Reactivity of Vinyl Sulphonic Esters. Part XVI.[1] Solvolytic Reactivity of β-Halogenovinyl Derivatives

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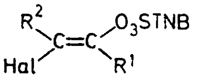
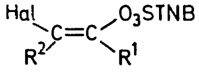
The solvolytic reactivity of *trans*- (I) and *cis*- (II) β-halogenovinyl 2,4,6-trinitrobenzenesulphonates, $R^2(Hal)C{:}C(O_3SAr)R^1$ [(I; Hal = Cl, Br, or I, R^1,R^2 = alkyl or aryl), (II; Hal = Cl or Br, R^1,R^2 = aryl)], has been investigated in acetic acid and in nitromethane–methanol. The kinetics and products indicate that the solvolysis in both solvents proceeds by S_N1 and S_N1–$E1$ mechanisms in the case of some β-iodovinyl derivatives. The reactivity of esters (I) strongly depends on the nature of the halogen and follows the order I $\gg$ Br > Cl. The *trans*-esters (I: R^1,R^2 = aryl) are more reactive than the corresponding *cis*-isomers when Hal = Br [$k_{(I)}/k_{(II)}$ = 10—15] and almost equally reactive when Hal = Cl. The substitution products from (I: Hal = I) retain the *trans*-geometry, whereas the substitutions of esters (I) and (II) (R^1,R^2 = aryl), when Hal = Br or Cl, are not stereospecific. Anchimeric assistance due to iodine and, to a much lesser extent, to bromine are suggested to be involved. The results are also discussed in terms of bridged *versus* open geometry for the intermediate vinyl cations and compared with those for electrophilic additions of halogens to the C≡C triple bond.

In spite of the large number of recent studies [2] on the S_N1-type reactivity of vinyl derivatives, the available data do not allow one to draw satisfactory conclusions on the effect of β-substituents. Except for RS or ArS groups (when *trans* to the leaving group) which can promote large increases in reactivity (up to 10^4—10^5) because of anchimeric assistance by the sulphur atom,[3,4] the observed effects due to changes at the β-carbon are quite small. A systematic set of data is available [5] only for the series of α-bromo-*p*-methoxystyrenes: the solvolysis rate changes in 4 : 1 ethanol–water at 120° on going from β,β′-dimethyl to β,β′-di-*p*-methoxyphenyl, to β,β′-diphenyl, and to β-unsubstituted derivatives are within a factor of 4. Also by taking into account the levelling effect of the α-*p*-methoxyphenyl group and the limited range of inductive effects of the β-substituents, such small changes would indicate a surprising insensivity of the solvolytic reactivity to the polar effect of β-substituents. However, as further studies [6] have recently brought to light, the operation of other factors, steric in origin, may compensate for polar or neighbouring group participation phenomena.

We have studied the effect of β-halogen atoms: their strong inductive electron-withdrawing ability as well as their implication in anchimeric assistance are well documented [7] in the solvolysis of saturated systems. This paper reports the reactivity of *trans*- (I) and *cis*- (II) β-halogenovinyl 2,4,6-trinitrobenzenesulphonates.† Their synthesis [9] and a preliminary account [10] of their chemical properties have been presented.


(I)


(II)

a; Hal = I
b; Hal = Br
c; Hal = Cl
TNB = 2,4,6-$(NO_2)_3C_6H_2$

RESULTS

Esters (Ia—c) and (IIb and c) have been synthesized as described.[9] The *cis*-esters could be obtained mixed with the corresponding *trans*-isomers only in the synthesis of 1,2-diarylvinyl derivatives. In the case of β-bromovinyl esters the *trans*-isomer could be easily obtained pure and in one case ($R^1 = R^2 = p$-MeC_6H_4) both isomers (Ib) and (IIb) could be isolated. In the case of β-chlorovinyl derivatives the *cis*-isomer was isolated in each case and in one case ($R^1 = R^2 = p$-$MeOC_6H_4$) a mixture enriched in the *trans*-ester [(I) : (II) = 1·85 : 1] was obtained.

The kinetics of the reactions of the esters (I) and (II) were measured in nitromethane–methanol and in acetic acid since kinetic data for other vinyl trinitrobenzenesulphonates were obtained for these solvents and are available for comparison purposes.[3,4] Preliminary experiments showed that β-chloro- and β-bromo-vinyl esters are much less reactive than the corresponding β-iodo-derivatives: esters (Ic; R^1,R^2 = alkyl) and some of the less activated compounds [(IIc) or (Ic) (R^1,R^2 = aryl)] react at a measurable rate only well above 100° where decomposition of the trinitrobenzenesulphonate group has been shown [3d] to occur. Therefore, the rate of solvolysis for these compounds could not be measured.

Products.—(a) *From esters* (Ia). Acetolysis of ester (Ia; $R^1 = R^2 = Pr^n$) gave only the corresponding substitution product (IIIa) in one geometric form (by ^1H n.m.r. analysis). The *trans*-structure was tentatively assigned by analogy with that of the products derived from other esters (Ia) (see below). Acetolysis of 1,2-diphenyl- or 2-phenyl-1-*p*-tolyl-vinyl derivatives afforded mainly substitution products (IIIa) (by ^1H n.m.r.[11]) together with sizeable amounts (7—13%) of elimination products (V).

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† The leaving group ability [4,8] of the trinitrobenzenesulphonate group in vinylic S_N1-type reactions has been estimated to exceed that of the bromide ion by 10^5—10^6.

[1] Part XV, A. Burighel, G. Modena, and U. Tonellato, *J.C.S. Perkin II*, 1973, 1021.

[2] General references dealing with vinyl cations, (*a*) M. Hanack, *Accounts Chem. Res.*, 1970, **3**, 209; (*b*) G. Modena and U. Tonellato, *Adv. Phys. Org. Chem.*, 1971, **9**, 185; (*c*) P. J. Stang, *Progr. Phys. Org. Chem.*, 1973, **10**, 276.

[3] (*a*) G. Modena and U. Tonellato, *J. Chem. Soc.* (*B*), 1971, 374; (*b*) *ibid.*, p. 381; (*c*) G. Capozzi, G. Modena, and U. Tonellato, *ibid.*, p. 1700; (*d*) A. Burighel, G. Modena, and U. Tonellato, *J.C.S. Perkin II*, 1972, 2026.

[4] G. Modena and U. Tonellato, *J. Chem. Soc.* (*B*), 1971, 1569.

[5] Z. Rappoport and A. Gal, *J. Org. Chem.*, 1972, **37**, 1174, and references cited therein.

[6] (*a*) Z. Rappoport and M. Atidia, *J.C.S. Perkin II*, 1972, 2316; (*b*) C. A. Grob and R. Nussbaumer, *Helv. Chim. Acta*, 1971, **54**, 2528; (*c*) D. R. Kelsey and R. G. Bergman, *J. Amer. Chem. Soc.*, 1970, **92**, 228; 1971, **93**, 1941.

[7] (*a*) A. Streitwieser, jun., 'Solvolytic Displacement Reactions,' McGraw-Hill, New York, 1962, pp. 120—126; (*b*) G. Modena and G. Scorrano, in 'The Chemistry of Carbon–Halogen Bonds,' ed. S. Patai, Interscience, London, 1973, pp. 301—406.

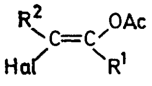
[8] Z. Rappoport and J. Kaspi, *J.C.S. Perkin II*, 1972, 1102.

[9] P. Bassi and U. Tonellato, *J.C.S. Perkin I*, 1973, 669.

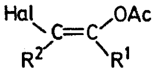
[10] P. Bassi, and U. Tonellato, *Gazzetta*, 1972, **102**, 387.

[11] Y. Ogata and I. Urasaki, *J. Org. Chem.*, 1971, **36**, 2164.

The reaction in 9 : 1 or 19 : 1 nitromethane–methanol afforded, besides the sulphonic acid, a complex mixture of products; free iodine was also present at the end of the reaction. In the case of the very reactive compound (Ia; $R^1 = R^2 = p\text{-}MeC_6H_4$) a clean mixture of elimination (V)



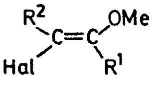
(III)



(IV)

$R^2C{\equiv}CR^1$

(V)



(VI)

$R^2(Hal)HC{\cdot}CO{\cdot}R^1$

(VII)

(42%) and substitution (VIa) (53%) products was obtained. Compound (VIa) is a very labile product [3b, 6a] and, on being left in the reaction medium, afforded benzil and benzilic acid derivatives.

(b) *From esters* (Ib) *and* (IIb). Acetolysis of 1,2-dialkyl or of the less activated 1,2-diaryl derivatives, in forcing conditions, afforded trinitrobenzenesulphonic acid and β-bromo-ketones [4, 12] (VIIb) in virtually quantitative yield.

Acetolysis of (Ib; $R^1 = R^2 = p\text{-}MeC_6H_4$) at 54·5° yielded after 70 h the corresponding vinyl acetates (IIIb) and (IVb) in the ratio 3·5 : 1. Further heating caused decomposition of both isomers to ketone (VIIb). ^1H N.m.r. analysis of the reaction mixture during decomposition of the ester showed that the *trans*-form isomerizes to the *cis* whereas the ratio of acetates (IIIb) : (IVb) is virtually constant during the reaction. Data are summarized in Figure 1. Both isomeric vinyl acetates were isolated and found to be stable under the reaction conditions. The *cis*-ester (IIb; $R^1 = R^2 = p\text{-}MeC_6H_4$) reacted at a slower rate than the *trans*-isomer and afforded on acetolysis the same mixture of vinyl acetates (IIIb) : (IVb) = 3·5 : 1.

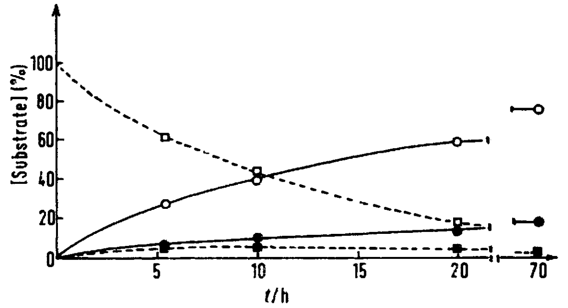


FIGURE 1 Composition of the reaction mixture during the acetolysis of the *trans*-2-bromo-1,2-di-*p*-tolyl-vinyl ester (Ib): □ *trans*-sulphonate (Ib); ■ *cis*-sulphonate (IIb); ○ *trans*-acetate (IIIb); ● *cis*-acetate (IVb)

Solvolysis in nitromethane–methanol of (Ib) and (IIb) gave ketone (VIIb) [3b] in high yield. Neither the expected primary solvolysis [(VIb) or its isomer] nor elimination products (V) were observed.

From esters (Ic) *and* (IIc). Acetolysis of the unreactive β-chlorovinyl esters gave only β-chloro-ketones (VIIc). In the case of (IIc; $R^1 = R^2 = p\text{-}MeOC_6H_4$) the corresponding vinyl acetates (IIIc) and (IVc) were obtained in virtually quantitative yield by complete acetolysis at 50°. Either the pure *cis*-isomer and a 1·85 : 1 mixture of *trans*- and *cis*-isomers gave the same ratio of isomeric acetates (IIIc) : (IVc) = 1 : 3·4. Extensive *cis* $\rightleftharpoons$ *trans*-isomerization was observed during the reaction (Figure 2). The two isomeric acetates were found to be stable under the reaction conditions.

On the other hand, in nitromethane–methanol, the main product of solvolysis from (Ic) and (IIc) was in each case the corresponding ketone (VIIc). Minor amounts of other unidentified products were isolated; the elimination products (V) were absent.

Kinetics.—Solvolysis in nitromethane–methanol was followed by conductometry and in acetic acid by spectrophotometry. First-order kinetics were obtained, in most cases up to at least 80% reaction. Table 1 lists the data for all the compounds for which measurements were taken. The rate of acetolysis of the 1,2-diarylvinyl derivatives (Ia), (Ib), and (IIc) is increased slightly by the addition of sodium acetate; the observed increase is <25% for salt concentrations up to 2 × 10^{-2}M. A smooth, virtually linear increase of the rate of acetolysis with $LiClO_4$ concentration was also observed for esters (Ib; $R^1 = R^2 = Ph$ and $R^1 = R^2 = p\text{-}MeC_6H_4$): no 'special' salt effect [13] was therefore evident. In the case of esters (Ia) the rate of solvolysis was not appreciably affected by air or light nor by the addition of radical scavengers or cyclohexene.

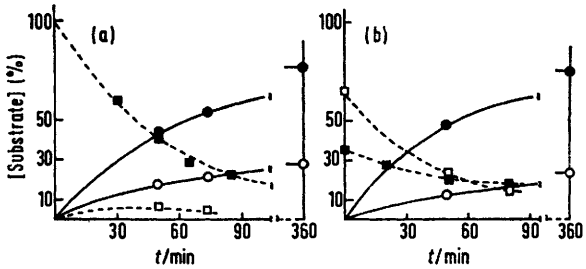


FIGURE 2 Composition of the reaction mixture during the acetolysis of (a) *cis*-2-chloro-1,2-bis-*p*-methoxyphenyl-vinyl ester (IIc) and (b) of a 1·8 : 1 mixture of *trans*-(Ic) and *cis*-(IIc) isomers: □ *trans*-sulphonate (Ic); ■ *cis*-sulphonate (IIc); ○ *trans*-acetate (IIIc); ● *cis*-acetate (IVc)

Structural Effects.—The rates of 1,2-diarylvinyl derivatives are strongly dependent on the nature of the substituents on the α-phenyl ring; the effect of substituents on the β-phenyl ring is much more attenuated. The rate constants for both symmetrically ($R^1 = R^2$) and asymmetrically ($R^1 \neq R^2$) substituted compounds can be correlated by means of a composite Hammett equation (1) [3a]

$$\log k_{\alpha,\beta} = \log k_0 + \rho(\sigma_\alpha^+ + A\sigma_\beta) \qquad (1)$$

where $k_{\alpha,\beta}$ is the rate constant for a substituted term, σ_α^+ is Brown's constant [14] for substituents on the α-ring, σ_β and A are the Hammett constant [14] and the attenuation coefficient, respectively, for substituents on the β-aryl ring. The values obtained from the best fit of data are given in Table 2. Owing to the limited number of terms for each series the A values are approximate figures.

DISCUSSION

Reaction Mechanism.—The strictly parallel kinetic behaviour of each ester investigated in nitromethane–methanol and in acetic acid indicates that the same reaction mechanism operates in the two media. The mechanism involves rate-limiting heterolysis of the α-

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[12] Z. Rappoport and Y. Apeloig, *J. Amer. Chem. Soc.*, 1969, **91**, 6734.

[13] S. Winstein, E. Clippinger, A. Fainberg, and G. C. Robinson, *J. Amer. Chem. Soc.*, 1954, **76**, 2597 and subsequent papers of the series.

[14] Taken from J. E. Leffler and E. Grunwald 'Rates and Equilibria of Organic Reactions,' Wiley, New York, 1963.

TABLE 1

Solvolysis of esters (I) and (II) in nitromethane (N)–methanol (M) and in acetic acid

Ester	R^1	R^2	Solvent	$10^5k/\text{s}^{-1}$ [a]						E_a/kcal mol^{-1} [b]	$\Delta S^\ddagger$/cal K^{-1} mol^{-1} [c]
				25°	35°	45°	100°				
(Ia)	Me	Me	N–M (9 : 1)	0·48	1·55	4·31	(520) [d]			20·6	−15
			HOAc		0·27	0·96				21·6	−15
(Ia)	Pr^n	Pr^n	N–M (9 : 1)	7·8	21·8	77·1	(13,000) [d]			22·4	−4·5
			HOAc	0·64							
(Ia)	Ph	Ph	N–M (19 : 1)	17·5	47·5	170				21·4	−6
			HOAc	1·27	5·0 [e]	14·9				23·2	−5
(Ia)	*p*-MeC_6H_4	Ph	N–M (19 : 1)	335							
			HOAc	22·6							
(Ia)	*p*-MeC_6H_4	*p*-MeC_6H_4	N–M (19 : 1)	405 [f]							
			HOAc	31·6							
(Ia)	*m*-MeC_6H_4	*m*-MeC_6H_4	N–M (19 : 1)	37·5							
			HOAc	2·36							
(Ia)	Ph	*m*-ClC_6H_4	N–M (19 : 1)	12·2							
				25°	55°	70°	80°	100°			
(Ib)	Me	Me	N–M (9 : 1)					0·13			
(Ib)	Pr^n	Pr^n	N–M (9 : 1)					0·19			
(Ib)	Ph	Ph	N–M (19 : 1)	(0·014) [d]	0·58	2·75	6·70			23·6	−12·5
			HOAc	(0·00063) [d]		0·35	1·1				
(Ib)	*p*-MeC_6H_4	*p*-MeC_6H_4	N–M (19 : 1)	0·62	21·5	91·0	(250)			22·7	−8·5
			HOAc	(0·029) [d]	2·2	14·6 [g]	42·8				
(IIb)	*p*-MeC_6H_4	*p*-MeC_6H_4	N–M (19 : 1)		1·82						
			HOAc		0·20 [h]		4·63				
(Ib)	*p*-MeC_6H_4	Ph	N–M (19 : 1)	0·44							
			HOAc	(0·020) [d]	1·52		31·0				
(Ib)	*m*-MeC_6H_4	*m*-MeC_6H_4	N–M (19 : 1)	(0·033) [d]	1·24	5·91	15·3			23·4	−12
				25°	40°	50°	60°	70°	80°		
(Ic)	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	N–M (19 : 1)	12·0	74	219				22·0	−6·5
(IIc)	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	N–M (19 : 1)	10·5	54	160			(4000) [d]	20·7	−9·5
			HOAc	1·1	6·7	18·7	50·0		(340) [d]		
(IIc)	*p*-$MeOC_6H_4$	Ph	N–M (19 : 1)	6·86	43·9	120			(2400) [d]		
			HOAc	0·83	6·2	14·1	45·6		230	22·7	−8·5
(IIc)	*p*-MeC_6H_4	*p*-MeC_6H_4	N–M (19 : 1)				2·0	6·1	14·3	22·1	−15·5
			HOAc						1·47		
(IIc)	*p*-MeC_6H_4	Ph	N–M (19 : 1)				1·22	3·31	9·47	23·3	−13
			HOAc						0·94		

[a] Average of at least two runns. [b] Estimated ±0·7—1 kcal mol^{-1}. [c] At 25° for esters (Ia and b); at 80° for (IIc); estimated ±1·5—2 cal mol^{-1} K^{-1}. [d] Extrapolated from higher or lower temperature measurements. [e] In the presence of [NaOAc] $(10^5k/\text{s}^{-1})$: 2·3 × 10^{-3}M, 5·2; 8·3 × 10^{-3}M, 5·6; 1·9 × 10^{-2}M, 6·2. [f] In the presence of [cyclohexene] 3 × 10^{-3}M, $10^5k/\text{s}^{-1}$ = 410. [g] In the presence of [$LiClO_4$] $(10^5k/\text{s}^{-1})$: 1 × 10^{-3}M, 15·0; 2 × 10^{-3}M, 15·0; 8 × 10^{-3}M, 16·1. [h] In the presence of [$LiClO_4$] $(10^5k/\text{s}^{-1})$: 0·6 × 10^{-3}M, 0·20; 1·5 × 10^{-3}M, 0·20; 8·5 × 10^{-3}M, 0·22.

carbon–oxygen bond. The following results are strongly indicative: (a) the large negative ρ values and the use of σ^+ constants for substituents on the α-aryl ring of 1,2-diaryl derivatives; (b) the positive solvent and salt effects of a magnitude already observed [3a,c,4] for unimolecular solvolyses of other vinyl trinitrobenzenesulphonates; and (c) the relative insensitivity to added base and radical scavengers [for esters (Ia)]. The last point rules out either the addition–elimination route [5,15] (Ad_E–$E1$ or Ad_N–$E1$) or a homolytic process.[16] On the other hand, product analysis shows that in all cases except esters (Ia; R^1,R^2 = aryl) only substitution products, vinyl acetates and methyl vinyl ethers or their decomposition products, are formed. In the case of 1,2-diaryl-2-iodovinyl derivatives, elimination products (V) have been isolated. The relative yield of elimination products increases on going from acetic acid (7—11%), to nitromethane–methanol (40—50%), to nitromethane–methanol containing cyclohexene (>70%), yet the rate of solvolysis is insensitive to these changes except for the solvent effect which is that observed [4] for other vinyl esters. The elimination pathway, at least in the absence of iodide ions, is therefore still governed by the rate-limiting ionization of the substrate to give a vinyl cation from which the iodine cation is lost.

TABLE 2

Substituent effects for the solvolysis of 1,2-diaryl-2-halogenovinyl derivatives

Ester	Solvent [a]	*T*/°C	ρ	*A*	*r* [b]	No. of compounds studied
(Ia)	N–M (19 : 1)	25	−4·1	$0{\cdot}2_2$	0·9993	5
	HOAc	25	−4·1	$0{\cdot}2_1$	0·9995	5
(Ib)	N–M (19 : 1)	25	−4·8	$0{\cdot}1_8$	0·9988	4
	HOAc	25	−4·9	$0{\cdot}2_2$		
		80	−4·5	$0{\cdot}2_3$		
(IIc)	N–M (19 : 1)	80	−5·1	$0{\cdot}1_7$	0·9986	4
	HOAc	80	−5·0	$0{\cdot}1_8$	0·9990	4

[a] See Table 1. [b] Correlation coefficient (H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191).

Reactivity.—The effect of changing the β-halogen atom in the 1,2-dialkyl and 1,2-diaryl derivatives is given in Table 3 which shows relative rate data including those for non-halogenated reference compounds. β-Bromo- and β-chloro-derivatives (I) and, in particular, (II) are less reactive than the reference compounds. This is

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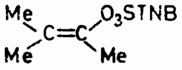
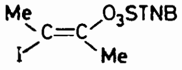
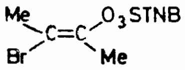
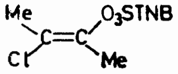
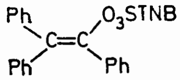
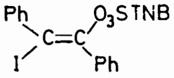
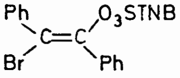
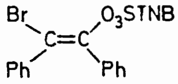
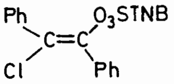
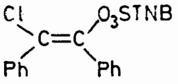
[15] Z. Rappoport, T. Bassler, and M. Hanack, *J. Amer. Chem. Soc.*, 1970, **92**, 4985.

[16] N. Frydman and Y. Mazur, *J. Amer. Chem. Soc.*, 1970, **92**, 3203.

expected in view of the strong electron-withdrawing inductive effect due to the β-halogen atom, although the observed retardation is much larger than predicted on the basis of literature data (see above). The polar effect of iodine is known [7] to be only slightly less than that of bromine and chlorine. Esters (Ia; $R^1 = R^2 =$ Ph) are, instead, *ca.* 10^4 times more reactive than the corresponding β-chlorovinyl derivatives and also more reactive than the reference compounds. There is little doubt that an anchimerically assisted [17] process is responsible for the rate enhancement. Between the two extremes, *i.e.*, esters (Ia) which follow the anchimerically assisted route (k_Δ) and esters (IIb and c) which undergo an anchimerically (and nucleophilically) unassisted [8,18] solvolysis (k_c) the reactivities of esters (Ib and c) may be taken as the intermediate cases. Esters (Ic; $R^1 = R^2 =$ Ar) react only 20—30% faster than the corresponding *cis*-isomers and anchimeric assistance, if any, is virtually negligible; the analogous esters (Ib) react 10—15 times faster than the *cis*-isomers and the difference in reactivity may be explained by assuming that substantial anchimeric assistance due to the bromine atom. The above picture may be complicated by steric effects which could alter the reactivity of geometrical isomers. Molecular models show that the *cis*-esters (IIb; $R^1 = R^2 =$ Ar) deviate from coplanarity slightly more than the *trans*-analogues (Ib). Steric factors alone would make the *cis*-isomer more reactive than the *trans*.[6a,8] Therefore, the $k_{trans} : k_{cis}$ ratio observed for the β-bromovinyl esters should be set as the lower limit of rate enhancement due to a β-bromine atom in the series of 1,2-diarylvinyl derivatives.

TABLE 3

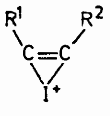
Relative rates of solvolysis of some vinyl trinitrobenzenesulphonates

Solvent [a]	T/°C				
					
N–M (9 : 1)	100	1·0 [b]	93	$2{\cdot}7 \times 10^{-2}$	[c]
					
N–M (19 : 1)	25	1·0 [d]	9·6	$7{\cdot}6 \times 10^{-3}$	
HOAc	80	1·0 [d]	6·0	$1{\cdot}2 \times 10^{-2}$	
					
N–M (19 : 1)	25	$6{\cdot}4 \times 10^{-4}$ [e]	$3{\cdot}2 \times 10^{-4}$ [e]	$2{\cdot}8 \times 10^{-4}$ [f]	
HOAc	80	$1{\cdot}0 \times 10^{-3}$ [e]	$2{\cdot}8 \times 10^{-4}$ [e]	$2{\cdot}4 \times 10^{-4}$ [f]	

[a] See Table 1. [b] Ref. 3*d*. [c] Too slow to measure. [d] Ref. 4. [e] Approximate values: estimated assuming the same $k_{trans} : k_{cis}$ ratio for the unsubstituted compound observed for substituted derivatives. [f] Estimated from the ρ values of Table 2.

For the 1,2-dimethyl compounds the β-iodo-ester is more reactive by a factor of 10^2 and the β-bromo-derivative is only 30 times less reactive than the non-halogenated compound. Although a direct estimate of the reactivity of the *trans*-β-chloro-derivatives is impossible and the *cis*-isomers are inaccessible, a rough estimate indicates that anchimeric assistance for (Ia and b) is larger than for the 1,2-diarylvinyl derivatives, as expected.[3d]

Stereochemistry.—Esters (Ia) give *trans*-substitution products. The complete retention of the original geometry strongly indicates β-iodine participation, *i.e.* the bridged intermediate cation (VIII) is formed. Nucleophilic attack of the solvent may occur either at the unsaturated carbon atoms from the unhindered side or at the iodine atom thus determining the formation of elimination products. Similar behaviour was observed [19] for arylthiovinyl cations for which a stable bridged structure has been proposed.



(VIII)

The acetolysis of esters (Ib) and (IIb) ($R^1 = R^2 = p$-MeC_6H_4) and of esters (Ic) and (IIc) ($R^1 = R^2 = p$-$MeOC_6H_4$) is, instead, non-stereospecific. Both isomers gave the same ratio of *trans*- and *cis*-acetates under kinetic control. Moreover, isomerization occurs during the reaction. In the case of β-bromovinyl esters the *trans*-acetate predominates by a factor of 3·5, a value much lower than expected if a stable bridged cation intermediate is invoked. The experimental facts can be accommodated by Scheme 1 in which oriented ion-pairs [20,21] are initially formed and may revert to products or give solvated ions prior to collapse to products. The

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[17] S. Winstein, A. H. Fainberg, and E. Grunwald, *J. Amer. Chem. Soc.*, 1957, **79**, 4146.

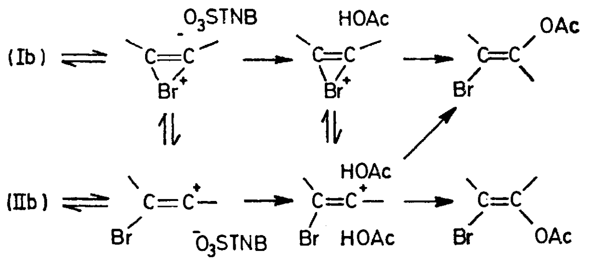
[18] P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *J. Amer. Chem. Soc.*, 1970, **92**, 2542.

[19] G. Modena, G. Scorrano, and U. Tonellato, *J.C.S. Perkin II*, 1973, 493.

[20] R. C. Fahey and D. J. Lee, *J. Amer. Chem. Soc.*, 1966, **88**, 6595.

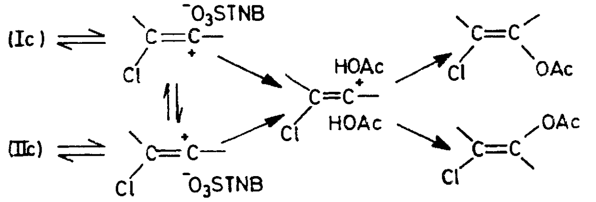
[21] J. A. Pincock and K. Yates, *Canad. J. Chem.*, 1970, **48**, 3332.

cation generated from the *trans*-ester may have a bridged structure only slightly more stable than that of the open one and rapid equilibrium between the two forms may be achieved. Nucleophilic attack by the solvent is likely to occur at the open rather than at the bridged ion: S_N1 opening of three-membered ring would precede the product-determining step. The bromine atom only partially hinders its side of the cation thus determining a relatively low *trans* : *cis* ratio in the products.



SCHEME 1

The acetolysis of β-chlorovinyl esters fits the analogous Scheme 2: here, however, the very small difference in reactivity between the two isomeric esters does not require a bridged structure for the intermediate cation. The relative abundance of the *cis*-acetate is somewhat difficult to explain. Steric or stereo-electronic arguments [6a,22] may be invoked: these would make the *cis*-(relative to the halogen) lobe of the p_π orbital of the α-carbon atom more accessible to nucleophilic attack by the solvent than the *trans*-lobe.



SCHEME 2

Conclusions.—The results allow the following conclusion. (a) The inductive effect of β-substituents, in the absence of participation, is quite remarkable and, as far as the effect of chlorine or bromine is concerned, it is of the magnitude observed in the solvolysis of saturated systems.[7,23] (b) Anchimeric assistance due to (*trans*) β-halogen atoms may also be relevant, as already observed in the case of β-sulphur [3] and follows the order I > Br > Cl.

A general trend is apparent in the vinyl cations from an open to a bridged intermediate on going from chlorine to bromine and iodine, and from arylvinyl to alkylvinyl cations. The 1,2-diarylbromovinyl cations are suggested as the mid-point in which however anchimeric assistance is still effective. Virtually the same trend was proposed for the intermediates in the electrophilc addition of halogens or pseudo-halogens [2b,9] to acetylenes at least in media of low polarity.[24]

Closer comparison of the results of vinylic solvolyses and electrophilic additions to triple bonds reveals other common facets and suggests a substantially similar mechanism leading to vinyl cations in the two reactions. The ρ values (see Table 2 and refs. 4 and 24) and the stereochemical results [21,25] of solvolyses and electrophilic additions for analogous systems are similar. Thus, for the acetolysis of 1,2-diaryl-2-bromovinyl esters (Ib) and for the bromination of arylacetylenes the ρ values are —4·9 and —5·2 and the stereochemical outcome is non-stereospecificity and non-stereoselectivity.

EXPERIMENTAL

Chemical shifts are relative to tetramethylsilane as internal standard for solutions in deuteriochloroform (unless otherwise specified). The solvents used in the kinetic experiments were purified as described. The synthesis of the esters, the methods used to achieve the separation of *trans*- and *cis*-isomers [(Ib) and (IIb) ($R^1 = R^2 = p$-MeC_6H_4) and (Ic) and (IIc) ($R^1 = R^2 = p$-$MeOC_6H_4$)], and the assignment of the geometrical structures have been discussed.[9]

Product Analysis.—(a) *Acetolysis*. (i) Esters (Ia). Ester (Ia; $R^1 = R^2 =$ Ph) (0·558 g) was dissolved in acetic acid (150 ml) and kept at 35° for 48 h. The solution was then poured into dichloromethane–water, the organic layer washed with water, sodium carbonate, and water, and dried (Na_2SO_4). Evaporation of the solvent left a solid residue from which, by chromatography on silica gel (hexane–benzene as eluant) the following products were isolated and identified: diphenylacetylene (22 mg, 13%) by comparison of its i.r. spectrum with that of an authentic sample, and *trans*-1,2-diphenyl-2-iodovinyl acetate (275 mg, 81%), m.p. 145—146° (lit.,[11] 146—146·5°), τ 2·4—3·0 (10H, m) and 8·27 (3H, s). Trace amounts of unidentified material were also isolated.

By the same procedure, from (Ia; $R^2 =$ Ph, $R^1 = p$-MeC_6H_4) (0·265 g) in acetic acid (100 ml) at 25° for 6 h the products isolated and identified were: phenyl-*p*-tolylacetylene (6 mg, 7%) by comparison of its i.r. spectrum with that of an authentic sample and trans-*2-iodo-2-phenyl-1-*p-*tolylvinyl acetate* (139 mg, 84%), τ 2·4—2·9 (9H, m), 7·63 (3H, s), and 8·21 (3H, s) (Found: C, 54·3; H, 4·05; I, 33·65. $C_{17}H_{15}IO_2$ requires C, 54·15; H, 4·0; I, 33·4%). From (Ia; $R^1 = R^2 = \mathrm{Pr}^n$) (0·41 g) in acetic acid (100 ml) at 35° for 90 h, the only product identified was *2-iodo-1,2-di-n-propylvinyl acetate*, one isomer from its ^{1}H n.m.r. spectrum, τ 7·3—7·8 (4H, m), 7·83 (3H, s), 8·2—8·8 (4H, m), and 8·9—9·25 (6H, 2 t) (195 mg; 84%). The product was unstable at room temperature and poor analyses were obtained (Found: C, 41·35; H, 6·05; I, 43·0. $C_{10}H_{17}IO_2$ requires C, 40·55; H, 5·8; I, 42·85%).

(ii) Esters (Ib) and (IIb). From ester (Ib; $R^1 = R^2 = p$-MeC_6H_4) (0·594 g) in acetic acid (150 ml) at 54·5° for 70 h, following the procedure described above, the products isolated and identified were: the *cis*-ester (IIb; $R^1 = R^2 = p$-MeC_6H_4) τ[9] 1·39 (2H, s), 2·8—3·1 (8H, m), and 7·69 and 7·76 (each 3H, 2 s), and *2-bromo-1,2-di-*p*-tolylvinyl acetate*

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[22] G. Maroni, G. Melloni, and G. Modena, *J.C.S. Chem. Comm.*, 1972, 857.

[23] S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Amer. Chem. Soc.*, 1948, **70**, 821; S. Winstein and E. Grunwald, *ibid.*, p. 828; E. Grunwald, *ibid.*, 1951, **73**, 5458.

[24] K. Yates, G. H. Schmid, T. W. Regulski, D. G. Garratt, H.-W. Leung, and R. S. McDonald, *J. Amer. Chem. Soc.*, 1973, **95**, 160.

[25] K. Yates and R. S. McDonald, *J. Org. Chem.*, 1973, **38**, 2465

(305 mg, 86%), *trans-* and *cis*-isomers in the ratio 3·5 : 1 (n.m.r.). The isomeric acetates were then separated by fractional crystallization from hexane. The trans-*isomer* m.p. 89—90° (Found: C, 63·0; H, 5·1; Br, 23·15. $C_{18}H_{17}BrO_2$ requires: C, 62·8; H, 4·95; Br, 23·05%) has τ (CCl_4) 2·45—2·95 (8H, m), 7·65 (6H, s), and 8·19 (3H, s). Almost pure (>93% by n.m.r.) *cis*-isomer was recovered from the mother liquors of several crystallizations, τ (CCl_4) 2·75—2·95 (8H, m), 7·70 (3H, s), 7·75 (3H, s), and 7·80 (3H, s).

The configurations of the two isomers were assigned by analogy with the chemical shifts of the AcO protons with those reported [26] for *trans-* and *cis*-2-bromo-1,2-diphenylvinyl acetates. Both isomers (40 mg) were recovered unchanged (n.m.r.) after having been dissolved separately in acetic acid (20 ml) containing an equimolar amount of trinitrobenzenesulphonic acid and heated at 54·5° for 70 h. The product distribution from ester (Ib) at different times was determined by n.m.r. analysis of the crude reaction mixture, using aliquot samples of 200 mg of ester in *ca.* 80 ml of solvent; the results are summarized in Figure 1. From pure ester (IIb; $R^1 = R^2 = p\text{-MeC}_6H_4$) (388 mg) in acetic acid (120 ml), after 70 h (corresponding to *ca.* 30% reaction) at 54·5°, the mixture contained only the unchanged ester and the two isomeric β-bromovinyl acetates, both in the ratio *trans* : *cis* = 3·5 : 1. 2-Bromo-*p*-methyl-2-*p*-tolylacetophenone was also isolated and identified by comparison of its n.m.r. and i.r. spectra with those of an authentic sample, when the acetolysis of esters (Ib) and (IIb) was prolonged at 54·5° or carried out at higher temperature.

From the less reactive compound (Ib; $R^1 = R^2 = Ph$) (0·559 g) after four days at 80°, the only product isolated was 2-bromo-2-phenylacetophenone (216 mg, 78%) by comparison of its i.r. spectrum with that of an authentic sample.

(iii) Esters (Ic) and (IIc). By the same procedure, from (IIc; $R^1 = R^2 = p\text{-MeOC}_6H_4$) (0·45 g) in acetic acid (150 ml) at 49·8° for 6 h, the products isolated and identified were: 2-chloro-1,2-bis-*p*-methoxyphenylvinyl acetate (228 mg, 26%), both *trans-* and *cis*-isomers in the ratio 1 : 3·6 (Found: C, 64·8; H, 5·4; Cl, 10·85. Calc. for $C_{18}H_{17}ClO_4$: C, 65·0; H, 5·15; Cl, 10·65%). The two isomers could not be separated in pure forms; by fractional crystallization from hexane, mixtures enriched in one of other isomer could be obtained and the n.m.r. signals were assigned as above, *trans*-isomer τ 2·4—3·4 (8H, m), 6·18 (6H, 2 superimposed s), and 8·05 (3H, s); *cis*-isomer τ 2·45—3·45 (8H, m), 6·22 (6H, 2 superimposed s), and 7·75 (3H, s). The isomeric composition of the enriched mixtures of the vinyl acetates remained unchanged in acetic acid (containing trinitrobenzenesulphonic acid) after 6 h at 50°.

From a 1·85 : 1 mixture of [(Ic) and (IIc) ($R^1 = R^2 = p\text{-MeOC}_6H_4$)] at 50° for 6 h the products isolated were the corresponding acetates in the ratio *trans* : *cis* = 1 : 3·6.

The analysis of the product distribution at different times was carried out as above and the results are summarized in Figure 2.

When the acetolysis was carried out at higher temperature, 2-bromo-*p*-methoxy-2-*p*-methoxyphenylacetophenone was also isolated, τ 1·95—2·1 (2H, m), 2·45—3·45 (9H, m), and 6·26 (6H, 2 superimposed s).

(b) *Solvolysis in* 19 : 1 *nitromethane–methanol.* (i) Esters (Ia). Ester (Ia; $R^1 = R^2 = p\text{-MeC}_6H_4$) (0·88 g) was dissolved in solvent (200 ml) and kept at 25° for 20 min. Preliminary experiments based on t.l.c. tests showed that the product distribution of the reaction mixture may change greatly on simply removing the solvent by vacuum distillation. Therefore the following procedure was used: the solution was extracted 12—15 times with *ca.* 100 ml portions of pentane. The combined pentane extracts were washed with water, sodium thiosulphate solution, and water, dried (Na_2SO_4), and the solvent removed under reduced pressure. Chromatography on a short silica gel column (hexane–ether as eluant) allowed the isolation and identification of di-*p*-tolylacetylene (122 mg, 42%), by comparison of its i.r. spectrum with that of an authentic sample; and *methyl 2-iodo-*1,2-*di-*p-*tolylvinyl ether* (271 mg, 53%) in one isomeric form, presumably *trans*, 2·9—3·0 (8H), 6·52 (3H, s), and 7·73 (6H, 2 superimposed s). This product decomposed readily at room temperature and poor analyses were therefore obtained (Found: C, 57·3; H, 4·9; I, 36·05. $C_{17}H_{17}IO$ requires C, 56·05; H, 4·7; I, 34·85%); it decomposes in solution to give mainly 4,4′-dimethylbenzil, τ 2·1—2·3 (4H, d), 2·7—2·9 (4H, d), and 7·58 (6H, s), and unidentified material. In separate experiments, by vacuum distillation of the solvent and crystallization of the residue with dichloromethane, trinitrobenzenesulphonic acid was isolated in virtually quantitative (94—96%) yield.

From the same ester (Ia) (0·52 g) in solvent (200 ml) containing cyclohexene (500 mg), after 30 min at 25°, the main product isolated following the procedure described above was di-*p*-tolylacetylene (124 mg, 72%) together with a mixture of the vinyl methyl ether and its decomposition products.

(ii) Ester (Ib) and (IIb). Ester (Ib; $R^1 = R^2 = p\text{-MeC}_6H_4$) (568 mg) was dissolved in solvent (150 ml) and kept at 45° for 18 h. The only product isolated and identified was: 2-bromo-*p*-methyl-2-*p*-tolylacetophenone (235 mg, 78%). The same product in 82% yield was also obtained from the *cis*-isomer.

(iii) Esters (Ic) and (IIc). From (IIc; $R^1 = R^2 = p\text{-MeOC}_6H_4$) (0·35 g) in solvent (100 ml) kept for 150 min at 40·5°, the only product isolated and identified was 2-chloro-*p*-methoxy-2-*p*-methoxyphenylacetophenone (127 mg, 71%). A viscous yellow material was also isolated but not identified. Virtually the same products were obtained under the same conditions from a 1·85 : 1 mixture of *trans-* and *cis*-isomers of this ester.

Kinetics.—The conductometric (in nitromethane–methanol) and spectrophotometric (in acetic acid) methods have been described. Both methods were occasionally used for solvolytic runs in nitromethane–methanol and the rate constants obtained with the two techniques were identical within experimental error (±3—4%). The kinetic runs at temperatures higher than 50° were carried out in sealed vials. Conductivity or absorbance measurements on the quenched samples were made at 25°.

First-order coefficients were calculated by use of a graphic method or a least-squares computer program. When mixtures of isomeric esters [(Ic) and (IIc) ($R^1 = R^2 = p\text{-MeOC}_6H_4$)] were measured, data were treated as described for two parallel first-order reactions producing a common product.[3a] The individual rate constant for the *trans*-isomer was easily obtained by graphic interpolation from the first-order rate plot.

We thank Professor G. Modena for advice and discussions.

[3/2425 *Received*, 26*th November*, 1973]

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[26] A. Jovtsheff and S. L. Spassov, *Monatsh.*, 1967, **98**, 2272.