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THE STABILITY OF PHENYLISOCYANATE IN DIMETHYLSULPHOXIDE SOLUTION

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Reactive isocyanates such as sulphonyl or acyl isocyanates undergo reaction with dimethylsulphoxide (DMSO) to yield the dimethylsulphilimine and carbon dioxide.[1,2,3] As a result of these facile reactions, the avoidance of DMSO as a solvent for isocyanate reactions has been suggested.[4] Moreover, a recent claim has been made that phenylisocyanate (PhNCO) is thermolysed under modest (3 hr at 80°) conditions in DMSO *via* a nitrenoid intermediate to yield aniline and *sym*- diphenyl urea.[5]

We have successfully used DMSO as a solvent for isocyanate reactions and have found it particularly useful as a solvent for the titrimetric estimation of NCO groups in compounds not soluble in the more usual solvents (dioxan or tetrahydrofuran) for such estimations.[6] Provided the DMSO is rigorously dried, no complications arise with isocyanates of moderate reactivity, and the rates of reactions with nucleophilic reagents are greatly increased over those in other solvents. Contrary to recently published findings we have also found PhNCO to be completely stable in DMSO for at least 16 hrs at 80° and 4 hrs at 100°.

The DMSO used for our reactions was dried by allowing a solution of 4,4′-diisocyanatodiphenyl methane in DMSO to stand for 48 hr. at 30°. It was confirmed that the solution contained isocyanate groups after this treatment by observing the i.r. absorption bands at 4.4μ[7] and further purification was then effected by distillation.

A solution of PhNCO in DMSO (10% v/v) was prepared and sealed under high vacuum in glass tubes, which had previously been dried under high vacuum. The tubes were immersed in oil baths at 80° for up to 16 hrs. and 100° for up to 4 hrs. The residual isocyanate content was determined by i.r. spectroscopy[7] and found in all cases to be identical to that of the control solution, which was not heated.

We further found that the addition of a small amount of water (c. 1% v/v) to a solution of PhNCO in DMSO at 25° resulted in the instantaneous loss of isocyanate absorptions. This solution was then examined by thin layer chromatography which showed the presence of aniline and sym-diphenyl urea.

It is suggested that the findings of previous workers[5] are consistent with their DMSO containing water and the products they observed are those expected from the hydrolysis of isocyanates.[8]

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