Vinyl Cations. Part 13.[1] Secondary Kinetic Deuterium Isotope Effects in the Solvolysis of Ring-substituted β-Styryl Trifluoromethanesulphonates [1,2]

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The β-kinetic deuterium isotope effects have been measured in the solvolysis of a series of ring-substituted β-styryl trifluoromethanesulphonates. At 75 °C in aqueous 80% ethanol for the parent compound. $k_H/k_D = 1.45$: for *p*-Cl. $k_H/k_D = 1.74$: for *m*-Cl. $k_H/k_D = 1.61$: for *p*-CF_3. $k_H/k_D = 1.64$: for *p*-NO_2. $k_H/k_D = 1.71$. Both the protio- and deuterio-series gave an excellent Hammett correlation with σ^+ (ρ −4.12 and −4.17, respectively). The products of solvolysis were the corresponding acetophenones and phenylacetylenes. The significance of these results is discussed.

DEUTERIUM isotope effects have been extensively employed as mechanistic probes in chemical reactions in general and in solvolysis reactions in particular.[3] In recent years besides solvolysis of saturated substrates there has been considerable interest and activity in the solvolysis of unsaturated systems and the attendant generation of vinyl cations.[4]

The first solvolytic generation of a vinyl cation was reported by Grob and Cseh [5] on a series of ring-substituted β-styryl bromides. Despite continued interest and a considerable amount of work on such aryl [6] and other stabilized [7] vinyl cations a number of questions such as the extent of bond breaking in transition state, the degree of phenyl rotation in the transition state, the effect of substituents on the stabilities of the intermediate

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[1] Part 12, P. J. Stang and T. E. Deuber, *J. Amer. Chem. Soc.*, 1977, **99**, 2602. Preliminary communication, R. J. Hargrove, T. E. Deuber, and P. J. Stang, *Chem. Comm.*, 1970, 1614.

[2] Abstracted in part from the Ph.D. Thesis of R. J. Hargrove, The University of Utah, 1974.

[3] For reviews see (*a*) S. E. Scheppele, *Chem. Rev.*, 1972, **72**, 511; (*b*) C. J. Collins and N. S. Bowman, 'Isotope Effects in Chemical Reactions,' Van Nostrand Reinhold, New York, 1970; (*c*) M. Wolfsberg, *Ann. Rev. Phys. Chem.*, 1968, **19**, 449; (*d*) E. F. Thornton, *ibid.*, 1966, **17**, 349; (*e*) P. Laszlo and Z. Welvart, *Bull. Soc. chim. France*, 1966, 2412; (*f*) E. A. Halevi, *Progr. Phys. Org. Chem.*, 1963, **1**, 109; (*g*) A. Streitwieser, jun., 'Solvolytic Displacement Reactions,' McGraw-Hill, New York, 1962; (*h*) F. W. Westheimer, *Chem. Rev.*, 1961, **61**, 265; (*i*) L. Melander, 'Isotope Effects on Reaction Rates,' Ronald Press, New York, 1960.

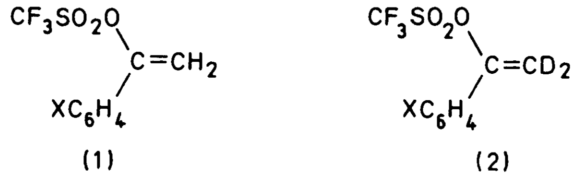
[4] For reviews see (*a*) L. R. Subramanian and M. Hanack, *J. Chem. Educ.*, 1975, **52**, 80; (*b*) P. J. Stang, *Progr. Phys. Org. Chem.*, 1973, **10**, 205; (*c*) G. Modena and U. Tonellato, *Adv. Phys. Org. Chem.*, 1971, **9**, 185; (*d*) M. Hanack, *Accounts Chem. Res.*, 1970, **3**, 209.

[5] C. A. Grob and C. Cseh, *Helv. Chim. Acta*, 1964, **47**, 194.

[6] Z. Rappoport, *Accounts Chem. Res.*, 1976, **9**, 265.

[7] M. Hanack, *Accounts Chem. Res.*, 1976, **9**, 364.

ions, *etc.*, remain largely unanswered. Hence in order to gain a better insight into these questions we investigated the solvolytic behaviour of a series of ring substituted β-styryltrifluoromethanesulphonates (triflates) (1) and their dideuterio-analogues (2).



(1) (2)

a; X = H
b; X = *p*—Cl
c; X = *m*—Cl
d; X = *p*—CF_3
e; X = *p*—NO_2

RESULTS AND DISCUSSION

Vinyl triflates (1) and (2) were prepared from the corresponding acetophenones and their deuterio-analogues, respectively, and the anhydride of trifluoromethanesulphonic acid according to literature procedures.[8] The appropriate deuterioacetophenones were prepared by repeated exchange of the enolizable hydrogens of the corresponding acetophenones with D_2O and NaOD.

TABLE 1

Rates of reaction of vinyl triflates (1) and (2) in 80% EtOH

Compd.	t/°C	k/s^{-1}	$\Delta H^‡$/ kcal mol^{-1}	$\Delta S^‡$/ cal mol^{-1} K^{-1}
(1a)	25.00	$(1.11 \pm 0.01) \times 10^{-4}$		
	49.93	$(2.31 \pm 0.04) \times 10^{-3}$		
	75.0 *	3.15×10^{-2}	22.6 ± 0.2	-0.8 ± 0.7
(1b)	49.99	$(8.70 \pm 0.14) \times 10^{-4}$		
	75.0 *	1.33×10^{-2}	23.7 ± 0.4	0.6 ± 1.0
	75.09	$(1.34 \pm 0.03) \times 10^{-2}$		
(1c)	49.97	$(6.80 \pm 0.15) \times 10^{-5}$		
	75.0 *	1.10×10^{-3}	24.1 ± 0.2	-3.1 ± 0.7
	76.84	$(1.34 \pm 0.01) \times 10^{-3}$		
	85.27	$(3.04 \pm 0.05) \times 10^{-3}$		
(1d)	75.00	$(9.83 \pm 0.76) \times 10^{-5}$	24.6 ± 1.2	-6.6 ± 3.5
	100.00	$(1.13 \pm 0.05) \times 10^{-3}$		
(1e)	75.0 *	1.96×10^{-5}	29.0 ± 0.3	3.1 ± 0.6
	75.15	$(2.00 \pm 0.02) \times 10^{-5}$		
	100.06	$(3.52 \pm 0.03) \times 10^{-4}$		
(2a)	25.00	$(7.83 \pm 0.13) \times 10^{-5}$		
	49.93	$(1.63 \pm 0.05) \times 10^{-3}$		
	75.0 *	2.20×10^{-2}	22.6 ± 0.4	-1.6 ± 1.2
(2b)	49.96	$(6.05 \pm 0.13) \times 10^{-3}$		
	75.00	$(7.93 \pm 0.31) \times 10^{-3}$	22.3 ± 0.5	-4.5 ± 1.7
(2c)	49.94	$(3.89 \pm 0.08) \times 10^{-5}$		
	75.0 *	6.97×10^{-4}	25.1 ± 0.2	-1.3 ± 0.7
	75.03	$(7.01 \pm 0.14) \times 10^{-4}$		
	85.27	$(2.02 \pm 0.04) \times 10^{-3}$		
(2d)	75.00	$(6.08 \pm 0.47) \times 10^{-5}$	25.2 ± 1.1	-5.8 ± 4.0
	100.00	$(7.44 \pm 0.45) \times 10^{-4}$		
(2e)	75.0 *	1.17×10^{-5}	27.2 ± 0.5	-3.3 ± 1.2
	75.29	$(1.21 \pm 0.02) \times 10^{-5}$		
	100.02	$(1.75 \pm 0.05) \times 10^{-4}$		

* Extrapolated.

Rates were measured conductometrically in aqueous 80% ethanol and are averages of 2—6 determinations. The results are summarized in Table 1.

Product studies were carried out for representative β-styryl triflates in buffered and unbuffered media. The products in all cases consisted of the corresponding arylacetylene and acetophenones and their deuterio-analogues as shown in Table 2.

Perusal of these data reveals a number of interesting facts and trends. The rate data of both (1) and (2) give an excellent Hammett correlation with σ^+ [9] as shown in Figures 1 and 2.

The observed ρ value of —4.1 indicates considerable charge development in the transition state consistent with a vinyl cation mechanism. The value of ρ in this work is in reasonable agreement with the value (—5.1) observed by Grob and his co-workers [5,10] in the solvolysis of β-styryl bromide, and the value (—3.8) observed by Noyce and Schlavelli [11] in the acid-catalysed hydration of arylacetylene, considering the differences in solvolysis

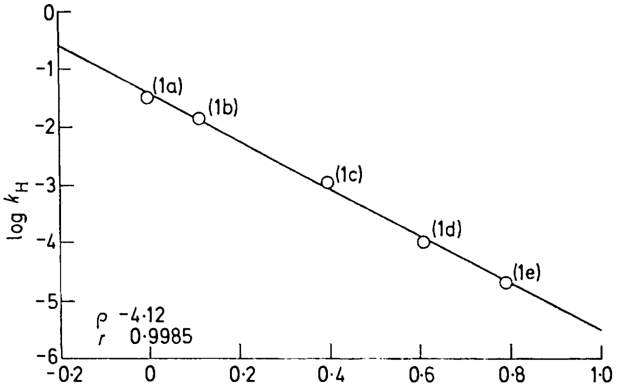


FIGURE 1 Hammett plot of log k_H *versus* σ^+ of substituted β-styryl triflates

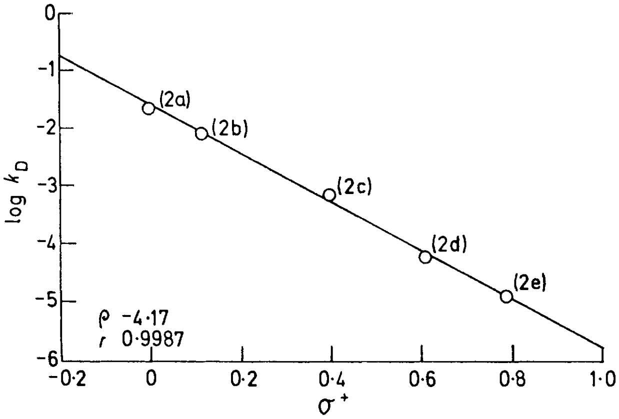


FIGURE 2 Hammett plot of log k_D *versus* σ^+ of substituted β-styryl triflates

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[8] P. J. Stang and T. E. Dueber, *Org. Synth.*, 1974, **54**, 79; T. E. Dueber, P. J. Stang, W. D. Pfeiffer, R. H. Summerville, M. A. Imhoff, P. V. R. Schleyer, K. Hummel, S. Bocher, C. E. Harding, and M. Hanack, *Angew. Chem. Internat. Edn.*, 1970, **9**, 521.

[9] C. W. McGary, Y. Okamoto, and H. C. Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 3037; H. C. Brown and Y. Okamoto, *ibid.*, 1958, **80**, 4980.

[10] C. A. Grob and H. R. Pfaendler, *Helv. Chim. Acta*, 1974, **54**, 2060; C. A. Grob, and R. Nussbaumer *ibid.*, 1971, **54**, 2528.

[11] D. S. Noyce and M. D. Schiavelli, *J. Amer. Chem. Soc.*, 1968, **90**, 1020.

media, temperature, and substrates. The somewhat surprising aspect of this data is that even the strongly destabilizing *p*-nitro-substituent falls on the correlation line and hence must react *via* the same type of vinyl cation mechanism as the parent system and the activated substrates of Grob and Noyce.

The rate data in the Table 1 allow calculation of the β-deuterium isotope effects given in Table **3**. The isotope effect of $k_H/k_D = 1.45$ for the parent compound is in good agreement with the values observed by Jones [12] and Maness [13] for the acetolysis of this compound.

TABLE 2

Product study of representative vinyl triflates (1) and (2)

Starting triflate	Reaction conditions	$XC_6H_4C{\equiv}CH$ (%)	$XC_6H_4\overset{O}{\overset{\|\|}{C}}CH_3$ (%)
(1a)	80% EtOH, 50.0°	35.1 ± 0.4	64.8 ± 0.4
	80% EtOH + 1 equiv. Et_3N, 50.0°	38.2 ± 0.4	61.8 ± 0.4
(1c)	80% EtOH, 50.0°	39.5 ± 0.4	60.5 ± 0.1
	80% EtOH + 1 equiv. Et_3N, 50.0°	43.2 ± 0.5	56.8 ± 0.1
(1e)	70% Acetone, 75.0°	58.1 *	9.3 *
	70% Acetone + 1 equiv. Et_3N, 75.0°	0 *	9.3 *
(2c)	80% EtOH, 50.0°	36.0 ± 0.8	64.0 ± 0.9
	80% EtOH + 1 equiv. Et_3N, 50.0°	37.7 ± 0.6	62.3 ± 0.6
(2e)	70% Acetone, 75.0°	41.8 *	14.2 *
	70% Acetone + 1 equiv. Et_3N, 75.0°	14.2 *	10.7 *

* Product not stable under reaction conditions employed.

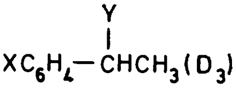
TABLE 3

Kinetic deuterium isotope effects for triflates (1) and (2) in 80% EtOH at 75 °C

Compound	k_H/k_D *	$\Delta\Delta F^{\ddagger}$/cal mol^{-1} per D *
(1a)/(2a)	1.45 ± 0.05	128
(1b)/(2b)	1.74 ± 0.10	191
(1c)/(2c)	1.61 ± 0.04	165
(1d)/(2d)	1.64 ± 0.23	171
(1e)/(2e)	1.71 ± 0.04	185

* Corrected to 100% D. See Experimental section.

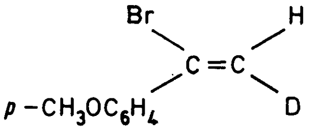
β-Deuterium isotope effects in solvolytic reactions have been ascribed to differential hyperconjugative overlap of the C–H(D) bond with the developing vacant *p*-orbital at the reaction site.[3] It has been shown that such β-isotope effects are strongly dependent upon the dihedral angle between the empty *p*-orbital and the β-C–H bond with maximum effects observed with a dihedral angle of 0°.[14] Owing to their linear geometry vinyl cations satisfy this requirement perfectly, hence one observes much larger β-deuterium effects in the present substrates than Shiner and his co-workers [15] observed in the solvolysis of 1-aryl-1-halogenoethanes (3) where k_H/k_{D_3} effects varied from 1.113 for the *p*-methoxy-isomer to 1.224 for the parent compound and 1.151 for the *p*-nitro-isomer. Such enhanced β-deuterium isotope effects have also been observed in the solvolytic generation of simple alkylvinyl cations compared to their saturated analogues.[16] The effect of substituents upon the isotope effect is revealing. The more destabilizing substituents such as *p*-NO_2 and *p*-CF_3 result in increased isotope effects indicating a greater need for hyperconjugative stabilization of the developing empty *p*-orbital with increasing electron withdrawal by the substituents. This trend is the same as that observed by Shiner [15] in the saturated substrates (3), but of a much larger magnitude. The fact that the isotope effects, with the exception of the *p*-chloro-isomer, correlate with σ^+ as shown in Figure **3** is in accord with the Hammond [17] and Swain–Thornton [18] postulates. Such deuterium isotope effects have also been observed in the ionization of diphenylmethanols [19] and the hydrolysis of acetals and orthoformates.[20]



$$XC_6H_4{-}\overset{\displaystyle Y}{\overset{|}{C}}HCH_3(D_3)$$

(3)

Y=Cl or Br



(4)

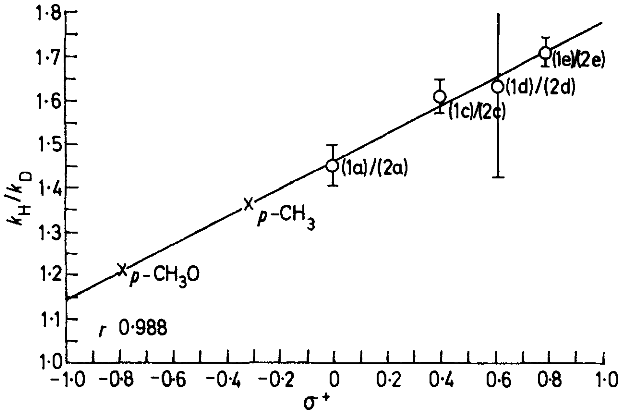


FIGURE 3 β-Deuterium isotope effects *versus* σ^+ for substituted β-styryl triflates: ○, experimental; ×, calculated

Extrapolation of our data as shown in Figure **3** predicts k_H/k_D 1.36 for *p*-CH_3 and k_H/k_D 1.21 for *p*-CH_3O. Unfortunately these activated triflates (1) and (2) could not be prepared owing to their very high reactivity and we were equally unsuccessful in preparing less reactive

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[12] W. M. Jones and D. D. Maness, *J. Amer. Chem. Soc.*, 1970, **92**, 5457.

[13] D. D. Maness and L. D. Turrentine, *Tetrahedron Letters*, 1973, 755.

[14] A. Streitwiesser, jun., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Amer. Chem. Soc.*, 1958, **80**, 2326; V. J. Shiner, jun., *ibid.*, 1960, **80**, 2655; V. J. Shiner, jun., and J. S. Humphrey, *ibid.*, 1963, **85**, 2416; V. J. Shiner, jun., and J. G. Jewett, *ibid.*, 1964, **86**, 945; J. G. Jewett and R. P. Dunlap, *ibid.*, 1968, **90**, 809; B. L. Murr and J. A. Conklin, *ibid.*, 1970, **92**, 3464.

[15] V. J. Shiner, jun., W. E. Buddenbaum, B. L. Murr, and G. Lamaty, *J. Amer. Chem. Soc.*, 1968, **90**, 418.

[16] P. J. Stang, R. J. Hargrove, and T. E. Dueber, *J.C.S. Perkin II*, 1974, 843.

[17] G. S. Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.

[18] C. G. Swain and E. R. Thornton, *J. Amer. Chem. Soc.*, 1962, **84**, 822; E. R. Thornton, *ibid.*, 1967, **89**, 2915.

[19] M. M. Mocek and R. Stewart, *Canad. J. Chem.*, 1963, **41**, 1641.

[20] H. Bull, T. C. Pletcher, and E. H. Cordes, *Chem. Comm.*, 1970, 527.

sulphonate esters such as βββ-trifluoroethanesulphonates.[21] However, the value of $k_H/k_D = 1.20$ for the p-methoxystyryl system is in reasonable agreement with the value predicted by Noyce and Schiavelli [22] from the hydration of p-$CH_3OC_6H_4C{\equiv}CH$ and the value of $k_H/k_D = 1.20$ observed by Rappoport and Apeloig [23] in the acetolysis of a mixture of *E*- and *Z*-deuterio-β-methoxystyryl bromide (4). Hence the full range of the effects of substituents upon the β-deuterium isotope effects in the solvolysis of the styryl triflates (1) and (2) would be 3.5-fold from k_H/k_D 1.21 for p-CH_3O to k_H/k_D 1.71 for p-NO_2.

Finally, both the excellent Hammett correlation (Figure 1) as well as the linearity of the correlation between k_H/k_D and σ^+ (Figure 3) suggest that rotation of the aryl group to deconjugate with the C=C double bond and conjugate with the nascent empty p-orbital occurs early on the reaction co-ordinate and must be complete, or nearly complete, at the transition state leading to the intermediate vinyl cations.

EXPERIMENTAL

All b.p.s are uncorrected. N.m.r. spectra were recorded on a Varian A-60 spectrometer using tetramethylsilane as internal standard and i.r. spectra were obtained on a Beckman IR-5A spectrometer. Mass spectra were obtained on an AEI MS-30 mass spectrometer. G.l.c. was performed on a Varian Aerograph 90-P unit using the following aluminium columns: A, 0.375 in × 15 ft, 15% SF-96 on 45–60 Chromosorb W; B, 0.25 in × 5 ft, 10% SF-96 on 60–80 Chromosorb W; C, 0.25 in × 10 ft, 10% SF-96 on 60–80 Chromosorb W; D, 0.375 in × 15 ft, 15% Carbowax 20 M on 45–60 Chromosorb W.

Materials.—Trifluoromethanesulphonic acid was purchased from 3M Company and used without further purification. Acetophenone was purchased from Matheson, Coleman and Bell, p-chloro- and p-nitro-acetophenone were obtained from Aldrich Chemical Company, m-chloroacetophenone was purchased from Eastman Kodak Company, and p-trifluoromethylacetophenone from Pierce Chemical Company and all were used without further purification.

Preparation of Trideuterioacetophenones.—Each of the acetophenones (*ca.* 0.02—0.09 mol) were exchanged with D_2O and NaOD as follows. A stock solution of 0.5M-NaOD was prepared by reacting sodium metal with D_2O. Each ketone was placed in a 25 ml Erlenmeyer flask with a wired-on serum cap and 0.5M-NaOD (4—6 ml) was added with a syringe; the mixture was stirred for 24 h at room temperature, the spent D_2O removed, and new D_2O added. A total of 4—6 such exchanges were carried out on each ketone. At the end of the exchange the organic layer was separated, dissolved in dry ether or benzene, and dried ($MgSO_4$), the solvent evaporated, and the deuteriated ketone was vacuum distilled.

Synthesis of Vinyl Triflates (1) *and* (2).—Vinyl triflates (1a—e) were prepared from the appropriate acetophenones and (2a—e) from the corresponding deuterioacetophenones according to the following general procedure.[8] A solution of the ketone (10—30 mmol) and anhydrous pyridine (1.1 equiv.) in anhydrous CCl_4 (15—30 ml) was cooled to −78° in a 50 ml Erlenmeyer flask stoppered with a wired-on cap. To the cooled solution was added triflic anhydride (1.1 equiv.; from CF_3SO_3H–P_2O_5) over a 5—10 min period with a syringe. The mixture was kept at −20° overnight, then allowed to stand at room temperature for 1—14 days until an intense dark colour developed. At the end of this period the mixture was diluted with additional CCl_4, filtered, the organic layer quickly washed with ice-cold water, and dried ($MgSO_4$). After filtration, the solvent was evaporated and the residue vacuum distilled. Yields averaged *ca.* 35%. The physical and spectral properties of these triflates are given in Table 4.

TABLE 4

Physical and spectral properties of vinyl triflates (1) and (2)

Compd.	B.p. (°C) [p/Torr]	Chemical shift δ C=CH$_2$	ArH	$\nu_{max.}$/cm^{-1} C=C	O=S=O	CF	CD	Other	%D *
(1a)	44—45 [0.3]	5.30, 5.45	7.30	1 655	1 431	1 224, 1 151			
(1b)	79—81 [0.9]	5.33, 5.53	7.27, 7.46	1 653	1 424	1 222, 1 145			
(1c)	52—56 [0.1]	5.42, 5.63	7.43	1 647	1 422	1 220, 1 141			
(1d)	39—44 [0.25]	5.62	7.57	1 626	1 404	1 221, 1 142			
(1e)	110—112 [0.1]	5.56, 5.80	7.67, 8.20	1 647	1 424	1 227, 1 144		1 531, 1 351 (NO_2)	
(2a)	45—46 [0.35]		7.46	1 613	1 424	1 264, 1 219	2 241		98 ± 3
(2b)	47—49 [0.07]		7.45	1 608	1 418	1 212, 1 143	2 237		92 ± 2
(2c)	43—47 [0.03]		7.15	1 610	1 422	1 221, 1 144	2 257		94 ± 2
(2d)	56—60 [0.5]		7.52	1 610	1 418	1 223, 1 147	2 232		97 ± 2
(2e)			8.30—9.81	1 595	1 426	1 225, 1 194	2 262	1 526, 1 351 (NO_2]	96 ± 2

* By integration of expanded n.m.r. spectra.

Kinetic Measurements.—Rate studies were carried out conductometrically in aqueous 80% ethanol (v/v), unbuffered, in 2 ml of stock solution in carefully controlled constant temperature baths containing 2 μl of substrate per 10 ml of solvent. Ethanol was purified by treating commercial 99.5% ethanol with sodium metal, then ethyl phthalate, according to the method of Wiberg.[24] Excellent first-order rates were observed in all instances for >5 half-lives. The rates were calculated by a non-linear, least squares program (LSKIN-1) [25] and are averages of 2—6 determinations. Results are given in Table 1.

Product Studies.—Product studies were carried out in all instances by means of inert internal standards and with the aid of authentic samples and analysed by g.l.c. Reactions

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[21] R. K. Crossland, W. E. Wells, and V. J. Shiner, jun., *J. Amer. Chem. Soc.*, 1971, **93**, 4217.

[22] D. S. Noyce and M. D. Schiavelli, *J. Amer. Chem. Soc.*, 1968, **90**, 1023.

[23] Z. Rappoport and Y. Apeloig, *J. Amer. Chem. Soc.*, 1974, **96**, 6428.

[24] K. Wiberg, 'Laboratory Techniques in Organic Chemistry,' McGraw-Hill, New York, 1960.

[25] D. F. DeTar and C. E. DeTar, 'Computer Programs in Chemistry,' Benjamin, New York, 1964.

were allowed to proceed for 3—4 half-lives and were carried out both buffered and unbuffered, in aqueous 80% ethanol at 50° for (1a), (1e), and (2c) and in aqueous 70% acetone at 75° for (1e) and (2e). The products, except for those resulting from (1e) and (2e) were found to be stable under the reaction conditions.

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