Trimethylammoniosulphate Esters

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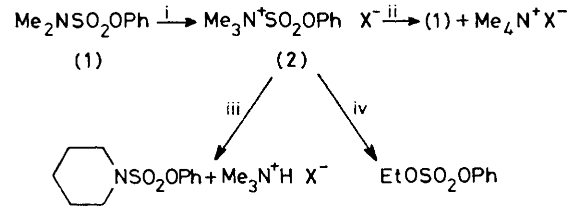
Summary *NN*-Dimethylsulphamate esters react with methyl fluorosulphate to give trimethylammoniosulphate esters; the phenyl ester (**2**) is readily characterized, but alkyl esters immediately give fluorosulphate esters or elimination products, showing that trimethylammoniosulphate is a very powerful leaving group.

BY analogy with fluorosulphates and trifluoromethanesulphonates ('triflates') it would be expected that the trialkylammoniosulphate ($R_3N^+SO_3^-$) function† would be a strong leaving group. We now provide evidence that this is indeed so and describe the first characterized compound containing this grouping.

Phenyl *NN*-dimethylsulphamate[1] (**1**) reacts with neat methyl fluorosulphate to give (**2**; X = FSO_3^-), m.p. 122—125 °C, in 88% yield. Proof of structure was obtained from (a) elemental analysis, (b) spectra [δ($CDCl_3$) 3·70 (s, 9H) and 7·56 (s, 5H); ν_{max} (Nujol) 1443 vs and 1282 vs cm^{-1}], and (c) the reactions shown in Scheme 1.



SCHEME 1. i, $MeOSO_2F$, 50 °C, 18 h; ii, Me_3N; iii, piperidine; iv, EtOH.

Methylation of alkyl *NN*-dimethylsulphamates (**3**) (Scheme 2) evidently yields trimethylammoniosulphate salts but these readily undergo further reaction to form the sulphobetaine (**4**), which precipitates from the medium, and products of substitution or elimination, sometimes with rearrangement. When R is a simple, straight-chain alkyl group, methyl fluorosulphate converts (**3**) into the

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† Trialkylammoniosulphates may be regarded as the first members of the '[*n*]-betylate' series, $R_3N^+[CH_2]_nSO_2OR$, in which $n = 0$. Previous representatives of the series are the '[2]-' and '[3]-betylates' (J. F. King and S. M. Loosmore, *J. C. S. Chem. Comm.*, 1976, 1011; J. F. King, S. M. Loosmore, and J. D. Lock, Abstracts, 2nd Joint CIC–ACS Meeting, Montreal, May—June, 1977, ORGN 15; see also P. Blumbergs, A. B. Ash, F. A. Daniher, C. L. Stevens, H. O. Michel, B. E. Hackley, Jr., and J. Epstein, *J. Org. Chem.*, 1969, **34**, 4065).

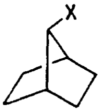
fluorosulphate (**5**); as may be seen from the isolated yields shown in Scheme 2, this procedure is a convenient route to the simple primary alkyl fluorosulphates.[2] With R = isobutyl or neopentyl, the only identified products in addition to (**4**) were, respectively, isobutene and isopentene. Similarly, reaction of methyl triflate, instead of fluorosulphate, with $Ph[CH_2]_3OSO_2NMe_2$ gave the triflate ester, $Ph[CH_2]_3OSO_2CF_3$.

$$\underset{(\mathbf{3})}{Me_2NSO_2OR} \xrightarrow{i} [Me_3N^+SO_2OR\ FSO_3^-] \rightarrow \underset{(\mathbf{4})}{Me_3N^+SO_3^-} + \underset{(\mathbf{5})}{ROSO_2F}$$

SCHEME 2. i, neat $MeOSO_2F$. Yield: R = Pr (45%), Bu (68%), $Ph[CH_2]_3$ (52%), CF_3CH_2 (36%).

Ammoniosulphate esters have been previously proposed[3] as intermediates in the reaction of alkyl chlorosulphates with tertiary amines. In agreement with this suggestion we have found that the reaction of trimethylamine and phenyl chlorosulphate, $PhOSO_2Cl$, (**6**) gives (**1**) and $Me_4N^+Cl^-$, as expected, assuming the initially formed trimethylammoniosulphate (**2**; X = Cl^-) reacts with more Me_3N, as shown in Scheme 1. In addition, the n.m.r. spectrum of the reaction mixture obtained from treating (**6**) with Me_3N and $AgClO_4$ showed the characteristic peak at δ 3·7 corresponding to *ca.* 5—10% of (**2**).

Reaction of 7-norbornyl *NN*-dimethylsulphamate (**7a**) in neat methyl fluorosulphate at 25 °C for 24 h gave the fluorosulphate (**7b**) in 65% yield, but in the presence of 2 equiv. of benzene gave a mixture of 7-phenylnorbornane (**7c**) (50%) and (**7b**) (15%). Control experiments showed that (**7c**) did not arise from (**7b**). We conclude that (**7a**) is converted into (**7d**) which then ionizes to form (**4**) and the 7-norbornyl cation, which may then yield (**7b**) or (**7c**).



(7)

a; X = OSO_2NMe_2
b; X = OSO_2F
c; X = Ph
d; X = $OSO_2N^+Me_3$
e; X = OSO_2CF_3
f; X = $OSO_2C_6H_4Me$-*p*

In view of the generally slow rate of formation of the 7-norbornyl cation in solvolyses,‡ these results suggest that the trimethylammoniosulphate group is one of the most powerful leaving groups of which a derivative has been isolated and characterized. We have as yet, however, seen no sign of the formation of phenyl cations from (**2**), and since phenyl cations are believed to be formed from benzenediazonium salts,[5] the latter presumably heterolyse more readily than trimethylammoniosulphates.

This work was supported by the National Research Council of Canada.

(*Received*, *5th October* 1977; *Com.* 1039.)

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‡ The estimated (T. M. Su, W. F. Sliwinski, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1969, **91**, 5386; S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, 1955, **77**, 4183) rate constants for acetolysis of (**7e**) and (**7f**) at 25 °C are, respectively, $1{\cdot}37 \times 10^{-9}$ and $6{\cdot}36 \times 10^{-15}\ s^{-1}$.

[1] The *NN*-dimethylsulphamate esters in this study were prepared essentially by the method of W. W. Binkley and E. F. Degering, *J. Amer. Chem. Soc.*, 1939, **61**, 3250.

[2] For other routes, see G. A. Olah, J. Nishimura, and Y. K. Mo, *Synthesis*, 1973, 661.

[3] J. Charalambous, M. J. Frazer, and W. Gerrard, *J. Chem. Soc.*, 1964, 5480.

[4] This result is similar to that reported in a recent exhaustive study with aryl triflates and related species: L. R. Subramanian, M. Hanack, L. W. K. Chang, M. A. Imhoff, P. v. R. Schleyer, F. Effenberger, W. Kurtz, P. J. Stang, and T. E. Dueber, *J. Org. Chem.*, 1976, **41**, 4099.

[5] C. G. Swain, J. E. Sheats, and K. G. Harbison, *J. Amer. Chem. Soc.*, 1975, **97**, 783, 796; C. G. Swain, J. E. Sheats, D. G. Gorenstein, and K. G. Harbison, *ibid.*, p. 791; R. G. Bergstrom, R. G. M. Landells, G. H. Wahl, Jr., and H. Zollinger, *ibid.*, 1976, **98**, 3301.