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TRIDEUTEROMETHYLATION IN DIMETHYL SULPHOXIDE

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Dimethyl sulphoxide is a very efficient solvent for the methylation of humic acids with dimethyl sulphate and alkali(1). We have found dimethyl sulphoxide is also an effective medium for the trideuteromethylation of sterically hindered(2) and strongly hydrogen-bonded(3) phenols which cannot be deuteromethylated by van der Merwe's method(4) using diazomethane and D_2O in dioxane.

Phenol (1 millimole), then CD_3I (2 mmole), were added to a suspension of finely powdered sodium hydroxide (4 mmole) in CH_3SOCH_3 (5 ml). The reaction mixture was stirred or shaken at room temperature for 30 minutes, diluted with water (5 ml) and extracted three times with CCl_4 (3 ml). The combined extracts were washed twice with water (5 ml) and dried. Removal of the solvent gave the trideuteromethylated phenol suitable for most spectrometric work. The product contained less than one percent each of the starting material and of CH_3 ether as shown by n.m.r. and mass spectrometry.

In this way, 2,6-di-tert-butyl-4-methylphenol and 2-hydroxybenzalaniline were trideuteromethylated in 90% yield. Acetophenone oxime gave the O-CD_3 ether free of N-CD_3 ether in 60% yield.

Dimethyl sulphoxide is a useful solvent for alkylation in general. The method described has been used successfully with one to ten millimoles of phenols, thiophenols, anthrols and oximes using methyl iodide and sulphate, ethyl iodide and sulphate and butyl iodide. Transmethylation from the solvent was never detected. However, since atmospheric oxygen, dimethyl sulphoxide and sodium hydroxide constitute a strong oxidising system(5), sensitive compounds should be handled under nitrogen.

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