S_N2' Catalysis and Sulphene Formation

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Summary Ethenesulphonyl chloride reacts with a mixture of a tertiary amine and an alcohol by S_N2' attack of the amine to form the positively charged sulphene which then gives a mixture of the ethenesulphonate and 2-trialkylammonioethanesulphonate esters.

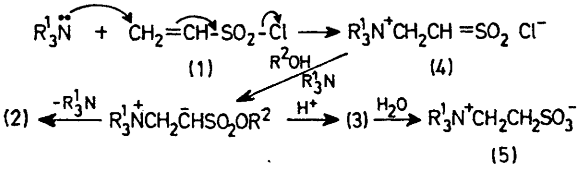
THE formation of alkyl ethenesulphonates (**2**) by the reaction of ethenesulphonyl chloride (**1**) with alcohols in the presence of a tertiary amine is apparently unreported, even though compounds (**2**) are made under similar conditions from 2-chloroethanesulphonyl chloride,[1] which is also known to give (**1**) readily with 2,6-lutidine.[2] A recent report,[3] in fact, claims 70—80% yields of the betaine ($Py^+CH_2CH_2SO_3^-$) from (**1**) and pyridine (Py) in methanol or ethanol. We report on our work on the products and the mechanism of the reaction of (**1**) with tertiary amines and alcohols. The reaction (in CH_2Cl_2 at 25 °C, for example) was found to occur very rapidly to give a mixture of esters (**2**) and (**3**, X = Cl) in *ca.* 60 and 40% yields, respectively [reaction (1)].

$$\underset{(\mathbf{1})}{CH_2{=}CHSO_2Cl} \xrightarrow[R^2OH]{R^1_3N} \underset{(\mathbf{2})}{CH_2{=}CH{-}SO_2OR^2} + \underset{(\mathbf{3})}{R^1_3N^+CH_2CH_2SO_2OR^2X^-} \qquad (1)$$

The neutral esters (**2**) are readily characterized but the presence of the ammonio esters (**3**) in the product was deduced (a) by formation of betaines (**5**) on hydrolysis, and (b) from the observation of characteristic n.m.r. peaks [*e.g.*, at δ 5·5 and 4·3 for (**3**, $R^1_3N^+ = Py^+$, $R^2 = Pr^i$, X = Cl)] as well as those appropriate to the alkyl group [in addition to those due to (**2**)]. The origin of these peaks was confirmed by the following synthesis. Reaction of (**2**, $R^2 = Pr^i$) [or the mixture of (**2**) and (**3**)] with dimethylamine gave $Me_2NCH_2CH_2SO_2OPr^i$ which on mixing with an equivalent amount of methyl fluorosulphonate[4] gave (**3**, R^2 = Me, R^2 = Pr^i, X = FSO_3), the n.m.r. spectrum of which was identical to that ascribed to (**3**, R^1 = Me, R^2 = Pr^i, X = Cl) in the product from (**1**).

Shaking with aqueous Na_2CO_3 readily converts (**3**) into (**2**), thereby enabling an alcohol to be converted into its ethenesulphonate ester by this route in excellent (*ca.* 90%) yield. The ester (**3**, R^1 = Me, R^2 = Pr^i, X = FSO_3) is hydrolysed to (**5**, R = Me) at *ca.* 40 times the rate of hydrolysis of isopropyl mesylate. Primary esters (**3**) are not as readily hydrolysed but react easily at room temperature with aqueous solutions of non-basic nucleophiles (*e.g.*, NaN_3, NaSCN, *etc.*) to give the corresponding alkyl derivatives in good yield. The ease of preparation of these ammonio esters (**3**) and their reactivity and amphiphilicity suggest potentially important applications which are now being investigated.

The ester (**2**, R^2 = Pr^i) obtained from reaction of (**1**) with Pr^iOD and either pyridine or triethylamine contained only small amounts of deuterium, thereby precluding significant intervention of the cumulated sulphene, $CH_2{=}C{=}SO_2$. Reaction of (**1**) with propan-2-ol and pyridine proceeds *ca.* 10^4 times faster than with 2,6-lutidine and about 500 times faster than that of prop-1-enesulphonyl chloride (Me-CH=$CHSO_2Cl$) with pyridine and propan-2-ol† (all at −70 °C in CH_2Cl_2). The same trend was also found in reactions of the same substrates catalysed by *NN*-dimethyl- and *NN*-diethyl-anilines. The reaction of either pyridine or 2,6-lutidine with (**1**) gave about the same proportion of (**2**) and the appropriate ammonio ester (**3**). We regard these observations as pointing strongly to a common rate-determining S_N2' attack‡ of the base in the formation of both (**2**) and (**3**), as in the Scheme; part of this sequence [(**1**) → (**4**) → (**3**) → (**5**)] is similar to that put forward to account for formation of (**5**) on reaction of (**1**) with tertiary amines in acetic acid.[3]



SCHEME

Nucleophilic catalysis *via* an S_N2' reaction has not to our knowledge been specifically proposed before, though it seems likely that the reaction will be found in other systems as well. A keten analogous to (**4**) has been implicated in the reaction of acryloyl chloride with alcohols and tertiary amines. Neither the mechanism of formation of this keten nor its involvement in reactions in which the base is lost (and hence functions as a true catalyst) has been explored, however. Our observations with (**1**) obviously raise the possibility of S_N2' catalysis in acyl transfer reactions as well.

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† The neutral product from this reaction was exclusively isopropyl prop-1-enesulphonate. Truce and Campbell (ref. 5) report that triethylamine and methanol give a mixture of the prop-1-ene- and prop-2-ene-sulphonates, the latter formed presumably from vinylsulphene ($CH_2{=}CHCH{=}SO_2$) and the former, in the light of the present study, by the S_N2' route and not by nucleophilic attack at sulphur as they previously suggested.

‡ 'S_N2'' is used here simply to indicate a bimolecular nucleophilic displacement with accompanying rearrangement of a double bond; no implication of the detailed mechanism is intended. (For a discussion of the mechanism of the S_N2' reaction, see F. G. Bordwell and T. G. Mecca, *J. Amer. Chem. Soc.*, 1972, **94**, 5825, and references cited therein.) An alternative term for the phenomenon described here might be 'vinylogous nucleophilic catalysis.'

[1] For a review see H. Distler, *Angew. Chem. Internat. Edn.*, 1965, **4**, 300; W. F. Whitmore and E. F. Landau, *J. Amer. Chem. Soc.*, 1946, **68**, 1797.
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[5] W. E. Truce and R. W. Campbell, *J. Amer. Chem. Soc.*, 1966, **88**, 3599.
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