
Nucleophilic Reactivity. Part VII.[1] The Mechanism of Hydrolysis of Some Unsaturated Esters of Methanesulphonic Acid

By R. F. Hudson and R. J. Withey

Allyl methanesulphonate gives the corresponding alcohol on alkaline hydrolysis, whereas the 1,4-dimethanesulphonates of *cis*- and *trans*-but-2-ene give high yields of but-2-enal which is probably formed by a 1,4-elimination followed by alkaline hydrolysis at sulphur. The diesters give the substituted products only on reaction with the sodium salts of *p*-nitrophenol and thiophenol. The mode of activation of sulphonate esters by vinylic and acetylenic groups is briefly discussed.

SUBSTITUTION at allylic systems has been widely investigated, and the electronic influence on reactivity of the vinyl group considered in some detail.[2] In general both S_N1 solvolyses and S_N2 displacements are activated by vinylic groups. On the other hand, an acetylenic group has little effect [3] on the rate of solvolysis but increases the rate of S_N2 displacements considerably, as shown by the data for methanesulphonates and chlorides in Table 1.

The chlorides and methanesulphonates show the same qualitative behaviour with the following quantitative differences. (a) $Pr^i \gg Et$ for methanesulphonate solvolysis, and the solvolytic reactivity of allyl sulphonate is greater than for the chloride. This indicates a greater tendency for the sulphonate esters to react by the ionisation, S_N1, mechanism. (b) The S_N2 reactivity of the methyl ester towards hydroxide ions is much greater

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[1] Part VI, P. A. Chopard, R. F. Hudson, and G. Klopman, *J. Chem. Soc.*, 1965, 1379.

[2] A. Streitwieser, *Chem. Rev.*, 1956, **56**, 650.

[3] M. Harfenist, *J. Amer. Chem. Soc.*, 1957, **79**, 4356; J. K. Kochi and G. S. Hammond, *ibid.*, 1953, **75**, 3452.

TABLE 1

Solvolysis and alkaline hydrolysis of halides and methanesulphonates (k_1 is the first-order constant relative to the ethyl compound for solvolysis; k_2 is the second-order constant relative to the ethyl compound for alkaline hydrolysis)

Subst.	Me	Et	Pr^i	CH=CH$_2$	C≡CH
Methanesulphonates					
k_1	3	1	23	76	0·87
k_2	3500	1	—	61	33
Chlorides					
k_1	—	1	1·7	14	0·7
k_2	13 *	1 *	0·16 †	35 †	35·5 †

* With EtO⁻ in EtOH. † With HO⁻ in 80% aqueous EtOH.

than that of the chloride ($k_{\text{Me}}/k_{\text{Et}} \sim 3{\cdot}5 \times 10^3$ for the methanesulphonate, and ~13 for the chloride).

It is not clear whether the unsaturated groups exert $+E$ or $-E$ effects in these reactions,[4] or whether the $+I$ effect increases or decreases the S_N2 reactivity. Some workers [5] consider that the inductive effect ($+I$) changes the reactivity in the order

$$\text{CH}_2\text{–CH}_3 < \text{CH}_2\text{C–H=CH}_3 \leqslant \text{CH}_2\text{–C≡CH}$$

and the conjugative effect ($-E$ as in S_N1 processes) as

$$\text{CH}_2\text{–CH}_3 \leqslant \text{CH}_2\text{–C≡CH} < \text{CH}_2\text{–CH=CH}_2$$

the combination of which gives the observed S_N2 reactivity order,

$$\text{CH}_2\text{–CH}_3 \leqslant \text{CH}_2\text{–CH=CH}_2 \sim \text{CH}_2\text{–C≡CH}$$

There are, however, indications that a $+I$ inductive effect, *e.g.*, as produced by the substitution of halogen atoms in alkyl halides, decreases the S_N2 reactivity,[6] by increasing the bond-breaking energy as first suggested by Polyanyi and his co-workers.[7]

The $-E$ contributions should be different for the chlorides and sulphonates in view of the more polar transition states of the esters, as indicated by the data of Table 1. Consequently, the similar S_N2 activation produced by alkyl and propargyl groups in both chlorides and sulphonates suggests that the rate increases are due to a $+E$ effect which could be similar for the two groups. The greater electronegativity of *sp*-carbon would tend to increase the $+E$ effect, thus counterbalancing the decrease in reactivity due to the $+I$ effect. In this way the activation produced by vinyl, 2-acetylenic, and carbonyl groups in the α-position may be reconciled with the deactivation by α- and β-halogen atoms.

The substitution of the $\text{CH}_2{\cdot}\text{O}{\cdot}\text{SO}_2{\cdot}\text{CH}_3$ group for a γ-hydrogen atom of the allylic ester has little effect on the rate of solvolysis (see Table 2).

A similar substitution of the γ-H atom by a CH_3 group increases the rate of solvolysis of allylic halides [1] by *ca.* 10^2. Unfortunately, but-2-enyl methanesulphonate could not be isolated. It seems, therefore, that the inductive effect of the $\text{O}{\cdot}\text{SO}_2{\cdot}\text{CH}_3$ group almost exactly opposes the hyperconjugation of a CH_2 group in the γ-position. Moreover, the rates of reaction of *cis*- and *trans*-but-2-ene 1,4-dimethanesulphonates with sodium *p*-nitrophenoxide, which lead to the corresponding diethers:

$$(\text{MeSO}_2{\cdot}\text{O}{\cdot}\text{CH}_2{\cdot}\text{CH}{:})_2 + 2\ \text{NO}_2{\cdot}\text{C}_6\text{H}_4{\cdot}\text{O}^- \longrightarrow (\text{NO}_2{\cdot}\text{C}_6\text{H}_4{\cdot}\text{O}{\cdot}\text{CH}_2{\cdot}\text{CH}{:})_2 + 2\text{MeSO}_3^-$$

are comparable to the rate of reaction with the allyl ester (Table 2). In both cases more than 90% of the diether was isolated, so the lower reactivity of the *cis*-compound is probably steric in origin. The *p*-nitrophenoxide and hydroxide ions have similar reactivities towards allyl methanesulphonate, in spite of the considerable difference in their basicities (pK_a of *p*-nitrophenol is 7·14 at 25° in water).

TABLE 2

Solvolysis and alkaline hydrolysis of (a) allyl methanesulphonate, and (b) but-2-ene 1,4-dimethanesulphonates

	(*a*)	(*b*)	
		cis	*trans*
10^5k_1 solvolysis (sec.$^{-1}$)	7·2	19·75	22·50
10^5k_2 (OH⁻) (l. mole^{-1} sec.$^{-1}$) ...	159·5	1016	1126
$10^5k_2'$ (*p*-Np) (l. mole^{-1} sec.$^{-1}$)	136·7	269·5	415·4
10^2k_2 (H$_2$O)/k_1 *	6·1	14·0	14·5
$10^2k_2'$ (H$_2$O)/k_1 *	5·3	3·8	5·6

* Per methanesulphonate group.

Similar observations have been made with allylic halides.[8] The low reactivity of the hydroxide ion may be attributed to its high solvation energy and low polarisability.[9]

Hydroxide ions are significantly more reactive towards the diester than towards allyl methanesulphonate (Table 2), indicating the incursion of an alternative mechanism. Analysis of the reaction mixture showed the presence of but-2-enal (*ca.* 70%) from both the *cis*- and *trans*-esters (see Experimental section).

By analogy with the facile dehydrohalogenation [10] of 1,4-dichlorobut-2-ene this reaction probably proceeds by a 1,4-elimination, followed by displacement on sulphur:

$$\begin{array}{c}
\text{MeSO}_2{\cdot}\text{O}{\cdot}\text{CH}_2{\cdot}\text{CH=CH}{\cdot}\text{CH}_2{\cdot}\text{O}{\cdot}\text{SO}_2\text{Me} + \text{OH}^- \\
\downarrow \\
\text{MeSO}_2{\cdot}\text{O}{\cdot}\text{CH=CH}{\cdot}\text{CH=CH}_2 + \text{MeSO}_3^- \\
\downarrow \text{OH}^- \\
\text{HO}{\cdot}\text{CH=CH}{\cdot}\text{CH=CH}_2 + \text{MeSO}_3^- \\
\downarrow \\
\text{CH}_3{\cdot}\text{CH=CH}{\cdot}\text{CHO} + 2\text{MeSO}_3^-
\end{array}$$

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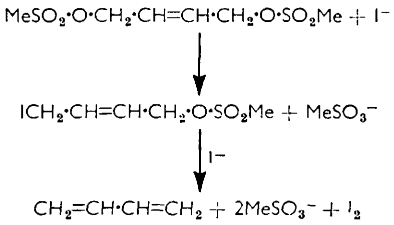
Although vinyl halides are very unreactive, vinyl methanesulphonate is rapidly hydrolysed in alkaline solution[11] (but not in neutral or acidic solution), to give acetaldehyde, presumably by attack on sulphur. Bunnett and Bassett[12] observed that methoxide ions react at the sulphur atom of phenyl toluenesulphonate whereas thioalkoxides react on carbon, and we find that thiophenoxide gives a quantitative yield of the dithioether with both *cis*- and *trans*-diesters. This mechanism of alkaline hydrolysis also explains the formation of acetaldehyde from ethane 1,2-disulphonates.[13]

The possible formation of 2,5-dihydrofuran as an intermediate was dismissed since this is highly unreactive in alkaline media.

p-Xylene αα′-dimethanesulphonate is hydrolysed 5 times more rapidly than the butene diesters, to give a small yield (*ca.* 1·5%) of *p*-tolualdehyde, presumably by a similar mechanism involving a xylylenic intermediate.

In the course of these investigations, the *cis*- and *trans*-but-2-ene disulphonates were treated with sodium iodide. A quantitative yield of iodine was produced within 5 min., probably by substitution followed by displacement on iodine:



$$\begin{tikzcd}
\mathrm{MeSO_2{\cdot}O{\cdot}CH_2{\cdot}CH{=}CH{\cdot}CH_2{\cdot}O{\cdot}SO_2Me + I^-} \arrow[d] \\
\mathrm{ICH_2{\cdot}CH{=}CH{\cdot}CH_2{\cdot}O{\cdot}SO_2Me + MeSO_3^-} \arrow[d, "I^-"] \\
\mathrm{CH_2{=}CH{\cdot}CH{=}CH_2 + 2MeSO_3^- + I_2}
\end{tikzcd}$$

This mechanism is similar to the well known formation of olefins from 1,2-dihalides by the action of iodide.[14a]

The decomposition of 1,4-dibromobut-2-ene by a mixture of sodium acetate and potassium iodide to give 100% butadiene presumably also proceeds by this kind of mechanism.[14b]

EXPERIMENTAL AND RESULTS

Preparation of the Esters.—Allyl methanesulphonate. A mixture of allyl alcohol (11·6 g., 0·2 mole), potassium hydroxide (20 g.), redistilled triethylamine (0·2 mole), and benzene (100 ml.) was stirred in a bath at −10°. Methanesulphonyl chloride (22·9 g.) was added slowly (2 hr.), and the hydrochloride filtered off. After removal of benzene, the residue was fractionally distilled. The *product* (61%) had b. p. 69°/15 mm. (Found: C, 34·9; H, 5·9; S, 23·6. $C_4H_8O_3S$ requires C, 35·3; H, 5·88; S, 23·5%

cis-*But-2-ene* 1,4-*dimethanesulphonate.* This reaction was carried out as above, using 10 g. of *cis*-but-2-ene-1,4-diol (General Aniline Film Corporation), b. p. 89°/0·05 mm., n_D^{20} 1·4765. At the end of the reaction, light petroleum (100 ml.; b. p. 40—60°) was added and the solid filtered off. The amine hydrochloride was removed by washing the solution with cold water (300 ml.), and the *ester* recrystallised from chloroform and light petroleum (b. p. 60—80°); yield 44%, m. p. 64° (Found: C, 29·6; H, 5·0; S, 26·0. $C_6H_{12}O_6S_2$ requires C, 29·5; H, 4·9; S, 26·2%).

trans-*But-2-ene* 1,4-*dimethanesulphonate.* The diol, prepared by the bromination of butadiene, followed by treatment with sodium acetate in glacial acetic acid, and sodium ethoxide in ethanol, had b. p. 100—102°/2·5 mm. (50%). The *ester* was prepared by the method given above; yield 58%, m. p. 106° (Found: C, 29·6; H, 5·1; S, 26·0%).

Xylene αα′-dimethanesulphonate. Silver methanesulphonate was prepared from freshly precipitated silver oxide and methanesulphonic acid, washed with ether, and dried at 100°. αα′-Dichloroxylene (17·5 g.) was added to a solution of silver methanesulphonate in acetonitrile (200 ml.), and the mixture boiled for 12 hr.[15] The solid was filtered off, and benzene and light petroleum (b. p. 40—60°) added to the solution, to precipitate the *diester.* This was recrystallised several times from a benzene–light petroleum mixture, m. p. 118—120° (83%) (Found: C, 40·4; H, 4·7; S, 21·4. $C_{10}H_{14}O_6S_2$ requires C, 40·8; H, 4·8; S, 21·8%).

Attempted preparation of but-2-enyl methanesulphonate. But-2-en-1-ol (0·5 mole) and trimethylamine (0·5 mole) were treated with methanesulphonyl chloride (0·5 mole) at −5°. Ether was added and the amine hydrochloride filtered off. The ether was removed, to give a clear pale yellow liquid which decomposed violently on attempted distillation (0·1 mm.).

Reaction Products.—Ethanolysis of allyl methanesulphonate. Allyl methanesulphonate (4·2 g.) was boiled in ethanol for 24 hr. Distillation gave 5·3 ml. of liquid, b. p. 68—69°, n_D^{20} 1·3851 (lit.,[16] b. p. 66—67°/743 mm., n_D^{20} 1·3856, for allyl ethyl ether).

Ethanolysis of cis-*but-2-ene* 1,4-*dimethanesulphonate.* The ester (4·04 g.) was boiled overnight in ethanol (100 ml.), and the resulting solution was neutralised with sodium ethoxide and distilled. Removal of the ethanol gave a viscous liquid (*ca.* 6 ml.) which was redistilled under reduced pressure, b. p. 61—63°/10 mm., n_D^{20} 1·4315 (lit.,[17] b. p. 61·7—62·5°/10 mm., n_D^{20} 1·4320, for 1,4-diethoxy-*cis*-but-2-ene).

Reactions of sodium p-*nitrophenoxide.* Allyl methanesulphonate (0·01M) was treated with sodium *p*-nitrophenoxide in (a) ethanol and (b) 50% aqueous acetone. Water was added at the end of the reaction. The precipitate was filtered off, washed with water, and recrystallised from ether, m. p. 35° (lit.,[18] m. p. of allyl *p*-nitrophenyl ether, 36°).

The *cis*- and *trans*-esters gave the *diethers*: 1,4-di-*p*-nitrophenoxy-*cis*-but-2-ene, m. p. 136—138° (Found: C, 58·0; H, 3·7. $C_{16}H_{14}N_2O_6$ requires C, 58·2; H, 3·4%); *trans*-diether, m. p. 128—130° (Found: C, 58·0; H, 3·7%).

Reactions of sodium thiophenoxide. The ester (0·01M) was treated under nitrogen with a solution (0·01M) of sodium thiophenoxide. Reaction was complete within 1 min., and the addition of water gave a white precipitate of *dithiophenoxy* trans-*but-2-ene* (98%) (Found: C, 69·1; H, 5·9; S, 25·2. $C_{16}H_{16}S_2$ requires C, 70·0; H, 5·9; S, 23·6%).

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Estimation of Aldehyde.—(a) *Ultraviolet spectra.* 0·01M-Solutions of *cis*- and *trans*-but-2-ene-1,4-diols in 50% aqueous ethanol are almost transparent between 218 and 360 mμ. Alkaline hydrolysates of the corresponding esters showed a peak at 228 mμ, corresponding to the main peak of but-2-enal. The aldehyde was estimated by hydrolysing a weighed quantity (0·01 mole) of ester in 50% aqueous ethanol containing 0·1N-sodium hydroxide at 60° for 2 hr. The spectrum of the solution was scanned between 210 and 320 mμ using a Unicam S.P. 100, and compared with a reference given by a 50% aqueous ethanol solution of but-2-enal (0·01M) which had been heated at 60° for 1 hr. The spectra of the corresponding esters and glycols were also taken. The spectrum of the hydrolysate of xylene αα′-dimethanesulphonate was followed over the 180—200 mμ range by an Optica CF4 spectrophotometer.

Solutions of the but-2-ene sulphonates were boiled in water for 12—16 hr. and the reaction mixture analysed similarly.

TABLE 3

Ultraviolet analyses of aldehyde formed in the neutral and alkaline hydrolyses of the disulphonates

Reaction	Extinction coefficients Aldehyde	Extinction coefficients Hydrolysate	% Aldehyde
Solvolysis (*cis*)	13,530	9·01	6·73
,, (*trans*)	,,	9·43	7·0
Alkaline (*cis*)	1446	962	66·5
hydrolysis (*trans*)	,,	973	67·0
(xylene ester)	15,950	257	1·6

(b) *Vapour-phase chromatography.* A solution of but-2-enal (0·01M) and *cis*-but-2-ene-1,4-diol (0·01M) in 50% aqueous acetone was analysed by means of a Pye Argon chromatograph using a 100—120 mesh column of Celite with stearic acid–silicone oil liquid phase, at 50°. A solution of *cis*-but-2-ene 1,4-dimethanesulphonate (2·25 g.) in 50% aqueous acetone (50 ml.) containing 2 equiv. of sodium hydroxide was boiled for 2 hr. The mixture was then subjected to a continuous ether extraction for 48 hr., and the concentrated solution analysed by vapour-phase chromatography. Comparison with the reference spectrum shows a product ratio of *ca.* 3 : 1 but-2-enal to 1,4-diol. Similar results were obtained from the *trans*-compound.

(c) *Isolation.* *cis*-But-2-ene 1,4-dimethanesulphonate (4 g.) in dioxan (50 ml.) was added to sodium hydroxide (1·32 g.) in water (50 ml.), and the mixture boiled for 3 hr. Distillation gave 50 ml. of azeotrope (b. p. 86—88°) of but-2-enal, dioxan, and water. Double-bond analysis gave 51% of but-2-enal [it is reasonable to assume that the 1,4-diol (b. p. 320°) is absent]. The azeotrope (10 ml.), treated with hydroxylamine hydrochloride in aqueous sodium carbonate (5 ml.), gave but-2-enal oxime, m. p. 119—121° (lit., 120—122°).

Kinetic Measurements.—The rates of hydrolysis were measured by standard procedures described elsewhere,[19] and the rate constants calculated from the appropriate first- and second-order equations. The rate of reaction of the esters with sodium *p*-nitrophenoxide was also determined acidimetrically, using potentiometric titration. The rate constants for the difunctional esters were determined from the initial part of the reaction only.

The reaction with sodium thiophenoxide was followed by the change in ultraviolet absorption at 500 mμ. A 10^{-3}M-solution of sodium thiophenoxide and the ester (10^{-3}M) in 50% aqueous ethanol was placed in a cell maintained at 1° ± 0·2°. The following rate constants were obtained: allyl methanesulphonate, $k_2 = 244 \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$; *cis*-but-2-ene dimethanesulphonate, $k_2 = 1294 \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$.

TABLE 4

Rate constants for the hydrolysis of methanesulphonate esters in 50% aqueous acetone at 35°

10^2[Ester] (M)	10^2[NaOH] (M)	10^5k_1 (sec.$^{-1}$)	10^2[Ester] (M)	10^2[NaOH] (M)	10^5k_1 (sec.$^{-1}$)
Allyl methanesulphonate			cis-*But-2-ene* (1,4-*dimethanesulphonate*		
1·04	—	7·2	0·57	—	19·2
0·87	—	7·2	0·45	—	20·3
1·23	1·96	10·3	0·49	1·97	40·3
1·41	2·00	10·4	0·48	1·98	40·2
Xylene αα′-dimethanesulphonate			trans-*But-2-ene* 1,4-*dimethanesulphonate*		
0·50	—	22·4	0·51	—	104
0·65	—	22·5	1·84	—	105
0·51	1·97	44·2	0·21	—	105
0·49	1·97	44·7	0·51	1·92	125
			0·50	1·92	126

TABLE 5

Rate constants for the reactions of sulphonate esters with sodium *p*-nitrophenoxide (PNP)

Solvent	10^2[Ester] (M)	10^2[PNP] (M)	10^5k_1 (sec.$^{-1}$)	10^5k_2 (l. mole^{-1} sec.$^{-1}$)
	Allyl methanesulphonate			
50% aq. acetone...	1·28	1·96	9·91	136·7
,, ,,	0·92	1·96	10·01	
100% ethanol......	1·40	—	1·11	28·7
	1·40	2·46	1·82	
	cis-*But-2-ene* 1,4-*dimethanesulphonate*			
50% aq. acetone...	0·50	1·98	24·0	269
100% ethanol......	0·60	—	2·56	253
	0·86	2·48	8·9	

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QUEEN MARY COLLEGE, MILE END ROAD, LONDON E.1.
[Present addresses (R. F. H.):
CYANAMID EUROPEAN RESEARCH INSTITUTE,
91 ROUTE DE LA CAPITE, COLOGNY-GENEVA,
SWITZERLAND.
(R. J. W.) CHEMICAL DEFENCE EXPERIMENTAL ESTABLISHMENT
PORTON DOWN,
WILTSHIRE.]

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