Vinylic Cations from Solvolysis. Part XIII.[1] S_N1 and Electrophilic Addition–Elimination Routes in the Solvolysis of α-Bromo- and α-Chloro-4-methoxystyrenes

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The solvolysis of α-chloro- (3) and α-bromo-4-methoxystyrene (4) in 80% EtOH gives 4-methoxyacetophenone and 4-methoxyphenylacetylene and is mechanistically S_N1. The solvolysis is enhanced by two β-methyl substituents; the Winstein–Grunwald *m* values are 0·76—1·00 at 25 °C and $k_1(4)/k_1(3) = 54$. In the acetolysis of compounds (3) and (4), 4'-methoxyacetophenone is formed, $k_1(4)/k_1(3) = 0{\cdot}46$—$0{\cdot}56$, $k_1(80\%\ EtOH)/k_1(AcOH) = 0{\cdot}13$ for (3) and 15 for (4), $k_{1AcOH}/k_{1AcoD} = 1{\cdot}94$ for (3) and 1·45 for (4), and deuterium is not incorporated in the unchanged (3) and (4). The hydrolysis of α-acetoxy-4-methoxystyrene and the addition of AcOH to 4-methoxyphenylacetylene and 4-methoxystyrene in AcOH are faster than the solvolyses of (3) and (4). These data suggest that the acetolysis of the chlorostyrene (3) is by concomitant S_N1 and electrophilic addition–elimination (Ad_E–E) routes, while that of (4) is mainly S_N1. The competition between the two routes is discussed.

It has been shown that S_N1 solvolysis of vinyl halides [2] may compete both with substitution by nucleophilic addition–elimination [3,4] and with $E2$ elimination.[1,5] An additional route, electrophilic addition–elimination [6] [equation (1)] rather than the S_N1 route [7] [equation (2)] was suggested for the solvolysis of 4-amino-α-bromostyrene in 80% EtOH. Although it is now clear that the S_N1 route prevails for this compound,[8] the electrophilic addition–elimination route (designated here Ad_E–E) was observed in another system [9] and should be considered especially in solvolysis in acidic media. Criteria for distinguishing between the two mechanisms were suggested [10] and we planned to study some of them with α-halogenostyrenes, a system in which presumably both routes can operate.

$$\mathrm{ArCX{=}CH_2} \xrightarrow{+H^+} \mathrm{Ar\overset{+}{C}XMe} \xrightarrow{+Nu^-} \mathrm{ArCX(Nu)Me} \xrightarrow{-HX} \mathrm{ArC(Nu){=}CH_2} \quad (1)$$

$$\underset{(1)}{\mathrm{ArCX{=}CH_2}} \xrightarrow{-X^-} \underset{(2)}{\mathrm{Ar\overset{+}{C}{=}CH_2}} \xrightarrow{+Nu^-} \mathrm{ArC(Nu){=}CH_2} \quad (2)$$

The α-arylvinyl cation (2) derived by S_N1 solvolysis of the chlorostyrene (1) is the simplest member of a series of polyarylvinyl cations such as $Ar^1C^+{=}CHAr^2$ and $Ar^1C^+{=}CAr^2_2$, the formation of which from vinyl halides and sulphonates was studied in recent years.[1-3,5-8,11] Since the selectivity of these ions and the low *m* values in some vinylic solvolyses [1,3,5,11b-g] were partially ascribed to steric effects of the β-substituents it was of interest to study reaction (2) where these effects are minimised. Since electrophilic addition to terminal acetylenes is faster than to internal acetylenes,[12] another substitution mechanism, consisting of $E1$ elimination followed by electrophilic addition to the acetylene [$E1$–Ad_E2, equation (3)], may also operate for system (1). This route is complementary to the nucleophilic elimination–addition [$E1cB$–Ad_N or $E2$–Ad_N, equation (4)] which was recognised previously.[4]

$$\mathrm{ArCX{=}CH_2} \xrightarrow{-X^-} \mathrm{Ar\overset{+}{C}{=}CH_2} \xrightarrow{-H^+} \mathrm{ArC{\equiv}CH} \xrightarrow[(2)\ +Nu^-]{(1)\ +H^+} \mathrm{ArC(Nu){=}CH_2} \quad (3)$$

$$\mathrm{R^1CH{=}CR^2X} \xrightarrow[-HX]{Base} \mathrm{R^1C{\equiv}CR^2} \xrightarrow{+Nu^-} \mathrm{R^1\bar{C}{=}CR^2Nu} \xrightarrow{+H^+} \mathrm{R^1CH{=}CR^2Nu} \quad (4)$$

We therefore studied the solvolysis of α-chloro- (3) and α-bromo-4-methoxystyrene (4) both in aqueous EtOH and in AcOH. The solvolyses of 1-(4-methoxyphenyl)-2-methylprop-1-enyl chloride (5) and bromide (6) in aqueous EtOH as well as reactions of related compounds in AcOH were investigated for comparison.

RESULTS

α-Chloro- and α-bromo-4-methoxystyrenes were prepared by the addition of the appropriate acid to 4-methoxyphenylacetylene in AcOH. 4-Methoxyacetophenone was

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[2] (*a*) M. Hanack, *Accounts Chem. Res.*, 1970, **3**, 209; (*b*) C. A. Grob, *Chimia*, 1971, **25**, 87; (*c*) G. Modena and U. Tonellato, *Adv. Phys. Org. Chem.*, 1971, **9**, 185; (*d*) P. G. Stang, *Progr. Phys. Org. Chem.*, in the press. We thank Professor Stang for a preprint.

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

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

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

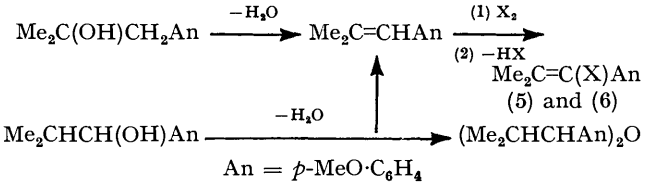
[9] P. E. Peterson and J. M. Indelicato, *J. Amer. Chem. Soc.*, 1968, **90**, 6515.

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

[11] (*a*) L. L. Miller and D. A. Kaufman, *J. Amer. Chem. Soc.*, 1968, **90**, 7282; (*b*) Z. Rappoport and A. Gal, *ibid.*, 1969, **91**, 5246; (*c*) Z. Rappoport and Y. Apeloig, *ibid.*, p. 6734; (*d*) Z. Rappoport and J. Kaspi, *ibid.*, 1970, **92**, 3220; (*e*) Z. Rappoport and Y. Apeloig, *Tetrahedron Letters*, 1970, 1817; (*f*) Z. Rappoport and Y. Apeloig, *ibid.*, p. 1845; (*g*) Z. Rappoport and A. Gal, *ibid.*, p. 3233; (*h*) W. M. Jones and D. D. Maness, *J. Amer. Chem. Soc.*, 1968, **90**, 4314; 1970, **92**, 5457.

[12] *E.g.*, E. J. Stamhuis and W. Drenth, *Rec. Trav. chim.*, 1961, **80**, 797; G. L. Hekkert and W. Drenth, *ibid.*, 1963, **82**, 405; D. S. Noyce, M. A. Matesich, M. D. Schiavelli, and P. E. Peterson, *J. Amer. Chem. Soc.*, 1965, **87**, 2295; D. S. Noyce and M. D. Schiavelli, *J. Org. Chem.*, 1968, **33**, 845.

a minor product in the additions. 1-(4-Methoxyphenyl)-2-methylprop-1-enyl chloride and bromide were prepared by halogenation–dehydrohalogenation of 1-(4-methoxyphenyl)-2-methylpropene, which in turn was obtained by dehydration of 1-(4-methoxyphenyl)-2-methylpropan-2-ol. Attempts to prepare the ethylene by dehydration of 1-(4-methoxyphenyl)-2-methylpropan-1-ol gave mixtures of the ethylene and the corresponding ether.



Solvolysis in Aqueous EtOH.—The solvolytic data in aqueous EtOH are in Table 1. Compounds (3), (4), and (6) showed first-order kinetics in the presence of NaOAc. The rate was independent of the base concentration and that of (4) was unchanged by the addition of excess of Bu_4NBr. The reaction of compound (5) gave strongly decreasing rate coefficients with the progress of the reaction, and recheck of our sample of (5) showed that this is not due to impurities, as shown by the analysis, the spectra, and the chloride infinity titre. This behaviour was ascribed to common-ion rate depression by the Cl^- formed, and this was verified by the 36% reduction in k_1 on addition of 0·08M-Bu_4NCl. In Table 1 the initial, extrapolated (to zero reaction time) k_1 values are given.

The bromide : chloride reactivity ratios were 54 for the styrenes (3) and (4), and 20 for (5) and (6). A Winstein–Grunwald mY plot [13] for (4) in 70—90% EtOH was curved, giving $m = 0·58$ for 80—90% EtOH and 0·77 for 70—80% EtOH at 120 °C. For compound (6), $m = 0·70$ for 80—90% EtOH at 110 °C and 0·73 for 70—80% EtOH at 100 °C.

The solvolysis products (Table 1) of α-halogeno-4-methoxystyrenes at 120 °C consist of 56—62% of 4-methoxyacetophenone (7) and 38—44% of 4-methoxyphenylacetylene (8) [equation (5)]. The product ratio was nearly independent of the leaving group and of the water content of the solvent. Under our conditions (8) is stable and does not form the ketone (7).

$$\underset{}{AnCX{=}CH_2} \xrightarrow[NaOAc]{80\%\ EtOH} \underset{(7)}{AnCOMe} + \underset{(8)}{AnC{\equiv}CH} \quad (5)$$

No vinyl ether or vinyl acetate were formed in the solvolysis. We found that α-acetoxy-4-methoxystyrene gave 63% of (7) after 2·5 h at 120 °C in the presence of 0·17M-NaOAc. Since this hydrolysis is slower than the solvolysis of (3), <5% of the vinyl acetate are formed during the solvolysis. Attempts to prepare the vinyl ether by the reaction of silver carbonate with (4) in absolute EtOH (a method which gave triarylvinyl ethers) [11b] gave only the acetophenone (7), suggesting that α-ethoxy-4-methoxystyrene is unstable under the reaction conditions.

The products obtained from compounds (5) and (6) [equation (6)] are the ketone (9), the vinyl ether (10),

TABLE 1

Rates and products in the solvolysis of $AnCX{=}CR_2$ [a] in aqueous EtOH

									Products, %			
R	X	10^3[AnCX=CR$_2$] M	10^2[NaOAc] M	% EtOH [b]	t/°C	10^5k_1/ s^{-1}	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ (120 °C) cal mol^{-1} K^{-1}	Ether X = OEt	Ketone X = OH	Acetate X = OAc	Acetylene
H	Cl	32·6	17	80	120·0	0·45 ± 0·006	26·8	−12		56		44
H	Cl	32·6	17	80	141·0	2·66 ± 0·01				50		50
H	Cl	32·6	36	80	140·5	2·32 ± 0·02				57		43
H	Br	26·5	18	80	120·1	24·8 ± 0·10 [c]	27·8 [d]	−7 [d]		58		42
H	Br	24·2	18	80	119·9	24·2 ± 0·10 [e]						
H	Br	27·0	18	90	120·0	9·20 ± 0·10				56		44
H	Br	30·3	18	70	120·1	71·8 ± 3·65				62		38
Me	Cl	35·0	17	80	120·3	4·4 [f]	28·6	−5	28	72		
Me	Cl	35·0	17	80	140·3	27·5 [f]						
Me	Cl	35·0	17	80	140·3	17·5 [f,g]						
Me	Br	35·0	8·6	80	120·3	87·8 ± 1·16	20·8	−19	48	42	10	
Me	Br	35·0	8·6	80	110·1	40·6 ± 1·13						
Me	Br	35·0	17	80	110·1	39·5 ± 2·40						
Me	Br	35·0	23	80	99·7	19·0 ± 0·13						
Me	Br	35·0	8·6	90	110·1	12·3 ± 0·24						
Me	Br	35·0	23	70	99·7	43·8 ± 0·58						

[a] [AnCX=CR$_2$] = 0·024—0·036M. [b] % EtOH is v/v of EtOH in the EtOH–H_2O mixture. [c] Literature value: 24×10^{-5} s^{-1} in the presence of 0·01M-Et_3N.[7] [d] Literature value.[7] [e] In the presence of 0·073M-Bu_4NBr. [f] Extrapolated from k_1 against time graphs. [g] In the presence of 0·08M-Bu_4NCl.

The rate was independent of the base concentration and that of (4) was unchanged by the addition of excess of Bu_4NBr. The reaction of compound (5) gave strongly decreasing rate coefficients with the progress of the reaction, and recheck of our sample of (5) showed that this is not due to impurities, as shown by the analysis, the spectra, and the chloride infinity titre. This behaviour was ascribed to common-ion rate depression by the Cl^- formed, and this was verified by the 36% reduction in k_1 on addition of 0·08M-Bu_4NCl. In Table 1 the initial, extrapolated (to zero reaction time) k_1 values are given.

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and occasionally the vinyl acetate (11) (Table 1). The ketone : ether ratios which were determined at infinity

$$\underset{(5)\text{ and }(6)}{Me_2C{=}C(X)An} \xrightarrow[NaOAc]{80\%\ EtOH} \underset{(9)}{Me_2CHCOAn} + \underset{(10)}{Me_2C{=}C(OEt)An} + \underset{(11)}{Me_2C{=}C(OAc)An} \quad (6)$$

were higher for (5) than for (6), but this may be due to partial hydrolysis of (10) to (9), since the ratios for the slower styrene (5) were determined after longer reaction times.

Acetolysis.—The acetolysis of α-halogeno-4-methoxystyrenes gives exclusively 4-methoxyacetophenone. The kinetic data are in Table 2. In the presence of NaOAc the reaction was usually of the first order, although in two runs k_1 increased slightly during the run and extrapolated, initial values are given. Addition of NaOAc or Bu_4NBr increased k_1. The reaction is slower in AcOD and the

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

solvent isotope effect k_{AcOH}/k_{AcOD} is 1·94 ± 0·06 for (3) and 1·45 ± 0·15 for (4) at 140·5 °C. The k_{Br}/k_{Cl} ratio is 0·46 at 120 °C and 0·56 at 141 °C.

The unbuffered acetolysis showed strong autocatalysis: k_1 increased >28-fold with the progress of the acetolysis of (4) (Table 3). The product is again the acetophenone (7).

TABLE 2

Acetolysis of AnCX=CH_2 in the presence of NaOAc

X	Solvent	10^2[AnCX=CH_2]/M	10^2[NaOAc]/M	t/°C	10^5k_1/s^{-1}	$\Delta H^\ddagger$/kcal mol^{-1}	$\Delta S^\ddagger$(120 °C)/cal mol^{-1} K^{-1}
Br	AcOH	3·5	4·0	120·3	1·52 [a,b]	23·2	−20·9
Br	AcOH	3·5	8·4	120·3	1·63 ± 0·02		
Br	AcOH	3·5	4·0	120·4	2·62 [c]		
Br	AcOH	3·5	4·0	141·0	7·50 [a,d]		
Br	AcOH	2·6	8·4	140·0	7·75 ± 0·60		
Br	AcOD	2·8	8·4	140·0	5·96 ± 0·03		
Br	AcOH	3·5	8·4	141·0	7·58 ± 0·16		
Br	AcOH	3·3	8·4	142·0	9·20 ± 0·12		
Br	AcOH	3·1	16·0	140·5	7·96 ± 0·15		
Br	AcOD	2·6	16·0	140·5	4·96 ± 0·24		
Br	AcOD	2·5	16·0	140·6	5·25 ± 0·16		
Cl	AcOH	3·6	8·8	120·1	3·51 ± 0·12	20·1	−28·7
Cl	AcOH	3·6	8·8	141·0	13·61 ± 0·18		
Cl	AcOD	3·2	8·7	140·5	6·23 ± 0·02		
Cl	AcOH	3·2	12·0	140·5	13·04 ± 0·46		
Cl	AcOD	3·2	12·0	140·5	6·93 ± 0·14		
Cl	AcOH	3·6	16·0	141·0	14·45 ± 0·49		

[a] Extrapolated, initial value. The integrated rate coefficient increases during the run. [b] 10^5k_1 Are 1·66 and 1·88 s^{-1} at 14·5 and 38% reaction, respectively. [c] In the presence of 0·04M-Bu_4NBr. [d] 10^5k_1 Values are 7·60 and 8·96 at 11·6 and 81·4% reaction, respectively.

When the reactions of (3) and (4) were followed by n.m.r. in AcOD no deuterium incorporation into the unchanged

TABLE 3

Acetolysis of 0·035M-α-bromo-4-methoxystyrene in unbuffered AcOH at 120·3 °C

Time/min	% Reaction	10^4k_1/s^{-1}
4	<1	<0·4
15	17·8	2·19
22	44·3	4·43
34	90·4	11·4
50	100	

vinyl halide was observed up to 40% reaction within the limit of detection. The accuracy of the measurement which is based on comparison of the signals for the vinylic protons with those for the methoxy-protons is lower at higher reaction percentages. 4-Methoxyacetophenone showed extensive deuteriation at the methyl group. In order to establish whether this incorporation is part of the solvolytic reaction or whether it occurs at a later stage, we studied the rates of the electrophilic reactions (exchange, addition, hydrolysis) and the rates of deuterium incorporation into the product, the possible intermediates, and related substrates under the reaction conditions (AcOH–NaOAc at 120 °C, Table 4). It was found that (*a*) 4-methoxyacetophenone is formed from 4-methoxyphenylacetylene in AcOH–NaOAc, and this reaction is 17 times faster than the solvolysis of (4) and shows a solvent isotope effect (SIE) k_{AcOH}/k_{AcOD} of 2·7 at 120 °C. (*b*) α-Acetoxy-4-methoxystyrene, the expected primary acetolysis product, also gives 4-methoxyacetophenone in a reaction which is 314 times faster than the acetolysis of (4), and k_{AcOH}/k_{AcOD} = 3·45 at 80·3 °C. (*c*) The rate of exchange of a single proton in the methyl group of 4-methoxyacetophenone is 51 times faster than the acetolysis of (4). This is based on the rate coefficient measured (by n.m.r.) for the exchange of the three protons of the methyl group together, it being assumed that the secondary isotope effects by the hydrogens on the methyl group are unity. (*d*) The addition of AcOH to 4-methoxystyrene to form 1-(4-methoxyphenyl)ethyl acetate gave an equilibrium mixture (as observed under related conditions [14]) of *ca.* 1 part of styrene to 2 of acetate starting from either substrate. The equilibrium position could not be determined accurately since 4-methoxy-

TABLE 4

Electrophilic reactions of 4-methoxyphenyl (An) substrates in AcOH–NaOAc [a]

Substrate	Solvent	t/°C	10^4k_1/s^{-1}	Product
AnC≡CH	AcOH	119·6	2·74 ± 0·18	AnCO·CH_3
AnC≡CH	AcOD	120·4	1·13 ± 0·15 [b]	AnCO·CD_3 [b,c]
AnC(OAc)=CH_2	AcOH	80·3	2·76 ± 0·17 [d]	AnCO·CH_3
AnC(OAc)=CH_2	AcOH	120·0	51·2 ± 4·7	AnCO·CH_3
AnC(OAc)=CH_2	AcOD	80·3	0·80 ± 0·08 [b]	AnCO·CH_2D
AnCOCH_3	AcOD	120·4	2·70 ± 0·09 [e]	AnCO·CD_3
AnCH=CH_2	AcOH	120·4	1·85 ± 0·15 [f]	AnCH(OAc)·CH_3
AnCH=CH_2	AcOD	120·4	0·55 ± 0·03 [f]	AnCH(OAc)·CD_3 [g]

[a] [Substrate] = 0·035M; [NaOAc] = 0·084M. [b] The k_1 values are for the formation of the initial product AnCO·CH_2D. [c] AnCOCD_3 is formed by further exchange of AnCOCH_2D. [d] $\Delta H^\ddagger$ = 19·4 kcal mol^{-1}; $\Delta S^\ddagger$(120°) = −19·6 cal mol^{-1} K^{-1}. [e] The k_1 is for the process AnCO·CH_3 ⟶ AnCO·CD_3. The decay of the Me signal in the n.m.r. spectrum was followed. [f] Based on initial rates up to 20% reaction. [g] After long reaction times.

[14] M. Mollard, B. Torck, M. Hellin, and F. Coussemant, *Bull. Soc. chim. France*, 1966, 83.

styrene undergoes a competing reaction, as shown by the gradual disappearance of the signals for the vinylic protons after longer reaction times. In the acid-catalysed addition [14] this was ascribed to dimerisation and polymerisation. Owing to these difficulties rate coefficients based only on points up to 20% reaction are given. However we found that the k_{AcOH}/k_{AcOD} value would not change appreciably even if the equilibrium value estimated above will be used.

As required by the 4-methoxystyrene + AcOD ⇌ 1-(4-methoxyphenyl)ethyl acetate equilibrium, deuterium incorporation into the methyl group of the acetate takes place in AcOD. The loss of the vinylic protons of 4-methoxystyrene by exchange is superimposed on their loss by the above-mentioned side reactions.

Reaction of the α-Bromostyrene (4) *in Formic Acid and in 2,2,2-Trifluoroethanol.*—Dissolution of (4) in HCO_2H immediately gives a violet colour [$\lambda_{max.}$ 540sh (log ε 1·48), 485 (1·60), and 262 nm (4·16)] and (7) was isolated after 2 h at room temperature. A blue colour [$\lambda_{max.}$ 550 (log ε *ca.* 3·0) and 257 nm (*ca.* 4·2)] was obtained on dissolving (3) and (4) in 2,2,2-trifluoroethanol. Only the low-wavelength absorption [$\lambda_{max.}$ 262 nm (log ε 4·30)] was observed in AcOH, where solutions of (3) and (4) are colourless.

Acetolysis of 4-Methoxybenzyl Halides.—The acetolyses of 4-methoxybenzyl chloride and bromide were studied for comparison. The only product was 4-methoxybenzyl acetate. No rate depression during a run or by added bromide ion was observed, and increase in the salt (NaOAc, Bu_4NBr) concentration increased the solvolysis rate (Table 5). The k_{Br}/k_{Cl} ratio is *ca.* 2·0.

TABLE 5

Acetolysis of 4-methoxybenzyl halides ($AnCH_2X$) in AcOH–NaOAc at 45·4 °C

X	$[AnCH_2X]$/ M	[NaOAc]/ M	$[Bu_4NBr]$/ M	10^5k_1/s^{-1}
Cl	0·04	0·08		2·73 ± 0·04 [a]
Br	0·13	0·065		3·75 [b]
Br	0·04	0·08		5·39 ± 0·21
Br	0·04	0·16		8·16 ± 0·27
Br	0·13	0·065	0·065	7·60 [b]
Br	0·13	0·065	0·13	10·28 [b]
Br	0·13	0·065	0·26	12·58 [b]

[a] Literature value: $k_1 = 1·9 \times 10^{-3}$ at 60° (ref. 29). [b] Based on a one-point experiment at 25—38% reaction.

DISCUSSION

Solvolysis in 80% EtOH.—The lack of dependence on the NaOAc concentration eliminates the nucleophilic addition–elimination route. An S_Ni route is supported by the first-order kinetics, the solvent and the β-substituent effect, the k_{Br}/k_{Cl} ratio, and the nature of the product. Several of these criteria suggest more specifically that the solvolysis is by the solvent unassisted (k_c) variant.[15,16]

k_{Br}/k_{Cl} *Ratios.*—The k_{Br}/k_{Cl} ratio of 54 for compounds (3) and (4) is similar to the ratios observed (53—82) for the S_Ni solvolyses of triarylvinyl halides [3,11b,f] and 1-halogeno-3-phenyl-1,3-di-t-butylallenes [17] in 80% EtOH, and to the ratios (30—58) for several saturated systems,[18,19] some of which solvolyse *via* the k_c route.[18c] The similar ratios for the crowded triarylvinyl halides and the much less crowded compounds (3) and (4) suggest that steric effects of these leaving groups play little role in determining the ratios. The lower value of 20 for the ββ-dimethyl derivatives is similar to $k_{Br}/k_{Cl} = 19$ for α-phenylethyl halides.[19a]

The Effect of β-*Substituents.*—β-Methyl substituents increase the solvolytic reactivity: $k_1(6)/k_1(4) = 3·7$ with NaOAc and 3·5 with Et_3N, when the data for α-bromo-4-methoxystyrene [7] were used. The complete reactivity scale for β-hydrogen atoms β-methyl groups in the α-bromo-4-methoxyphenylvinyl system is: [7,20,21] H, H (1·0), *cis*-Me,H (6·43), H,*trans*-Me (0·78), and *cis*-Me,*trans*-Me (3·7), where *cis* and *trans* designate the relative positions of the methyl and the 4-methoxyphenyl groups. As discussed elsewhere [1,3] these differences reflect the combination of inductive and steric (buttressing) effect of the methyl groups. The main effect is the increase of the reactivity by the *cis*-β-methyl group which by sterically increasing the 4-methoxyphenyl–double bond deconjugation raises the energy of the ground state and lowers that of the transition state. Two β-methyl groups show near-additivity of the effects of the *cis*- and the *trans*-methyl groups, as observed also with triarylvinyl halides.[11e]

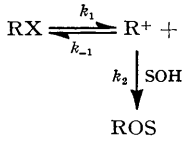
m *Values.*—The solvent effect is discussed in terms of the *m* values of the Winstein–Grunwald equation $\log(k/k_0) = mY$.[13] Extrapolation of the *m* values to 25 °C with the aid of the approximate relationship $m_1/m_2 = T_2/T_1$ [11b,22] gives $m = 0·76$—1·00 for (4) and $m = 0·90$ for (3). These values fit the k_c variant of the S_Ni route for which *m* values of 0·7—1·0 were assigned.[13,23] They are higher than the *m* values for more hindered systems [*e.g.*, m(25 °C) = 0·50 for $An_2C{=}C(Br)An$] [11b] supporting the previous observation that *m* values in aqueous ethanol decrease on increasing the bulk of β-substituents.[1,5,11b–d]

Products.—The formation of acetylene and ketone in ratios which are independent of the leaving group are characteristic of an S_Ni–$E1$ reaction *via* a 'free' carbonium ion. It was noted [8] that the acetylene : ketone ratio in the solvolysis of 4-amino-α-bromostyrene in 80% EtOH increases with the basicity of the medium. The formation of 42% acetylene from (4) in the presence

[15] S. Winstein, E. Allerd, R. Heck, and R. Glick, *Tetrahedron*, 1958, **3**, 1.
[16] P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C J. Lancelot, *J. Amer. Chem. Soc.*, 1970, **92**, 2542.
[17] M. D. Schiavelli, R. P. Gilbert, W. A. Boynton, and C. J. Boswell, *J. Amer. Chem. Soc.*, 1972, **94**, 5061.
[18] (*a*) K. A. Copper and E. D. Hughes, *J. Chem. Soc.*, 1937, 1183; E. D. Hughes and U. G. Shapiro, *ibid.*, p. 1177; (*b*) P. v. R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, 1961, **83**, 2700; (*c*) R. C. Bingham and P. v. R. Schleyer, *ibid.*, 1971, **93**, 3189.
[19] (*a*) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 1957, **79**, 1597, 1602; (*b*) A. H. Fainberg and S. Winstein, *ibid.*, p. 1608; (*c*) S. Winstein, A. H. Fainberg, and E. Grunwald, *ibid.*, p. 4146.
[20] C. A. Grob and R. Nussbaumer, *Helv. Chim. Acta*, 1971, **54**, 2528.
[21] Y. Apeloig, unpublished results.
[22] S. Winstein and A. H. Fainberg, *J. Amer. Chem. Soc.*, 1957, **79**, 5937.
[23] K. B. Wiberg, 'Physical Organic Chemistry,' Wiley, New York, 1964, p. 417.

of NaOAc and none in the presence of Et_3N in 80% EtOH [7] [as also observed for 1-(4-methoxyphenyl)-1-bromopropene [20,21]] is another indication to the sensitivity of the product composition to the nature of the medium.

Effect of the Common Ion.—The absence of common-ion rate depression for compounds (3), (4), and (6) points to a low selectivity of the intermediate for the leaving group as opposed to the solvent or its conjugate base. This should not be surprising in our nucleophilic solvent, although common-ion rate depression was observed for triarylvinyl bromides and iodides in aqueous ethanol [21] and dimethylformamide.[11a] The absence of ion return for the strain-free ion (2) supports the suggestion that part of the selectivity of the vinyl cation is due to the shielding of the cationic orbital by bulky β-substituents.[11g] This is also in line with the α value of 7·5 calculated for (5) [by Scheme 1 and equation (8)], which is lower than the α values for 1-(4-methoxyphenyl)-2,2-diphenylvinyl iodide (30—50) and bromide (10) in 70% dimethylformamide,[11a] but higher than $\alpha = 0$ for (4). However, the ion return for (5) is unexpected since it was not observed for the bromo-compound (6), or for tris-(4-methoxyphenyl)vinyl bromide [11b,24] (which has bulkier β-substituents), although Br^- should be more nucleophilic than Cl^- in aqueous EtOH (*cf.* the α values above). A scheme including both ion pairs [20] and dissociated ions may be implied, and although there are not sufficient data to support it, it is clear that at least part of the product arises from ' dissociated ' ions.



SCHEME 1

$$k_{obs} = k_1/(1 + \alpha[X^-]) \qquad \alpha = k_{-1}/k_2 \qquad (8)$$

Acetolysis.—*A priori*, the acetolysis of (3) and (4) in the less nucleophilic AcOH should be more S_N1-like than in 80% EtOH. However, for our terminal olefins, competition with the electrophilic addition–elimination (Ad_E–E) route [equation (1)] which would also give the acetophenone (7) should be considered. The products and the first-order kinetics are consistent with both routes but the results presented below enable us to apply several distinguishing criteria, which were discussed [10] but not investigated in detail. These show that both routes contribute appreciably to the solvolysis of (3), while the Ad_E–E route is a minor contributor (if at all) to the acetolysis of (4).

(a) *The element effect.* The k_{Br}/k_{Cl} ratios in AcOH are much lower than in 80% EtOH. This was observed earlier for the S_N1 route (*e.g.*, for diphenylmethyl halides in AcOH $k_{Br}/k_{Cl} = 3$) [19c] and was ascribed to more efficient hydrogen bonding of the incipient smaller chloride ion with the electrophilic solvent.[19c] For triarylvinyl halides which react *via* S_N1, $k_{Br}/k_{Cl} = 5$—42 in AcOH.[3,11f,11g,21] The lowest ratio which we are aware of is 1·7 for the acetolysis of *exo*-7-norcaryl halides.[25] Since all these values are higher than our ratios of 0·46—0·56 (the chloride is faster than the bromide) we studied the similarly activated 4-methoxybenzyl halides which react *via* the S_N1 route in 90% EtOH [26,27] and 80% dioxan [28] and found a k_{Br}/k_{Cl} ratio of 2. Our k_1(45·4 °C) for 4-methoxybenzyl chloride with 0·08M-NaOAc is 70 times lower than the k_1(60 °C) reported with 0·06M-NaOAc,[29] but the data in 80% dioxan [28] are more consistent with our value.

The similar electronic effects of the two halogens, as reflected by the k_{Br}/k_{Cl} ratios in nucleophilic vinylic substitition,[4] suggest that the ratios will be unity or slightly lower for the Ad_E–E route. The only data which we found for electrophilic addition to halogenoolefins are the relative reactivities of X in the addition of the solvent CF_3CO_2H to 2-X-propenes: [30] H (1), Cl (0·35), Br (0·082), *i.e.*, $k_{Br}/k_{Cl} = 0·23$.

(b) *Solvent effect.* The Ad_E–E route should be faster in AcOH than in 80% EtOH. Indeed, *cis*-but-2-enyl toluene-*p*-sulphonate reacts 100 times more rapidly *via* the Ad_E–E route in HCO_2H [9] than *via* the S_N1 route in 50% MeOH.[31] The rate ratio k_1(80% EtOH)/k_1(AcOH) for (4) is 15, *i.e.*, in the range of 6—25 found for α-(4-methoxyphenyl)vinyl substrates solvolysing *via* S_N1,[3,11b,11e,11h,24] and near the estimated value of 20 for α-phenylvinyl trifluoromethanesulphonate [11h,32] which it resembles structurally. The ratio for (3), however, is 0·13, much lower than the ratio of 10 observed for (5) which solvolyses *via* S_N1.[24] The reaction of (3) is therefore accelerated by incursion of the Ad_E–E route.

(c) k_X/k_H *Ratios.* Halogen substituents decrease the rate of electrophilic addition to the double bond [33,34] (see ref. 35 for an exception). The ratios of k_X for the acetolysis of (3) and (4) to k_H for the addition of AcOH to 4-methoxystyrene are $k_{Br}/k_H = 0·09$ and $k_{Cl}/k_H = 0·19$. Comparison with $k_{Br}/k_H = 0·08$ and $k_{Cl}/k_H =$

[24] A. Gal, Ph.D. Thesis, The Hebrew University, Jerusalem, 1972.
[25] W. F. Sliwinski, T. M. Su, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1972, **94**, 133.
[26] J. W. Baker, *J. Chem. Soc.*, 1951, 2506.
[27] A. Streitwieser, 'Solvolytic Displacement Reactions,' McGraw-Hill, New York, 1962, p. 19.
[28] J. W. Hill and A. Fry, *J. Amer. Chem. Soc.*, 1962, **84**, 2763.
[29] M. Hojo, T. Ichi, Y. Tamaru, and Z. Yoshida, *J. Amer. Chem. Soc.*, 1969, **91**, 5170.
[30] P. E. Peterson and R. I. Bopp, *J. Amer. Chem. Soc.*, 1967, **89**, 1283.
[31] P. E. Peterson and J. M. Indelicato, *J. Amer. Chem. Soc.*, 1969, **91**, 6194.
[32] R. G. Hargrove, T. E. Dueber, and P. G. Stang, *Chem. Comm.*, 1970, 1614.
[33] P. B. D. de la Mare and R. Bolton, 'Electrophilic Additions to Unsaturated Systems,' Elsevier, Amsterdam, 1966, pp. 27, 84; J. Burgin, G. Hearne, and F. F. Rust, *Ind. Eng. Chem.*, 1941, **33**, 385.
[34] R. N. Haszeldine and J. E. Osborne, *J. Chem. Soc.*, 1956, 61; A. L. Henne and E. P. Plueddeman, *J. Amer. Chem. Soc.*, 1943, **65**, 1271; A. L. Henne and R. C. Arnold, *ibid.*, 1948, **70**, 758; M. Loizos, A. F. Hegarty, and J. E. Dubois, *Bull. Soc. chim. France*, 1969, 2747.
[35] A. N. Bose and S. W. Benson, *J. Chem. Phys.*, 1963, **38**, 878.

0·35 for the addition of $CF_3{\cdot}CO_2H$ to 2-substituted propenes [30] supports the incursion of the Ad_E–E route.

(d) *Solvent isotope effect (SIE) and deuterium incorporation.* A rate-determining protonation is slower in *O*-deuteriated than in undeuteriated solvents.[36a] For typical reactions, *e.g.*, the acid-catalysed isomerisation of stilbenes,[37] $k_{H_2O}/k_{D_2O} = 2{\cdot}4$—$6{\cdot}0$ [37b] and a slow proton transfer from a carboxylic acid in water gives $k_{RCO_2H}/k_{RCO_2D} = 2{\cdot}95$—$6{\cdot}8$.[38] The SIE for S_N1 solvolyses are much lower: $k_{H_2O}/k_{D_2O} = 1{\cdot}06$—$1{\cdot}49$ for saturated substrates [36b] and 1·33 for 4-amino-α-bromostyrene in 50% aqueous dioxan.[8]

the SIE in AcOH for the Ad_E reactions of two compounds which may serve as adequate models for our compounds. One is expected to give a much more stabilised carbonium ion, and the other only a slightly more stabilised ion than those derived by β-protonation of our α-halogeno-4-methoxystyrenes. The first reaction is the hydrolysis of α-acetoxy-4-methoxystyrene in AcOH to 4-methoxyacetophenone which gave a SIE of 3·45. Noyce and Pollack [42] suggested an Ad_E (A–S_E2 in their terminology) mechanism for this reaction in water on the basis of the $k_{H_2O}/k_{D_2O} = 2{\cdot}50$, the substituent effects, and the sensitivity of the

TABLE 6

Solvent isotope effects in carboxylic acid solvents

Substrate	Solvent	Process	Mechanism	k_{RCO_2H}/k_{RCO_2D}	Ref.
AnC(Ph):C(An)Br	AcOH	Solvolysis	S_N1	1·1	*a*
Ph_2C:C(Ph)OSO_2F	AcOH	Solvolysis	S_N1	1·04	*b*
Ph_2C:C(OTs)Ph	AcOH	Solvolysis	S_N1	0·93	*b*
AnC(OTs):CMe_2	$CF_3{\cdot}CO_2H$	Solvolysis	S_N1	1·07	*c*
AnC(OTs):CMe_2	AcOH	Solvolysis	S_N1	0·85	*d*
AnC(OBs):CMe_2	AcOH	Solvolysis	S_N1	1·05	*d*
AnC(Br):CMe_2 [e]	AcOH	Solvolysis	S_N1	0·85	*f*
Fl:C(Br)An [e,g]	AcOH	Solvolysis	S_N1	1·20	*f*
AnC(Ph):CHAn	AcOH	Isomerisation	Ad_E	2·55	*h*
$CH_3{\cdot}(CH_2)_3{\cdot}$C(OAc):CHD	AcOH	Hydrolysis	Ad_E (AS_E2)	3	*i*
XC_6H_4CH:CH_2	AcOH–H_2SO_4	Addition	Ad_E	1·55—2·26 [j]	*k*
AnCH:CH_2	AcOH–H_2SO_4	Addition	Ad_E	2·16	*k*
AnCH:CH_2	AcOH	Addition	Ad_E	3·4	*l*
AnC≡CH	AcOH	Addition	Ad_E	2·7	*l*
AnC(OAc):CH_2	AcOH	Hydrolysis	Ad_E (AS_E2)	3·45	*l*
m-$Me_2C_6H_4$	$CF_3{\cdot}CO_2H$	H-Exchange	S_E (reversible)	1·75	*m*
p-$ClC_6H_4SiMe_3$	$CF_3{\cdot}CO_2H$	Desilylation	S_E	6·2	*m*
MeCH—CH_2 (O)	AcOH	Acetolysis	Ad_E (reversible)	1·53	*n*

[a] Ref. 11*f*. [b] Ref. 11*h*. [c] Z. Rappoport and J. Kaspi, *Tetrahedron Letters*, 1971, 4039. [d] Z. Rappoport and J. Kaspi, *J.C.S. Perkin II*, 1972, 1102. [e] The SIE is based on extrapolated k_1 values since the reactions show common-ion rate depression. [f] Ref. 24. [g] Fl = fluorenylidene. [h] Ref. 21. [i] R. H. Summerville and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1972, **94**, 3629. [j] The SIE depends on the substituent X. [k] Ref. 43. [l] This work. [m] C. Eaborn, P. M. Jackson, and R. Taylor, *J. Chem. Soc.* (*B*), 1966, 613. [n] Ref. 44*a*.

These data combined with our SIE of $1{\cdot}94 \pm 0{\cdot}06$ for (3) point to a contribution of the Ad_E–E route. However, for estimating this contribution [and that for (4) where the SIE is only $1{\cdot}45 \pm 0{\cdot}15$] the maximum expected SIE in AcOH for both the S_N1 and the Ad_E–E routes are required. Since the maximum SIE calculated for water (3·6) [39] cannot be used in AcOH, we collected data on SIE in RCO_2H. Table 6 shows that the SIE for vinylic S_N1 solvolyses are $\leqslant 1{\cdot}2$, and for the various Ad_E reactions the values are 1·55—6·2. However, the degree of proton transfer in the transition states of these Ad_E addition may differ appreciably from that in our system. The Hammond principle [40] implies that the transition state for the proton transfer will become closer to the reactant when the stability of the resulting carbonium ion is increased.[37b,41] We therefore studied hydrolysis rate to the nature of the vinylic substituents. Similar arguments (the SIE and the much slower hydrolysis of triarylvinyl acetates [24] than that of α-acetoxy-4-methoxystyrene) support a rate-determining protonation in AcOH also. The second reaction is the addition of AcOH to 4-methoxystyrene which gave a solvent isotope effect of 3·4. A rate-determining protonation is assumed here by analogy with the Ad_E routes suggested for the acid-catalysed addition of AcOH in AcOH ($k_{AcOH}/k_{AcOD} = 2{\cdot}16$).[43] An SIE of 3·4 for the Ad_E route with a proton transfer in the transition state similar to that expected for (3) and (4) should therefore be a good estimate. Using a tentative SIE of 1·2 (Table 6) for the S_N1 route we conclude that the Ad_E–E route contributes appreciably (*ca.* 35% of k_1) to the acetolysis of (3), but much less ($\leqslant$10%) to that of (4), and this is supported by (*a*)—(*c*) above.

[36] P. M. Laughton and R. E. Robertson, in 'Solute–Solvent Interactions,' eds. J. F. Coetzee and C. D. Ritchie, Marcel Dekker, New York, 1969, (*a*) chap. 7; (*b*) p. 429.

[37] *E.g.*, D. S. Noyce, D. R. Hartter, and F. B. Miles, (*a*) *J. Amer. Chem. Soc.*, 1968, **90**, 4633; (*b*) *J. Org. Chem.*, 1968, **33**, 4260.

[38] (*a*) A. J. Kresge and Y. Chiang, *J. Chem. Soc.* (*B*), 1967, 58; (*b*) F. A. Long and D. Watson, *J. Chem. Soc.*, 1958, 2019; (*c*) B. D. Batts and V. Gold, *J. Chem. Soc.*, 1964, 4284; (*d*) V. Gold and D. C. A. Waterman, *J. Chem. Soc.* (*B*), 1968, 839, 849.

[39] C. A. Bunton and V. J. Shiner, jun., *J. Amer. Chem. Soc.*, 1961, **83**, 42, 3207, 3214.

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

[41] W. M. Schubert and J. R. Keefe, *J. Amer. Chem. Soc.*, 1972, **94**, 559.

[42] D. S. Noyce and R. M. Pollack, *J. Amer. Chem. Soc.*, 1969, **91**, 119.

[43] R. Corriu and J. Guenzet, *Tetrahedron*, 1970, **26**, 671.

The small deuterium isotope effect could also be due to an initial reversible protonation.[44] However, the absence of deuteriation in the unchanged vinyl halide up to 40% reaction shows that the reaction is practically irreversible, as observed also in the early stages of the acid-catalysed hydration of styrenes [41,45] and phenylacetylenes [46] in water.

For an irreversible addition, deuterium incorporation in the methylene group of the primary acetolysis product is an integral part of the mechanism. However, since the observed acetolysis product (7) is formed by hydrolysis of α-acetoxy-4-methoxystyrene which is 314 times faster than the acetolysis of (4), the methyl group should be 33% deuteriated. Further deuterium incorporation during the exchange is masked by the much faster deuterium incorporation of (7) than in the acetolysis of (4).

Ad_E–E vs. S_N1 Routes in Vinylic Systems.—A change from a sluggish leaving group X to a good one will enhance the S_N1 route and if the electron-attracting ability of X also increases, a simultaneous Ad_E–E route would be inhibited. For α-arylvinyl systems there are two extreme situations: (*a*) α-phenylvinyl fluorosulphonate with a highly electron-attracting excellent leaving group which solvolyses exclusively *via* S_N1;[11h] and (*b*) α-acetoxy-4-methoxystyrene (or α-arylvinyl phosphates [47]) with a sluggish leaving group which protonates easily {*e.g.*, in protonation k[MeC(OAc):CH_2]/k(MeCH:CH_2) = 1300 [48] and k[AnC(OAc):CH_2]/k(AnCH:CH_2) = 28} and reacts exclusively *via* Ad_E–E.[42] Our α-arylvinyl halides are then in the range of shifting mechanism. Comparison of the activation enthalpies and the SIE shows (Table 7) that a gradual change in these parameters accompanies the change in the leaving group. Such data can be useful in evaluation of either route for α-arylvinyl systems.

Our results are relevant for the possible occurrence of the Ad_E–E route in other vinylic solvolyses. Electrophilic bromination,[33,49] chromyl chloride oxidation,[50] and addition of 2,4-dinitrobenzenediazonium salts [51] to styrenes are slightly affected by β-methyl substitution,[52] but are retarded by β-phenyl substituents and the reactivity of these systems is decreased by further substitution. Since the S_N1 route of α-arylvinyl halides is usually accelerated (except for mono-*trans*-substituents),[1,5,20] by β-alkyl and aryl groups [1,3,5,11b,20] the ArCX=CR^1R^2 (R ≠ H) systems would most likely acetolyse *via* S_N1, while the Ad_E–E route should be considered for *trans*-α-aryl-α-halogeno-β-phenyl(or alkyl)-ethylenes.

The solvent change AcOH ⟶ HCO_2H ⟶ CF_3·CO_2H should increase the rates of both routes, and which one predominates depends on the relative *m* values of the Winstein–Grunwald equation for both. While trifluoroacetolysis of 1-(4-methoxyphenyl)-2-methylprop-1-enyl arenesulphonates is mechanistically S_N1,[53] an Ad_E–E route for (4) in HCO_2H is likely. We attribute the colour observed on dissolution of (4) in HCO_2H (and probably also in 2,2,2-trifluoroethanol) to the cation ArC^+XMe which is formed by protonation of (4), by analogy with the positions of the long-wavelength maxima to those found in the spectra of the stable 1,1-bis-(4-methoxyphenyl)ethyl cations.[54] If similar ε values are assumed, the protonation proceeds to *ca.* 0·1%.

Catalysis by strong acid in AcOH also diverts the reaction of (4) into the Ad_E–E route which is more responsive to acid-catalysis than the S_N1 route. This is realised in the autocatalysis of the reaction of (4) in unbuffered AcOH (Table 3) with the formed HBr as the catalyst.

Intermediates in the Solvolysis and the Addition.—If the bromo-compound (4) acetolyses mainly *via* the relatively strain-free vinyl cation (2; Ar = 4-MeO·C_6H_4) the absence of common-ion rate depression, which was observed with the AnC^+=CAr_2 and AnC^+=CHAr cations [1,3,5,11a,11d–g] fits the suggestion of a steric contribution of the β-substituents to the selectivity of the cations. An apparent discrepancy is that the ion formed on solvolysis is captured preferentially by AcO^- (or AcOH) while the kinetically controlled products

TABLE 7

Structure, rate parameters, and mechanisms for the acetolysis of $ArCX=CH_2$

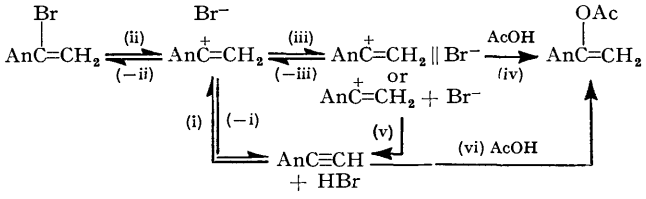
Ar	X	k_{AcOH}/k_{AcOD}	$\Delta H^{\ddagger}$ / kcal mol^{-1}	$\Delta S^{\ddagger}$(120°) / cal mol^{-1} K^{-1}	Mechanism
An	OAc	3·45	19·4	−19·6	Ad_E
An	Cl	1·94	20·1	−28·7	Ad_E–E + S_N1
An	Br	1·45	23·2	−20·9	S_N1 (+some Ad_E–E)
Ph [a]	OSO_2F		25·4	−0·4	S_N1

[a] Data from ref. 11h.

[44] N. S. Isaacs, *Tetrahedron Letters*, 1965, (*a*) 4549, (*b*) 4553.
[45] W. M. Schubert, B. Lamm, and J. R. Keefe, *J. Amer. Chem. Soc.*, 1964, **86**, 4727; W. M. Schubert and B. Lamm, *ibid.*, 1966, **88**, 120; N. C. Deno, A. Kish, and H. J. Peterson, *ibid.*, 1965, **87**, 2157.
[46] D. S. Noyce and M. D. Schiavelli, *J. Amer. Chem. Soc.*, 1968, **90**, 1020.
[47] R. D. Frampton, T. T. Tidwell, and V. A. Young, *J. Amer. Chem. Soc.*, 1972, **94**, 1271.
[48] D. S. Noyce and R. M. Pollack, *J. Amer. Chem. Soc.*, 1969, **91**, 7158.
[49] J. E. Dubois and A. Schwarcz, *Compt. rend.*, 1964, **259**, 2227.
[50] F. Freeman and N. J. Yamachika, *J. Amer. Chem. Soc.*, 1972, **94**, 1214.
[51] H. Marxmeier and E. Pfeil, *Annalen*, 1964, **678**, 28.
[52] J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, 1969, **91**, 1483.
[53] Z. Rappoport and J. Kaspi, *Tetrahedron Letters*, 1971, 4039.
[54] N. C. Deno, P. T. Groves, and G. Saines, *J. Amer. Chem. Soc.*, 1959, **81**, 5790; Z. Rappoport and I. Schnabel, *J.C.S. Perkin II*, 1972, 146.

in the addition of HBr to 4-methoxyphenylacetylene in AcOH are 87% of the bromide-captured product (4) and only 13% of (7). The latter reaction is complete at room temperature at equimolar concentrations in 1 min, while the addition of AcOH to (8) has a half-life of 43 min at 120 °C. Evidence for an intermediate vinyl cation in the addition is the SIE of 2·7 in the addition of AcOH and the similarity to the hydration of acetylenes in water [46,55] or in aqueous AcOH [56] where the evidence for intermediate vinyl cation is strong.

Our interpretation (Scheme 2) is similar to that invoked for explaining the analogous behaviour of the isopropyl *p*-bromobenzenesulphonate–propene–*p*-bromobenzenesulphonic acid system in trifluoroacetic acid.[57] Undissociated HBr and (8) react directly (i) to give an intimate ion pair which collapses (—ii) to the vinyl bromide more rapidly than it dissociates (iii). The solvolysis product arises from a more dissociated intermediate (by ii ⟶ iii ⟶ iv). This may be a solvent-separated ion pair where return (—iii) and solvent capture (iv) may compete, or a dissociated ion which is captured more rapidly than it returns, as shown by the absence of common-ion rate depression. Vinyl cation ion pairs were suggested in the addition of HCl to 1-phenylpropyne in AcOH.[58]



SCHEME 2

The formation of 4-methoxyphenylacetylene in aqueous EtOH but not in AcOH and of internal acetylenes in AcOH [1,5,21] raises the possibility of a third route [(—i) ⟶ (vi) or (v) ⟶ (vi)] for the formation of the product. A reversible *E*1 elimination of the cation or the ion pair to form 4-methoxyphenylacetylene, followed by addition of AcOH, competes with the irreversible capture by AcOH (iv). Such a pathway is plausible since it was shown in the acid-catalysed hydration of phenylacetylene in water that the energy of the transition state leading to phenylacetylene from the α-phenylvinyl cation is only 1—2 kcal mol^{-1} higher than that of the transition state for the capture of the ion by water, while the reverse reaction is 28 kcal mol^{-1} easier.[46] This *E*1–Ad_E route would be hidden in our system since the addition of AcOH to 4-methoxyphenylacetylene is 17 times faster than the solvolysis. The deuterium incorporation by 4-methoxyacetophenone prevents its study by labelling experiments.

EXPERIMENTAL

M.p.s are uncorrected. U.v. spectra were recorded 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 spectrometer and are given in τ values.

Materials.—4-Methoxyphenylacetylene, b.p. 80—82 °C at 10 mmHg (lit.,[29] 89—94 °C at 15 mmHg) was prepared according to the literature, τ (CCl_4) 2·90 (4H, q, Ar), 6·33 (3H, s, MeO), and 7·07 (1H, s, ≡CH).[59] 4-Methoxystyrene, b.p. 78—80 °C at 8 mmHg (Fluka) was redistilled before use, τ (CCl_4) 3·19 (4H, q, *J* 8·5 Hz, Ar), 3·63, 3·80, 4·48, 4·77, 5·00, 5·16 (4H, m, vinyl), and 6·39 (3H, s, MeO). α-Acetoxy-4-methoxystyrene, m.p. 68 °C (lit.,[42] 77—78 °C) was prepared according to Noyce and Pollack, τ (CCl_4) 3·09 (4H, q, Ar), 5·01 (2H, d, *J* 1 Hz, $=CH_2$), 6·28 (3H, s, MeO), and 7·85 (3H, s, AcO).[42] 4-Methoxyacetophenone, m.p. 38—39 °C, was commercial (Fluka), $\lambda_{max.}$ (EtOH) 271·5 nm (ε 16,500), ν 1675 cm^{-1}, τ (CCl_4) 2·70 (4H, q, Ar), 6·22 (3H, s, MeO), and 7·60 (3H, s, Me). 4-Methoxyisobutyrophenone, b.p. 146 °C at 13 mmHg (lit.,[60] 158 °C at 25 mmHg), was prepared according to Sosa, τ (CCl_4) 2·80 (4H, q, Ar), 6·27 (3H, s, MeO), 6·40—6·90 (1H, m, CH), and 8·90 (6H, d, 2Me).[60] 4-Methoxybenzyl chloride, b.p. 85—86 °C at 8 mmHg (lit.,[61] 93 °C at 2·5 mmHg), and 4-methoxybenzyl bromide, b.p. 90 °C at 6 mmHg (lit.,[62] 126 °C at 12 mmHg) were prepared according to Spath,[62] and 1-(4-methoxyphenyl)-2-methylpropen-1-yl acetate was prepared from the bromide and silver acetate.[24] 1-(4-Methoxyphenyl)ethanol [63] was prepared by lithium aluminium hydride reduction of 4-methoxyacetophenone, τ (CCl_4) 3·20 (4H, q, Ar), 5·50 (1H, q, CH), 6·38 (3H, s, MeO), 7·0br (1H, s, OH), and 8·72 (3H, s, Me). 1-(4-Methoxyphenyl)ethyl acetate, b.p. 125—128 °C at 5 mmHg (lit.,[64] 111·5 °C at 3·5 mmHg) was prepared in 80% yield from the reaction of 1-(4-methoxyphenyl)ethanol with acetic anhydride, τ (CCl_4) 3·17 (4H, q, Ar), 4·37 (1H, d, CH), 6·37 (3H, s, MeO), 8·05 (3H, s, AcO), and 8·52 (3H, d, Me). α-Chloro-4-methoxystyrene, m.p. 41—42 °C (lit.,[65] 45 °C) was prepared from 4-methoxyphenylacetylene by the addition of equimolar quantity of dry hydrogen chloride dissolved in glacial acetic acid. The solid is unstable and decomposes within a few hours at room temperature. Its solutions are more stable, τ (CCl_4) 2·54 (4H, d, Ar), 4·13, 4·64 (2H, 2d, CH_2), and 6·02 (3H, s, MeO).

Solvents.—Ethanol–water mixtures were prepared according to Grob and Cseh.[7] The basic solutions were prepared from AnalaR NaOAc (B.D.H.). Dry AcOH (containing 1—2% of acetic anhydride) was prepared as described.[11c] Acetic [$^2H_1$]acid was prepared according to Jones and Maness.[11h] It contained (in different preparations) 5—13% of undeuteriated acid (by n.m.r.). Solutions of NaOAc in AcOH were prepared by dissolving AnalaR Na_2CO_3 in the AcOH.

α-Bromo-4-methoxystyrene.—This was prepared by a

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modification of the method of Grob and Cseh.[7] 4-Methoxyphenylacetylene (2·6 g, 20 mmol) was dissolved in dry acetic acid (25 ml) and the solution was cooled to 0 °C. A cold solution of dry hydrogen bromide (2·4 g, 30 mmol) in acetic acid (25 ml) was added with stirring, and after 3 min the mixture was poured into ice–water. The solid which separated was collected immediately, dissolved in methanol, and precipitated by cooling the solution in liquid air. α-Bromo-4-methoxystyrene (2·2 g, 65%), m.p. 34—35 °C (lit.,[7] 35—36°) was obtained as crystals. The compound is unstable and begins to decompose within few hours at room temperature. It is more stable in solution, $\lambda_{max.}$ (cyclohexane) 262 nm (ε 14,500), $\lambda_{max.}$ (AcOH) 262 nm (ε 20,000), ν ($CHCl_3$) 1605 cm^{-1} (C=C), τ (CCl_4) 2·88 (4H, q, Ar), 4·02, 4·26 (2H, 2d, CH_2), and 6·25 (3H, s, MeO).

The product distribution in the addition was obtained as follows: to 4-methoxyphenylacetylene (0·42 g, 2 mmol) in dry acetic acid (20 ml), dry hydrobromic acid (0·24 g, 3 mmol) in acetic acid (20 ml) was added at 10 °C. The solution turned violet immediately. After 1 min the mixture was poured into ice–water (200 ml) and the organic layer was extracted immediately with carbon tetrachloride (100 ml), dried ($CaCl_2$), and evaporated. N.m.r. of the remaining oil showed the formation of 87% of α-bromo-4-methoxystyrene and 13% of 4-methoxyacetophenone and none of the starting material.

1-(4-*Methoxyphenyl*)-2-*methylprop*-1-*enyl Chloride and Bromide*.—(a) 1-(4-*Methoxyphenyl*)-2-*methylpropan*-2-*ol*. To methylmagnesium iodide (68 g, 0·41 mol) in dry ether (200 ml), ethyl 4-methoxyphenylacetate (29·1 g, 0·15 mol) in dry ether (100 ml) was added slowly with cooling during 1 h. The mixture was poured into aqueous 0·4M-ammonium chloride (200 ml), and the organic layer was separated, washed with water, and dried ($MgSO_4$). The solvent was evaporated and the remaining oil was distilled, giving 21·6 g (87% yield) of 1-(4-*methoxyphenyl*)-2-*methylpropan*-2-*ol*, b.p. 118 °C at 3 mmHg (Found: C, 73·2, H, 9·05. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·95%) τ (CCl_4) 3·61 (4H, centre of q, Ar), 6·27 (3H, s, MeO), 7·38 (2H, s, CH_2), 8·38 (1H, s, OH), and 8·85 (6H, s, 2Me).

(b) 1-(4-*Methoxyphenyl*)-2-*methylpropene*. This was prepared by the dehydration of 1-(4-methoxyphenyl)-2-methylpropan-2-ol (20 g) in 20% sulphuric acid (120 ml) at reflux for 2 h, extraction with chloroform, drying, evaporation of the solvent, and distillation of the remaining oil (87%), b.p. 82—86 °C at 4 mmHg (lit.[60] 116—118 °C at 18 mmHg), τ (CCl_4) 3·00 (4H, q, Ar), 3·83br (1H, s, CH), 6·28 (3H, s, MeO), and 8·20—8·23 (6H, m, 2Me).

(c) 1-(4-*Methoxyphenyl*)-2-*methylprop*-1-*enyl bromide*. To 1-(4-methoxyphenyl)-2-methylpropene (8 g, 50 mmol) in carbon tetrachloride (50 ml), bromine (8·4 g, 52 mmol) was added slowly with stirring. The mixture was then washed with a dilute solution of sodium hydroxide and with water and dried ($MgSO_4$). The solvent was evaporated and the remaining oil [probably the dibromide, τ (CCl_4) 2·92 (4H, centre of q, Ar), 4·80 (1H, s, CH), 6·17 (3H, s, MeO), 8·00 (3H, s, Me), and 8·14 (3H, s, Me)] was dissolved in t-butyl alcohol (75 ml), to which potassium t-butoxide (7 g, 60 mmol) in t-butyl alcohol (25 ml) was added. The mixture was shaken overnight at room temperature, poured into water, extracted with benzene, and the organic layer washed with water and dried ($MgSO_4$). The solvent was evaporated, the remaining oil was dissolved in methanol, and on cooling with liquid air for a few minutes 9·3 g (77% yield) of crystals of 1-(4-*methoxyphenyl*)-2-*methylprop*-1-*enyl bromide*, m.p. 42—43°, were obtained (Found: C, 54·9; H, 5·3; Br, 32·7. $C_{11}H_{13}BrO$ requires C, 54·8; H, 5·4; Br, 33·2%), τ (CCl_4) 3·00 (4H, centre of q, Ar), 6·08 (3H, s, MeO), 8·00 (3H, s, Me), and 8·30 (3H, s, Me).

(d) 1-(4-*Methoxyphenyl*)-2-*methylprop*-1-*enyl chloride*. This was prepared in 57% yield from the reaction of equimolar amounts of 1-(4-methoxyphenyl)-2-methylpropene and chlorine in carbon tetrachloride in an analogous manner to the preparation of the bromide, as *crystals*, m.p. 37—38 °C (from methanol) (Found: C, 67·4; H, 6·5; Cl, 17·7; OMe, 15·3. $C_{11}H_{13}ClO$ requires C, 67·1; H, 6·7, Cl, 18·0; OMe, 15·8%), τ (CCl_4) 2·99 (4H, centre of q, Ar), 6·08 (3H, s, MeO), 8·03 (3H, s, Me), and 8·27 (3H, s, Me).

Ethyl 1-(4-*Methoxyphenyl*)-2-*methylprop*-1-*enyl Ether*.—Silver carbonate (556 mg, 2 mmol) and 1-(4-methoxyphenyl)-2-methylprop-1-enyl bromide (444 mg, 1·84 mmol) in absolute ethanol (70 ml) were refluxed in the dark for 2 h. The hot mixture was filtered, the solvent was evaporated, and the remainder dissolved in chloroform, filtered from the residual silver salts, and the chloroform was evaporated and the oil was distilled *in vacuo* giving 160 mg (42% yield) of *ethyl* 1-(4-*methoxyphenyl*)-2-*methylprop*-1-*enyl ether*, b.p. 138—140 °C at 25 mmHg, which is the exclusive product according to n.m.r. (Found: C, 75·75; H, 8·5. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·8%), τ (CCl_4) 2·23 (4H, centre of q, Ar), 6·28 (3H, s, MeO), 6·38 (2H, q, CH_2, *J* 6·5 Hz), 8·25 (3H, s, Me), 8·40 (3H, s, Me), and 8·83 (3H, t, Me, *J* 6·5 Hz).

Reaction of Silver Carbonate with α-*Bromo*-4-*methoxystyrene*.—α-Bromo-4-methoxystyrene (213 mg, 1 mmol) was added to silver carbonate (1·65 g, 6 mmol) in absolute ethanol (25 ml). The mixture was refluxed for 15 h, filtered, and the solvent was evaporated. N.m.r. showed that the residue is exclusively 4-methoxyacetophenone.

Hydrolysis of α-*Acetoxy*-4-*methoxystyrene*.—An ampoule containing α-acetoxy-4-methoxystyrene (64 mg, 0·35 mmol) in 80% ethanol (10 ml) containing sodium acetate (0·17M) was kept at 120 °C for 150 min. The mixture was poured into water and extracted with carbon tetrachloride. The extract was dried ($CaCl_2$) and evaporated. N.m.r. (CCl_4) of the remaining oil showed the formation of 63% of 4-methoxyacetophenone and 37% of unchanged starting material.

Dehydration of 1-(4-*Methoxyphenyl*)-2-*methylpropan*-1-*ol*.—This alcohol, b.p. 130—132 °C at 15 mmHg (lit.,[60] b.p. 157—158 °C at 21 mmHg), was prepared from the Grignard reaction of 4-methoxybenzaldehyde and isopropyl bromide. Attempted dehydration under the conditions described above for 1-(4-methoxyphenyl)-2-methylpropan-2-ol gave two fractions, one with b.p. 82—86 °C at 4 mmHg (40%) which was identified as 1-(4-methoxyphenyl)-2-methylpropene, and another, b.p. 175—190 °C at 4 mmHg (60%) which is probably bis-[1-(4-methoxyphenyl)-2-methylpropyl] ether (lit.,[60] 210—235 °C at 13 mmHg).

Kinetics.—The sealed-ampoule technique (Corning glass ampoules) was used. Stock solutions of the vinyl halides were used. The formation of the bromide ion was followed by titration with silver nitrate with eosin as indicator, and the chloride ion was titrated potentiometrically with a Radiometer TTT 1C. The reactions were usually followed to 60—90% reaction and the infinity values were measured after 10 or more half-lives. The addition of acetic acid to 4-methoxyphenylacetylene was followed by n.m.r. by observing the disappearance of the signal for the acetylenic proton and the formation of the methoxy and the methyl

signals. In deuterioacetic acid the formation of the new methoxy-signal was followed. The addition of acetic acid to 4-methoxystyrene was followed by observing the methyl, the acetoxy, and the vinyl protons in the n.m.r. spectrum. The hydrolysis of α-acetoxy-4-methoxystyrene was followed by observing the CH_2D signal formed and the decay of the acetoxy-signal. Whenever two signals were followed in the same run, the rate coefficients calculated for both were similar.

Product Analysis.—Except for the run when products were isolated (a single run for each compound) the product analysis was performed by n.m.r. on the oil obtained after extraction of the reaction mixture with carbon tetrachloride or chloroform, drying, and evaporation of the solvent.

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