

19

formed by exchange. Once again the compound 19 is quite unstable and it decomposes readily to tetravalent phosphorus compounds.

The relative instability of the compounds with amino nitrogen bonded to phosphorus is not unexpected. Amino nitrogen can stabilize a positive charge on phosphorus and therefore enhance dissociation to phosphonium salts which can undergo further decomposition to tetravalent phosphorus compounds.

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## Experimental Section

**Materials.** The starting phosphines were prepared by standard techniques or purchased when possible. Their  $^1\text{H}$  and  $^{31}\text{P}$  nmr spectra agreed with literature values.

**Reactions.** Equimolar quantities (*ca.*  $5 \times 10^{-3}$  mol of the phosphine and diethyl peroxide) were allowed to react in methylene chloride. Usually the reactants were cooled to at least  $0^\circ$  before mixing. The reactions were monitored by  $^1\text{H}$  and  $^{31}\text{P}$  nmr spectroscopy. In those studies in which other solvents were used the methylene chloride was evaporated at room temperature *in vacuo* and the residue was dissolved in the appropriate solvent. Benzoic acid was added to each reaction mixture and the formation of ethyl benzoate was demonstrated by glpc.

## Vinyl Cations from Solvolysis. I. The Trianisylvinyl Halide System<sup>1</sup>

Zvi Rappoport and Aharon Gal

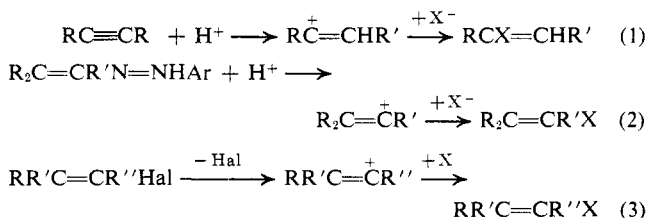
Contribution from the Department of Organic Chemistry,  
The Hebrew University, Jerusalem, Israel. Received March 24, 1969

**Abstract:** Solvolysis of trianisylvinyl chloride (1-Cl) and bromide (1-Br) and of 1-anisyl-2,2-diphenylvinyl bromide (7) in 80% ethanol follows a first-order course in the substrate, is independent of the concentration of added sodium hydroxide, and is only slightly dependent on that of added *p*-toluenethiolate ion. The solvolysis of 1-Br is 1.75 times faster than that of  $\alpha$ -bromo-*p*-methoxystyrene, excluding the addition-elimination mechanism. The similar rates for 1-Br and 7 point to the absence of  $\beta$ -aryl participation. The Grunwald-Winstein *m* values of 0.34–0.53 and the  $k_{1-\text{Br}}/k_{1-\text{Cl}}$  value of 58 at  $120^\circ$  are discussed in terms of intermediate vinyl cations in the solvolysis. The reactivity difference between  $\alpha$ -bromostyrene and  $\alpha$ -phenylethyl bromide is entirely due to activation energy difference. Vinyl cations and saturated cations are compared.

Vinyl cations were studied very little until recent years. Lately, they were suggested as intermediates in electrophilic additions to alkenes and acetylenes (eq 1),<sup>2</sup> in the deamination of vinylamines,<sup>3</sup> or in the reaction of 2-oxazolidones in basic solution<sup>4</sup> or vinyltriazenes in acidic solution<sup>5</sup> (eq 2). Ions with contributing vinyl cation structures were observed by nmr,<sup>6</sup> and solvolysis products of acetylenic sulfonates

may arise from vinyl cations formed by triple bond participation.<sup>7</sup>

Solvolytic formation of vinyl cations (eq 3) was studied even less. This may be due to the belief that vinyl halides are not easily solvolyzed, although the only evidence is the inertness of simple vinyl halides toward alcoholic silver nitrate.<sup>8</sup> The solvolysis of a vinyl ha-



lide may be more difficult than that of a saturated one owing to the partial carbon-halogen double bond in the former,<sup>9</sup> but the relative values were not determined.

(1) Presented in part at the XXXVIII meeting of the Israel Chemical Society, Beersheba, Oct 1968; Z. Rappoport, A. Gal, and Y. Apeloig, *Israel J. Chem. Proc.*, **6**, 16p (1968).

(2) T. L. Jacobs and S. Searles, *J. Amer. Chem. Soc.*, **66**, 686 (1944); W. Drenth and H. Hogeveen, *Rec. Trav. Chim. Pays-Bas*, **79**, 1002 (1960); E. J. Stamhuis and W. Drenth, *ibid.*, **80**, 797 (1961); H. Hogeveen and W. Drenth, *ibid.*, **82**, 375 (1963); P. E. Peterson and J. E. Dudley, *J. Amer. Chem. Soc.*, **85**, 2865 (1963); **88**, 4990 (1966); R. W. Bott, C. Eaborn, and D. R. M. Walton, *J. Organometal. Chem.*, **1**, 420 (1964); *J. Chem. Soc.*, 384 (1966); K. Griesbaum, *Angew. Chem. Intern. Ed. Engl.*, **3**, 697 (1964); *J. Amer. Chem. Soc.*, **86**, 2301 (1964); K. Griesbaum, W. Naegel, and G. G. Wanless, *ibid.*, **87**, 3151 (1965); R. L. Letsinger, E. N. Oftedahl, and J. R. Nazy, *ibid.*, **87**, 742 (1965); R. C. Fahey and D. J. Lee, *ibid.*, **88**, 5555 (1966); **90**, 372 (1968); H. W. Whitlock, Jr., and P. E. Sandvick, *ibid.*, **88**, 4525 (1966); D. S. Noyce, M. A. Matesich, M. D. Schiavelli, and P. E. Peterson, *ibid.*, **87**, 2295 (1965); D. S. Noyce, M. A. Matesich, and P. E. Peterson, *ibid.*, **89**, 6225 (1967); D. S. Noyce and K. E. Debruin, *ibid.*, **90**, 372 (1968); D. S. Noyce and M. D. Schiavelli, *ibid.*, **90**, 1020, 1023 (1968); T. Sasaki, S. Eguchi, and T. Toru, *Chem. Commun.*, 780 (1968).

(3) D. Y. Curtin, J. A. Kampmeier, and B. R. O'Connor, *J. Amer. Chem. Soc.*, **87**, 863 (1965).

(4) M. S. Newman and A. Kutner, *ibid.*, **73**, 4199 (1951); M. S. Newman and A. E. Weinberg, *ibid.*, **78**, 4654 (1956).

(5) W. M. Jones and F. W. Miller, *ibid.*, **89**, 1960 (1967).

(6) H. G. Richey, Jr., J. C. Phillips, and L. E. Rennick, *ibid.*, **87**, 1381 (1965); H. G. Richey, Jr., L. E. Rennick, A. S. Kushner, J. M. Richey, and J. C. Phillips, *ibid.*, **87**, 4017 (1965).

(7) M. Hanack, J. Haeflner, and I. Herterich, *Tetrahedron Lett.*, 875 (1965); P. E. Peterson and R. J. Kamat, *J. Amer. Chem. Soc.*, **88**, 3152 (1966).

(8) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley & Sons, Inc., New York, N. Y., 1956, p 141.

(9) E. D. Hughes, *Trans. Faraday Soc.*, **34**, 185 (1938); **37**, 603 (1941).

Solvolysis of triphenylhaloallenes was suggested to progress *via* an allenic cation,<sup>10</sup> but the suggestion is only tentative. Kinetic arguments suggested SN1 solvolysis for  $\beta$ -aroyl- $\beta$ -bromoacrylic acid salts,<sup>11</sup> but substituent and temperature effects are compatible with a different reaction course.<sup>12</sup> Modena's work<sup>13</sup> shows that vinylic solvolysis may be facile even at room temperature in a system with good leaving and activating groups.

In Grob's work<sup>14</sup> on the solvolysis of  $\alpha$ -bromostyrenes in 80% ethanol, and in Modena's work on 1,2-diaryl-2-arylmecapto-2,4,6-trinitrobenzenesulfonates<sup>13</sup> from the first-order kinetics, the accelerating effect of electron-donating substituents and of polar medium, vinylic cations are required. Solvolysis of  $\beta$ -halo- $\alpha,\beta$ -unsaturated carboxylate ions in the same conditions<sup>15</sup> is interpreted similarly.

For study of vinylic cations formed by solvolysis, a system is required in which the stereochemistry, the possibility of anchimeric assistance, and the reactivity ratio of leaving groups could be investigated without interference from other reaction routes. There are many pathways for nucleophilic vinylic substitution,<sup>12</sup> such as "addition-elimination,"<sup>16</sup> "elimination-addition" routes,<sup>17</sup> primary rearrangement followed by solvolysis,<sup>18</sup> and others.<sup>12</sup> The absence of vinylic and allylic hydrogens will exclude the "elimination-addition" ones, while electron-donating substituents would suppress the nucleophilic "addition-elimination."

The triarylvinylic halide system with electron-donating substituents is compatible with these requirements.<sup>19</sup> This paper describes the SN1 solvolysis of trianisylvinyl halides, in relation to solvent, common ion, and leaving group effects, and in connection with  $\beta$ -aryl participation.

## Results

**Solvolysis Products.** The expected solvolysis intermediate of trianisylvinyl halides (**1**) in basic 80% ethanol is the vinylic cation **2**. Capture of **2** by water will

(10) T. L. Jacobs and D. M. Fenton, *J. Org. Chem.*, **30**, 1808 (1965).  
 (11) I. Zugravescu, R. Ralea, and M. Petroveanu, *Analele Stiint. Univ. A. I. Cuza, Iasi, Sect. I*, **4**, 181 (1958); *Chem. Abstr.*, **53**, 19955 (1959).

(12) Z. Rappoport, *Advan. Phys. Org. Chem.*, **7**, 1 (1969).

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

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

(15) C. A. Grob, J. Csapilla, and G. Cseh, *ibid.*, **47**, 1590 (1964).

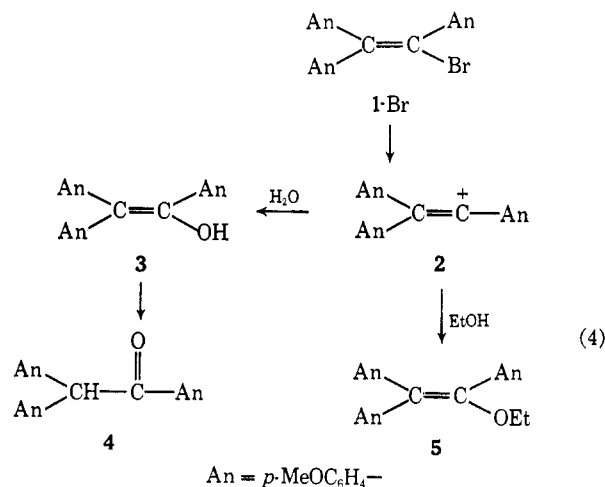
(16) *E.g.*, S. I. Miller and P. K. Yonan, *J. Amer. Chem. Soc.*, **79**, 5931 (1957); D. E. Jones, R. O. Morris, C. A. Vernon, and R. F. M. White, *J. Chem. Soc.*, 2349 (1960); G. Modena, *et al.*, *Gazz. Chim. Ital.*, **89**, 854, 866, 878 (1959), and following papers in the series; P. Beltrame, *et al.*, *J. Chem. Soc., B*, 1103, 1108 (1967), and preceding papers in the series.

(17) *E.g.*, W. E. Truce, *et al.*, *J. Amer. Chem. Soc.*, **78**, 2743, 2752 (1956); **80**, 1916 (1958); W. C. Kuryla and D. G. Leis, *J. Org. Chem.*, **29**, 2773 (1964); W. C. Kuryla, *ibid.*, **30**, 3926 (1965); L. K. Montgomery, *et al.*, *J. Amer. Chem. Soc.*, **87**, 1917 (1965); **89**, 2952, 3453 (1967); S. Gheresetti, G. Modena, P. E. Todesco, and P. Vivarelli, *Gazz. Chim. Ital.*, **91**, 620 (1961); L. DiNunno, G. Modena, and G. Scoranno, *J. Chem. Soc., B*, 1186 (1966); P. Beltrame, D. Pitea, A. Marzo, and M. Simonetta, *ibid.*, **71** (1967); V. J. Shiner, Jr., and J. S. Humphrey, Jr., *J. Amer. Chem. Soc.*, **89**, 622 (1967); A. T. Bottini and R. E. Olsen, *ibid.*, **84**, 195 (1962), and following papers in the series.

(18) F. Theron, Ph.D. Thesis, University of Clermont-Ferrand, France, 1967; L. N. Owen and M. U. S. Sultanbawa, *J. Chem. Soc.*, 3089 (1949).

(19) After this paper was sent to publication it was brought to our attention that very recently L. L. Miller and D. A. Kaufman [*J. Amer. Chem. Soc.*, **90**, 7282 (1968)] had studied triarylvinylic iodides in aqueous dimethylformamide. Some of their results are similar to ours.

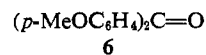
give  $\alpha,\alpha$ -bis(4-methoxyphenyl)-4-methoxyacetophenone (**4**) *via* ketonization of the enol (**3**), and capture by ethanol would give the ethyl ether **5** (eq 4).



Spectrophotometric study in the presence of triethylamine had shown a regular increase at  $\lambda$  276 m $\mu$ , the long-wave maxima of the anisolate of **4**, while the absorption of **1-Br** at 248 m $\mu$  decreased. Spectra at more than 50% reaction resemble that of the anisolate of **4** after allowance for the remaining **1-Br**.

However, pure **4** could not be obtained from the reaction of 0.06–0.09 *M* of **1-Br** with 0.25 *M* sodium hydroxide, triethylamine, or silver carbonate. Instead, work-up of the basic reaction mixture after several half-lives gives an oil with C=O absorption at 1670 cm<sup>-1</sup> in chloroform and  $\lambda_{\max}$  276 m $\mu$  in 95% ethanol. Nmr showed three singlets at 3.78, 3.81, and 5.96 and a multiplet at 6.8–7.3, 8.0–8.1 ppm downfield from tetramethylsilane in a ratio of 6:3:1:12. These were assigned, respectively, to the  $\beta$ - and the  $\alpha$ -anisyl methoxyls, the  $\beta$  hydrogen, and the aromatic protons of **4**. There are three AA'BB' quartets, *J* = 9 cps, the  $\beta$ -anisyl hydrogens at  $\delta$  6.91 and 7.25 and the  $\alpha$ -anisyl ones at 8.07 (*ortho*) and 6.93 (*meta*). The spectra are similar to that of the anisolate of **4** apart from the additional anisole signals and to that of  $\alpha,\alpha$ -diphenyl-*p*-methoxyacetophenone except for the change of anisyls to phenyls, and **4** is therefore the main initial solvolysis product.

The mass spectra of crude reaction mixture depends on the reaction times and base concentrations but showed peaks at *m/e* 362 (P for **4**, *ca.* 1–2%), at 361 (P – 1, 3–7%), at 347 and 346 (P – Me, P – 1 – Me) and at 227 (An<sub>2</sub>CH<sup>+</sup>) and 135 (AnCO<sup>+</sup>), each of which was the base peak in a different analysis. In an analysis of a sample taken after several half-lives *m/e* 242 was strong (36%) and was ascribed to 4,4'-dimethoxybenzophenone (**6**). Two weak peaks at 390 and at 375 are due to the ether **5**.



When the reaction mixture was left for long reaction times, or even from kinetic runs, a solid (yield up to 48%) which was identified by its melting point, mixture melting point, ir, and nmr as **6** was separated. It was also obtained from chromatography of the initially formed oil.

The ketone **4** was prepared earlier as its anisolate by condensing anisole and anisoin in phosphoric acid, but

could not be induced to crystallize.<sup>20</sup> In polyphosphoric acid we obtained anisil, probably from acid-catalyzed disproportionation of the anisoin,<sup>21</sup> and a white solid with correct analysis, ir, and melting point for **4**, and nmr of the anisolate of **4**.<sup>20</sup> The highest peak in the mass spectra is at 362. When this compound was steam distilled or refluxed with sodium hydroxide, **6** was formed. Basic hydrolysis of trianisylvinyl acetate in 80% ethanol gave **6** and anisic acid, and the behavior of **4** formed during solvolysis or independently prepared is therefore similar.

Only **4** was cleaved in 80% ethanol, since benzhydryl phenyl ketone, benzhydryl anisyl ketone, and *p*-methoxybenzhydryl anisyl ketone were recovered unchanged on reflux.

The ether **5** is a minor solvolysis product, and it was isolated from chromatography of the reaction mixture. However, in the presence of silver salts, especially at low temperature, it was one of the main products.

**Solvolysis.** In initial experiments, when triethylamine was used to neutralize the acid formed, both the bromide titer and the absorption at 276 m $\mu$  increased up to 50–60% reaction. At higher reaction percentage both began to decrease. The inorganic bromide is probably lost by the dissociation of triethylamine hydrobromide, followed by alkylation of the solvent to form ethyl bromide. Such complications had been noted by Grob<sup>14</sup> at higher temperature. The spectral changes may be due to the **4**  $\rightarrow$  **6** reaction. Sodium hydroxide was therefore used for neutralization. Constant ionic strength was not kept since some of the base was lost during a run by reaction with the ampoule glass, but the rate was quite independent of the base concentration. The reactions were of first order in either (**1**-Cl) or (**1**-Br). The error in the rate constants is somewhat higher than usual in solvolysis, since owing to the low solubility, material for every kinetic point was weighted independently.

In solvolysis of **1**-Br in the presence of 2.5–4 times molar concentrations of sodium *p*-toluenethiolate (0.11–0.13 *M*) the reaction is first order, independent of the thiolate concentration. The rate coefficient at the high thiolate concentration is similar to that in the presence of sodium hydroxide if the calculated infinity is used, but is 10–15% lower when using the observed infinity. The reaction reached only 83–94% of the calculated value, and the rate dropped toward the end of the reaction. At higher thiolate concentration the rate

(20) (a) E. C. Dodds, L. Goldberg, E. I. Grünfeld, W. Lawson, C. M. Saffer, Jr., and R. Robinson [*Proc. Roy. Soc. (London)*, **132B**, 83 (1944)] reported that the ketone **4** is difficult to purify and gave only its boiling point at reduced pressure. (b) G. Sumrell and G. E. Goheen [*J. Amer. Chem. Soc.*, **77**, 3805 (1955)] prepared the ketone as an anisolate, mp 77–79°, and on removing the anisole by distillation obtained an oil which did not crystallize. (c) K. Sisido, K. Okano, T. Isida, and H. Nozaki [*J. Amer. Chem. Soc.*, **77**, 6580 (1955)] reported that by condensation of *p*-methoxyacetophenone and *p*-anisylglyoxal they obtained the ketone as a yellow oil which could not be crystallized. In a later patent, K. Sisido, H. Nozaki, and K. Okano [Japan Patent 6633 (1957); *Chem. Abstr.*, **52**, 12918 (1958)] obtained a solid, mp 77–78°, by the same method. However, the authors claimed that they obtained the free ketone **4**, mp 82–83°, by reaction of *N,N*-dimethylaminophenyl- $\alpha$ -*p*-anisoylnitrone and anisole in sulfuric acid. The analysis of **4** and its anisolate is very similar and the results given fit more the anisolate than the free ketone. Since the ir, uv, and mass spectra of **4** and its anisolate would be similar, differentiation can be made by nmr. Our nmr evidence shows that the compound, mp 77–79°, is indeed the anisolate. It seems therefore that **4** was not obtained yet as a solid.

(21) D. R. Berger and R. K. Summerbell, *J. Org. Chem.*, **24**, 1881 (1959); Y. Halpern, M. Michman, and S. Patai, *J. Chem. Soc., B*, 149 (1966).

coefficients are constant within the first 70% of each run, but are lower than those at low thiolate concentration. This effect is now investigated. The rate data in 80% ethanol are summarized in Table I and typical runs are given in Table VI.

Table I. Solvolysis of An<sub>2</sub>C=CAnX (**1**) in 80% Ethanol

X	<b>1</b> , <i>M</i> $\times$ 10 <sup>3</sup>	Added base	Concn, <i>M</i> $\times$ 10 <sup>2</sup>	<i>T</i> , °C	<i>k</i> <sub>1</sub> $\times$ 10 <sup>4</sup> , sec <sup>-1</sup>
Cl	29	NaOH	37	120	0.070 $\pm$ 0.004
	29	NaOH	56	120	0.071 $\pm$ 0.005
	29	NaOH	31	141	0.422 $\pm$ 0.004
Br	31	NaOH	29	109.3	1.86 $\pm$ 0.04
	31	NaOH	52	120	4.09 $\pm$ 0.27
	31	NaOH	20	120	4.25 $\pm$ 0.20
	31	NaOH	18	120	3.91 $\pm$ 0.16
	60	NaOH	68	120	3.37 $\pm$ 0.05 <sup>a</sup>
	29 <sup>b</sup>	NaOH	31	119.8	3.80 $\pm$ 0.12
	43	NaSC <sub>6</sub> H <sub>4</sub> Me- <i>p</i>	11	120.3	4.61 $\pm$ 0.19 <sup>c,d</sup>
	29	NaSC <sub>6</sub> H <sub>4</sub> Me- <i>p</i>	13	120.3	4.44 $\pm$ 0.13 <sup>e</sup>
	29	NaSC <sub>6</sub> H <sub>4</sub> Me- <i>p</i>	23	120.3	4.10 $\pm$ 0.26 <sup>f</sup>

<sup>a</sup> The low value may be due to a slow dissolution of the high substrate concentration. <sup>b</sup> In the presence of 0.032 *M* NaBr. <sup>c</sup> Average value of the first 65% reaction, based on the observed infinity. <sup>d</sup> Observed infinity, 86.5%; 10<sup>4</sup>*k*<sub>1</sub> based on the calculated infinity = 3.99  $\pm$  0.17. <sup>e</sup> Observed infinity, 92.5%; 10<sup>4</sup>*k*<sub>1</sub> based on the calculated infinity = 3.89  $\pm$  0.06. <sup>f</sup> Observed infinity, 78.3%; 10<sup>4</sup>*k*<sub>1</sub> based on the calculated infinity = 4.10  $\pm$  0.26.

Bromide/chloride reactivity ratio at 120° is 57.6. It should be somewhat temperature dependent owing to the difference in the activation energies. Common ion rate depression during a run was not observed; the rate constants were steady up to 75–90% reaction. To ascertain that the steady low constant observed with 0.06 *M* **1**-Br is due to solubility difficulties, 0.03 *M* sodium bromide was added to a reaction mixture containing 0.029 *M* **1**-Br. The rate constant is slightly lower than usual, but within the combined errors, suggesting that common ion rate depression is unimportant.

Solvent effects were studied with **1**-Cl in 65, 80, and 90% ethanol, and with **1**-Br in 80 and 90% ethanol (Table II). A plot of log *k* for the chloride *vs.* Grun-

Table II. Solvolysis of An<sub>2</sub>C=CAnX in Aqueous Ethanol at 120°

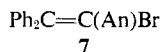
X	Solvent	<i>Y</i> <sup>a</sup>	<i>k</i> <sub>1</sub> $\times$ 10 <sup>4</sup> , sec <sup>-1</sup>
Cl	65% EtOH	0.860 <sup>b</sup>	0.202 $\pm$ 0.005
	80% EtOH	0.000	0.071 $\pm$ 0.005
	90% EtOH	-0.747	0.035 $\pm$ 0.002
Br	80% EtOH	0.000	4.08 $\pm$ 0.27
	90% EtOH	-0.747	2.27 $\pm$ 0.04

<sup>a</sup> Values taken from ref 22. <sup>b</sup> Average of *Y* values at 60 and 70% ethanol.

wald-Winstein's *Y*<sup>22</sup> is concave, *m* = 0.53 for 65–80% aqueous ethanol and 0.42 for 80–90% ethanol, while for the bromide *m* = 0.34.

**1**-Anisyl-2,2-diphenylvinyl bromide (**7**) was studied in order to evaluate  $\beta$ -anisyl participation and showed first-order kinetics. The products are  $\alpha,\alpha$ -diphenyl-*p*-methoxyacetophenone, which is also formed by sol-

(22) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2770 (1956).



volyzing 7 in formic acid, and 1-anisyl 2,2-diphenylvinyl ether, which is the main product in solvolysis in the presence of silver carbonate. With sodium *p*-toluenethiolate nearly quantitative yield of 1-anisyl-2,2-diphenylvinyl *p*-toluenethiolate was formed. First-order dependence on 7, independence of the low *p*-toluenethiolate concentration, and similar rate coefficients to those in the presence of sodium hydroxide were observed (Table III).

**Table III.** Solvolysis of 1-Anisyl-2,2-diphenylvinyl Bromide (7) in 80% Ethanol

7, $M \times 10^3$	Added base	Concn, $M \times 10^2$	$T, ^\circ\text{C}$	$k_1 \times 10^4, \text{sec}^{-1}$	$A_v, k_1 \times 10^4$
29	NaOH	30	120.3	$1.97 \pm 0.04$	
40	NaOH	38	120.3	$1.86 \pm 0.03$	1.92
29	NaOH	50	120.3	$1.92 \pm 0.02$	
33	$\text{NaSC}_6\text{H}_4\text{Me-}p$	12	120.3	$2.05 \pm 0.10^{a,b}$	
43	$\text{NaSC}_6\text{H}_4\text{Me-}p$	11	120.3	$1.88 \pm 0.07^{a,c}$	1.97
40	NaOH	29	127.8	$3.46 \pm 0.02$	
29	NaOH	44	127.8	$3.49 \pm 0.12$	3.48
40	NaOH	29	139.8	$7.63 \pm 0.14$	
57	NaOH	29	139.8	$7.62 \pm 0.28$	7.70
57	NaOH	36	139.8	$7.86 \pm 0.10$	

<sup>a</sup> Average value of the rate constants for the first 60–75% reaction. Value given is based on the observed infinity. <sup>b</sup> Observed infinity, 82%;  $10^4 k_1$  based on the calculated infinity =  $1.68 \pm 0.08$ . <sup>c</sup> Observed infinity, 88%;  $10^4 k_1$  based on the calculated infinity =  $1.66 \pm 0.06$ .

The rate data and the activation parameters for the solvolysis of 1-Cl, 1-Br, 7, and  $\alpha$ -bromo-*p*-methoxystyrene are given in Table IV.

**Table IV.** Rate Data for the Solvolysis of  $\text{R}_2\text{C}=\text{CAnX}$  in 80% Ethanol

R	X	$k_1 \times 10^4$ at $120^\circ$	$\Delta H^\ddagger, ^\circ\text{kcal mol}^{-1}$	$\Delta S^\ddagger$ at $120^\circ, ^\circ\text{eu}$
An	Cl	0.07	26.8	-14
An	Br	4.08	21.2	-20
Ph	Br	1.92	22.3	-19
H	Br	$2.40^c$	$27.0^c$	$-7^c$

<sup>a</sup> Estimated error,  $\pm 1.5 \text{ kcal mol}^{-1}$ . <sup>b</sup> Estimated error,  $\pm 4 \text{ eu}$ . <sup>c</sup> Taken from ref 14.

Triphenylvinyl bromide was recovered unchanged from reaction in 80% ethanol in the presence of triethylamine at  $150^\circ$  for 20 hr, or from acetic acid containing sodium acetate after 15 hr at  $150^\circ$ . Under these conditions 1-Br and 7 give at least 80% vinylic acetates. The uncatalyzed acetolysis of 1-Br shows external return and will be reported soon.

The solvolysis of triphenylvinyl bromide is accelerated by silver acetate. Reflux for 10 hr of 0.02 *M* triphenylvinyl bromide and 0.02 *M* silver acetate gave 74% of triphenylvinyl acetate. Triphenylvinyl chloride was recovered unchanged under the same conditions.

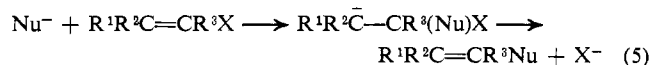
The reactivity of 1-Br, 1-Cl, and 7 in acetic acid containing silver acetate is also much enhanced. Vinylic acetates are formed quantitatively in 1 hr at reflux

temperature. Silver acetate or silver oxide with 1-Br in ethanol give 4 and 5.

## Discussion

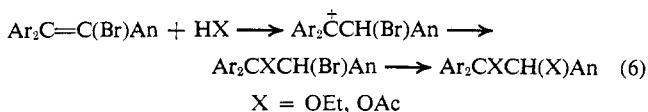
**Evidence for Carbonium Ion Intermediates.** Reported formation of vinylic ions during solvolysis is still rare. Our evidence is based on excluding competing pathways, and on the kinetics, products, and analogy with Grob's system.

The primary reaction products are the vinylic ether, enol, and acetate. The multiplicity of mechanisms for their formation is reduced by the absence of vinylic and allylic hydrogens essential for the "elimination-addition" and the prototropy-substitution routes.<sup>12</sup> Consecutive  $\text{SN}2'$  rearrangements<sup>23</sup> are impossible and vinylic anions are unlikely,<sup>24</sup> and the "addition-elimination" and the  $\text{SN}1$  reactions remain the likely mechanisms. The nucleophilic addition-elimination route (eq 5, Nu = nucleophile) is highly unlikely in 80% ethanol or in acetic acid, since in our systems the anisyl



groups enhance the nucleophilic rather than the electrophilic reactivity of the double bond. The nucleophilic addition-elimination mechanism observed in the reaction of the related 1,1-diaryl-2-haloethylenes with ethoxide ion<sup>25–27</sup> showed different kinetic behavior than our compounds. By using the Hammet equation for this reaction,  $10^8 k_2$  values at  $120^\circ$  are 120 and 1.8  $\text{l. mol}^{-1} \text{sec}^{-1}$  for 1,1-diphenyl-<sup>26</sup> and 1,1-dianisylvinyl bromide, respectively. At substrate and base concentrations similar to ours, the half-lifetimes for these two halides are *ca.*  $10^8$  and  $10^6$  sec compared to 1500 sec for 1-Br. The former values are lower limits for the half-lifetimes for the nucleophilic addition-elimination route for 1-Br and 7, owing to the higher nucleophilicity of ethoxide *vs.* hydroxide toward a carbonium ion,<sup>28</sup> the lower rates of the ion-molecule reaction in 80% ethanol compared to ethanol,<sup>29</sup> and the steric and electronic rate retardation of the  $\alpha$ -anisyl group.

An electrophilic addition-elimination (eq 6) is possible for 1, but the first-order kinetics are incompatible with the lower rates of the vinylic systems compared to the saturated ones, and with the similar rates of all the compounds of Table IV. Moreover, such addition to 1-Br would give 1,2-diols, 1,2-diethers, and 1,2-diacetates. None of these had been detected, although the mass spectra could detect 0.1% of the starting material. However, the electrophilic addition-elimination mech-



(23) W. T. Miller, Jr., J. H. Fried, and H. Goldwhite, *J. Amer. Chem. Soc.*, **82**, 3091 (1960).

(24) *E.g.*, D. Y. Curtin and E. E. Harris, *ibid.*, **73**, 2716, 4159 (1951); D. Y. Curtin, H. W. Johnson, Jr., and E. G. Steiner, *ibid.*, **77**, 4566 (1955).

(25) E. F. Silversmith and D. Smith, *J. Org. Chem.*, **23**, 427 (1958).

(26) P. Beltrame and G. Favini, *Gazz. Chim. Ital.*, **93**, 757 (1963).

(27) P. Beltrame, P. L. Beltrame, O. Sighinolfi, and M. Simonetta, *J. Chem. Soc., B*, 1103 (1967).

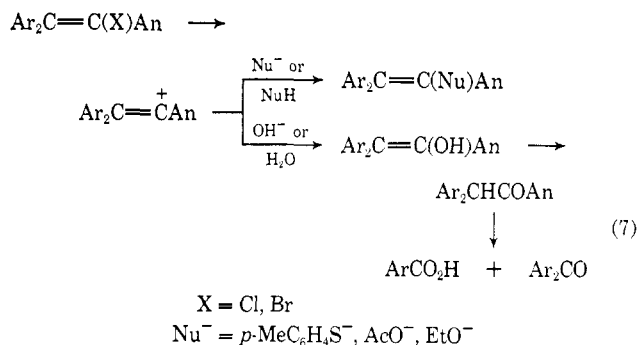
(28) W. Reeve and P. F. Alutoo, *Tetrahedron Lett.*, 2557 (1968).

(29) K. B. Wiberg, "Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1964, p 388.

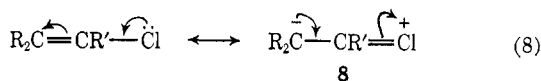
anism may predominate in solvents such as trifluoroacetic or formic acid.<sup>30</sup>

On the other hand, the absence of kinetic dependence (reaction order and rate coefficients) on the nucleophile at low nucleophile concentration, while the product is nucleophile dependent, is typical for a cationic intermediate, formed in a rate-determining step and captured by nucleophiles in a product-determining step. The  $k_{\text{Br}}/k_{\text{Cl}}$  rate ratio, the solvent effect, the electrophilic catalysis by silver acetate, and the similarity in activation at the  $\alpha$  position to that in *p*-methoxy- $\alpha$ -bromostyrene for which the  $\text{S}_{\text{N}}1$  mechanism was established by substituent effects support this suggestion.

The solvolysis is summarized in eq 7. The carbonium ion is drawn as linear, based on product distribution studies in the solvolysis of *cis*- and *trans*-1,2-dianisyl-2-phenylvinyl bromides.<sup>1,31</sup>

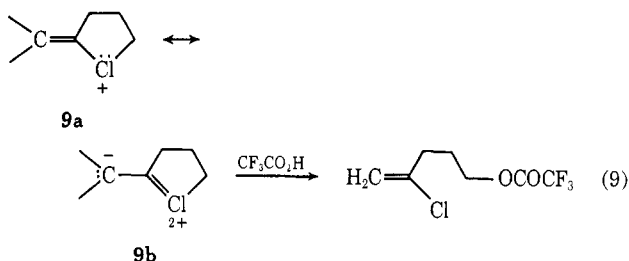


**Vinylic vs. Saturated Carbonium Ions.** The inertness of vinyl halides to solvolysis is ascribed to structure **8** with the partial double bond between the  $\alpha$ -carbon and



the halogen<sup>9</sup> (eq 8).

The C-Cl bond in vinyl chloride is shortened from 1.76 to 1.69 Å and in vinyl bromide from 1.91 to 1.86 Å.<sup>32</sup> The evidence is not conclusive since there is no independent support that this is not a result of a change in the valency state of the carbon atom.<sup>33</sup> From the observation that the chloronium ion **9a** ↔ **9b** ring opens



in trifluoroacetic acid only with the cleavage of the non-vinylic C-Cl bond (eq 9), Peterson suggested<sup>34</sup> that the

(30) P. E. Peterson and J. M. Indelicato, *J. Amer. Chem. Soc.*, **90**, 6515 (1968).

(31) Z. Rappoport and Y. Apeloig, to be published. On acetolysis of this system equal amounts of *cis* and *trans* acetates are formed from either *cis* or *trans* starting bromoethylene.

(32) J. A. C. Hugill, I. E. Coop, and L. E. Sutton, *Trans. Faraday Soc.*, **34**, 1518 (1938); L. O. Brockway, J. Y. Beach, and L. Pauling, *J. Amer. Chem. Soc.*, **57**, 2693 (1935).

(33) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1955, p 176.

(34) P. E. Peterson and J. E. Dudley, *J. Amer. Chem. Soc.*, **88**, 4990 (1966).

"unreactivity of vinylic halides may be primarily a consequence of the strength of the  $\sigma$ -bond to the  $\text{sp}^2$ -carbon," since a structure such as **8** is unlikely owing to unfavorable charge repulsion on the doubly charged chlorine of **9b**.

The importance of structure **8** in affecting the reactivity may be evaluated in three ways: (a) by measuring and calculating the energy difference required for breaking the C-leaving group bond in vinylic and saturated systems; (b) by changing the charge spreading ability of the  $\beta$  substituents; (c) by changing the  $\alpha$ -leaving group, and comparing the "element effect" to that in saturated systems.

(a) **The Energetics of the  $\text{RX} \rightarrow \text{R}^+ + \text{X}^-$  Process.** Data for our compounds are not available, but the gas phase data can be calculated and compared with solvolytic data. The energy of the process  $\text{RX} \rightarrow \text{R}^+ + \text{X}^-$  is composed from the dissociation energy  $D$ , the ionization potential  $I_p$  of the R radical, and the electron affinity of the X radical which is cancelled in comparing ethyl and vinyl bromide. From electron impact,  $I_p = 217.9^{35}$  and  $202.4^{36}$  kcal mol<sup>-1</sup> for the vinyl and ethyl radical, respectively. The C-Br bond energies in ethyl and vinyl bromides are 69 and 73.4 kcal mol<sup>-1</sup>.<sup>38,39</sup> Formation of the vinyl cation in the gas phase costs 20 kcal mol<sup>-1</sup> more than for the ethyl ion.<sup>40</sup>

Application of this value to our system is questionable due to substituent effects. For example, it can be calculated<sup>41</sup> that 65 kcal mol<sup>-1</sup> less are required to form the *p* methoxybenzyl ion than the ethyl ion. It is not clear if the difference prevails between vinyl halide and a system with  $\alpha$ -halogen and  $\alpha$ -anisyl, which may compete as electron donors.

The reduced reactivity of unsubstituted vinyl halides due to inductive effects alone is estimated from Taft's inductive substituent constants  $\sigma^*$ <sup>42</sup> of the ethyl (-0.100)<sup>43</sup> and the vinyl (0.653)<sup>44</sup> groups. If a linear  $\sigma^*\rho^*$  relationship holds, and  $\rho^*$  is approximated by that for the solvolysis of secondary brosylates in acetic acid<sup>45</sup> or tertiary halides in 80% ethanol<sup>45</sup> ( $\rho^* = -3.3$  to  $-3.5$ ), vinyl halide is two to three orders of magnitude less reactive than ethyl halide. This difference is sufficient to account for a complete cleavage of **9** in the direction observed, and the contribution of structure **8** cannot be deduced from the cleavage of **9**.

Comparison should be made between  $\alpha$ -bromostyrene and  $\alpha$ -phenylethyl bromide, since **1** or **7** has to be com-

(35) A. G. Harrison and F. P. Lossing, *ibid.*, **82**, 519 (1960).

(36) J. B. Farmer and F. P. Lossing, *Can. J. Chem.*, **33**, 861 (1955). The more accurate photoionization value is  $\leq 193.2$  kcal mol<sup>-1</sup> [F. A. Elder, C. Giese, B. Steiner, and M. Ingrham, *J. Chem. Phys.*, **36**, 3292 (1962)]. Nevertheless we prefer to use values derived from the same experimental method,<sup>37</sup> acknowledging that our final value will be the lower estimate.

(37) A. Streitwieser Jr., *Progr. Phys. Org. Chem.*, **1**, 14 (1963).

(38) J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.*, **45**, 339 (1949).

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

(40) From the large difference in the ionization potentials compared to the small difference in the bond energies, Miller<sup>19</sup> had concluded that hybridization rather than resonance stabilization is the factor responsible to the vinylic unreactivity.

(41) A. G. Harrison, P. Kebarle, and F. P. Lossing, *J. Amer. Chem. Soc.*, **83**, 777 (1961); F. P. Lossing, K. U. Ingold, and J. H. S. Hender-son, *J. Chem. Phys.*, **22**, 1489 (1954).

(42) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, Chapter 13.

(43) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **75**, 4231 (1953).

(44) J. Hine and W. C. Bailey, *ibid.*, **81**, 2075 (1959).

(45) A. Streitwieser, Jr., *ibid.*, **78**, 4935 (1956).

pared to the  $\alpha,\beta,\beta$ -triarylethyl system, in which superimposed accelerating effects (due to participation<sup>46</sup> or steric effects<sup>47</sup>) are evident. Extrapolated  $k_1$  values for  $\alpha$ -bromostyrene<sup>14</sup> and for  $\alpha$ -phenylethyl bromide<sup>48</sup> at 25° in 80% ethanol are  $10^{-14}$  and  $2 \times 10^{-4}$ , respectively. The difference is entirely due to the activation energies (34.1 vs. 20.2 kcal mol<sup>-1</sup>), the activation entropies being similar (ca. 8 eu). By assuming a  $\sigma\rho$  relationship for  $\alpha$ -phenylethyl bromides,<sup>48</sup> the corresponding *p*-methoxy derivatives differ by eight orders of magnitude. Most of the gas phase difference is still present in solution. The differences may be due to an earlier transition state in the more endothermic vinylic solvolysis, or to a more efficient solvation of the vinylic ion owing to lower hindrance to back solvation and to the absence of two hydrogens.

(b) **The Effect of  $\beta$  Substituents.** With the increased negative charge spreading ability of a  $\beta$  substituent the reactivity will be reduced due to increased importance of structure 8. A large structural change is not safe, however, since, e.g., a *p*-nitrophenyl group activates arylhaloethylenes in the nucleophilic addition-elimination route.<sup>49,50</sup> The rate similarity of our  $\beta,\beta$ -diphenyl and  $\beta,\beta$ -dianisyl derivatives does not argue against contribution from 8, since the above-mentioned differences are counterbalanced by opposite inductive effects.

(c)  **$k_{\text{Br}}/k_{\text{Cl}}$  Ratios.** Changing a leaving group from X to Y causes an "element effect"  $k_{\text{X}}/k_{\text{Y}}$ . If X and Y differ markedly in their electron-donating ability, the element effects will differ in saturated and vinylic systems.

The observed  $k_{\text{Br}}/k_{\text{Cl}} = 58$  is similar to those found in 80% ethanol for solvolyzing saturated systems, e.g., 42, 32, 34, 58, and 19 for *t*-butyl,<sup>51</sup> isopropyl,<sup>52</sup> neophyl,<sup>53</sup> adamantyl,<sup>54</sup> and  $\alpha$ -phenylethyl<sup>55</sup> halides, respectively. Indeed, similarity of the values is expected from Taft's  $\sigma_{\text{R}}^{\text{p}}$ <sup>56</sup> or  $\sigma_{\text{R}}^0$ <sup>57</sup> values, which are assumed to measure the resonance contribution of a substituent on the aromatic nucleus. In each reaction class  $\sigma_{\text{R}}^{\text{p-Cl}} \sim \sigma_{\text{R}}^{\text{p-Br}}$ <sup>58</sup> and the  $\sigma_{\text{R}}^0$  values are almost the same.<sup>57</sup> A different approach is to use bond energy data. The difference in the bond energies of the vinylic bromide and chloride on the one hand and the saturated halides on the other is the energy difference between the "element effect" in the two systems. The dissociation energies of vinyl chloride and bromide are 85.5 and 73.4 kcal mol<sup>-1</sup>,<sup>35</sup> i.e., the difference is 12.1 kcal mol<sup>-1</sup>. The bond energy difference between ethyl chloride and bromide is 12.5 kcal mol<sup>-1</sup>,<sup>39</sup> and the two element effects

are similar. Large differences in solution are not expected, as found, since solvation energies would be cancelled out. Estimation of mesomeric electron donation from element effects requires different leaving groups.<sup>58</sup>

**$\beta$ -Aryl Participation.** The vinylic system is more rigid, but has shorter bonds than a saturated one. In trianisylvinyl halides there is always an aryl group *trans* to the leaving group. While our system is formally a secondary one, reactivity-wise it is similar to a primary one and these factors may be involved in a neighboring group participation, although this phenomena may not be very important in 80% ethanol.<sup>59</sup> For example,  $k_{\beta\text{-An}}/k_{\beta\text{-Ph}} = 97$  in 80% ethanol for the neophyl tosylate system and the reaction is completely anchimerically assisted<sup>60</sup> while it is mainly unassisted for  $\beta$ -anisylethyl tosylate in ethanol.<sup>61</sup>

The rate ratios for  $\beta,\beta$ -unsubstituted,  $\beta,\beta$ -diphenyl, and  $\beta,\beta$ -dianisyl derivatives (1:0.8:1.7 at 120°) should be corrected for the inductive effects of the aryl groups in order to estimate the amount of participation. The rate-retarding effect of  $\beta$ -Ph in saturated systems is estimated between 8 and 10<sup>62</sup> and it is assumed that the value for  $\beta$ -An is similar. This is based on  $\text{p}K_{\text{a}}$ 's of  $\beta$ -phenylacetic acids, and the values for vinylic systems may be derived from those for acrylic acids. We assume that the effect of  $\beta$ -*trans* substituents is mainly inductive and that dipolar structures in the acid are unimportant. From the  $\text{p}K_{\text{a}}$ 's in water at 25° of acrylic (4.25), *trans*-cinnamic (4.44), and *trans-p*-methoxycinnamic (4.38)<sup>63</sup> the inductive effects of vinylic  $\beta$ -H,  $\beta$ -Ph, and  $\beta$ -An are similar<sup>64</sup> and the solvolysis ratios are close to the corrected ones. Both  $\beta$ -phenyl and  $\beta$ -anisyl participation are therefore unimportant in 80% ethanol, in line with the similarity of the activation parameters for the  $\beta,\beta$ -diphenyl and the  $\beta,\beta$ -dianisyl compounds. We hesitate to attribute too much meaning to this similarity, and to the difference from the monoaryl derivative, since the temperature range investigated was rather small, and a serious error may be introduced into the activation parameters.<sup>65</sup>

The absence of participation may be due to the high nucleophilicity of the solvent and to the  $\alpha$ -activating anisyl group which may dump participation from substituents in further away positions.<sup>66</sup>

**Solvent Effects.** The solvolysis rate of 1-Cl and 1-Br increases with the solvent polarity, but the Grunwald-Winstein *m* values are lower than expected for an SN1 reaction (0.7–1.0).<sup>67</sup> A value such as for 1-Br is usu-

(46) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 513–514.

(47) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Amer. Chem. Soc.*, **74**, 1113 (1952); H. C. Brown, Special Publication No. 16, The Chemical Society, London, 1962, pp 148–150; H. C. Brown, R. Bernheimer, and K. J. Morgan, *J. Amer. Chem. Soc.*, **87**, 1280 (1965).

(48) V. J. Shiner Jr., W. E. Buddenbaum, B. L. Murr, and G. Lamaty, *ibid.*, **90**, 418 (1968).

(49) P. Beltrame, P. L. Beltrame, O. Sighinolfi, and M. Simonetta, *J. Chem. Soc., B*, 1103 (1967).

(50) G. Marchese, G. Modena, and F. Naso, *Tetrahedron*, **24**, 663 (1968).

(51) K. A. Copper and E. D. Hughes, *J. Chem. Soc.*, 1183 (1937).

(52) E. D. Hughes and U. G. Shapiro, *ibid.*, 1177 (1937).

(53) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 1608 (1957).

(54) P. von R. Schleyer and R. D. Nicholas, *ibid.*, **83**, 2700 (1961).

(55) A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1597, 1602 (1957).

(56) R. W. Taft, Jr., and I. C. Lewis, *ibid.*, **81**, 5343 (1959).

(57) R. W. Taft Jr., S. Ehrenson, I. C. Lewis, and R. E. Glick, *ibid.*, **81**, 5352 (1959).

(58) We are now studying halide and neutral mercury as leaving groups, toward this goal.

(59) S. Winstein, C. R. Lindgren, H. Marshall, and L. L. Ingraham, *J. Amer. Chem. Soc.*, **75**, 147 (1953).

(60) S. G. Smith, A. H. Fainberg, and S. Winstein, *ibid.*, **83**, 618 (1961).

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

(62) H. C. Brown and C. J. Kim, *ibid.*, **90**, 2082 (1968).

(63) Z. Rappoport, "Handbook of Tables for Organic Compounds Identification," 3rd ed, The Chemical Rubber Co., Cleveland, Ohio, 1967, pp 431, 432.

(64) Information related to our compounds with the two aryl groups is that the  $\text{p}K_{\text{a}}$ 's of  $\beta$ -phenylcinnamic acid (4.77) and of cinnamic acid (4.75) in 20% ethanol are the same: R. Carrié, *Bull. Soc. Sci. Bretagne*, **37**, 99 (1962).

(65) R. C. Peterson, J. H. Markgraf, and S. D. Ross, *J. Amer. Chem. Soc.*, **83**, 3819 (1961). Using this method, with a fractional error in the rate constant  $\alpha = 0.06$ , the maximum error in the activation energy  $2\delta = 3$  kcal mol<sup>-1</sup>.

(66) P. G. Gassman, J. Zeller, and J. Lumb, *Chem. Commun.*, **69** (1968).

ally associated with SN2 reactions<sup>67</sup> while that for 1-Cl is in an intermediate region. In addition, the *mY* plot is curved.

These aspects do not contradict the SN1 mechanism. Both the *Y* scale and most of the *m* values by which the mechanistic categories had been assigned were measured at 0–50°. Since it is assumed that the relationship  $(m_1/m_2) = (T_2/T_1)^a$  holds,<sup>68</sup> our *m* values at 25° should be higher than at 120°. From the *m* values for  $\alpha$ -phenylethyl bromide<sup>55</sup> and related systems,  $a \sim 1$  and *m* is calculated to be 0.60–0.76 and 0.50 for 1-Cl and 1-Br, respectively, at 25°, values which are closer to the SN1 range.

Moreover, for *exo*-norbornyl *p*-trifluoromethylthionbenzoate *m* = 0.45 in the same solvent mixtures “consistent with an ionization process,”<sup>69</sup> and “the sensitivity of the ionization rate to the solvent change tends to be less for the methoxylated than for the parent structures.”<sup>61</sup> For *p*-methoxyneophyl tosylate, a model for SN1 reactions, *m*  $\sim$  0.4 at 25°, lower than our extrapolated value.<sup>60</sup> This may be explained by participation, but the higher *m* value for  $\alpha$ -bromostyrene (0.60 at 170°) supports the generalization for vinylic systems without the need to invoke participation.

Curved *mY* plots in ethanol–water mixtures were found for  $\alpha$ -phenylethyl chloride, bromide,<sup>55</sup> and presumably for *p*-methoxyneophyl tosylate.<sup>60</sup> The reasons for this were discussed.<sup>55</sup>

**The Question of Ion Pairs.** No common ion rate depression during a run or by added external bromide ion to 1-Br was observed. The solvolysis products are either formed *via* dissociated ions, which are captured faster than they return to ion pairs, or they are exclusively formed *via* ion pairs.<sup>70</sup> Although the solvolysis products in acetic acid are mainly formed *via* dissociated ions,<sup>71</sup> decision between these two alternatives is not yet possible. It is important, however, that the intermediates are selective enough to be captured by thio nucleophile in competition with the lyate ions. Along the ionization–dissociation pathway they are advanced enough to give products selectively, but not to be returnable externally. More data are needed to establish if analogy to “solvent separated ion pairs”<sup>70</sup> is justified.

**Side Reaction.** Alkaline cleavage of the triaryl ketone was observed in refluxing basic ethanol only with 4. Several mechanistic routes for the cleavage predict that the triphenyl ketone would be cleaved as easily as 4. Nucleophilic attack by hydroxide at the benzydrylic carbon atom of 3, followed by cleavage as found with activated carbon–carbon double bonds,<sup>72</sup> would give 6 and *p*-methoxybenzyl alcohol, which may give anisic acid by the Canizzaro reaction. Air oxidation of the enolate was suggested for a similar cleavage by sodium in toluene.<sup>73</sup>

Hydroxide ion may also attack the carbonyl group of 4 with the expulsion of the dianisylmethide ion, which

(67) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 846 (1948); S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951); ref 29, p 417.

(68) S. Winstein and A. H. Fainberg, *J. Amer. Chem. Soc.*, **79**, 5397 (1957).

(69) S. G. Smith and J. Petrovich, *J. Org. Chem.*, **30**, 2882 (1965).

(70) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *J. Amer. Chem. Soc.*, **78**, 328 (1956).

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(72) S. Patai and Z. Rappoport, *J. Chem. Soc.*, 383, 392 (1962).

(73) C. F. Koelsch, *J. Amer. Chem. Soc.*, **54**, 2049 (1932).

in turn is air oxidized to 6. The first step is analogous to the reported cleavage of similar ketones to benzoic acid and diarylmethane by alkali in ethanol.<sup>73,74</sup> However, in our ampoules there is much less oxygen than that required for the 48% yield of 6, while these examples show that the oxidation of the carbanion does not necessarily take place.

## Experimental Section

Melting points are uncorrected. Nuclear magnetic resonance spectra were recorded with a Varian A56/60 spectrometer and are given in cycles per second downfield from internal tetramethylsilane.

**Materials.** Trianisylvinyl chloride (mp 113°, from ethanol) was prepared according to Shelton, *et al.*,<sup>75</sup> and trianisylvinyl bromide (mp 118–119°, from 95% ethanol) according to Sisido, *et al.*,<sup>76</sup> Both had the correct analysis and the expected uv, ir, nmr, and mass spectra.

**Solvents.** The 80% ethanol and the aqueous ethanolic mixtures were prepared according to Grob.<sup>14</sup>

**1-Anisyl-2,2-diphenylvinyl Bromide (7).** (a) **1-Anisyl-2,2-diphenylethanol.** Ethyl *p*-methoxyphenylacetate (14 g, 0.07 *M*) in ether (50 ml) was added slowly to phenylmagnesium bromide (25 g, 0.14 *M*) in ether (100 ml) at gentle reflux. The mixture was refluxed 1 additional hr, poured into a 3 *M* solution of ammonium chloride (250 ml), and separated, and the ethereal fraction was washed, dried, and evaporated. The solid obtained was recrystallized (ethanol) giving white needles, mp 137–139°, of 1-anisyl-2,2-diphenylethanol (12.5 g, 59%): nmr (carbon tetrachloride) 1:2:3 singlets at 127 cps (OH), 215 cps (CH<sub>2</sub>), and 224 cps (OMe).

*Anal.* Calcd for C<sub>21</sub>H<sub>20</sub>O<sub>2</sub>: C, 82.85; H, 6.62. Found: C, 82.95; H, 6.36.

(b) **1-Anisyl-2,2-diphenylvinyl Bromide (7).** To 2-anisyl-1,1-diphenylethanol (11 g, 0.036 *M*) in acetic acid (50 ml), bromine (6 g, 0.037 *M*) in acetic acid (25 ml) was added with stirring which continued for additional 30 min. Half of the solvent was removed, the residue was cooled, and water was added to turbidity. The yellow solid was filtered and recrystallized (ethanol) giving 1-anisyl-2,2-diphenylvinyl bromide: mp 130–131° (lit.<sup>19</sup> 128–130°); 8.5 g, 68%.

*Anal.* Calcd for C<sub>21</sub>H<sub>17</sub>BrO: C, 69.02; H, 4.69; Br, 21.87. Found: C, 69.20; H, 4.48; Br, 21.63.

The nmr spectrum (deuteriochloroform) exhibited a 3 H singlet at 220 cps (OMe), two 5 H singlets at 401 and 440 cps (Ph), and a quartet at 400.3, 435.7 (*J* = 9 cps) (An).

**1,2,2-Trianisylvinyl 1-*p*-Toluenethiolate.** Trianisylvinyl bromide (180 mg) in 80% ethanol (7 ml) containing sodium *p*-toluenethiolate (0.12 *M*) in a sealed ampoule was kept at 120° for 20 hr. On cooling, a solid, mp 45–50° (200 mg, 100%), was separated. Crystallization (ether–petroleum ether (bp 40–60°)) gave a white solid, mp 94–96° (115 mg, 58%).

*Anal.* Calcd for C<sub>30</sub>H<sub>28</sub>SO<sub>3</sub>: C, 76.90; H, 6.03; S, 6.84. Found: C, 76.78; H, 6.26; S, 6.38.

The nmr spectrum (deuteriochloroform) exhibited a 3 H singlet at 130 cps (Me), three 3 H singlets at 218, 221, and 227 cps (MeO), and a 16 H multiplet at 384–430 cps (Ar). In kinetic runs the yield was over 90%.

**1,2,2-Trianisyl 1-Ethyl Ether.** Trianisylvinyl bromide (670 mg, 1.57 *mM*) and silver carbonate (425 mg, 1.54 *mM*) in 95% ethanol (50 ml) were refluxed for 2 hr. The solution was filtered, water was added and the precipitate was recrystallized (petroleum ether, bp 40–60°) giving a white solid: mp 102–103° (250 mg, 41%);  $\lambda_{\text{max}}^{\text{C}_6\text{H}_5}$ : 247  $\mu\text{m}$  ( $\epsilon$  19,500), 305 (18,300); C=C stretching at 1605  $\text{cm}^{-1}$ .

*Anal.* Calcd for C<sub>25</sub>H<sub>26</sub>O<sub>4</sub>: C, 76.90; H, 6.71. Found: C, 76.62; H, 6.45.

The nmr spectrum (deuteriochloroform) exhibited a 3 H triplet at 71 cps (Me), three 3 H singlets at 221, 223, and 226 cps (MeO), a 2 H quartet at ca. 221 cps (CH<sub>2</sub>), and a 12 H multiplet at 390–435 cps (aromatic).

**1-Anisyl-2,2-diphenylvinyl 1-*p*-Toluenethiolate.** An ampoule containing 1-anisyl-2,2-diphenylvinyl bromide (100 mg) and sodium *p*-toluenethiolate (0.08 *M*) in 80% ethanol (7 ml) was kept at 128°

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Table V. Mass Spectra of Crude Reaction Mixture from Solvolysis of 1-Br

<i>m/e</i>	390	375	362	361	347	346	333	242	227	135	107
Relative abundance											
<i>a</i>	12	2	1.5	7	6	7	12.5	36	5	100	16
<i>b</i>	<0.03	0.3	1	3	1	4	1	0.5	100	28	2
Assignment	5	5-Me	4	4-H	4-Me	4-Me-H	An <sub>3</sub> C <sup>+</sup>	An <sub>2</sub> CO <sup>+</sup>	An <sub>2</sub> CH <sup>+</sup>	AnCO <sup>+</sup>	An <sup>+</sup>

<sup>a</sup> Reaction with 0.054 *M* 1-Br, 0.3 *M* NaOH, six half-lives at 120°. <sup>b</sup> Reaction with 0.06 *M* 1-Br, 0.25 *M* NaOH, 165 half-lives at 120°.

for 5 hr. On cooling, a white solid, mp 145–147°, was separated (105 mg, 94%). Recrystallization (95% ethanol) gave 1-anisyl-2,2-diphenylvinyl 1-*p*-toluenethiolate: mp 147–148°;  $\lambda_{\text{max}}^{\text{C}_6\text{H}_5\text{S}^-}$  235 m $\mu$  ( $\epsilon$  23,400), 253 sh (18,100), 339 (10,300).

*Anal.* Calcd for C<sub>23</sub>H<sub>24</sub>O<sub>2</sub>: C, 82.28; H, 5.92; S, 7.85. Found: C, 82.06; H, 5.78; S, 7.43.

The nmr spectrum (deuteriochloroform) exhibited two 3 H singlets at 129 (Me) and 215 cps (MeO), two 5 H singlets at 417.5 and 433 cps (Ph), one 4 H quartet at 409 and 429 cps (*p*-MeC<sub>6</sub>H<sub>4</sub>S<sup>-</sup>), and half of another quartet at 385 and 394 cps (the other half is buried under other peaks).

**1-Anisyl-2,2-diphenyl 1-Ethyl Ether.** 1-Anisyl-2,2-diphenylvinyl bromide (365 mg, 1 mM) and silver carbonate (280 mg, 1 mM) in 80% ethanol (70 ml) were refluxed for 4 hr. The hot solution was filtered and rinsed with warm ethanol, and water was added to turbidity. On cooling, 1-anisyl-2,2-diphenylvinyl 1-ethyl ether (197 mg, 60%), mp 100–101° (from ethanol), was obtained.

*Anal.* Calcd for C<sub>23</sub>H<sub>26</sub>O<sub>2</sub>: C, 83.62; H, 6.69; OMe + OEt (calcd as MeO), 19.62. Found: C, 83.53; H, 6.38; OMe + OEt, 19.6.

The nmr spectrum (deuteriochloroform) exhibited a 3 H triplet at 71 cps (*J* = 6.5 cps, Me), a 3 H singlet at 223 cps (MeO), a 2 H quartet at 220 cps (CH<sub>2</sub>), two 5 H singlets at 420 and 435 cps (Ph), and two overlapping 4 H quartets (protons at 402 and 427 cps, An).

**$\alpha,\alpha$ -Diphenyl-*p*-methoxyacetophenone.** 1-Anisyl-2,2-diphenylvinyl bromide (3.65 g, 0.01 *M*) and sodium formate (0.7 g, 0.01 *M*) in formic acid (100 ml) were refluxed for 48 hr. On cooling and addition of water  $\alpha,\alpha$ -diphenyl-*p*-methoxyacetophenone (3.1 g, 100%), mp 126–127°, was separated. Recrystallization (ethanol) gave white crystals, mp 127–128° (lit.<sup>19</sup> mp 128.5–129.5°); parent peak at *m/e* 302; C=O stretching at 1680 cm<sup>-1</sup>; nmr (deuteriochloroform) 3 H singlet at 228 cps (MeO), 1 H singlet at 363 cps (CH), 10 H singlet at 442 cps (two Ph), and two overlapping quartets, *J* = 8 cps (protons at 416 and 484 cps, An).

**Solvolysis of Trianisylvinyl Bromide. (a) Formation of 4.** Many experiments had been done in order to isolate 4. In a typical one, 12 ampoules, each containing trianisylvinyl bromide (180 mg) in basic (0.25 *N* sodium hydroxide) 80% ethanol (7 ml), were kept 80 hr at 120°. Then, they were cooled and combined, the solvent was evaporated, acetone was added, the inorganic salts were filtered, and the acetone was evaporated. Attempts to crystallize the residue gave only oil with C=O absorption at 1670 cm<sup>-1</sup> and nmr consistent with 4 as described in the Results.

**(b) Isolation of 5 from Chromatography.** Trianisylvinyl bromide (1.6 g) in basic (0.35 *N* sodium hydroxide) 80% ethanol (60 ml) was kept at 120° for 2.5 hr, poured into water, and extracted with chloroform which was dried and evaporated. The formed oil was chromatographed on a silica gel column (50 g, Fischer) using benzene, chloroform–benzene, and chloroform. Only oils were obtained except for one of the chloroform fractions which gave a solid, mp ca. 90° (30 mg), which was identified as the ethyl ether 5 by its nmr.

**(c) Mass Spectral Analysis.** The mass spectra of different crude reaction mixtures were dependent on the relative concentrations of the reactants and on the reaction times. Two typical examples with the suggested assignments are given in Table V.

**(d) Formation of 4,4'-Dimethoxybenzophenone (6).** Trianisylvinyl bromide (1.48 g, 3.5 mM) was added to a solution of sodium hydroxide (0.25 *N*) in 80% ethanol (40 ml) in a pressure bottle. After 6 hr at 120° the solution was cooled, and the solid (400 mg) was crystallized (ethanol). The white solid, mp 142–144°, was identified as 4,4'-dimethoxybenzophenone (6) by undepressed melting point with an authentic sample and identical ir, by nmr (3:4 ratio of OMe at 228 cps to an aromatic multiplet at 408–466 cps), and by mass spectra (base peak at *m/e* 242, other ones at *m/e* 227, 212, and 211).

**Solvolysis of 1-Br and 1-Cl in the Presence of Silver Salts.** The solvolysis of 1-Br was conducted in 80% ethanol up to several half-

lives in the presence of different silver salts. The silver bromide was filtered, the solvent was evaporated, and the oil was analyzed by nmr for the ketone 4 and the ether 5. Some ketone 6 may also be analyzed as 4 since differentiation between the two is difficult. With silver carbonate or silver acetate at 120° in 80% ethanol the ether/ketone ratio is 2:3 while with silver carbonate or silver oxide at reflux the ether was almost the exclusive product.

With sodium hydroxide, the ketone was the main product and the ether was formed only in minor quantities at 120°, but at reflux they were formed in a ratio of 1:1. In the presence of sodium hydroxide at 140° 1-Cl gave an ether/ketone ratio of 2:1.

**Formation of 4 from 1-Br in Formic Acid.** Trianisylvinyl bromide (2.06 g, 4.7 mM) in formic acid (75 ml) containing sodium formate (500 mg) was refluxed for 24 hr. The oil formed on evaporation of the solvent was dissolved in chloroform, which was washed, dried, and evaporated. The oil formed showed an nmr similar to that from solvolysis of 1-Br in 80% ethanol, which was ascribed to 4. Crystallization attempts failed.

**Trianisylvinyl Acetate.** Trianisylvinyl bromide (1.8 g, 4.2 mM) and silver acetate (0.72 g, 4.3 mM) in glacial acetic acid (25 ml) and acetic anhydride (2 ml) were refluxed for 2 hr. The hot solution was filtered, evaporated, dissolved in cyclohexane, and filtered, the solvent evaporated, and the oil obtained crystallized (ethanol) giving trianisylvinyl acetate, white crystals, mp 97–98° (1.55 g, 91%).

*Anal.* Calcd for C<sub>25</sub>H<sub>24</sub>O<sub>5</sub>: C, 74.23; H, 5.92. Found: C, 73.88; H, 5.92.

The ir spectrum exhibited C=O stretching at 1765 cm<sup>-1</sup>; nmr (deuteriochloroform) 3 H singlet at 121 cps (CH<sub>3</sub>CO<sub>2</sub>), two singlets (9 H) at 227 and 231 cps (MeO), and a 12 H multiplet at 402–441 cps (An).

**Basic Hydrolysis of Trianisylvinyl Acetate.** Trianisylvinyl acetate (600 mg) in 80% ethanol (50 ml) containing sodium hydroxide (1 g) was refluxed for 3 hr. Water was added to turbidity and the solution was left for 1 week, giving then white solid, mp 142–143°. This was identified as 4,4'-dimethoxybenzophenone by melting point, mixture melting point, ir, and nmr spectra. The filtrate was extracted with chloroform and washed with aqueous sodium carbonate, and the aqueous phase was acidified with hydrochloric acid until it was acidic. A solid, mp 182–183°, was obtained and identified as anisic acid by ir and undepressed melting point with an authentic sample. The oil in the chloroform solution could not be induced to crystallize.

**$\alpha,\alpha$ -Dianisyl-*p*-methoxyacetophenone Anisolate.** Anisoin (10 g, 0.06 *M*) was added with vigorous stirring to anisole (54 g, 0.5 *M*) in polyphosphoric acid (70 g) at 90°. After 0.5 hr the solution was poured slowly into ice–water, and the white solid (13.1 g, 100%) was filtered, washed with dilute sodium hydroxide, and crystallized from alcohol, acetic acid, or chlorobenzene–hexane. White crystals, mp 77–79° (lit.<sup>20b</sup> mp 77–79°), of 4-anisolate were obtained:  $\lambda_{\text{max}}^{95\% \text{ EtOH}}$  276 m $\mu$  (shoulders at 249, 255, 261 m $\mu$ ); ir (chloroform) 1670 cm<sup>-1</sup>; nmr 12 H (MeO, three singlets, 225–230 cps), 1 H (CH singlet, 358 cps), 17 H (aromatic multiplet, 408–486 cps).

**Steam Distillation of the Anisolate.** The anisolate (6 g) was steam distilled, the remaining oil was extracted with chloroform and dried, and the solvent was evaporated. Crystallization (ethanol) did not give immediately any solid. After 2 months, crystals, mp 135–137°, separated and were identified as 4,4'-dimethoxybenzophenone by mixture melting point.

**Reaction of the Anisolate with Base.** The anisolate (1 g) in 80% ethanol (40 ml) and sodium hydroxide (1 g) was refluxed for 4 hr. On cooling, a solid, mp 134–136° (a few milligrams), was precipitated, and identified by mixture melting point, ir, and thin layer chromatography as 4,4'-dimethoxybenzophenone.

**Solvolysis Products from 1-Anisyl-2,2-diphenylvinyl Bromide.** 1-Anisyl-2,2-diphenylvinyl bromide (2.5 g) in 80% ethanol (140 ml) containing sodium hydroxide (0.29 *N*) in a pressure bottle was kept at 128° for 6 hr. The solvent was evaporated and the



oil was extracted with chloroform which was dried and evaporated. Most of the compound was precipitated as an oil on crystallization from dilute ethanol, but a solid, mp ca. 110°, with  $C=O$  absorption at 1680  $cm^{-1}$  and the same nmr as  $\alpha, \alpha$ -diphenyl-*p*-methoxyacetophenone was formed. In a similar experiment the ir of the chloroform-extracted oil showed absorptions at 1605 and 1680  $cm^{-1}$ , and an nmr consistent with a mixture of the ketone and 1-anisyl-2,2-diphenyl 1-ethyl ether. For example, a ketone-ether ratio of 1:1 was obtained from the bromide in refluxing basic 80% ethanol for 140 hr.

**Attempts for Uncatalyzed Solvolysis of Triphenylvinyl Bromide.** Triphenylvinyl bromide and excess triethylamine in 80% ethanol were kept for 20 hr at 150°, for 10 hr with potassium hydroxide in 50% ethanol, or with sodium or lithium acetate in acetic acid at 150° for 7 hr. The starting material was recovered always unchanged in yields higher than 90%.

**Solvolysis of Triphenylvinyl Halides in the Presence of Silver Salts.** After reflux for 12 hr of triphenylvinyl chloride in acetic acid containing silver acetate, or in 50% ethanol containing silver oxide, the starting material was recovered unchanged. Reaction of triphenylvinyl bromide (6.7 g, 20 mM) with silver acetate (3.5 g, 21 mM) in acetic acid (50 ml) and acetic anhydride (1 ml), for 10 hr at 118°, followed by filtration and addition of water gave triphenylvinyl acetate: mp 104° (lit.<sup>77</sup> mp 104.5–105.5°) (4.6 g, 74%); ir (Nujol) 1780  $cm^{-1}$ ; nmr signals in the ratio 1:5 at 114 cps ( $CO_2Me$ ) and 426–450 cps (aromatic).

**Kinetic Runs.** Triarylvinyll halide was weighted individually (90–180 mg) into each of seven to eight glass ampoules, prepared according to Grob.<sup>14</sup> Basic 80% ethanol (7 ml) was added, and the cooled (liquid air) ampoule was sealed. The ampoules were heated for a few minutes to ca. 60–70° in order to facilitate dissolution, and introduced into the oil bath. When thermal equilibrium was achieved (0.5–2 min) the ampoules were shaken vigorously until all the oily substrate was dissolved. If this is not done, much lower steady first-order rate coefficients are obtained. The slow solubility causes apparent lower rate coefficients for the first kinetic point compared to later ones. At appropriate intervals the am-

poules were taken out, cooled, and opened, and 5-ml samples were titrated against standard silver nitrate using eosin and dichlorofluorescein indicators for the bromide and the chloride ions, respectively.

Halide analyses in experiments with *p*-toluenethiolate ion cannot be performed similarly since the sulfur compounds reacted with silver nitrate. In these cases, excess aqueous cupric nitrate was added to the sample to trap all the free *p*-toluenethiolate ion, the solid obtained was filtered, and the filtrate was titrated as usual. When *p*-toluenethiolate ion, bromide free, was treated with aqueous cupric nitrate and eosin, a temporary violet color, which disappeared after few minutes, was formed. This was absent in the titrations of the kinetic points, and in control experiments the method gave satisfactory bromide analysis. However, in infinity kinetic points the bromide was less than calculated for 100% reaction. It is not known if this is due to the method, or inherent in the reaction.

**Table VI.** Kinetic Experiments

(a) $31 \times 10^{-3} M$ trianisylvinyl bromide, $29 \times 10^{-2} M$ sodium hydroxide, 109.3°						
Time, min	19	33	44	60	87	137
% reaction	18.1	31.7	39.5	49.6	62.8	79.0
$k_1 \times 10^4 \text{ sec}^{-1}$	1.75	1.90	1.90	1.90	1.89	1.89
Av $k_1 = (1.87 \pm 0.04) \times 10^{-4}$						
(b) $43 \times 10^{-3} M$ 1-anisyl-2,2-diphenylvinyl bromide, $11 \times 10^{-2} M$ sodium <i>p</i> -toluenethiolate, 120.3°						
Time, min	24	30	40	65	92	133
% reaction	20.1	26.1	33.6	49.1	58.4	66.4
$k_1 \times 10^4 \text{ sec}^{-1}$						
<i>a</i>	1.78	1.91	1.93	1.97	1.81	1.76
<i>b</i>	1.57	1.68	1.70	1.73	1.59	1.40
Av $k_1 = (1.86 \pm 0.08) \times 10^{-4}$ <sup>a</sup>						
Av $k_1 = (1.61 \pm 0.09) \times 10^{-4}$ <sup>b</sup>						

<sup>a</sup> Based on measured infinity. <sup>b</sup> Based on calculated infinity.

**Sample Runs.** Table VI gives two samples of the kinetic experiments.

(77) H. Biltz, *Ann.*, **296**, 219 (1897).

## Deuterium-Labeling Studies of Intramolecular Hydrogen Transfer Reactions and the Problem of Hydrogen-Deuterium Rearrangement in Mass Spectra. The Case of Isopropyl *n*-Butyl Ether

G. A. Smith and Dudley H. Williams

Contribution from the University Chemical Laboratory, Cambridge, England.  
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**Abstract:** In the mass spectrum of isopropyl *n*-butyl ether, the origin of the hydrogen atom transferred in the loss of  $C_4H_8$  from the  $M^+ - CH_3$  ion has been studied as a function of the internal energies of the  $M^+ - CH_3$  ions. Strong evidence in favor of intramolecular H-H rearrangements within the *n*-butyl chain prior to loss of  $C_4H_8$  (or  $H_2O$ ) is forthcoming. As a consequence of the internal hydrogen exchange reactions which probably occur, it is concluded that deuterium-labeling studies of hydrogen rearrangement processes do not in the present case allow one to infer the size (assumed) of cyclic transition states where several carbon loci are apparently involved. Competing metastable transitions are utilized to establish that after a few microseconds, the  $M^+ - CD_3$  ions from  $(CD_3)_2CDOCH_2CH_2CH_2CH_3$  and  $(CD_3)_2CDOCH(CH_3)CH_2CH_3$  have not undergone, to any large extent, isomerization of the four-carbon atom chain to give common structures.

As first pointed out by McLafferty,<sup>1</sup> the two most characteristic reactions undergone by simple aliphatic ethers upon electron impact are  $\alpha$  cleavage in the molecular ion (e.g., **1**  $\rightarrow$  **a**), followed by elimination of

(1) F. W. McLafferty, *Anal. Chem.* **29**, 1782 (1957).

the remaining alkyl chain as a neutral particle with associated hydrogen migration (e.g., **a**  $\rightarrow$  **b**).

Although deuterium labeling clearly establishes which portions of the molecule are eliminated in the above two steps,<sup>2</sup> the structures of the ions **a** and **b** are only plau-