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DIARYL SULPHONES : A SYNTHESIS FROM ARYLTHALLIUMS

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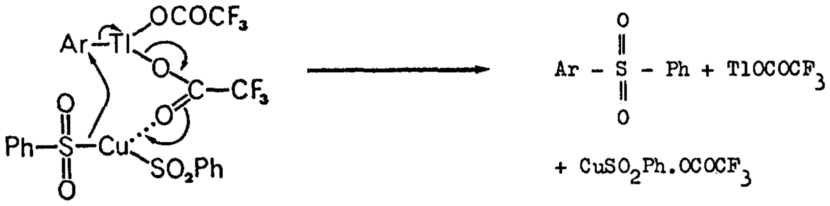
2,4-dimethyl-, 2,4,6-trimethyl- and 4-chloro- phenylthallium bis (trifluoracetate) separately react with cupric benzenesulphinate to give unsymmetrical sulphones. An explanation for the requirement of Cu^{2+} in the reactions is given.

Most synthetic routes for the direct preparation of unsymmetrical diaryl sulphones, i.e. not those requiring the oxidation of the corresponding sulphide or sulphoxide, are based upon reactions of derivatives of aryl sulphonic acids. These may be reacted with aromatic compounds e.g. in the presence of trifluoroacetic anhydride,[1] or else converted to the corresponding halides and, particularly when electron releasing substituents are present, made to undergo Friedel-Crafts type reactions.[2] Alternatively these halides, including the fluoride[3] will react with numerous aromatic organometallic compounds[4-7] to give diaryl sulphones. Nucleophilic substitutions, using arylsulphinate salts with suitably activated arylhalides provide a further but not very widely applicable route.[8]

Following the successful preparation of arylthallium compounds by McKillop[9] ten years ago, there has been considerable interest in methods of transforming arylthallium bis (trifluoroacetates) into a range of monoaryl derivatives. The variety of the reactions with various nucleophiles leading to these compounds has been reviewed.[10] We report here some preliminary results for the preparation of some unsymmetrical diaryl sulphones.

The direct interaction between arylthalliums, e.g. 2,4-dimethylphenylthallium bis (trifluoroacetate) and sodium benzenesulphinate proved to be unsuccessful. Since good yields have been reported for the formation of arylcyanates[11] and selenocyanates[12] using the appropriate copper salts, it was thought worthwhile examining the effect of using the corresponding copper salt of benzenesulphinic acid. Aqueous solutions containing sodium benzenesulphinate and cupric sulphate (4:1) were reacted with arylthalliums dissolved in dioxan, in the absence of light, by gentle heating for 24 hr. The following sulphones were so prepared: 2,4-dimethyl-, 2,4,6-trimethyl- and 4-chloro- diphenylsulphone. Assuming conversions of m-xylene, mesitylene and chlorobenzene to the intermediate arylthalliums to be better than 80%,[13] then we have found that the subsequent sulphinatodethallation reactions occur to the extent of c.a. 60%. No attempt has so far been made to maximise these yields, particularly by changing the solvent from aqueous dioxan which permitted considerable ammounts of material to remain suspended throughout the procedure.

The important part played by copper in this sulphinatodethallation reaction is thought to be its co-ordination with one of the trifluoroacetate groups of the arylthallium bis (trifluoroacetate) thereby aiding the nucleophilic displacement of the thallium by the sulphinate anion.



The mild conditions used in this sulphonylation provide some advantages over the more usual preparative methods for unsymmetrical sulphones, and a further advantage of the intermediacy of an arylthallium is that thallation does not always occur at the positions most activated towards electrophilic attack e.g. thallation at position 2 in benzoate esters.[10] Substituted benzene sulphinates are readily prepared by the reduction of the corresponding sulphonyl chlorides.[14]

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