Arylthiotrialkylammonium Ions and Chlorides

By JAN H. WEVERS and HENDRIK KLOOSTERZIEL*

(*Gorlaeus Laboratories, The University of Leiden, P.O. Box 75, The Netherlands*)

Summary Arylthiotrialkylammonium ions (**2**) are formed in solution from arylarenethiolsulphonates (**1**) and trialkylamines, and as solid chlorides from arylsulphenyl chlorides and trialkylamines.

WHEN a tertiary amine is added to a solution of an arylarenethiolsulphonate (**1**) in acetonitrile, dimethylformamide (DMF), dimethylsulphoxide (DMSO) or ethanol the u.v. extinction changes and the electrical conductivity increases strongly as a function of time. By analogy with the reaction of (**1**) with secondary amines, which yields sulphenamides,[1] nucleophilic substitution at the bivalent sulphur atom with formation of the novel arylthiotrialkylammonium ions (**2**) seems indicated. The reaction is an equilibrium. If excess NEt_3 is added to a solution of (**1**) in DMSO and then when no change is observed, NEt_3 is removed by distilling in vacuo the extinction and conductivity revert to the values of the original solution.

$$\underset{(\mathbf{1})}{Ar^1SO_2Ar^2} + NR_3 \rightleftharpoons \underset{(\mathbf{2})}{Ar^1S\overset{+}{N}R_3} + Ar^2SO_2^- \qquad (1)$$

$Ar^1 = Ph, C_6H_4Me, 2,4,6\text{-}(MeO)_3C_6H_2$
$Ar^2 = Ph, 2,3,4\text{-}Cl_3C_6H_2, 2,4,6\text{-}Cl_3C_6H_2, 2\text{-}NO_2 4\text{-}ClC_6H_3$

The presence of the ion (**2**) is indicated by the ^1H n.m.r.

spectrum in deuteriated DMF which shows additional resonances due to methyl and methylene groups.

This reaction (equation 1) explains the beneficial effect of NEt_3 on the formation of sulphenate esters from (**1**) and alcohols.[2]† (**1**) precipitates out on addition of water to a solution of (**1**) in DMF or DMSO. If a trialkylamine is added first and then water, aryldisulphide, a known product of decomposition of sulphenic acid precipitates.

The reaction of arylsulphenyl chlorides with NEt_3 gave the ions (**2**) as salts. Slow addition of NEt_3 to a solution of the chloride in dry ether at −10°C gives a white precipitate instantaneously. Using a slight excess of NEt_3, filtration (under N_2) and drying (in vacuo, 20°C) the arylthiotriethylammonium chlorides are formed in quantitative yields (equation 2).‡

$$\mathrm{ArSCl} + \mathrm{NEt_3} \rightarrow \mathrm{ArS\overset{+}{N}Et_3Cl^-} \qquad (2)$$

The salts are hygroscopic (though less than the corresponding sulphenyl chlorides). On heating decomposition occurs at *ca.* 100 °C. ^1H n.m.r. spectra ($CDCl_3$) of the salts show δ 1·41 (t, Me) and 3·12 (q, CH_2) (at 0·3 and 0·5 p.p.m. lower field than NEt_3). The solutions in $CDCl_3$ do not, unlike solutions in DMF, show any reversal of equation 2. Addition of water to solutions in DMF leads to rapid precipitation of the aryldisulphide. Addition of an excess of Ar^2SO_2Na, stirring for one hour, distilling off the NEt_3 in vacuo and addition of water yields (**1**).

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† Numerical values for the rate constants of the reaction (equation 1) (to be published) prove that (**2**) plays no role in the reaction of bisphenylsulphonylmethane and (**1**) in the presence of NEt_3, *cf.* J. K. Bosscher and H. Kloosterziel, *Rec. Trav. Chim.*, 1970, **89**, 402, and ref. 2.

‡ Satisfactory elemental analyses were obtained.

[1] E. Ciuffarin, L. Senatore, and G. Giovannini, *J.C.S. Perkin II*, 1972, 2314.
[2] B. G. Boldyrev, L. C. Vid, and S. A. Kolesnikova, *J. Org. Chem.*, (*U.S.S.R.*), 1974, **10**, 405.