Formation of Triaminosulphonium and Alkoxydiaminosulphonium Ions

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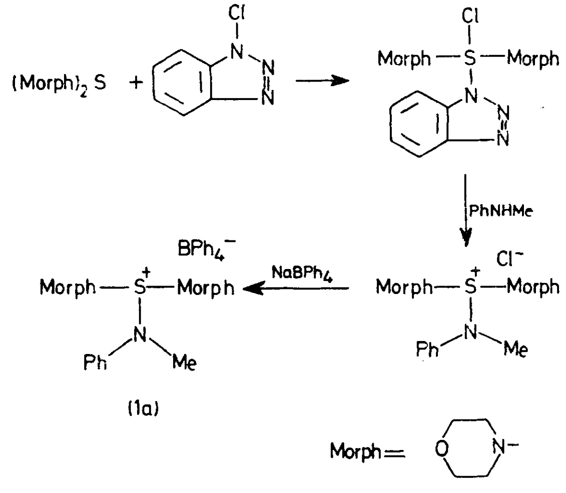
Summary Triaminosulphonium and alkoxydiaminosulphonium ions have been prepared; the former are stable towards nucleophiles whereas the latter are readily hydrolysed by the moisture in air.

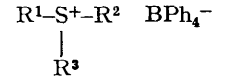
ALTHOUGH hetero-substituted sulphonium ions are of interest and the disubstituted ions $RS^+(OMe)_2$[1] and $R^1S^+(NR^2{}_2)_2$[2] have been reported, tri-hetero-substituted sulphonium ions have not yet been reported. We now describe their synthesis.

When a solution of 1-chlorobenzotriazole (1 equiv.) in CH_2Cl_2 was added to a solution of dimorpholino sulphide (1 equiv.) in CH_2Cl_2 at −70 °C, the solution turned pale yellow, indicating the formation of an adduct. Addition of a solution of *N*-methylaniline (1 equiv.) in CH_2Cl_2 at − 70 °C discharged the colour immediately. The solution was then warmed to room temperature and a solution of $NaBPh_4$ in acetone was added followed by n-hexane; a mixture of NaCl and the triaminosulphonium tetraphenylborate (**1a**) was precipitated. The salt (**1a**) was dissolved in acetone, and reprecipitated with n-hexane. The triaminosulphonium salts (**1b**—**e**) were prepared similarly.



In the case of (**1b**), *N*-chloromorpholine could be used instead of 1-chlorobenzotriazole; simple mixing of R_2N-S-NR_2 and R_2N-Cl yielded $(R_2N)_3S^+Cl^-$, which was converted into (**1b**) by $NaBPh_4$.

After reprecipitation from acetone, compounds (**1a**—**e**) all gave satisfactory C, H, and N analyses, and their ^1H and ^{13}C n.m.r. and ir. spectra are consistent with the triaminosulphonium ion structure.



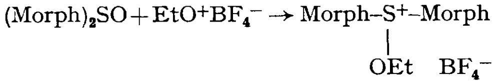
$$\underset{\displaystyle R^3}{R^1\text{–}\overset{|}{S}{}^+\text{–}R^2}\quad BPh_4^-$$

(**1**)

a; $R^1 = R^2 =$ Morph; $R^3 =$ PhMeN
b; $R^1 = R^2 = R^3 =$ Morph
c; $R^1 = R^2 =$ Morph; $R^3 =$ piperidino
d; $R^1 = R^2 = Et_2N$; $R^3 =$ piperidino
e; $R^1 = R^2 = R^3 =$ piperidino

These triaminosulphonium ions are unique in that they are very stable towards nucleophiles. Even when they were left with Ph_3P in $(CD_3)CO$ for 3 days or when they were refluxed in MeOH for several hours, no change was observed in their n.m.r. spectra. Mixing with Me_2S or Et_2NH also caused no change. The dialkoxysulphonium ions $R^1S^+(OR^2)_2$ react instantaneously with Me_2S.[1]

A solution of dimorpholino sulphoxide (0·04 mol) in CH_2Cl_2 and triethyloxonium tetrafluoroborate (0·042 mol) was refluxed for 2 h, and then ether was added. The brown-black oil which was formed was recrystallized from MeOH in the dry. Pale yellow crystals of the salt (**2**) were obtained (24·6%). Its ^1H and ^{13}C n.m.r. spectra were consistent with this structure, but its C, H, and N analyses were somewhat removed from the theoretical values because of its extreme moisture sensitivity. This decomposition is probably catalysed by the HBF_4 formed in the hydrolysis. The salt (**2**) must be synthesized in a well dried solvent in a dry box. Attempts to exchange its anion with BPh_4^- resulted in its hydrolysis.



$$(Morph)_2SO + EtO^+BF_4^- \rightarrow \text{Morph–}\underset{\displaystyle OEt}{\overset{}{S}}{}^+\text{–Morph}\quad BF_4^-$$

(**2**)

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[1] H. Minato, K. Yamaguchi, and M. Kobayashi, *Chemistry Letters*, 1975, 307.

[2] J. L. Richards and D. S. Tarbell, *J. Org. Chem.*, 1970, **35**, 2079.