Vinylic Cations from Solvolysis. Part XI.[1,2] Solvolysis of Triarylvinyl Arenesulphonates and Bromides

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Triarylvinyl arenesulphonates and bromides, $Ar^2_2C=C(Ar^1)X$ (X = Br or $O{\cdot}SO_2Ar^3$), were solvolysed in 70% acetone, and tris-*p*-methoxyphenylvinyl tosylate (II–OTs) and brosylate were solvolysed in acetic acid. The products were 2,2-diarylacetophenones and tris-*p*-methoxyphenylvinyl acetate, respectively. The solvolysis of (II–OTs) shows common ion rate depression and the intermediate vinyl cation is captured by bromide and tosylate ions. For change in Ar^3 of the leaving group, the Hammett ρ value is 1·91 at 50 and 1·67 at 75°. For 60—90% aqueous acetone a Winstein–Grunwald *mY* plot is linear with $m = 0{\cdot}42$. The reaction rate is sensitive to the α-activating substituent with $k_{\alpha\text{-}p\text{-MeO}\cdot C_6H_4}/k_{\alpha\text{-Ph}} = 630$, and much less sensitive to the nature of the β-aryl groups. Solvent isotope effects are small. It is suggested that the reaction has an S_N1 mechanism with an intermediate ' selective ' vinyl cation. The solvent effect and the $k_{OBs} : k_{OTs}$ and the $k_{OTs} : k_{Br}$ reactivity ratios are discussed and it is concluded that the solvolysis is anchimerically and nucleophilically unassisted.

THERE is now ample evidence for the formation of vinyl cations as intermediates in the solvolysis of vinylic systems substituted with the appropriate leaving group.[3-5] While vinylic solvolyses are usually much slower than those of the corresponding saturated analogues,[3,4,6-8] the effect of substituents[7,9,10] and solvents,[6,9,10] the secondary hydrogen isotope effect,[11] the stereochemistry of the solvolysis,[12] and the occurrence of common ion rate depression,[13] *cis–trans* isomerisation,[14] and rearrangements[15] suggests a qualitative similarity of the trigonal and digonal carbonium ions and of the transition states for their formation. However, solvolysis of triarylvinyl[6,8] and diarylvinyl halides[16] gave low Winstein–Grunwald *m* values[17] while the α-anisylvinyl cations are more selective towards nucleophiles than expected by their sluggish formation.[7,13] These phenomena, at least in part, are connected with the high steric crowding in the vinylic cations and in the transition states for their formation. Accordingly, the *m* values decrease,[6,9,16] the selectivity of the ion increases,[13] and the competing *E*1 elimination becomes dominant[5,9,16] on increasing the bulk and the number of the vinylic substituents.

Alternative explanations for the low *m* values are nucleophilic solvent assistance or formation of a transition state with low polarity. Additional information on the polarity of the transition state of the solvolysis can be obtained from the relative reactivity ratios of the same substrate with different leaving groups, $k_{OBs} : k_{OTs}$ and $k_{OTs} : k_{Br}$.[18,19] The $k_{OBs} : k_{OTs}$ ratios can be also used[20] to differentiate between the S_N1 route and the electrophilic addition–elimination route which gives the same product. The present work was initiated in order to gain more information on the effect of the arenesulphonate leaving groups and the solvent in vinylic solvolyses, and on the selectivity of the intermediate cations.

RESULTS

Preparation of the Triarylvinyl Arenesulphonates.—Nine triarylvinyl arenesulphonates (II), (III-OTs), (IV-OTs), and (V-OTs) and tris-*p*-methoxyphenylvinyl methanesulphonate (mesylate) $An_2C=C(An)O{\cdot}SO_2Me$ were prepared from the triarylvinyl bromides and silver arenesulphonates (or mesylate) in dry acetonitrile in moderate to good yields (equation 1). Triphenylvinyl bromide is much less reactive and the tosylate is obtained only after prolonged reaction times in a sealed ampoule at 120°. Our method is simpler than that of Jones and Maness[8] who prepared analogous sulphonates by a three-step synthesis *via* the triazene from the vinyl bromide.

$$Ar^2_2C=C(Ar^1)Br + AgO{\cdot}SO_2Ar^3 \longrightarrow Ar^2_2C=C(Ar^1)O{\cdot}SO_2Ar^3 + AgBr \quad (1)$$

(II) $Ar^1 = Ar^2 = An$
(II-OTs) $Ar^3 = C_6H_4Me\text{-}p$
(II-OBs) $Ar^3 = C_6H_4Br\text{-}p$
(II-*p*-ONs) $Ar^3 = C_6H_4{\cdot}NO_2\text{-}p$
(II-*o*-ONs) $Ar^3 = C_6H_4{\cdot}NO_2\text{-}o$
(II-OPh) $Ar^3 = Ph$
(II-OAn) $Ar^3 = C_6H_4{\cdot}OMe\text{-}p$
(III-OTs) $Ar^1 = An$; $Ar^2 = Ph$; $Ar^3 = C_6H_4Me\text{-}p$
(IV-OTs) $Ar^1 = Ar^2 = Ph$; $Ar^3 = C_6H_4Me\text{-}p$
(V-OTs) $Ar^1 = An$; Ar^2_2C = fluorenylidene; $Ar^3 = C_6H_4Me\text{-}p$
$An = p\text{-MeO}{\cdot}C_6H_4$

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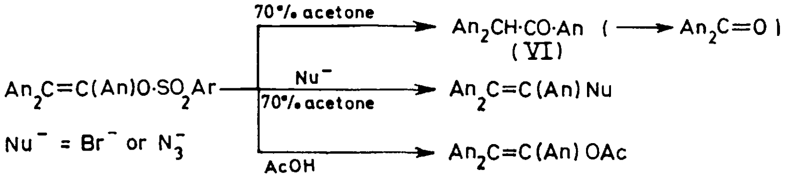
Solvolysis Products.—Compounds (II)—(V-OTs) were solvolysed in aqueous acetone and in acetic acid. In aqueous acetone the n.m.r. spectra of the solvolysis mixtures of tris-*p*-methoxyphenylvinyl tosylate, *o*-nitrobenzenesulphonate and bromide were taken after 10 half-lives. The n.m.r. spectra were identical with that of 4′-methoxy-2,2-bis-*p*-methoxyphenylacetophenone (VI) which was also obtained from the solvolysis of tris-*p*-methoxyphenylvinyl bromide and chloride in aqueous ethanol.[6] No attempt was made to isolate (VI) which has not been obtained previously as a solid (see discussion in footnote 20 of ref. 6).

The acetophenone (which was reported to cleave by sodium hydroxide to 4,4′-dimethoxybenzophenone during its formation in the solvolysis of tris-*p*-methoxyphenylvinyl bromide in 80% ethanol) [6] was usually stable in our mild reaction conditions. However, when (II-OBs) was left for two months at room temperature in 70% acetone containing 2,6-lutidine, 4,4′-dimethoxybenzophenone was formed. The mechanism of this fragmentation was discussed earlier.[6]



SCHEME 1

TABLE 1

Solvolysis of $Ar^2_2C{=}C(Ar^1)O{\cdot}SO_2R$ in 70% acetone [a]

Ar^1	Ar^2	R	t/°C	10^5k_1/s^{-1}	t/°C	10^5k_1/s^{-1}	$\Delta H^‡$/kcal mol^{-1}	$\Delta S^‡$/cal K^{-1} mol^{-1}
An	An	*p*-MeC_6H_4	50	0·413 ± 0·005	75	8·38 ± 0·39 [b]	25·9	−2·8
			75	6·87 ± 0·04 [c]	75	7·35 ± 0·25 [d]		
An	Ph	*p*-MeC_6H_4	75	2·84 ± 0·02	90	13·0 ± 0·7	24·5	−9·2
Ph	Ph	*p*-MeC_6H_4			120	0·298 ± 0·027		
An	Fl [e]	*p*-MeC_6H_4	75	0·380 ± 0·011	100	7·48 ± 0·24	29·8	−2·3
An	An	*p*-$MeO{\cdot}C_6H_4$	50	0·227 ± 0·015	75	4·96 ± 0·16	24·9	−6·9
An	An	Ph	50	0·715 ± 0·006	75	14·8 ± 0·3	26·1	−1·8
An	An	*p*-BrC_6H_4	50	2·29 ± 0·002	75	42·1 ± 2·1	25·1	−2·1
An	An	*p*-$O_2N{\cdot}C_6H_4$	50	2·80 ± 0·01 [f]	75	46·8 ± 1·0 [f]	24·3 [f]	−4·2 [f]
					75	320 [g]		
An	An	*o*-$O_2N{\cdot}C_6H_4$	50	5·64 ± 0·03 [f]	60	18·8 ± 0·2 [f]	24·9 [f]	−0·9 [f]
An	An	Me			75	4·78 ± 0·18		

[a] [2,6-Lutidine] = 0·016—0·020M; [vinyl sulphonate] = 0·008M. [b] [2,6-Lutidine] = 0·0166M. [c] The solvent is acetone–D_2O (7 : 3, v/v). [d] [2,6-Lutidine] = 0·0704M. [e] Fl = $Ar^2_2C{=}$ = Fluorenylidene [f] In 90% acetone. [g] Extrapolated (from data in 90% acetone) to 70% acetone, by taking m = 0·42.

Solvolysis of fluorenylidene-(*p*-methoxyphenyl)methyl tosylate (V-OTs) in 70% acetone gave only 9-anisoylfluorene, and acetolysis of (II-OTs) and (II-OBs) gave tris-*p*-methoxyphenylvinyl acetate.[6]

When the solvolysis of (II-OTs) was conducted in 70% acetone in the presence of 20 molar excess of tetrabutylammonium bromide, only tris-*p*-methoxyphenvinyl bromide was isolated in 77% yield. Likewise, when (II-*o*-ONs) was solvolysed in the presence of excess of sodium azide, the organic product showed absorption of azido-group in the i.r. spectrum, and no C=O absorption of the ketone (VI) (Scheme 1).

Kinetics.—The solvolysis was followed in 60—90% aqueous acetone mixtures, in aqueous ethanol and in acetic acid. In aqueous acetone, 2,6-lutidine was used for neutralisation of the liberated arenesulphonic acid and the reaction was followed by the increase in the conductance of the 2,6-lutidinium arenesulphonate. This method could not be used in the presence of an excess of salts, and under these conditions the reaction was followed by n.m.r. spectroscopy. When 2,6-lutidine or triethylamine were used in aqueous ethanol, the conductance of the solution increased steadily up to 40—50% reaction, after which it remained constant. This may be due to esterification of the formed sulphonic acid by the alcohol. Sodium acetate was therefore used for the neutralisation and the reaction was followed titrimetrically both in 90% ethanol and in acetic acid.

Solvolysis in Aqueous Acetone.—All reactions were first order in the sulphonate and no common ion rate depression was detected within a kinetic run by the formed arenesulphonate ion. The concentration of the ester was usually 0·008M and that of 2,6-lutidine 0·0166M. When the concentration of the 2,6-lutidine was increased 4·2-fold, the rate coefficient for the reaction of (II-OTs) in 70% acetone was *ca.* 12% lower. Table 1 lists the data for all the compounds studied in 70% (v/v) acetone. The rate coefficients were calculated with the aid of the computer program KINDAT for the first-order reaction,[21] which searches and uses the best infinity value. These rate coefficients are therefore slightly different from those reported earlier,[2] which were calculated by averaging k_1 for individual points.

From Table 1 the Hammett ρ value for changes in the arenesulphonate leaving group for four compounds is 1·91 at 50° (correlation coefficient r = 0·994). At 75°, data for the reactive *p*-nitrobenzenesulphonate could be extrapolated from that in 90% acetone with the aid of the Winstein–Grunwald equation.[17] For the five points ρ = 1·67 and r = 0·997. From the data for (II-OTs) and (II-*p*-ONs) in 90% acetone ρ = 1·68. The *o*-nitrobenzenesulphonate is twice as reactive as the *para*-isomer while the mesylate is about half as reactive as the tosylate. Most of the

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

activation enthalpies are 25 ± 1 kcal mol^{-1}, with the most reactive compounds having the lower $\Delta H^{\ddagger}$. For (V-OTs) the activation enthalpy is much higher than those for the other compounds. Usually the spread in the activation entropies is larger than in the energy terms. The solvent isotope effect, when D_2O is the co-solvent instead of H_2O is $k_H : k_D$ = 1·22 ± 0·06.

The α-substituent effect is pronounced, $k_{\alpha\text{-An}} : k_{\alpha\text{-Ph}}$ = 630 ($\rho^+ = -3{\cdot}6$). β-Aryl groups have a small effect, provided that the geometry is retained. However, the β-fluorenyl derivative (V-OTs) is 22 times less reactive than the β,β-bis-*p*-methoxyphenyl compound (II-OTs).

Table 2 gives the data for (II-OTs) in the presence of added salts. The concentrations of the arylsulphonate and the base are 2·5 times higher than those of Table 1 since the n.m.r. method required the use of higher concentrations. Sodium perchlorate (0·38M) increases the solvolysis rate, but by less than that found in many solvolyses of saturated compounds.[22] Tetrabutylammonium bromide which diverts the product to tris-*p*-methoxyphenylvinyl bromide gives a reduced rate. The rate coefficients are also much lower in the presence of tetraethylammonium tosylate; with 0·414M-Et_4NOTs k_1 is 29% of its value in the absence of salt. This common ion rate depression is practically absent for (IV-OTs); at 0·414M-Et_4NOTs the rate coefficient is only 4% lower than that in the absence of the salt.

TABLE 2

Solvolysis of $Ar_2C{=}C(Ar)OTs$ [a] in the presence of added salts in 70% acetone

Ar	Added salt (10^{2}M)	t/°C	10$^5k_1$/s^{-1}
An		75	8·38 ± 0·39
An	Bu_4NBr [b]	75	7·43 ± 0·57
An	$NaClO_4$ (38)	75	10·1 ± 0·6
An	Et_4NOTs (13·8)	75	3·65 ± 0·08
An	Et_4NOTs (41·4)	75	2·43 ± 0·22
Ph		120	0·298 ± 0·027
Ph	Et_4NOTs (41·4)	120	0·287 ± 0·025

[a] [$Ar_2C{=}C(Ar)OTs$] = 0·02M; [2,6-lutidine] = 0·04M. Product, tris-*p*-methoxyphenylvinyl bromide.

Table 3 gives the data for (II-OTs) in four aqueous acetone mixtures covering 2·66 units in the ionisation power, Y.[17] The reaction is faster in the more aqueous solvent, and the plot of log k *vs.* Y is linear (r = 0·992), with a Winstein–Grunwald slope of m = 0·42 (Figure). A run in 90% ethanol is also included in Table 3.

TABLE 3

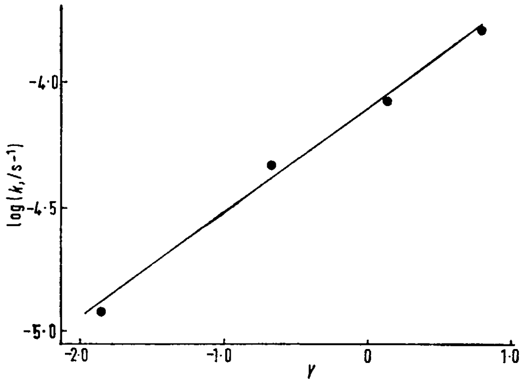
Solvolysis of compound (II-OTs) in aqueous–organic media at 75°

Solvent (v/v) [a]	Y	10$^5k_1$/s^{-1}
$Me_2CO–H_2O$ (9 : 1)	−1·86	1·18 ± 0·02
$Me_2CO–H_2O$ (4 : 1)	−0·67	4·59 ± 0·13
$Me_2CO–H_2O$ (7 : 3)	0·13	8·38 ± 0·39
$Me_2CO–H_2O$ (3 : 2)	0·80	16·1 ± 0·7
$EtOH–H_2O$ (9 : 1)	−0·75	11·8 ± 0·6

[a] The base is 2,6-lutidine, except in $EtOH–H_2O$ (9 : 1) where it is NaOAc.

Acetolysis.—The acetolysis of (II-OTs) and (II-OBs) is summarised in Table 4. For (II-OTs) $\Delta H^{\ddagger}$ = 22·1 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −15·4 cal K^{-1} mol^{-1}. The reaction was also conducted in AcOD and the solvent isotope effects $k_{AcOH} : k_{AcOD}$ are 0·85 ± 0·08 for (II-OTs) and 1·05 ± 0·05 for (II-OBs).

Solvolysis of Triarylvinyl Bromides.—Tris-*p*-methoxyphenylvinyl bromide, 2,2-diphenyl-1-(*p*-methoxyphenyl)-vinyl bromide, and fluorenylidene-(*p*-methoxyphenyl)-methyl bromide were solvolysed in 70% acetone. Table 5 also contains extrapolated data for the corresponding tosylates to the same temperature, and $k_{OTs} : k_{Br}$ ratios. For tris-*p*-methoxyphenylvinyl bromide k_1 increases only by 7·5% on increasing the concentration of the 2,6-lutidine 5·7-fold, and the activation parameters are $\Delta H^{\ddagger}$ = 28·2 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −4·1 cal K^{-1} mol^{-1}. The $k_{OTs} : k_{Br}$ ratios are 19·1—87 for different substrates, solvents, and temperatures.



mY Plot for the solvolysis of (II-OTs) in aqueous acetone at 75°

TABLE 4

Acetolysis of tris-*p*-methoxyphenylvinyl arenesulphonates [a]

Compound	Solvent	t/°C	10$^5k_1$/s^{-1}
(II-OTs)	AcOH	60	3·20 ± 0·06
(II-OTs)	AcOH	75	13·5 ± 0·9
(II-OTs)	AcOD	75	16·0 ± 0·5
(II-OBs)	AcOH	75	51·7 ± 1·0
(II-OBs)	AcOD	75	49·1 ± 1·7

[a] [Vinyl ester] = 0·02M; [base] = [NaOAc] = 0·04M.

DISCUSSION

Evidence for Vinylic Carbonium Ion Intermediates.—A multiplicity of mechanistic routes may lead to an overall nucleophilic vinylic substitution by a nucleophile or by the lyate ion.[23] Some of these (*e.g.*, elimination–additions, rearrangement–substitution) require vinylic or allylic hydrogen and are excluded in our system, leaving four routes (Scheme 2); (*a*) nucleophilic addition–elimination,[23] (*b*) attack on sulphur, (*c*) electrophilic addition–elimination, and (*d*) S_N1 reaction *via* the ion (VII). As discussed below our data only fit route (*d*).

Route (*a*) dominates the reaction of fluorenylidene-(*p*-methoxyphenyl)methyl halides with thio-nucleophiles in aqueous ethanol.[1] However, it is incompatible with the low (II-OTs) : (III-OTs) reactivity ratio and with the predominance of the S_N1 route for 2,2-diphenyl-1-(*p*-methoxyphenyl)vinyl bromide with thio-nucleophiles.[1]

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[22] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 2763, 2780.

[23] Z. Rappoport, *Adv. Phys. Org. Chem.*, 1969, **7**, 1.

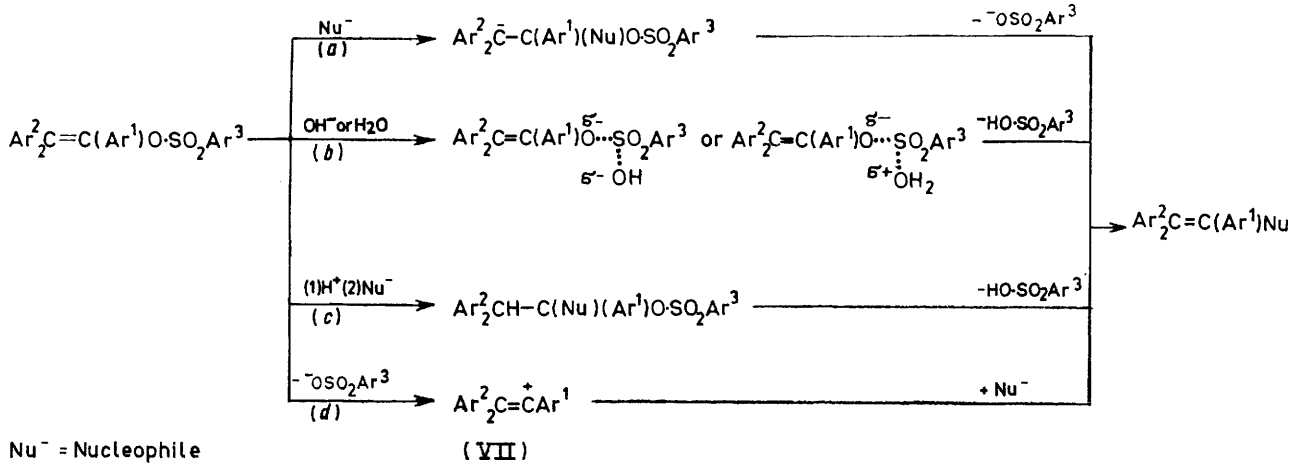
Moreover, route (*a*) is first order in the nucleophile while k_1 for (II-OTs) falls by 12% on increasing the 2,6-lutidine (and correspondingly the OH^-) concentration 4·2-fold.

Table 5

Solvolysis of $Ar_2C{=}C(An)X$ and tosylate : bromide reactivity ratios

Ar	Solvent (v/v)	t/°C	X = Br [a] $10^5k_1/s^{-1}$	X = OTs $10^5k_1/s^{-1}$	$k_{OTs} : k_{Br}$
An	$Me_2CO–H_2O$ (7 : 3)	95·1	1·68 ± 0·10 [b]		
		120·3	21·4 ± 0·7 [b]	680 [d]	31·8
		120·3	23·0 ± 1·1 [c]		
An	$EtOH–H_2O$ (9 : 1)	75·0	0·43 [d,e] (0·61) [f]	11·8	27·0 (19·4)
An	AcOH	120·3	6·7 [g]	582 [d]	87·0
Ph	$Me_2CO–H_2O$ (7 : 3)	120·3	7·5 ± 0·17 [b]	188 [d]	25·1
Fl [h]	$Me_2CO–H_2O$ (7 : 3)	120·3	3·22 ± 0·07 [b]	61·5 [d]	19·1

[a] $[Ar_2C{=}C(An)Br]$ = 0·008M. [b] Base = [2,6-lutidine] = 0·016M. [c] [2,6-Lutidine] = 0·092M. [d] Extrapolated from data at lower temperatures. [e] Rappoport and Gal, unpublished results. The base is NaOAc. [f] From ref. 6. Data in the presence of NaOH. [g] Extrapolated k_1 value from ref. 13. [h] Fl = $Ar_2C{=}$ = Fluorenylidene.



Scheme 2

Precedents for route (*b*) under strongly nucleophilic conditions are known for phenyl-,[24] neophyl-,[25] and tertiary saturated [26] tosylates and even for a cyclic vinyl tosylate.[27] Attack on sulphur by hydroxide ion is excluded since it would be first order in the nucleophile and slower in the more aqueous solvents. An O–S cleavage by water *via* a zwitterionic transition state requires α-An : α-Ph and β-An : β-Ph reactivity ratios lower than 1 for the triarylvinylethoxide leaving group, contrary to what was observed. Moreover, analogy with the basic hydrolysis of benzoates [28] suggests the reactivity order (II-*o*-ONs) : (II-*p*-ONs) < 1 while the actual ratio is 2·04. In AcOH, route (*b*) cannot explain the products and the $k_{OTs} : k_{Br}$ ratio.

Route (*c*),[20,29,30] should be always considered in solvents such as AcOH. While Markovnikov addition *via* $Ar^2{}_2C(Nu)CH(Ar^1)O{\cdot}SO_2Ar^3$ does not give the observed product, the anti-Markovnikov addition would show the same solvent and substituent effects and would give the same product as route (*d*). Peterson and Indelicato [20] argued that the $k_{OBs} : k_{OTs}$ ratios should be *ca.* 3 for route (*d*) as found for saturated systems,[31] while the ratios would be lower than 1 for route (*c*) since the brosylate is more electronegative than the tosylate group. This was observed in the aqueous methanolysis [$k_{OBs} : k_{OTs}$ = 3, route (*d*)] [32] and the formolysis [$k_{OBs} : k_{OTs}$ = 0·3, route (*c*)] [20] of but-2-enyl and cyclohex-1-enyl arenesulphonates. Our $k_{OBs} : k_{OTs}$ ratios of 3·42 and 3·16 in AcOH and AcOD at 120° and 5·55 (ρ = 1·91) and 5·03 (ρ = 1·67) in 70% acetone at 50 and 75° eliminate route (*c*).

The solvent isotope effects $k_{AcOH} : k_{AcOD}$ of 0·85 and 1·05 for (II-OTs) and (II-OBs) are contradictory to a

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[24] J. Ferns and A. Lapworth, *J. Chem. Soc. Trans.*, 1912, **101**, 273; C. A. Bunton and Y. F. Frei, *J. Chem. Soc.*, 1951, 1872; J. F. Bunnett and J. Y. Bassett, jun., *J. Amer. Chem. Soc.*, 1959, **81**, 2104; *J. Org. Chem.*, 1962, **27**, 1887, 2345; T. J. Broxton, Y. C. Mac, A. J. Parker, and M. Ruane, *Austral. J. Chem.*, 1966, **19**, 521.

[25] F. C. Bordwell, B. M. Pitt, and M. Knell, *J. Amer. Chem. Soc.*, 1951, **73**, 5004.

[26] P. G. Gassman, J. M. Hornback, and J. M. Pascone, *Tetrahedron Letters*, 1971, 1425.

[27] N. Frydman, R. Bixon, M. Sprecher, and Y. Mazur, *Chem. Comm.*, 1969, 1044.

[28] J. D. Roberts and M. C. Caserio, 'Basic Principles of Organic Chemistry,' Benjamin, New York, 1965, p. 961.

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

[30] See also W. M. Schubert and G. W. Barfknecht, *J. Amer. Chem. Soc.*, 1970, **92**, 207.

[31] S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *J. Amer. Chem. Soc.*, 1956, **78**, 328.

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

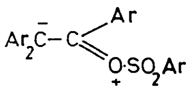
rate-determining protonation [route (*c*)].[33] Similar reasoning was employed for the acetolysis of triphenylvinyl sulphonates.[8]

Route (*d*) fits the kinetics, the effects of the solvent, the leaving group, and the α- and β-substituents and the rate-product criterion. The solvolysis rate of (II-OTs) is unchanged by the addition of $\mathrm{Bu^n_4NBr}$ but the product is diverted from the acetophenone (VI) to tris-*p*-methoxyphenylvinyl bromide.

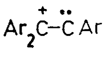
The k_Δ, k_s, *and* k_c *Routes*.—Solvolysis is often discussed in terms of three processes with their corresponding rate coefficients; (*a*) anchimerically assisted, k_Δ, (*b*) nucleophilically solvent assisted, k_s, and (*c*) anchimerically and nucleophilically unassisted, k_c.[34,35] Tertiary or bridgehead systems react *via* the k_c route, while the k_s route is important for secondary systems,[36] except for the 2-adamantyl system which solvolyses by the k_c route since the k_s process is hindered. Our vinylic systems are unique in showing contradictory response to the different criteria used for designating mechanistic categories for the saturated substrates. The m and the $k_{\mathrm{OTs}} : k_{\mathrm{Br}}$ values fit the k_Δ or the k_s process, while the $(k_{\mathrm{aq.\,Me_2CO}} : k_{\mathrm{AcOH}})_Y$ and the ρ values for the leaving group fit the k_Δ or the k_c processes better. As elaborated below, our triarylvinyl systems are at least as hindered as the 2-adamantyl system and accordingly they solvolyse *via* the k_c route.

Effect of the α- *and* β-*Substituents*.—The reactivity ratio (II-OTs) 2280 : (III-OTs) 630 : (V-OTs) 206 : (IV-OTs) 1 at 120° in 70% acetone suggests a small effect of the β-aryl substituents as found for the corresponding bromides[6] and iodides.[7] The reactivity ratios (III-OTs) : (V-OTs) of 3 at 120 and 7·5 at 75° are far from reflecting the enormous difference in the negative charge dispersal ability of the β-substituents (which is shown in the pK_a values of fluorene and diphenylmethane).[37] Consequently, contributions to the ground state by electron donation from the leaving group [*e.g.* (VIII)][38] cannot be dominant.[6,8] To the degree that the transition state resembles the ion, electron transfer to the cationic orbital as in (IX) is of little importance.[7,8]

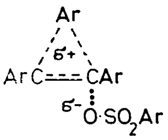
A priori, the (II-OTs) : (III-OTs) reactivity ratio of 3·6 may be due to β-*p*-methoxyphenyl participation since even small rate accelerations can indicate strong participation.[39] However, the k_Δ route [transition state (X)] should have little importance since α-*p*-methoxyphenyl group 'overcomes' the double bond participation in the norbornen-7-yl system by $>10^{10}$.[40] Moreover, kinetic and stereochemical evidence in the closely related *cis*- and *trans*-1,2-bis-*p*-methoxyphenyl-2-phenylvinyl bromides[14,41] and mesylates[42] exclude β-*p*-methoxyphenyl participation. The lower reactivity of (V-OTs) compared with (III-OTs) probably reflects a smaller twist of the α-*p*-methoxyphenyl group from the plane of the double bond in (V-OTs),[1] which amounts to a lower ground-state energy.



(VIII)



(IX)



(X)

The activation by the α-aryl substituents corresponds to a ρ^+ value of $-3{\cdot}6$ at 120° using σ^+ values for the two substituents. Comparable ρ^+ values ($-3{\cdot}6$ to $-4{\cdot}6$)[1,7,9,43] were observed for the formation of vinyl cations in solvolyses and in additions to acetylenes. These values argue for a development of a substantial positive charge in the transition state of the solvolysis.

Reactivity of the Leaving Groups.—(a) *Sulphonate leaving groups*. Fleming[44] argued that low ρ values for the arenesulphonate leaving groups are associated with high degree of solvent participation in the transition state for the ionisation. Among the few such ρ values available are 1·168, 1·248, and 1·565 for the hydrolysis of methyl,[45] ethyl,[46] and isopropyl[45] arenesulphonates in aqueous ethanol and methanol and 1·16 for the decarboxylative elimination of p-$\mathrm{MeC_6H_4{\cdot}C(O{\cdot}SO_2Ar){:}C(CO_2^-)_2}$ in 10% dioxan.[44] All are lower than our values (1·67 and 1·91) which are the highest known to us for solvolyses, except for that in the solvolysis of 1-(*p*-methoxyphenyl)-2-methylpropen-1-yl arenesulphonates in acetone–water (7 : 3).[47] * The $k_{\mathrm{OMs}} : k_{\mathrm{OTs}}$ ratio of 0·58 is within the range 0·48—1·2 found for several secondary systems.[48]

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* In ref. 47, the $k_{\mathrm{OBs}} : k_{\mathrm{OTs}}$ value in acetone–water 7 : 3 was erroneously reported as 5·03. The correct value is 5·70.

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[48] (*a*) D. S. Noyce, B. E. Johnston, and B. Weinstein, *J. Org. Chem.*, 1969, **34**, 463; (*b*) F. J. Choupek and G. Zweifel, *ibid.*, 1964, **29**, 2092; (*c*) R. M. deSousa and R. M. Moriarity, *ibid.*, 1965, **30**, 1509; J. F. Biellman and G. Ourisson, *Bull. Soc. chim. France*, 1962, 341; (*d*) K. T. Leffek, R. E. Heppolette, and R. E. Robertson, *Canad. J. Chem.*, 1966, **44**, 677; R. E. Robertson, *Progr. Phys. Org. Chem.*, 1967, **4**, 213; (*e*) R. S. Bly and R. Veazey, *J. Amer. Chem. Soc.*, 1969, **91**, 4221; (*f*) R. S. Bly, R. C. Strickland, R. T. Swindell, and R. L. Veazey, *ibid.*, 1970, **92**, 3722.

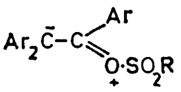
The 2·04-fold higher reactivity of (II-*o*-ONs) compared with (II-*p*-ONs) and the similar activation parameters suggest a relatively minor steric effect of the arenesulphonate group, and some stabilisation of the *o*-nitrobenzenesulphonate ion by sulphonate-*ortho*-nitro interaction. In contrast, the 10-times faster basic hydrolysis of ethyl *p*-nitrobenzoate compared with the *ortho*-isomer was ascribed to steric hindrance to attack on the *ortho*-ester.[28] If the analogy prevails, it excludes route (*b*) of Scheme 2.

From the value of ρ $(+10{\cdot}3)$ for the approximate linear relationship $(r = 0{\cdot}988)$ between $\log k$ for the solvolysis of the saturated $X{\cdot}SO_3R$ compounds with σ_m of X, it was concluded that a substantial negative charge develops on sulphur in the transition state.[49] We used data from the literature [8] for the acetolysis of triphenylvinyl tosylate, fluorosulphonate, and trifluoromethanesulphonate at 150° in combination with our relative reactivity for the mesylate (calculated from the $k_{\mathrm{OMs}}:k_{\mathrm{OTs}}$ ratio) to obtain a similar plot with $\rho = +11{\cdot}0$ $(r = 0{\cdot}986)$. We took $\sigma_m(p\text{-}MeC_6H_4) = 0{\cdot}04$ instead of 0·06 which was used earlier [assuming that $\sigma_m(\mathrm{Ph}) = \sigma_m(\mathrm{Tolyl})$],[49] since the tolyl group is electron donating compared with phenyl. From the similarity of the ρ values the magnitude of charge developed in the transition states of the solvolyses of the vinylic and the saturated substrates seems comparable.

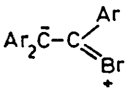
(b) *Tosylate* : *bromide ratio*. Hoffmann [19] (following DePuy and Bishop [18]) has suggested the use of the $k_{\mathrm{OTs}}:k_{\mathrm{Br}}$ ratios as a probe for the degree of charge separation in the transition state. The ratios are $\lesssim 1$ for S_N2 reactions and are 15—4000 for the S_N1 reactions and ' in good approximation the faster an S_N1 reaction the more ionic its transition state ' and the higher is the $k_{\mathrm{OTs}}:k_{\mathrm{Br}}$ ratio.[19] Bingham and Schleyer ascribe part of the variations in these ratios to nucleophilic solvent participation, and part of the high ratios found for bridgehead systems to a relief of ground-state strain in the tosylates.[50] A tentative value of $k_{\mathrm{OTs}}:k_{\mathrm{Br}} = 231$ was taken as typical for the k_c process, while lower values indicate nucleophilic solvent participation.[50]

Our $k_{\mathrm{OTs}}:k_{\mathrm{Br}}$ ratios in nucleophilic solvents (Table 5) which are close to those for the hydrolysis [51] and the formolysis [52] of ethyl and propyl derivatives may point to a nucleophilic solvent participation in our compounds. However, models of triarylvinyl bromides and tosylates show that the approach of the solvent from the back side in the plane of the double bond is completely hindered. The rear is a *cis*-stilbene system, where the steric hindrance, even without the added solvent molecules, is sufficient to twist the aryl groups from the plane of the double bond. The *cis* aryl–aryl interaction which is reduced in the transition state, is responsible for the higher solvolytic reactivity of *cis*-1,2-bis-*p*-methoxyphenylvinyl bromide compared with the *trans*-isomer.[16] Moreover, there is also an electronic repulsion between the π-electrons of the twisted aryl groups and the lone pair of the nucleophilic solvent. The k_s route is therefore improbable on both steric and electronic grounds in these systems.*

Low $k_{\mathrm{OTs}}:k_{\mathrm{Br}}$ ratios will be obtained if, in spite of the low contribution of structure (VIII), (VIIIa) contributes



(VIIIa)



(VIIIb)

1—2 kcal mol⁻¹ more than (VIIIb) to the ground states. This effect is absent in saturated systems.

Alternative explanation suggests that the triarylvinyl bromides are sterically accelerated compared with the tosylates. Molecular models show that non-bonded interactions between the oxygens of the tosylate and remote hydrogens are small in the triarylvinyl systems but that the bromide is more crowded than the tosylate at the region of the C–X bond. Loss of ground state *cis*-aryl–double bond conjugation by twist of the *cis*-aryl group from the plane of the double bond is higher for the bromide than for the tosylate and may be sufficient to explain the low $k_{\mathrm{OTs}}:k_{\mathrm{Br}}$ ratios. We note that each of the above explanations predicts a different change in the direction of the $k_{\mathrm{OTs}}:k_{\mathrm{Br}}$ ratios when the size of the β-substituents is reduced. Data on this are being collected.

The $k_{\mathrm{OTs}}:k_{\mathrm{Br}}$ ratios in saturated systems (the quinuclidin-4-yl system is an exception) [53] are mainly entropy controlled. For the 1-adamantyl-,[54] the 2-adamantyl-,[36] and the bicyclo[2,2,2]oct-1-yl [53] systems $\Delta\Delta S^{\ddagger} = \Delta S^{\ddagger}(\mathrm{Br}) - \Delta S^{\ddagger}(\mathrm{OTs}) = ca.\ -10$ cal K⁻¹ mol⁻¹, while $\Delta\Delta H^{\ddagger} = \Delta H^{\ddagger}(\mathrm{Br}) - \Delta H^{\ddagger}(\mathrm{OTs}) = 0{\cdot}6$—2·3 kcal mol⁻¹. In contrast, $\Delta\Delta S^{\ddagger} = -1$ cal K⁻¹ mol⁻¹ and $\Delta\Delta H^{\ddagger} = 2{\cdot}3$ kcal mol⁻¹ for the tris-*p*-methoxyphenylvinyl system in 70% acetone, probably reflecting the different factors affecting the $k_{\mathrm{OTs}}:k_{\mathrm{Br}}$ ratios in the vinylic systems.

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* A referee has suggested that a simple explanation for the relatively small $k_{\mathrm{OTs}}:k_{\mathrm{Br}}$ ratios and the relatively low m values is that the transition state is not very ionic. We note that even if Hoffmann's interpretation of the low $k_{\mathrm{OTs}}:k_{\mathrm{Br}}$ values holds for saturated systems (*cf.* ref. 50) it should not be used without caution for vinylic systems which differ from saturated systems in their geometry and in the resonative interaction of the leaving group with the double bond. Moreover, low m values are not necessarily connected with transition state of low polarity, as shown by the lower m values for tosylates compared with bromides, and by the lower m values for β-methoxyaryl derivatives compared with β-aryl derivatives (*cf.* D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1970, **92**, 5977). The high negative 'ρ^+' value for the α-activating group and the higher positive 'ρ' values for the sulphonate leaving groups point to a transition state with a rather high polarity in our system.

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Solvent Effects.—The two criteria based on solvent effects for judging the importance of the k_s route gave contradictory results. The m value[17] in aqueous acetone (0·42) is low, and even extrapolation by the relationship $m_1/m_2 = (T_2/T_1)^a$ [55] (taking $a = 1$)[6] still gives $m = 0{\cdot}48$, a value somewhat higher than those usually associated with the k_s route.[17] On the other hand, a low reactivity ratio in an aqueous nucleophilic solvent *vs*. that in an electrophilic solvent with the same ionisation power (Y) is taken as evidence for the k_c route.[17b,36] For tris-*p*-methoxyphenylvinyl tosylate $(k_{\text{aq Me}_2\text{CO}} : k_{\text{AcOH}})_{Y=-1{\cdot}63} = 0{\cdot}12$ and if m in aqueous EtOH is taken as 0·4 ($m = 0{\cdot}34$ for tris-*p*-methoxyphenylvinyl bromide)[6] $(k_{\text{aq. EtOH}} : k_{\text{AcOH}})_Y = 0{\cdot}4$ for the tosylate at 75 and 1·2 for the bromide at 120°.[6] These values are among the lowest reported for these leaving groups (even lower than those for the 1- and 2-adamantyl systems[36]) and therefore argue strongly for the k_c route for our compounds. Higher response to the change in the electrophilicity compared with a change in the nucleophilicity of the solvent was recorded for other vinylic solvolyses.[41,47]

It was suggested that the low m values for vinylic solvolyses are connected with hindrance to back-solvation.[4,6–8,16] This explanation cannot hold as such (however, see below) since nucleophilic solvent assistance is expected to reduce the m values. Higher effectivity of the α-substituent in charge dispersal would result in a lower m value, judging by the lower sensitivity to the solvent change of β-methoxyaryl compounds compared with their β-aryl analogues in systems where positive charge dispersal in the transition state occurs by β-*p*-methoxyphenyl participation.[56,57] This should contribute to our low m values since almost all our compounds are α-*p*-methoxyphenyl derivatives.[6,12a,13,14,16]

An additional factor is that m values in vinylic systems increase with the decrease in the size of the β-substituents.[6,9,16] If the crowded transition state is specifically solvated by the small water molecules, the dielectric constant at the vicinity of the transition state would change less on changing the solvent than the macroscopic dielectric constant and m values would be low and dependent on the bulk of the vinylic substituents. However, hydrogen bonding to the leaving group are from the less hindered front-side, and are probably responsible for the higher rate in acetic acid ($Y = -1{\cdot}63$) than in 80% acetone ($Y = -0{\cdot}67$).

The solvent isotope effect in 70% acetone containing either 30% of D_2O or H_2O ($k_H : k_D = 1{\cdot}22 \pm 0{\cdot}06$) is higher than the values (1·08—1·12) observed for simple alkyl benzenesulphonates in water. The origin of these effects was discussed.[58]

Selectivity of the Tris-p-*methoxyphenylvinyl Cation*.—Several vinyl halides show common ion rate depression in aqueous dimethylformamide (DMF)[7] and in AcOH.[13,14,16] The ion return increases with the increased stabilisation by the α-substituent; it was observed for 1-(*p*-methoxyphenyl)-2,2-diphenyl- but not with triphenyl-vinyl iodide.[7] In the acetolysis of the $R^1R^2C{=}CR^3Br$ system the ion return also increases with the increasing bulk of R^1 and R^2 in the order An,An > An,H > Me,Me > H,H.[13] In non-nucleophilic media even the 2,4,6-trinitrobenzenesulphonate ion captures a vinylic cation.[10,59]

Table 2 demonstrates that ion return takes place with tosylate ion in solvolytic media. The simplified solvolysis scheme, considering only 'dissociated ions' [equation (2)][31,60] gives the depressed rate coefficient

$$\text{ROTs} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{R}^+ + \text{OTs}^- \xrightarrow[\text{H}_2\text{O}]{k_2} \text{ROH} \qquad (2)$$

k_d of equation (3) when $\alpha = k_{-1}/k_2$ is the selectivity of the

$$k_d = k_1/(1 + \alpha[\text{OTs}^-]) \qquad (3)$$

OTs^- ion *vs*. water. Neglecting the ionic strength effect (since salt effects are specific and the presence of $\text{Bu}^n{}_4\text{NBr}$ lowers k_1), the use of equation (3) and the data of Table 2 gives $\alpha = 8 \pm 2$. Tosylates are less sensitive to salt effects than perchlorates.[22] An upper limit for the undepressed k_1 in the presence of Et_4NOTs was therefore estimated by assuming a 'normal salt effect'[22] behaviour $k_1 = k_1^0(1 + b[\text{Salt}])$ for Et_4NOTs and using $b = 0{\cdot}54$ as calculated for $NaClO_4$. The α values calculated by using these corrected higher k_1 values are 10 and 8, respectively, for the low and the high added concentrations of Et_4NOTs. The average ($\alpha = 9 \pm 1$) shows that the correction for the salt effect is small.

No rate decrease was observed on addition of Et_4NOTs to solvolysing triphenylvinyl tosylate. Thus, if the salt effect resembles that of $NaClO_4$, α = *ca*. 0·6, but if it is low, α = *ca*. 0.

The α value for (II-OTs) in 70% acetone is lower than those observed (30—50) for competition between iodide ion and water with 1-(*p*-methoxyphenyl)-2,2-diphenylvinyl iodide in 70% DMF.[7] The ratio of the two α values gives $k_2(\text{I}^-)/k_2(\text{OTs}^-) = 4$—6 for the capture of the triarylvinyl cation by the two nucleophiles. The high reactivity difference between iodide and tosylate ions towards saturated carbon atom (Swain–Scott n values are 5·04 and <1, respectively)[61] is much reduced, but is still apparent in their reaction with the triarylvinyl cations.

Bromide is also more reactive than tosylate towards the tris-*p*-methoxyphenylvinyl cation. The cation is completely captured by a 20-fold excess of bromide, while capture by added tosylate is not complete at similar concentrations.

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The present data show that at least 70—75% of the product arises from 'dissociated' (or 'free') tris-*p*-methoxyphenylvinyl cations. This behaviour is reminiscent of that of the triarylvinyl cations in acetic acid, where >90% of the products arise from 'dissociated' ions.[14]

Our vinyl cation is much more selective than expected from its sluggish formation. We attribute the high selectivity and the long life-time of the cation to two reasons; (*a*) The α-*p*-methoxyphenyl group effectively delocalises the positive charge, and the lower α for the α-phenyl derivative reflects the lower efficiency of the phenyl group in charge dispersal. (*b*) For α-*p*-methoxyphenyl compounds part of the selectivity is due to steric effects. The arguments used to discard the k_s route in the transition state apply here for the ion. The *p*-orbital of the carbonium ion is sterically shielded by the β-substituents from approach of the nucleophile from the plane of the double bond, and the π-electrons of the aryl groups exert electrostatic repulsion on the approaching nucleophile. This picture is consistent with the absence of common ion rate depression in the acetolysis of the much less hindered α-bromo-*p*-methoxystyrene.[13]

EXPERIMENTAL

M.p.s were taken with a Kofler hot-stage microscope and are corrected. I.r. spectra were measured with a Perkin-Elmer 337 spectrometer, u.v. spectra with a Perkin-Elmer 450 spectrometer, n.m.r. spectra with a Varian T-60 spectrometer, and mass spectra with an Atlas C4 spectrometer at 70 eV.

Solvents.—Acetone (AnalaR) was dried for a few days over potassium carbonate, filtered, and distilled. The middle fraction, b.p. 54°, was collected. The aqueous acetone mixtures were prepared by mixing the appropriate volumes of dry acetone with conductivity water. 90% Ethanol was prepared similarly. Dry ethanol was prepared by refluxing commercial absolute ethanol (Frutarom) for 5 h over calcium oxide, distilling, and collecting the middle cut, b.p. 76°. Acetic acid (Frutarom) was refluxed with 2—3% acetic anhydride for 2 days, fractionated, and the middle cut, b.p. 114°, was used. The acid contains 1% of acetic anhydride by g.l.c. AcOD Was prepared according to Weltner.[62] Acetic anhydride (Frutarom) was distilled and to the fraction boiling at 81° and 50 mmHg (300 ml), deuterium oxide (50 ml) was added. After 15 h, the homogeneous mixture was refluxed for 5 h, fractionated twice, and the fraction boiling at 113—114° was used. The i.r. spectrum showed strong C–D absorption at 2200 cm^{-1} and a small absorption at 1760 cm^{-1} from the residual anhydride. The n.m.r. showed no O–H signal.

Triarylvinyl Arenesulphonates.—(a) *Silver arenesulphonates*. Silver tosylate was prepared by Kornblum's method [63] from toluene-*p*-sulphonic acid and silver oxide. The other silver sulphonates were prepared by the following method exemplified for silver *p*-bromobenzenesulphonate. *p*-Bromobenzenesulphonyl chloride (4 g, 16 mmol), silver oxide (4 g, 17 mmol) and water (0·5 g, 0·03 mol) in acetonitrile (50 ml) were refluxed for 30 min in a flask protected from the light. The mixture was cooled to 0°, the silver chloride and oxide were filtered off, the solvent was evaporated, and silver *p*-bromobenzenesulphonate (4·5—5·2 g, 80—95% in different experiments) was obtained. The yield depends on the amount of silver salt coprecipitated with the silver chloride. The silver arenesulphonates are high melting solids (>300°), very soluble in water, and although they contain traces of silver chloride they can be used without further purification.

(b) *Triarylvinyl arenesulphonates*. Tris-*p*-methoxyphenylvinyl bromide and 1-(*p*-methoxyphenyl)-2,2-diphenylvinyl bromide were prepared as described previously.[6] The bromides (0·01 mol) were dissolved in boiling acetonitrile (30 ml), and a solution of the silver arenesulphonate (0·12 mmol) in acetonitrile (30 ml) was added. Turbidity formed within a few s, and the mixture was refluxed until the precipitation of silver bromide ceased (15—30 min). The inorganic salts were filtered, the solvent was evaporated, and the dry residue was dissolved in acetone, filtered from the remaining silver salts, and evaporated. The vinyl sulphonates were crystallised from ethanol except for the sensitive *o*-nitrobenzenesulphonate which was crystallised from non-solvolysing chloroform–petroleum ether.

The preparation of tris-*p*-methoxyphenylvinyl mesylate and fluorenylidene-(*p*-methoxyphenyl)methyl tosylate was similar but refluxing for 2 h was required to obtain yields similar to those for the other esters.

Triphenylvinyl bromide was recovered unchanged from reflux of a similar mixture for 48 h. When the bromide (2 g, 4·7 mmol) and silver tosylate (1·3 g, 4·7 mmol) in acetonitrile (10 ml) were kept in a sealed ampoule for 48 h at 120° and the mixture was worked-up as usual, triphenylvinyl tosylate (1·2 g, 60%) was formed. The analytical data for the arenesulphonates are in Table 6. For carbon disulphide solutions the main absorptions in the i.r. spectra are at 2840 (C–H of the methoxy-group) and 1360 cm^{-1} (sulphonyl). The C=C absorption at 1600 cm^{-1} is covered by that of the solvent, but it is observed for all compounds in chloroform. The fingerprint region of the vinyl sulphonates is similar with strong absorptions at 770, 810, 830, 930, 940, 1000, 1020, 1040, 1160, 1170, 1190, 1250, and 1300 cm^{-1}.

The n.m.r., u.v., and mass spectral data are in Table 7. The parent peak is small and the base peak which is common for all the four compounds studied corresponds to $An_2C=C(Me)An$, which should be formed by an extensive rearrangement. The second most abundant peak corresponds to the tris-*p*-methoxyphenylvinyl cation. Other peaks (which are not recorded in Table 7) correspond to the loss of one or several methyl and methoxy-substituents, and to the loss of the substituent on the arenesulphonate residue.

Solvolysis Products.—Tris-*p*-methoxyphenylvinyl bromide, tris-*p*-methoxyphenylvinyl tosylate and tris-*p*-methoxyphenylvinyl *o*-nitrobenzenesulphonate were solvolysed under kinetic conditions for 10 half-lives. The ampoules were opened, the acetone was evaporated *in vacuo* and the remainder was extracted with chloroform. The organic phase was washed with dilute hydrochloric acid, sodium hydrogen carbonate solution, and water, dried (Na_2SO_4), and evaporated. The residual oil showed strong absorption in chloroform at 1670 cm^{-1} (conjugated C=O) and n.m.r. [τ ($CDCl_3$) 6·27 (6H, s, 2 × MeO), 6·20 (3H, s, MeO), 5·10 (1H, s, CH), and 2·73—3·53 and 1·93—2·07

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[62] W. Weltner, *J. Amer. Chem. Soc.*, 1955, **77**, 3941.

[63] N. Kornblum, W. J. Jones, and G. J. Anderson, *J. Amer. Chem. Soc.*, 1959, **81**, 4113.

(12H, m, ArH)] which are identical with those of 4′-methoxy-2,2-bis-*p*-methoxyphenylacetophenone.[6]

From a solution of tris-*p*-methoxyphenylvinyl brosylate (46 mg) in 70% acetone (10 ml) containing 2,6-lutidine (17 mg) which was left at room temperature for 2 months, a precipitate of white crystals (10 mg), m.p. 142—144°, was formed. It was identified as 4,4′-dimethoxybenzophenone by mixed m.p. and by its i.r. spectrum (identical with that of an authentic sample).

Tris-*p*-methoxyphenylvinyl tosylate and brosylate were solvolysed in acetic acid at 120° for 10 half-lives. The ampoules were opened, water was added to give turbidity, and the precipitate was crystallised from petroleum ether, giving tris-*p*-methoxyphenylvinyl acetate, m.p. 97° (lit.,[6] 97—98°), mixed m.p. 97°, τ ($CDCl_3$) 7·98 (3H, s, OAc), 6·50, 6·53, and 6·57 (9H, 3 × s, 3 × MeO), and 2·67—3·30 (12H, m, ArH).

Fluorenylidene-(*p*-methoxyphenyl)methyl tosylate (150 mg) in 70% acetone (10 ml) was left at 120° for 24 h. After work-up as above, the compound was identified as 9-anisoylfluorene,[1] by n.m.r. [τ ($CDCl_3$) 6·20 (3H, s, OMe), 4·50 (1H, s, CH), and 2·03—3·27 (12H, m, ArH)] and by i.r. [$\nu_{max.}$ (KBr) 1653 cm^{-1} (C=O)].

Solvolysis in the Presence of Added Salts.—Tris-*p*-methoxyphenylvinyl tosylate (0·39 g, 0·74 mmol), 2,6-lutidine (0·165 g, 1·65 mmol), tetrabutylammonium bromide (5·72 g, 14·7 mmol), and 70% aqueous acetone (25 ml) were kept in a sealed ampoule at 75° for 24 h. Chloroform (25 ml) was added, the organic layer was separated, dried (Na_2SO_4), and evaporated. Crystallisation of the residue from ethanol gave tris-*p*-methoxyphenylvinyl bromide (240 mg, 77%), m.p. 118—119° (lit.,[6] 118—119°) which was identified by mixed m.p. and n.m.r.

Tris-*p*-methoxyphenylvinyl *o*-nitrobenzenesulphonate (133 mg, 0·24 mmol), 2,6-lutidine (50 mg, 0·47 mmol), and sodium azide (30·6 mg, 0·46 mmol) in 70% aqueous acetone (25 ml) were allowed to react at 35° for 24 h. The organic material was extracted by chloroform, and the solvent was evaporated. The i.r. spectrum of the remaining oil showed strong absorption at 2110 cm^{-1} (N_3), and none at 1670 cm^{-1} for the ketone (VI).

TABLE 6

Analytical data for the vinyl sulphonates $Ar^2_2C{=}C(Ar^1)O{\cdot}SO_2R$

Ar^1	Ar^2	R	M.p. (°C) [a]	Yield (%)	Formula	Calc. (%) C	H	S	N	Found (%) C	H	S	N
An	An	*p*-MeO·C_6H_4	133	57	$C_{30}H_{28}O_7S$	67·65	5·3	6·0		67·3	5·3	5·6	
An	An	*p*-MeC_6H_4	143	66	$C_{30}H_{28}O_6S$	69·75	5·45	6·2		70·0	5·4	6·6	
An	An	Ph	150	47	$C_{29}H_{26}O_6S$	69·3	5·2	6·6		69·5	5·05	5·7	
An [b]	An [b]	*p*-BrC_6H_4 [b]	110	60	$C_{29}H_{25}BrO_6S$	59·9	4·35	5·5		60·05	4·25	5·05	
An	An	*p*-$O_2N{\cdot}C_6H_4$	143 (decomp.)	66	$C_{29}H_{25}NO_8S$	63·6	4·6	5·85	2·55	64·3	4·85	4·9	2·6
An	An	*o*-$O_2N{\cdot}C_6H_4$	131 (decomp.) [c]	22	$C_{29}H_{25}NO_8S$	63·6	4·6	5·85	2·55	63·55	4·35	5·9	2·25
An	An	Me	143	60	$C_{24}H_{24}O_6S$	64·45	5·5	7·25		65·1	5·55	6·95	
An	Ph	*p*-MeC_6H_4	169	49	$C_{28}H_{24}O_4S$	73·7	5·3	7·05		73·45	5·2	6·6	
Ph	Ph	*p*-MeC_6H_4	172 [d]	60	$C_{27}H_{22}O_3S$	76·05	5·45	7·55		76·0	5·25	6·95	
An	Fl [e]	*p*-MeC_6H_4	191—192	64	$C_{28}H_{22}O_4S$	74·0	4·9	7·05		74·05	4·95	7·4	

[a] From ethanol. [b] Calc. for Br, 13·75%; found: 13·85%. [c] From chloroform–petroleum ether. [d] Lit.,[8a] 153°; [8b] 169°. [e] Fl = $Ar^2_2C{=}$ = Fluorenylidene.

TABLE 7

Spectral data for the vinyl sulphonates

$Ar^2_2C{=}C(Ar^1)X$ Ar^1	Ar^2	X	$\lambda_{max.}$ (MeCN)/nm (log ε)	τ($CDCl_3$) [a] MeO [b]	Me [b]	Ar [c]	Mass spectra B (*m/e*)	P (%)	C (*m/e*) (%) [i]
An	An	OAns	247 (4·55), 292·5 (4·21)	6·17 (2), 6·25 (2)		2·47—3·50	360	3·4	345 (72)
An	An	OTs	245 (4·41), 293 (4·24)	6·20 (1), 6·27 (2)	7·63	2·50—3·50	360	1·3	345 (53) [j]
An	An	OPhs	245 (4·37), 293 (4·23)	6·18 (1), 6·27 (2)		2·38—3·52			
An	An	OBs	239 (4·54), 292 (4·24)	6·17 (1), 6·23 (1), 6·25 (1)		2·50—3·50	360	36	345 (85) [k]
An	An	*p*-ONs	246·5 (4·51), 291 (4·29)	6·20 (1), 6·25 (2)		1·82—3·47 [f]	360	0·2	345 (42)
An	An	*o*-ONs	245 (4·43), 293 (4·27)	6·23 (2), 6·29 (1)		2·27—3·50			
An	Ph	OTs	282 (4·15)	5·90 (1)	7·62	2·50—3·50			
Ph	Ph	OTs	229 (4·46), 266 (4·06)		7·67	2·50—3·50			
An	An	OMs	245·5 (4·36), 294·5 (4·20)	6·23 (1), 6·27 (1), 6·30 (1)	7·68	2·67—3·55			
An	Fl [d]	OTs	250 (4·46), 259 (4·53), 319 (4·20) [e]	6·18 (1)	7·65	1·48—1·65, [g] 2·17—3·62 [h]			

[a] Integration fits the assignments. [b] Singlet. [c] Multiplet. [d] Fl = $Ar^2_2C{=}$ = Fluorenylidene. [e] In dioxan. [f] Contains a 4H AA′BB′ quartet for the *p*-nitrophenyl group centered at τ 3·13 with *J* 9 Hz. [g] One hydrogen showing unsymmetrical quartet. [h] 15H. [i] The second most abundant peak. [j] In another determination *m/e* 361 is 98, *m/e* 330 is 82, and *m/e* 345 is 80%. [k] In another determination *m/e* 345 is the base peak and the parent peak is <0·5%.

Kinetic Measurements.—Reactions <60° were followed conductometrically in a closed conductometric cell. For reactions >60° the sealed ampoule technique was used. The ampoules were pre-treated according to Grob.[9] For reactions in aqueous acetone the vinyl sulphonate was dissolved in dry acetone containing 2,6-lutidine, conductivity water was added, and the solution was divided into the ampoules. For reactions in 90% ethanol and in AcOH, the vinyl sulphonate was weighed individually into each ampoule. The ampoules were sealed at liquid air temperature, introduced to the thermostated bath, and shaken rapidly after 1—2 min for complete dissolution. At the appropriate intervals the ampoules were cooled rapidly, opened, and the reaction was followed by the four following methods.

(*a*) The conductometric method was used for measurements in aqueous acetone. Into a 10 ml conductivity cell, 5 ml of the mixture and 5 ml of the same aqueous acetone mixture were introduced and the conductance was followed at 0° with a Pye Conductance Bridge. Below 60° the mixture was introduced directly into the conductivity cell which was immersed in the thermostat and the reaction was followed directly without further dilution. The conductivity at zero time was obtained by extrapolation. Calibration curves showed that at our concentrations the conductivity is linear with the concentration of the 2,6-lutidinium arenesulphonate.

(*b*) Reactions in aqueous ethanol and sometimes in acetic acid–NaOAc were followed, after dilution, by potentiometric titration of the base with 0·1N-HCl, to pH 4·3, which was determined independently as the end point. TTT1c titrator (Radiometer) was used.

(*c*) Reactions in acetic acid were usually followed by back-titration of the excess of sodium acetate with perchloric acid in acetic acid. Indicators could not be used since the system itself developed a red colour with an excess of acid. This colour change was used as a self-indicator.

(*d*) Reactions in aqueous acetone in the presence of added salts could not be followed conductometrically. The content of each ampoule was extracted with chloroform, washed with dilute HCl, sodium hydrogen carbonate and water, dried (Na_2SO_4), and the solvent was evaporated. The oil was dissolved in $CDCl_3$, the n.m.r. spectrum was taken and the progress of the reaction was followed from the ratio of the methyl singlet of the tosylate to those of the methoxy-groups.

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