gas chromatography, column temperature 200°. The only new peak noted was that of triphenylvinyl acetate; none of the crossover acetate, 2,2-ditolyl-1-phenylethenyl acetate, could be detected.

**Stability of Triphenylvinyl Acetate under Acetolysis Conditions.** Triphenylvinyl acetate, 22.3 mg, was dissolved in 10 ml of dry acetic acid (*ca.* 0.008 M in NaOAc). A 5-ml sample of this solution was sealed in an ampoule and heated at 160° for 1400 min. The reaction mixture was cooled and analyzed by gas chromatography. The acetate showed no significant decomposition when compared to the unheated triphenylvinyl acetate solution.

## Kinetic Studies

**General.** Glacial acetic acid (reagent grade) was purified by refluxing for 1 hr in the presence of 10% acetic anhydride and 2 g of CrO<sub>3</sub>/100 ml. Fractional distillation afforded dry acetic acid. Acetic acid-*d* was prepared by reacting molar equivalents of acetic anhydride and deuterium oxide (99.77%, Columbia Organic Chemicals Co., Inc.). The product was fractionally distilled.

**A. Spectrophotometric Analysis.** In a typical run, 3.55 mg of triphenylvinyl fluorosulfonate was placed in a 10-ml volumetric flask along with 2.5 ml of a 0.10 M stock solution of sodium acetate in acetic acid. Dry

(50) (a) M. S. Newman and A. Kutner, *J. Amer. Chem. Soc.*, **73**, 4199 (1951); (b) R. S. Yost and C. R. Hausar, *ibid.*, **69**, 2325 (1947).

(51) C. Dufraisse and J. E. Viel, *Bull. Soc. Chim. Fr.*, **37**, 874 (1925).

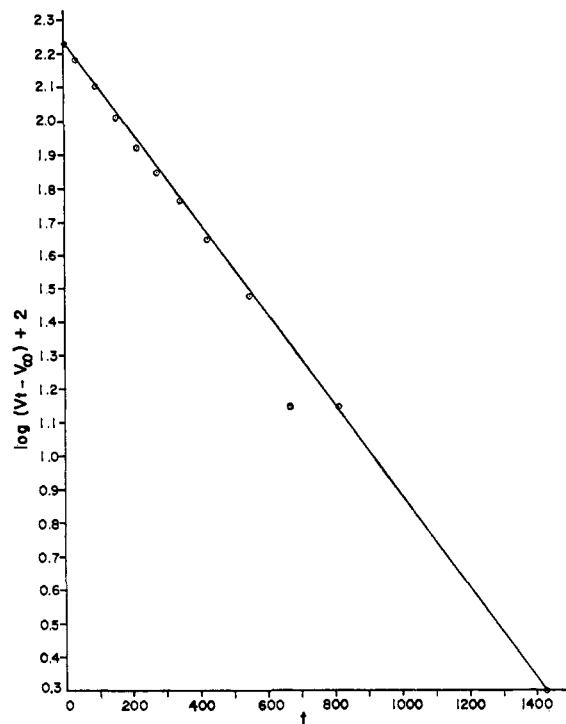


Figure 2. Acetolysis of triphenylethenyl tosylate at 150.8°.

acetic acid was added to make the final volume 10 ml. After the fluorosulfonate had dissolved, 1.0 ml of this solution was added to 9.0 ml of acetic acid heated to *ca.* 5° above the temperature of the kinetic run. The mixture was then rapidly transferred to a glass-stoppered uv cell, and placed in a thermostated cell holder. About 10 min was allowed for temperature equilibration, after which a time zero reading was taken on the Zeiss spectrophotometer. (The reference cell contained sufficient triphenylvinyl acetate so that its absorption reading was *ca.* 0.50. This allowed the time zero reading to have an absorption reading of 0.20–0.30.) At various time intervals, absorption readings were taken during the first three half-lives in a run. The time infinity reading was taken after ten half-lives. A typical run is shown in Figure 1.

**B. Titrimetric Analysis.** The acetolysis rates of triphenylvinyl tosylate, 1-phenylvinyl fluorosulfonate, and 1-phenylvinyl-2-*d* fluorosulfonate were more conveniently followed by a titrimetric procedure.

In a typical run, 253 mg of triphenylvinyl fluorosulfonate was dissolved in 100 ml of 0.00802 M sodium acetate buffered, acetic acid. About 17 ampoules containing *ca.* 5 ml of this solution were sealed and allowed to equilibrate for 15 min in the oil bath. At time zero an ampoule was withdrawn, and the reaction quenched by placing it in iced water. The ampoule was opened, and a 4-ml aliquot removed. Five drops of a saturated solution of bromophenol blue in acetic acid is added. The aliquot is titrated with 0.01000 N HClO<sub>4</sub> in acetic acid to the color change of yellow to colorless. At various time intervals, an aliquot is withdrawn and titrated to the end point. Generally 10–15 points are taken in a run during the first three half-lives. The time infinity reading was taken after ten half-lives. A typical plot is shown in Figure 2.

**Product Studies.** The amount of triphenylvinyl acetate produced in the acetolysis of triphenylvinyl



fluorosulfonate, triphenylvinyl trifluoromethanesulfonate, and triphenylvinyl tosylate was determined by gas chromatographic analysis, column temperature 196°. Triphenylethylene was used as an internal standard. The amount of 1-phenylvinyl acetate produced by the acetolysis of 1-phenylvinyl fluorosulfonate was determined titrimetrically. In all cases, tlc and gc showed only the acetate as a product.

In one instance, triphenylvinyl acetate was isolated in pure form from the acetolysis of triphenylvinyl fluorosulfonate in 93% yield. The fluorosulfonate, 38.8 mg, was dissolved in acetic acid along with 83.0 mg of sodium acetate. This solution was heated to 75° for 2 hr, poured into an equal volume of water, and extracted with ether. The solvent was removed on a rotary evaporator, and the resulting white solid was dried under vacuum for 2 days. This work-up afforded a product, 29.4 mg, whose melting point and mixture

melting point were identical with those of triphenylvinyl acetate. The infrared spectrum (Nujol) was superimposable upon that of an authentic sample of triphenylvinyl acetate.

In a similar manner, 1-phenylvinyl acetate was isolated from the acetolysis of 1-phenylvinyl fluorosulfonate. The light yellow oil had an infrared spectrum (neat) that was superimposable upon that of an authentic sample of 1-phenylvinyl acetate.

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## Thioacetal Hydrolysis. The Hydrolysis of Benzaldehyde Methyl S-(Substituted phenyl) Thioacetals

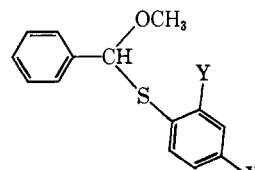
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**Abstract:** The rate constants for acid-catalyzed hydrolysis of a series of benzaldehyde methyl S-(substituted phenyl) thioacetals have been measured at 30° in 20% dioxane-H<sub>2</sub>O. General acid catalysis could not be detected with any of these compounds. The value of  $\Delta S^*$  for the hydronium ion catalyzed hydrolysis of the unsubstituted derivative is -4.8 eu. This reaction is much faster in D<sub>2</sub>O than H<sub>2</sub>O, the ratio  $k_D/k_H$  being 1.51. The  $\rho$  value for acid-catalyzed hydrolysis of the series is -1.0. An A1 mechanism is indicated with the carbon-sulfur bond breaking in the rate-determining step. The hydrolysis of the 2,4-dinitrophenyl derivative is pH independent from pH 1.5 to 0.1 M NaOH. This reaction proceeds at approximately the same rate in D<sub>2</sub>O as in H<sub>2</sub>O ( $k_{D_2O}/k_{H_2O} = 0.90$ ). The pH-independent reaction is therefore very likely a unimolecular decomposition to 2,4-dinitrothiophenoxide ion and a resonance-stabilized carbonium ion.

The generally accepted mechanism for the acid-catalyzed hydrolysis of simple acetals and ketals involves preequilibrium protonation by hydronium ion followed by rate-determining unimolecular decomposition to an alcohol and a resonance-stabilized carbonium ion.<sup>2</sup> Strong electron withdrawal in the leaving group, which greatly reduces the basicity of oxygen and at the same time facilitates breaking of the carbon-oxygen bond, will change the mechanism to one involving partially rate-determining protonation.<sup>3</sup> Replacement of an acetal oxygen by sulfur might therefore also be expected to give rise to a mechanism in which there is partially rate-determining proton transfer since sulfur is much less basic than is oxygen. However, general acid catalysis was not observed in the hydrolysis of 2-(substituted phenyl)-1,3-oxathiolanes.<sup>4,5</sup> Proton transfer from hydronium ion must be essentially

complete in the transition state for those compounds.<sup>4</sup> A simple replacement of oxygen by sulfur therefore does not reduce basicity sufficiently to produce clearly a mechanism change. It was thought that it would be of importance to study the hydrolysis of thioacetals of substituted thiophenols so that basicity and ease of bond breaking could be varied systematically by changing the substituent groups in the thiophenol portion of the molecule. Anderson and Capon<sup>6</sup> have



- I, X = OCH<sub>3</sub>; Y = H  
 II, X = CH<sub>3</sub>; Y = H  
 III, X = H; Y = H  
 IV, X = Cl; Y = H  
 V, X = NO<sub>2</sub>; Y = H  
 VI, X = NO<sub>2</sub>; Y = NO<sub>2</sub>

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