# Vinylic Cations from Solvolysis. Part XII.[1] Solvolysis of cis- and trans-α-Bromo- and -αβ-Dibromo-4,4'-dimethoxystilbenes

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Solvolysis of cis- and trans-α-bromo-4,4'-dimethoxystilbenes (3) and (4) in 80% and 90% EtOH and in AcOH gives mainly bis-4-methoxyphenylacetylene (8). The first order $k_{cis} : k_{trans}$ reactivity ratios in aqueous ethanol are 43·5—49 in the presence of sodium acetate and 19·7 in the acetolysis. With 0·5M-NaOH in 80% EtOH $k_{cis} : k_{trans}$ = 0·06 where k_{cis} is a first-order coefficient and k_{trans} is the second-order coefficient for the E2 reaction. Acetolysis of cis- and trans-αβ-dibromo-4,4'-dimethoxystilbenes (5) and (6) is slower than those of compounds (3) and (4). Values of $k(3)/k(5) = 187$, $k(4)/k(6) = 3·3$ and $k(5)/k(6) = 0·37$—$0·41$ were calculated. The products with sodium acetate are 4,4'-dimethoxybenzil, 4,4'-dimethoxybenzoin acetate, deoxy-4,4'-dimethoxybenzoin, and the acetylene (8), but in the presence of AgOAc, trans-α-acetoxy-β-bromo-4,4'-dimethoxystilbene (7) was formed. The acetolysis of all the compounds showed common ion rate depression and that of compound (7) gives similar products to those of (5) and (6). The mechanism of the reaction of compound (4) in the presence of sodium hydroxide is suggested to be E2 while all the other reactions are mechanistically S_N1–$E1$. The rate difference between compounds (3) and (4) in the E1 process is ascribed mainly to a rate enhancement of compound (3) due to ground-state steric interactions. No evidence for β-bromine participation was observed. The structure and the selectivity of the intermediate vinyl cations are discussed.

SOME mechanistic features in the solvolysis of α-p-methoxyphenylvinyl bromides change appreciably when the two β-hydrogen atoms of compound (1) are substituted by aryl groups as in compound (2). While compound (1) shows no common ion rate depression on acetolysis [2,3] compound (2) does so strongly [2-4] and the

AnC(Br):CH₂
(1)

AnC(Br):CAr₂
(2)

An = p-MeOC₆H₄
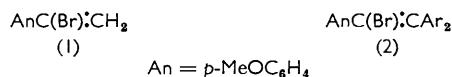
Winstein–Grunwald m values decrease with the change (1) ⟶ (2).[5,6] These phenomena were ascribed in part [3,7] to steric interaction between the bulky α- and β-aryl groups in compound (2) and its transition state. It was of interest to study a pair of cis–trans-isomers with only one β-aryl group, in order to see whether their

behaviour is intermediate between those of compounds (1) and (2) and to study the relationship between the geometry and the reactivity of the system.[8]
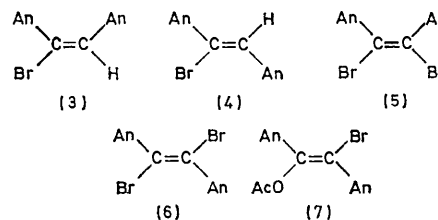
Another mechanistic question concerns the effect of introducing a β-electron-attracting group. This may cause a change in mechanism (e.g., to nucleophilic addition–elimination) [9] or only reduce the rate of the

[1] Part XI, Z. Rappoport and J. Kaspi, J.C.S. Perkin II, 1972, 1102.

[2] A. Gal, Ph.D. Thesis, The Hebrew University of Jerusalem, 1972.

[3] Z. Rappoport and A. Gal, Tetrahedron Letters, 1970, 3233.

[4] Z. Rappoport and Y. Apeloig, Tetrahedron Letters, 1970, 1817.

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

[6] Z. Rappoport and A. Gal, J. Amer. Chem. Soc., 1969, 91, 5246.

[7] Z. Rappoport and J. Kaspi, J. Amer. Chem. Soc., 1970, 92, 3220.

[8] For reviews dealing with vinyl cations see (a) M. Hanack, Accounts Chem. Res., 1970, 3, 209; (b) C. A. Grob, Chimia (Switz.), 1971, 25, 87; (c) G. Modena and U. Tonellato, Adv. Phys. Org. Chem., 1971, 9, 185; (d) P. J. Stang, Progr. Phys. Org. Chem., in the press.

[9] (a) Z. Rappoport, Adv. Phys. Org. Chem., 1969, 7, 1; (b) Z. Rappoport and A. Gal, J. Org. Chem., 1972, 37, 1174.

S_N1 process. If the β-group is in the *trans*-position and capable of neighbouring group participation, a rate enhancement may be observed.

We therefore studied the solvolyses of *cis*- and *trans*-α-bromo-4,4'-dimethoxystilbenes (3) and (4), *cis*- and *trans*-αβ-dibromo-4,4'-dimethoxystilbenes (5) and (6), and *trans*-α-acetoxy-β-bromo-4,4'-dimethoxystilbene (7). A preliminary account on the solvolysis of compounds (3) and (4) has appeared.[10]

RESULTS

cis- and *trans*-α-Bromo-4,4'-dimethoxystilbenes (3) and (4) were prepared by the addition of hydrobromic acid to bis-4-methoxyphenylacetylene (8) in acetic acid. Under kinetic control in the absence of excess of hydrobromic acid the addition is stereospecific, leading to >93% of the *cis*-isomer (3) [equation (1)]. The solvent incorporation products α-acetoxy-4,4'-dimethoxystilbenes (9) represent

$$AnC\equiv CAn + HBr \longrightarrow (3) + AnC(OAc):CHAn$$

$$(8) \qquad \qquad \qquad (9)$$

$$\downarrow HBr \qquad \qquad \qquad (1)$$

$$\underline{\quad excess\ of\ HBr\quad} \longrightarrow (4) + (3) + AnCBr_2CH_2An$$

at most 1·5% of the addition products. The addition product of compound (8) [or (3) itself] with excess of hydrobromic acid in acetic acid gives *cis–trans* isomerisation and a mixture richer in the thermodynamically more stable *trans*-isomer (4) is obtained. Excess of hydrobromic acid with compound (8) also gives a diadduct which was not investigated.

The assignments of the geometrical structures are based on the following data: (*a*) The λ_{max} and ε values of compound (3) are lower than those of (4). (*b*) The i.r. spectrum of the *trans*-isomer (4) is simpler. (*c*) The positions of the signals of the vinylic, methoxy, and aromatic protons of compound (4) are at lower field than those of (3). In addition, the aromatic multiplet of compound (4) is wider than that of (3), and (4) shows one methoxy-signal compared with two for the *cis*-isomer (3). These are in line with the spectra and the configuration assignments for the unsubstituted,[11] the *p*-methoxy, and other substituted stilbenes.[11b] (*d*) Compound (4) is thermodynamically more stable. (*e*) The melting point of the *trans*-isomer (4) is higher than that of (3), which according to models is less planar. (*f*) In the electrophilic addition to the acetylene (8), (3) is formed stereospecifically (see Discussion section).

cis- and *trans*-1,2-Bis-4-methoxyphenyl-1,2-dibromoethylenes (5) and (6) were obtained by the addition of bromine to the acetylene (8) in carbon tetrachloride [equation (2)]. The *cis–trans* ratio is solvent dependent. Reaction of 0·2mM-bromine with 0·2mM-(8) in 60 ml of several solvents gave only compounds (5) and (6) and the percentage of the *cis*-

$$(8) + Br_2 \longrightarrow (5) + (6) \qquad (2)$$

isomer (5) in the dibromide mixture is as follows: acetone (0), hexane (19), acetic acid, chloroform, ether, carbon disulphide (22—24), and carbon tetrachloride (45%).

Assignment of the geometrical configuration is based on the following data. (*a*) The m.p. of compound (6) (198°) is higher than that of (5) (116°) as found also for the αβ-dibromostilbenes.[12] (*b*) The methoxy and the aromatic protons of the *trans*-isomer (6) are at a lower field than those of (5). (*c*) More compound (6) is formed in the bromination of the acetylene (8) in the more polar solvents. (*d*) The λ_{max} of compound (6) is shorter than that of (5). This is in line with the generalisation [13] that the conjugation maxima of *trans*-αβ-dialkylstilbenes are at shorter wavelength than those for the *cis*-isomers.

trans-α-Acetoxy-β-bromo-4,4'-dimethoxystilbene (7) was prepared by treating a mixture of compounds (5) and (6) with silver acetate. Only one isomer was obtained. Tentatively this was assigned the *trans*-configuration by the similarity of the position of the methoxy-signal in the n.m.r. to that of *trans*-compound (6), and by the presence of only one high intensity u.v. absorption maximum as in (6).

Solvolysis Products.—Solvolysis of compounds (3) and (4) in basic 90% ethanol gave both the acetylene (8) and deoxy-4,4'-dimethoxybenzoin (10), but no vinyl ether was observed by n.m.r. spectroscopy. In the presence of 0·043M-sodium acetate the (8) : (10) ratio is 1·7 at 36—73% reaction of *cis*-isomer (3), and 3·5—5·2 at 45—86% reaction of (4). Similar product distributions were obtained in 80% ethanol. No *cis–trans* isomerisation of compounds (3) and (4) was detected by n.m.r. spectroscopy.

Acetolysis of compounds (3) and (4) gave 90—92% of the acetylene (8), the formation of which was followed by n.m.r. spectroscopy, and which was isolated. The remainder is a 9 : 1 mixture of two monoacetates (9) [ν (C=O) at 1750 cm⁻¹; acetoxy-signals at δ 2·10 and 2·30 in $CDCl_3$]. Some isomerisation of compound (3) to (4) took place during the acetolysis. After 63% solvolysis, 10% of compound (4) were observed. Acetolysis of compounds (3) and (4) in the presence of AgOAc gave 25—50% of the acetylene (8) and 50—75% of an 88 : 12 mixture of the two monoacetates (9). The predominant acetate has the higher acetoxy-signal and is probably the *cis*-isomer.

Acetolysis mixtures from compounds (5) and (6) which were analysed after several half-lives contained the deoxybenzoin (10), 4,4'-dimethoxybenzoin acetate (11), 4,4'-dimethoxybenzil (12), and (8) [equation (3)]. The product

$$\text{(5) and (6)} \xrightarrow{\text{AcOH–NaOAc}} AnCH_2COAn + AnCH(OAc)COAn +$$
$$(10) \qquad \qquad (11)$$
$$AnCOCOAn + (8) \quad (3)$$
$$(12)$$

distribution depends on the reaction time and the geometry of the starting material. In one experiment with the *cis*-isomer (5) the products were 30% (10), 33% (11), 24% (12), and 13% (8), while 15% (10), 35% (11), 19% (12), and 31% (8) were formed from compound (6) after seven half-lives. The percentage of the acetylene (8) (which was detected by i.r. spectroscopy) was calculated by difference, since it could not be determined by n.m.r. spectroscopy (see below).

Isomerisation, (5) ⇌ (6), accompanies the solvolysis. The n.m.r. spectra of the solvolysis mixture of compound (5) after 5 and 24% solvolysis showed the presence of 84 and 70% of the unchanged (5), the remainder being probably the *trans*-isomer (6). At 15 and 34% solvolysis of compound

[10] Z. Rappoport and M. Atidia, *Tetrahedron Letters*, 1970, 4085.
[11] (*a*) 'High Resolution N.M.R. Spectra Catalog,' Varian Associates, Palo Alto, California, 1962, Spectra Nos. 305 and 306; (*b*) H. Güsten and M. Salzwedel, *Tetrahedron*, 1967, **23**, 173, 187.
[12] I. Limpricht and I. Schwanert, *Ber.*, 1871, **4**, 379; E. Bergmann, *J. Chem. Soc.* 1936, 402.
[13] H. Suzuki, *Bull. Chem. Soc. Japan*, 1960, **33**, 396.

(6), (5) comprises 10 and 11% of the product, respectively. These values are approximate since the n.m.r. spectra of compounds (6) and (8) are identical.

Solvolysis of the *trans*-isomer (6) in acetic acid gave (at 90% reaction) 30% (10), 8% (11), 31% (12), 4% 4,4'-dimethoxybenzoin and probably 15% (8). Acetolysis of 0·04M-(7) in the presence of 0·08M-NaOAc at 140° gave compound (11) as the main product (90—95%) up to 55% reaction. 5—10% Of unidentified acetate was observed by n.m.r. spectroscopy. Later in the reaction compounds (10) and (12) are also formed, *e.g.*, at 85% reaction the (10) : (11) : (12) ratio is 3 : 4 : 4.

Isomerisation of compound (6) in refluxing 1,3-dichlorobenzene in the dark gave a 1 : 1 mixture of (5) and (6).

Kinetics.—All the kinetic data are in the Table. The values reported earlier were recalculated by the KINDAT

the ratios of the half-time to the initial rate coefficients as calculated by the first-order equation. These values are 0·69—0·75 in different runs and are similar for both isomers.

The kinetics of the solvolysis of compounds (5) and (6) are complicated by the presence of two leaving groups. We isolated >30% of (5) and (6) from the non-solvolysed fraction from a reaction of compound (5) in which 90% of one bromide ion was liberated. The kinetic data on the acetolysis of compound (7) also shows that partial solvolysis of the second bromide of compounds (5) and (6) took place. However, since compound (6) reacts faster than (7), reasonably constant rate coefficients for the solvolysis of the first bromide of the *trans*-compound (6) were calculated from data up to 40% liberation of one bromide ion. The similarly calculated k_1 values for the *cis*-isomer (5) increased slightly along the run, and the initial k_1 was obtained by

Solvolysis of α-bromo-4,4'-dimethoxystilbenes [a]

Compound	Added base	(Concn.)/M	[Bu$_4$NBr]/M	Solvent	T/°C [b]	$10^6 k_1$/s^{-1} [c]	k_{cis}/k_{trans}
(3)	NaOH	0·5		80% EtOH	120·2	1130 ± 210	*ca.* 0·06 [d]
	NaOAc	0·043		80% EtOH	120·2	1370 ± 40	49
	NaOAc	0·5		80% EtOH	120·2	1320 ± 90	43·5
	NaOAc	0·043		90% EtOH	120·2	460 ± 31	45·5
	NaOAc	0·08		AcOH	120·2	82·5 [e]	19·7
	NaOAc	0·16		AcOH	120·2	108 [e]	
	NaOAc	0·08		AcOH	140·0	347 [f]	
(4)	NaOH	0·5		80% EtOH	120·2	[g]	
	NaOAc	0·043		80% EtOH	120·2	27·8 ± 1·7	
	NaOAc	0·5		80% EtOH	120·2	30·3 ± 1·2	
	NaOAc	0·043		90% EtOH	120·2	10·1 ± 0·6	
	NaOAc	0·08		AcOH	120·2	4·2 [e]	
(5)	NaOAc	0·08		AcOH	141·4	2·27 ± 0·20	0·37
	NaOAc	0·16		AcOH	141·2	2·81 ± 0·31	0·41
	NaOAc	0·08	0·08	AcOH	142·0	2·45 ± 0·18	
	NaOAc	0·08		95% AcOH	140·2	9·25 ± 0·38 [h]	0·40
(6)	NaOAc	0·08		AcOH	141·0	6·06 ± 0·15	
	NaOAc	0·16		AcOH	141·0	6·90 ± 0·20	
	NaOAc	0·08	0·08	AcOH	144·4	4·59 ± 0·20	
	NaOAc	0·08		95% AcOH	140·2	23·1 ± 3·3	
(7)	NaOAc	0·08		AcOH	141·0	1·27 ± 0·05	
	NaOAc	0·16		AcOH	140·2	1·95 ± 0·09	
	NaOAc	0·08	0·08	AcOH	140·2	1·11 ± 0·07	

[a] [Vinyl bromide] = 0·04M. [b] ±0·2°. [c] Titrimetric value. [d] Estimated value. [e] Initial k_1 values (extrapolated). [f] Based on one kinetic point at 47% reaction. [g] Too fast to measure. [h] [Vinyl bromide] = 0·08M. Rates measured potentiometrically.

program.[14] The solvolysis of compound (3) in 80% EtOH is 15% slower in the presence of NaOH than with NaOAc at similar concentrations. The reaction of the *trans*-isomer (4) with NaOH in 80% EtOH is very fast; 84% of inorganic bromide was formed after 6 min at 97°, giving an approximate second order coefficient at 10^{-2} l mol^{-1} s^{-1}. This is a minimum value since a homogeneous solution was obtained only after 2 min. In the other cases first-order behaviour was obtained, and the error in the fast runs reflects a combination of low solubility and high reactivity. The reaction was slower in 90% EtOH, and *m* values of the Winstein-Grunwald equation [15] (in 80—90% EtOH) are 0·64 for compound (3) and 0·59 for (4) at 120°.

The first-order rate coefficients for the acetolysis decrease during the kinetic run and the initial values (Table) were obtained by extrapolation. The magnitude of this common ion rate depression [16] is given by $k_1^{50\%}/k_1^0$ values which are

extrapolation. The possible common ion rate depression was studied for compounds (6) and (7) by the addition of external bromide ion.

The reaction is faster in aqueous acetic acid, and Winstein-Grunwald *m* values for the pair AcOH–95% AcOH are 0·61 for (5) and 0·62 for (6) at 140°.

DISCUSSION

Solvolysis of Compounds (3) *and* (4) *in Aqueous Ethanol.* —The lack of dependence of the solvolysis rate on the nature and the concentration of added base is usually an important argument for the S_N1 route, and was used in the case of triarylvinyl halides.[6,9b] The solvolysis of α-bromo-4,4'-dimethoxystilbenes in aqueous ethanol is base dependent; $k_{cis}/k_{trans} = 43·5$—49 in the presence of NaOAc, but it is at most 0·06 in the presence of NaOH as estimated from the approximate second-order coefficients.

[14] R. C. Williams and J. W. Taylor, *J. Chem. Ed.*, 1970, **47**, 129.

[15] E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846; S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, 1951, **73**, 2700.

[16] S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *J. Amer. Chem. Soc.*, 1956, **78**, 328; S. Winstein, A. F. Diaz, B. R. Appel, and R. Baker, *Chem. Soc. Special Publ.*, No. 19, 1965, p. 109.

Although the acetylene (8) is the main product with both bases, the 720-fold decrease of the k_{cis}/k_{trans} ratio and the inverted reactivity order with NaOH suggest that a change of mechanism occurs with change in the base. We believe that both isomers with NaOAc and the *cis*-isomer with NaOH react *via* the $S_N1–E1$ route *via* the carbonium ion (13), but that the *trans*-isomer eliminates HBr *via* an $E2$ route (Scheme 1).

SCHEME 1
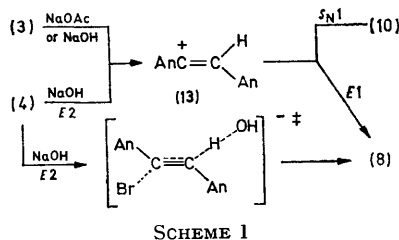
The evidence for the S_N1 route is as follows. (*a*) The reaction rates change only slightly on an eleven-fold increase in the NaOAc concentration with both compounds (3) and (4) and at similar concentrations the reaction of the *cis*-isomer is only 15% faster with NaOAc than with NaOH. (*b*) The formation of deoxy-4,4'-dimethoxybenzoin in the presence of NaOAc is consistent with an S_N1 route concomitant with the $E1$ elimination, but not with the $E2$ route. (*c*) The k_{cis}/k_{trans} ratio is similar to that in acetic acid, a solvent in which the $E1$ mechanism is more likely. (*d*) The actual rates of reaction of compounds (3) and (4) are consistent with those of other α-*p*-methoxyphenyl vinyl bromides which react by the S_N1 route (see below).[3-6] (*e*) The reaction rate increases with solvent polarity while a rate decrease is predicted for an $E2$ reaction between an ion and a neutral molecule.[17]

The $E2$ mechanism for compound (4) is consistent with the higher rate obtained with the stronger base, NaOH, as compared to NaOAc, and with the expected higher reactivity of compound (4) compared with (3) in a *trans*-$E2$ elimination.[18] For the closely related α-chlorostilbenes which probably react by the $E2$ route, $k_{trans}/k_{cis} = 208$ for NaOH in ethanol.[19]

An analogous multi-mechanism behaviour was observed and interpreted similarly with 1-methylprop-1-enyl trifluoromethanesulphonates[20] and tosylates[21] which in aqueous ethanol gave k_{trans}/k_{cis} ratios of 40 and 10, and acetylene from the *trans*-isomer and a mixture of acetylene and ketone from the *cis*-isomer. If the pro-

ducts of compound (3) are derived exclusively from the cation (13), the formation of 80% acetylene from *trans*-isomer (4) and only 63% acetylene from (3) with NaOAc may suggest an appreciable contribution (*ca.* 40%) of an $E2$ process for an overall reaction of (4). This is inconsistent with the magnitude of the m value and with its similarity to that of compound (3). The product distribution fits elimination from ion pairs with the solvent acting as a base since the incipient proton is less hindered to approach of the solvent in the ion pair derived from compound (4) than in that derived from (3).

Vinyl ethers are formed in the aqueous ethanolysis of triarylvinyl halides.[6,9,22] Their absence in the solvolyses of (3), (4), and α-bromostyrenes[2,5,23] may be due to their hydrolysis to the ketone by an $A–S_E2$ mechanism[24] which will be more hindered in triarylvinyl ethers. Some ethers were formed from 1-bromo-1-(p-methoxyphenyl)-propenes in the presence of triethylamine[25] but not with sodium acetate.[26]

Our k_{cis}/k_{trans} reactivity ratios are the highest known to us in vinylic solvolysis. They may be due to rate enhancement for compound (3) by β-p-methoxyphenyl participation[27] since β-phenyl participation was suggested for 1-methyl-2-phenylprop-1-enyl trifluoromethanesulphonates.[28] However, this is unlikely since an α-p-methoxyphenyl group outweighs β-double bond participation[29] by 10^{10}, and the stereochemical[22] and kinetic evidence ($k_{cis}/k_{trans} = 0.9$—1.15 in 80% EtOH and in AcOH)[4] in the related 1,2-bis-p-methoxyphenyl-2-phenylvinyl bromides and mesylates (14a) and (14b) (X = Br or OSO_2Me)[4,25] exclude β-p-methoxyphenyl participation.

(14a)   (14b)   (15)
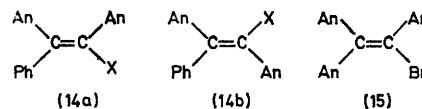
We ascribe the k_{cis}/k_{trans} ratio to a steric acceleration of the reaction of the *cis*-isomer and similar explanations hold for related systems.[26,30a] Molecular models of compounds (3) and (4) show a high departure from coplanarity of the p-methoxyphenyl groups of compound (3) with the double bond while (4) is nearly planar. Our isomerisation experiment shows that compound (4) is $\geqslant 1$ kcal mol^{-1} more stable than (3).

The ground state is most stabilised when the stilbene

[17] K. B. Wiberg, ' Physical Organic Chemistry,' Wiley, New York, 1963, p. 388.

[18] D. V. Banthorpe, ' Elimination Reactions,' Elsevier, London, 1963.

[19] S. J. Cristol and R. S. Bly, jun., *J. Amer. Chem. Soc.*, 1961, **83**, 4027.

[20] P. J. Stang and R. Summerville, *J. Amer. Chem. Soc.*, 1969, **91**, 4600.

[21] P. E. Peterson and J. M. Indelicato, *J. Amer. Chem. Soc.*, 1969, **91**, 6194.

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

[23] C. A. Grob and H. R. Pfaendler, *Helv. Chim. Acta*, 1971, **54**, 2060.

[24] D. S. Noyce and R. M. Pollack, *J. Amer. Chem. Soc.*, 1969, **91**, 7158.

[25] Z. Rappoport and Y. Apeloig, unpublished results.

[26] C. A. Grob and R. Nussbaumer, *Helv. Chim. Acta*, 1971, **54**, 2528.

[27] (*a*) A. Streitwieser, jun., ' Solvolytic Displacement Reactions,' McGraw-Hill, London, 1962, p. 144; (*b*) D. Bethell and V. Gold, ' Carbonium Ions,' Academic Press, London, 1967, ch. 7.

[28] P. J. Stang and T. E. Deuber, *J. Amer. Chem. Soc.*, 1972, **94**, in the press.

[29] P. G. Gassman, J. Zeller, and J. T. Lamb, *Chem. Comm.*, 1968, 69; P. G. Gassman and A. Fentiman, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 1545.

[30] (*a*) D. R. Kelsey and R. G. Bergman, *J. Amer. Chem. Soc.*, 1970, **92**, 228, 1971, **93**, 1941; (*b*) S. A. Sherrod and R. G. Bergman, *ibid.*, p. 1925.
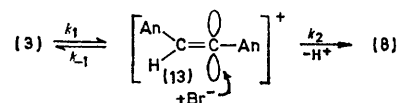
portion is coplanar while the transition state is most stabilised when the $\pi_{C=C}$ and the $\pi_{\alpha\text{-aryl}}$ orbitals are perpendicular, since overlap between the α-aryl and the incipient cationic orbital is maximised. Hence, steric interaction which results in deconjugation of the double bond and the α-aryl group increases the reactivity by raising the ground state and lowering the transition state energies. These effects lead to the reactivity order α-vinyl $\gg \alpha$-phenyl $\gg \alpha$-methyl in vinylic solvolysis.[8,31] The ground-state energy is also raised by a β-aryl–double bond deconjugation. The transition-state energy would be lowered by a relief of β-aryl–leaving group interaction, and by the gain in the β-aryl–double bond conjugation energy accompanying bending of the α-aryl group in the transition state leading to the linear cation.

In solvolysis in 80% EtOH compound (3) is 5·6 and $ca.$ 3 times faster and compound (4) is 8·3 and 14 times slower than α-bromo-4-methoxystyrene (1) and tris-p-methoxyphenylvinyl bromide (15) respectively.[5,6] Our considerations explain the $k_1(4)/k_1(15)$ ratio but not the low $k_1(4)/k_1(1)$ ratio since compound (4) is less planar than (1). We believe that this is due to the inductive effect of the β-p-methoxyphenyl group which was formerly underestimated[6] by using an inadequate model. The inductive rate retardation by β-phenyl in saturated systems was estimated as 8 or 10[32] and the value may be higher in β-p-methoxyphenylvinyl systems due to the shorter bonds and to the electron-attracting methoxy-substituent.

Extrapolation of Winstein–Grunwald m values via the approximate relationship[6,33] $(m_1/m_2) = (T_2/T_1)$ gives m values of 0·84 for compound (3) and 0·78 for (4) at 25°. These are higher than the m values for compounds (14) and (15)[4,6] and are in the region assigned for S_N1 reactions.[15]

Acetolysis of Compounds (3) *and* (4).—The discussion above of the *cis/trans* ratios is equally valid for the acetolysis. Evidence for a cationic intermediate is the slight rate enhancement with the increase of the added salt concentration and mainly the appearance of common ion rate depression.[16] The fall of the rate coefficient during the reaction was attributed earlier to the formation of a selective vinyl cation.[1-3,34,35] For the cation (13) it suggests that k_{-1} and k_2 in Scheme 2 for the *cis*-isomer are of comparable magnitude. Contrary to the cation derived from compounds (14a) and (14b),[34] the cation (13) is ' sterically asymmetrical ' and selective between the two in-plane directions of attack by the nucleophile. Attack from the side of the smaller group (indicated by the arrow in Scheme 2) would be favoured and *cis*-products should predominate. This was observed in the addition of HBr to the acetylene (8) where cation (13) is the most likely intermediate; >90% of (3)

and small amounts of the vinyl acetates [which are minor products in the acetyolysis of (3) and (4)] are formed.

$$(13) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \left[\begin{array}{c} An \\ H \end{array} \hspace{-0.3em} C = \overset{O}{\underset{O}{C}} - An \right]^+ \overset{k_2}{\underset{-H^+}{\longrightarrow}} (8)$$

SCHEME 2

As predicted, the acetolysis of compound (3) is accompanied by a rate depression due to a combination of the common ion effect and the formation of the less reactive (4), and by isomerisation to (4). The acetolysis of compound (4) shows no isomerisation as predicted, but the rate depression is similar in magnitude to that of (3), although only a small rate depression is predicted. As yet we have no explanation to offer for this.

The sequence of decreasing common ion rate depression for the $An\overset{+}{C}{=}CR^1R^2$ cations is therefore $R^1,R^2 =$ $Ar^1,Ar^2 >$ Me,Me $>$ An,H $>$ H,H, and it was ascribed to decreased shielding of the cationic orbital by the β-substituents. However, we note that while in other systems OAc^- and Br^- compete in capturing the cation, in our case Br^- captures cations (13) but OAc^- is mainly involved in proton abstraction. Likewise, the preference of elimination over substitution for $AnCBr{=}CHR$ increases with the bulk of R from 0% when R = H to 90% elimination for R = An,[2,25] reflecting the importance of steric effects in the formation of the strain-free acetylene. The predominance of the vinyl acetates in the presence of AgOAc is probably due to the lower basicity of the medium compared with NaOAc. By analogy with the behaviour of the bromides we believe that the acetate formed in excess is the *cis*-acetate.

Acetolysis of Compounds (5), (6) *and* (7).—Of the expected acetolysis products of compounds (5) and (6), only (7) was observed. The absence of the diacetates $AnC(OAc){:}C(OAc)An$ from the acetolysis of compounds (5), (6), and (7) may be accounted for by their further hydrolysis to 4,4'-dimethoxybenzoin acetate (11), since vinyl acetates form ketones in acetic acid.[2,22,30b] No 4,4'-dimethoxybenzil and only 12% of deoxy-4,4'-dimethoxybenzoin are formed from compound (7) up to two half-lives, and their formation in equal amounts after longer reaction times may mainly involve disproportionation of the acetate (11). However, this is not the route for the formation of compounds (10) and (12) from (5) and (6) at short reaction times since we found that (11) is stable for 48 h under our reaction conditions. Benzil derivatives were formed in other vinylic solvolyses of α,β-diaryl systems carrying two potential leaving groups.[36,37]

[31] M. D. Schiavelli, S. C. Hixon, and H. W. Moran, *J. Amer. Chem. Soc.*, 1970, **92**, 1082; M. D. Schiavelli, S. C. Hixon, H. W. Moran, and C. J. Boswell, *ibid.*, 1971, **93**, 6989.

[32] H. C. Brown and C. J. Kim, *J. Amer. Chem. Soc.*, 1968, **90**, 2082.

[33] S. Winstein and A. H. Fainberg, *J. Amer. Chem. Soc.*, 1957, **79**, 5397.

[34] Z. Rappoport and Y. Apeloig, *Tetrahedron Letters*, 1970, 1845.

[35] L. L. Miller and D. A. Kaufman, *J. Amer. Chem. Soc.*, 1968, **90**, 7282.

[36] S. J. Huang and M. V. Lessard, *J. Amer. Chem. Soc.*, 1968, **90**, 2432.

[37] G. Cappozi, G. Modena, and L. Ronzini, *J.C.S. Perkin I*, 1972, 1136.

We propose that compounds (10) and (12) are formed *via* a debromination–oxidation sequence. The cation (16) reacts with Br^- or AcO^- giving bromine (or AcOBr) and the acetylene (8) [equation (4)] which was indeed detected in the solvolysis mixtures of compounds (5), (6), and (7). 4,4'-Dimethoxybenzil is then formed by oxidation of (11) by bromine (or AcOBr) and we found that deoxy-4,4-dimethoxybenzoin is formed from (8) in acetic acid at 160°.

$$(5) \text{ and } (6) \longrightarrow \underset{(16)}{AnC(Br)\overset{+}{:}C\text{-}An} \xrightarrow{\ Br^-\ } (8) + Br_2 \quad (4)$$
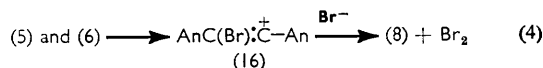
The Winstein–Grunwald *m* values for the AcOH–95% AcOH pair, extrapolated to 25° are 0·85 for (5) and 0·86 for (6). These values as well as the increase in k_1 with the salt concentration and the common ion rate depression fit the S_N1 mechanism. From the depressed k_1 value (k^d_1) we estimated the competition factors α as 0·2 for (5), *ca.* 0·8 for (6), and 0·75 for (7) by equations (5) and (6). We accounted for the salt effect by assuming that the increase in k_1 by the action of Br_4NBr is similar to that caused by NaOAc.

$$RBr \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^+ + Br^- \xrightarrow{\ k_2, OAc^-\ } \text{Products} \quad (5)$$
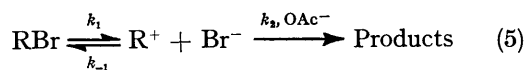
$$k^d_1 = k_1/(1 + \alpha[Br^-]/[OAc^-]) \quad \alpha = k_{-1}/k_2 \quad (6)$$

The lower α value for the slower reacting isomer (5) is expected. The bromide ion return to cation (16) gives mainly (6), as judged by its predominance in the (8)–Br_2 reaction, and the faster reacting isomer (6) should therefore experience a much larger rate depression. The α values are much lower than those for more reactive systems such as compounds (3), (4), or (15),[3,34] but the selectivity observed with our sluggish system suggests again a shielding effect of the cationic orbital by the β-bromo- and β-acetoxy-substituents.

Our ionisation experiment shows that the ground state energies of compounds (5) and (6) are similar. By analogy, the equilibrium amounts of the *cis*-isomer in α,β-disubstituted stilbenes PhCX:CXPh are 45% when X = Me and 75% when X = Cl.[13] Considerations similar to those discussed for compounds (3) and (4) explain the small reactivity differences between (5), (6), and (7) without the need to invoke β-bromine or β-acetoxy-participation. The question of neighbouring bromine in vinylic systems is not clear.[38]

A β-bromine atom reduces the solvolytic reactivity. Using activation energies of 25 kcal mol⁻¹ for compounds (5) and (6) we obtained $k_1(3)/k_1(5) = 187$ and $k_1(4)/k_1(6) = 3·3$ as average values. These ratios were multiplied by two for comparison purposes since compounds (5) and (6) have two equivalent leaving groups, and then $k_H/k_{Br} = 375$ and 6·6 for the *cis*- and the *trans*-

systems, respectively. The ratio for the *cis*-isomer is of the same magnitude as in the solvolysis of cyclohexyl brosylates,[39] or for the ethanolysis of an α-aryl system ($k_{MeCHBrPh}/k_{BrCH_2CHBrPh} = 10^3$).[40] However, the ratio for the *trans*-isomer is low for systems without anchimeric assistance. We believe that the difference of 4 kcal mol⁻¹ between the observed ratio and a hypothetical extreme value of 10^3 as above is accomodated by ground-state differences. The high angle of twist (54·5°) for *trans*-α,β-dibromostilbene[13] suggests a much higher departure from coplanarity for compound (6) compared with (4). The concomitant loss of conjugated energy should be at least similar to that between *cis*- and *trans*-stilbene which differ by at least 3·8 kcal mol⁻¹,[41] since the loss of conjugation is lower for *cis*-stilbene compared with the *trans*-compound (6).

EXPERIMENTAL

U.v. spectra were measured with a Perkin-Elmer 450 spectrometer, i.r. spectra with a Perkin-Elmer 337 spectrometer, and n.m.r. spectra with a Varian T-60 instrument. The chemical shifts are in p.p.m. downfield from tetramethylsilane.

Solvents.—Glacial acetic acid (Frutarom) was refluxed with acetic anhydride (1%) for 48 h and distilled, and the middle fraction was used. Absolute ethanol (Frutarom) was distilled. Aqueous solvents were prepared from the organic solvent and conductivity water. Solutions of NaOAc in acetic acid were prepared by dissolving analytical sodium carbonate in the acetic acid.

Bis-4-methoxyphenylacetylene (8).—(a) Bromination of 1,1-bis-*p*-methoxyphenylethylene[42] in carbon tetrachloride gave 1,1-bis-*p*-methoxyphenyl-2-bromoethylene, m.p. 84°,[42] δ (CDCl₃) 3·80 (3H, s, MeO), 3·85 (3H, s, MeO), and 6·63—7·37 (9H, m, Ar, :CH). (b) Sodium (9·2 g, 0·4 mol) was dissolved in ethylene glycol (2·5 l) and 1,1-bis-*p*-methoxyphenyl-2-bromoethylene (31·8 g, 0·1 mol) was added. The mixture was refluxed for 10 h, cooled, and filtered, giving the acetylene (8) (12 g, 50%), m.p. 143° (from ethanol) (lit.,[43] 143°), λ_{max.} (EtOH) 291 (ε 35,700) and 309·5 nm (29,500), δ (CDCl₃) 3·82 (s, MeO) and 6·83—7·57 (q, Ar).

cis-α-Bromo-4,4'-dimethoxystilbene (3).—To the acetylene (8) (2·88 g, 12 mmol) in acetic acid (300 ml), 6M-hydrobromic acid (12 mmol) in acetic acid (2 ml) was added. The mixture was stirred for 2 h and left overnight. The solvent was evaporated and the oil obtained was crystallised twice from ethanol giving cis-α-*bromo*-4,4'-*dimethoxystilbene* (3 g, 78%), m.p. 79—80° (Found: C, 60·4; H, 4·45; Br, 25·2. $C_{16}H_{15}BrO_2$ requires C, 60·2; H, 4·45; Br, 25·05%, λ_{max.} (hexane) 243 (ε 18,800) and 297 nm (13,800), λ_{max.} (EtOH) 243 (ε 18,200) and 296 nm (13,000), ν_{max.} (CS₂) spectrum similar to those of (4) and 1,1-bis-*p*-methoxyphenyl-2-bromoethylene except for absorptions at 1160m, 892m, and 788m cm⁻¹, δ (CDCl₃) 3·73 (3H, s, MeO), 3·82 (3H ,s, MeO), 6·87 (1H, s, CH:), and 6·63—7·43 (8H, 2AA'BB' q, 2 × Ar), *m/e* 318, 320 (*M*, 76%), 239 (*M* − Br, base peak), 224

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

[39] S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Amer. Chem. Soc.*, 1948, **70**, 821.

[40] S. Winstein and E. Grunwald, *J. Amer. Chem. Soc.*, 1948, **70**, 828.

[41] (*a*) C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' 2nd edn., Cornell University Press, Ithaca, 1969, pp. 139—141; (*b*) G. Fischer, K. A. Muszkat, and E. Fischer, *J. Chem. Soc.* (*B*), 1958, 1156.

[42] P. Pfeiffer and R. Wizinger, *Annalen*, 1928, **461**, 132.

[43] W. Tadros, A. B. Sakla, A. A. Helmy, and M. K. Khalil, *J. Chem. Soc.*, 1965, 3994.

(M — Br — Me, 19), 209 (M — Br — 2Me, 11), 152 (22), and 121 (methoxytropylium ion, 17).

trans-α-*Bromo*-4,4'-*dimethoxystilbene* (4).—(a) To the acetylene (8) (2·88 g, 12 mmol) in carbon tetrachloride (300 ml), 6M-hydrobromic acid (12 mmol) in acetic acid (2 ml) was added. The mixture was stirred for 2 h and left overnight. N.m.r. spectroscopy showed the formation of a 9 : 1 cis–trans mixture. 6M-Hydrobromic acid (1 ml) in acetic acid was then added and the mixture was refluxed for 4 h. N.m.r. spectroscopy showed the presence of 78% (4), 20% (3), and <2% of an organic acetate. The solvent was evaporated and the oil obtained was crystallised twice from ethanol giving trans-α-bromo-4,4'-dimethoxystilbene (2 g, 52%), m.p. 101—102° (Found: C, 60·45; H, 4·8; Br, 25·0%), $\lambda_{max.}$ (hexane) 299·5 nm (ε 27,000), $\lambda_{max.}$ (EtOH) 300 nm (ε 26,800), $\nu_{max.}$ (CS$_2$) identical with that of (3) except for bands at 750w and 583m cm^{-1}, δ (CDCl$_3$) 3·53 (6H, s, 2 × MeO), 7·10 (1H, s, CH:), and 6·90—7·77 (8H, 2AA'BB' q, 2 × Ar), m/e 320, 318 (M, base peak), 239 (M — Br, 99%), 224 (M — Br — Me, 93), 209 (M — Br — 2Me, 49), 152 (95), and 121 (methoxytropylium ion, 73).

(b) Gaseous hydrobromic acid was bubbled through the acetylene (8) (2·4 g, 10 mmol) in carbon tetrachloride (300 ml) during 1 h. The mixture was left overnight to give solid (2 g), m.p. 175°. The mother liquor was evaporated giving an oil which on recrystallisation from ethanol gave trans-α-bromo-4,4'-dimethoxystilbene (1·2 g, 37%), m.p. 101°.

The solid which melts at 175° is very insoluble in chloroform, acetone, carbon tetrachloride, and carbon disulphide and by its analysis it is probably bis-*p*-methoxyphenyldibromoethane (Found: C, 47·35; H, 3·75; Br, 38·75 without recrystallisation. C$_{16}$H$_{16}$Br$_2$O$_2$ requires C, 48·05; H, 4·05; Br, 39·95%).

cis- *and* trans-1,2-*Bis*-p-*methoxyphenyl*-1,2-*dibromoethylenes* (5) *and* (6).—Bromine (3 ml, 56 mmol) in carbon tetrachloride (200 ml) was added slowly to the acetylene (8) (13·1 g, 55 mmol) in carbon tetrachloride (800 ml). Crystals of the trans-dibromide separated towards the end of the addition. Most of the solution (800 ml) was evaporated and the solid was collected and recrystallised from ethanol, giving needles (9 g, 41%) of trans-*isomer* (6), m.p. 198° (Found: C, 48·05; H, 3·25; Br, 40·1. C$_{16}$H$_{14}$Br$_2$O$_2$ requires C, 48·25; H, 3·5; Br, 40·15%), $\lambda_{max.}$ (MeCN) 261·4 nm (ε 16,400); $\nu_{max.}$ (CS$_2$) 1300m, 1250s, 1185m, 1175s, 1110w, 1040m, 835m, *735m, 680*w, and *635*w cm^{-1}, δ (CDCl$_3$) 3·85 (3H, s, MeO), 7·22 (4H, centre of AA'BB' q, J 9 Hz, Ar).

The mother liquor was evaporated to dryness and the remainder was crystallised from ethanol giving yellow crystals of the cis-isomer (5) (7 g, 32%), m.p. 116° (Found: C, 48·5; H, 3·56; Br, 40·1%), $\lambda_{max.}$ (MeCN) 249 (ε 19,400) and 308 nm (6750), $\nu_{max.}$ (CS$_2$) similar to that of (6) except for the bands in italics and the presence of bands at 831m, 795m, and 555m cm^{-1}, δ (CDCl$_3$) 3·70 (3H, s, MeO) and 6·90 (4H, centre of AA'BB' q, J 9 Hz, Ar).

trans-α-*Acetoxy*-β-*bromo*-4,4'-*dimethoxystilbene* (7).—trans-1,2-Bis-*p*-methoxyphenyl-1,2-dibromoethylene (5 g, 12·5 mmol) in acetic acid (300 ml) and silver acetate (2·1 g, 12·5 mmol) were refluxed for 90 min. The solution was filtered and evaporated and the solid obtained was dissolved in carbon tetrachloride (200 ml). The solution was filtered and evaporated and the solid was crystallised twice from ethanol giving pale yellow crystals of the *acetate* (7) (4·4 g, 93%), m.p. 114° (Found: C, 57·5; H, 4·8; Br, 21·6. C$_{18}$H$_{17}$BrO$_4$ requires C, 57·3; H, 4·5; Br, 21·2%), $\lambda_{max.}$ 279

nm (ε 19,600), $\nu_{max.}$ (CS$_2$) 1770s (C=O), 1050m, 920m, 760m, and 555m cm^{-1}. δ (CDCl$_3$) 1·90 (3H, s, OCOMe), 3·82 (6H, s, MeO), and 6·80—7·67 (8H, m, Ar).

The n.m.r. spectrum of the mother liquor showed that it contained 25% (7), 50% 4,4'-dimethoxybenzoin acetate, and 25% of two unidentified acetates in the ratio 4 : 1.

Reaction of compound (3) with silver acetate gave similar results.

Reaction of α-*Bromo*-4,4'-*dimethoxystilbenes with Silver Acetate.*—A mixture of silver acetate (50 mg, 0·3 mmol) and compound (3) (96 mg, 0·3 mmol) was refluxed in acetic acid (50 ml) for 60 min, filtered, and evaporated. N.m.r. spectroscopy (CCl$_4$) showed the formation of 54% of two monoacetates. The predominant one (presumably the cis-isomer) had signals at δ 2·13 (OAc), 3·73 (MeO), 3·80 (MeO), 6·33 (CH:), and 6·77—7·75 (m, Ar). In the other acetate (presumably the trans-isomer) the acetoxy-peak is at δ 2·27.

Reaction with the trans-isomer (4) gave similar results.

In an experiment on a larger scale with (3) (1·56 g, 5 mmol) and silver acetate (81 mg, 5 mmol), acetylene (8) (0·24 g, 20%) was isolated. N.m.r. spectroscopy showed that the remainder was 35% (8) and 65% of acetates in the ratio of 88 (AcO at δ 2·13) : 12 (AcO at δ 2·27). Attempts to separate the acetates failed.

Reaction of trans-1,2-*Bis*-p-*methoxyphenyl*-1,2-*dibromoethylene with Silver Acetate.*—(a) Silver acetate (66·8 mg, 0·4 mmol) and (6) (79·6 mg, 0·2 mmol) in acetic acid (50 ml) were refluxed for 60 min. The mixture was filtered, evaporated to dryness, the remaining oil dissolved in carbon tetrachloride, and the organic layer was washed with water, dried, and evaporated. N.m.r. spectroscopy showed the formation of 82% monoacetates with two signals, one at δ 1·90 and the other at 2·23, in the ratio 3 : 1. According to the positions of the signals these are due to trans-α-acetoxy-β-bromo-4,4'-dimethoxystilbene (7) and the acetate (11), respectively. No diacetates were observed.

(b) Silver acetate (1·1 g, 12·5 mmol) and (6) (5 g, 12·5 mmol) were refluxed in the dark in acetic acid (50 ml) for 90 min. The mixture was filtered, and water (5 ml) was added slowly to the filtrate, giving (7) (2·3 g, 50%). On addition of water (5 ml), a yellow solid (1 g, 28%), m.p. 134° (from ethanol), identified as 4,4'-dimethoxybenzil, was obtained, δ (CDCl$_3$) 3·87 (3H, s, MeO) and 7·43 (4H, centre of q, Ar), $\nu_{max.}$ (CS$_2$) 1660 cm^{-1} (C=O).

Isomerisation of Compound (6).—Compound (6) (0·4 g, 1 mmol) was refluxed in 1,3-dichlorobenzene (100 ml) at 170° in the dark. Samples were analysed by n.m.r. spectroscopy after 24 and 48 h, and in both cases a 1 : 1 mixture of (5) and (6) was observed.

Reaction of Acetylene (8) *with Acetic Acid.*—The acetylene (8) (0·1 g, 0·42 mmol) and sodium acetate (0·1 g, 1·22 mmol) were kept in acetic acid (10 ml) in a sealed tube at 160° for 20 h. N.m.r. spectroscopy showed the formation of 82% deoxy-4,4'-dimethoxybenzoin by comparison of the spectrum with that of an authentic sample, δ (CDCl$_3$) 3·77 (3H, s, MeO), 3·85 (3H, s, MeO), 4·17 (1H, s, CH), 7·30—7·78 (6H, m, Ar), 7·93, and 8·08 (2H, half q, 2 × o-H in the *p*-MeOC$_6$H$_4$ group).

4,4'-*Dimethoxybenzoin Acetate* (11).—4,4'-Dimethoxybenzoin (0·3 g, 11 mmol) and sodium acetate (0·08 g, 1 mmol) in acetic acid (10 ml) were kept in a sealed ampoule at 160° for 20 or 48 h. N.m.r. of both reactions was identical with that of an authentic 4,4'-dimethoxybenzoin acetate, δ (CDCl$_3$) 2·23 (3H, s, OAc), 3·78 (3H, s, MeO), 3·82 (3H, s,

MeO), 6·66—6·83 (7H, m, CH:, Ar, half Ar q), 7·72, 8·03 (2H, half q, 2 × o-H in the p-MeOC$_6$H$_4$ group), $\nu_{max.}$ (CS$_2$) 1740 (C=O, AcO) and 1680 (C=O) cm^{-1}.

Hydrolysis of 4,4'-Dimethoxybenzoin Acetate.—Sodium acetate (0·08 g, 1 mmol) and 4,4'-dimethoxybenzoin acetate (0·31 g, 1 mmol) were kept in 80% aqueous acetic acid (80 ml) at 120° for 20 h. N.m.r. spectroscopy showed the presence of 80% 4,4'-dimethoxybenzoin and 20% of the acetate.

Kinetic Experiments.—The sealed ampoule technique was used. The ampoules were prepared according to Grob and Cseh.[5] Stock solutions of all the compounds [excluding (6)] in acetic acid were used. The solubility of compound (6) in acetic acid and of compounds (3) and (4) in aqueous ethanol is low and required independent weighing of each ampoule.

The formation of bromide ion was followed titrimetrically with silver nitrate using Eosin indicator or potentiometrically. First-order coefficients were calculated by use of the KINDAT program.[14]

Product Analysis.—Following the bromide titration the mixture was extracted twice with carbon tetrachloride (2 × 30 ml), the organic layer was separated, washed with sodium hydrogen carbonate solution and with water, dried (CaCl$_2$), and evaporated. N.m.r. and i.r. spectra of the

remaining oil were taken. Control experiments showed that the same product distribution was obtained from ampoules which were not subjected to titration.

The methoxy-signals of compounds (3) and (5) at δ 3·73 and 3·70 respectively were used for their determination in mixtures. The percentage of monoacetates was determined from the intensity ratios of the total acetate to the total methoxy-signals. The amounts of compounds (10) and (11) were calculated, respectively, from the ratio of the methylene protons of (10) at δ 4·17 and of the acetoxy-protons of (11) at δ 2·17 to the methoxy-protons. The amount of compound (12) was determined from the ratio of the half quartet o-hydrogen atom of the p-methoxybenzoyl group at δ 7·83—8·17 to the total aromatic protons, after subtracting the amounts of compounds (10) and (11) which were determined as above. Qualitative evidence for the appearance of (12) and of (8) [which has an n.m.r. spectrum identical to that of (6) in CDCl$_3$] was inferred from the presence of their characteristic absorptions at 600 and 750 cm^{-1}, respectively.