

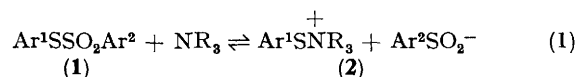
Arylthiotrialkylammonium Ions and Chlorides

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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 arylthiotrialkyl-



Ar¹ = Ph, C₆H₄Me, 2,4,6-(MeO)₃C₆H₂

Ar² = Ph, 2,3,4-Cl₃C₆H₂, 2,4,6-Cl₃C₆H₂, 2-NO₂-4-ClC₆H₃

ammonium ions (2) seems indicated. The reaction is an equilibrium. If excess NET₃ is added to a solution of (1) in DMSO and then when no change is observed, NET₃ is removed by distilling in vacuo the extinction and conductivity revert to the values of the original solution.

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).[‡]



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 $\text{Ar}^2\text{SO}_2\text{Na}$, 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.