# Activation of Dimethyl Sulphoxide by Crown Ethers

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Crown ethers activate dimethyl sulphoxide in reactions with aromatic amines to produce the coloured quinoneimmonium dyes.

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The reaction of dimethyl sulphoxide (DMSO) with alcohols,[1,2] phenols,[3] carbonyl compounds,[4] and amines[4] is a subject of current interest. Several methods of activating DMSO have been investigated. Recently, t-butyl bromide was found to be a particularly effective activator in reactions with nucleophiles under mild or weakly basic conditions.[5] In these reactions, the DMSO undergoes a Pummerer-like reaction.[6]

Recently we reported a new method of synthesis of coloured quinoneimmonium dyes based on the reaction of DMSO with *N*,*N*-dimethylaniline in the presence of a Lewis acid catalyst.[7]

We report here that the reaction of DMSO with aromatic amines can be catalysed by crown ethers. Thus, treatment of the *N*-phenylaza 15-crown-5, *N*-phenyl-13-aza-1,4,7,10-tetraoxacyclopentadecane, with DMSO leads to the formation of a blue compound similar to that obtained from the reaction of *N*,*N*-dimethylaniline with DMSO in the presence of Lewis acid.[8] A typical procedure for the reaction is as follows: A mixture of the *N*-phenylaza 15-crown-5 (1.00 g, 3.4 mmol) and anhydrous DMSO (20 ml) was refluxed for 2 h. During this time the reaction mixture turned deep blue. The DMSO was evaporated under vacuum and the residual gum-like product was washed several times with diethyl ether. The crude product was dissolved in chloroform and poured on a silica gel chromatographic column. The product was eluted with a 3 : 1

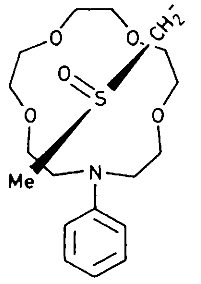

Figure 1

chloroform–ethanol mixture and precipitated with $KPF_6$ solution to give a blue crystalline product 1.56 g (35%), i.r.(KBr disc) 1600, 1340, and 1130 $cm^{-1}$; u.v.–visible (MeOH, $\lambda_{max.}$) 600, 580, and 264 nm; $^1H$ n.m.r. δ 3.7 (2-, 4-OH) and 6.6—7.3 (m, 9H); high resolution mass spectrum, *m/z* 602.3570 ($M^+ + 1$, calcd. for $C_{33}H_{49}N_2O_8$, 602.7666), 308.1879 (calcd. for $C_{17}H_{26}NO_4$, 308.3974), and 295.1767 (calcd. for $C_{16}H_{25}NO_4$, 295.1767).

In three separate trials, the reaction of DMSO with *N,N*-dimethylaniline was carried out in the presence of 18-crown-6, benzo-15-crown-5, and 15-crown-5 respectively. Surprisingly, a blue colour was obtained when the mixture was heated at *ca.* 150 °C for 30 min. After cooling, the blue compound was extracted with chloroform, which upon evaporation gave a gum-like product. This was then dissolved in methanol and a crystalline product precipitated on addition of $KPF_6$. The crystalline product was characterized as the quinone immonium salt from the following data: i.r. (KBr disc) 1580, 1350, and 2860 $cm^{-1}$; u.v.–visible (MeOH) 590, 310, and 264 nm; n.m.r. ($CDCl_3$) δ 2.91 (s, 12H), 3.81 (s, H), and 6.82—7.00 (m. 8H); mass *m/z* 253, 134, and 118. These results are in complete agreement with those reported previously.[7]

The above results clearly indicate that crown ethers can play the role of Lewis acids in the reactions of DMSO with aromatic amines. In the light of the previously published mechanism,[8] which requires the presence of nucleophilic species of the type $Me{-}S(O)(\cdots X){-}CH_2^-$ (where X is a Lewis acid), it is most likely that the crown ether ring complexes with DMSO through the sulphur atom, which in the presence of amine as a base produces nucleophilic species of the type shown in Figure 1. This nucleophile then reacts with the aromatic amine to produce products *via* the recently published mechanism.[8]

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