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REDUCTION OF NITRILE OXIDES WITH ISONITRILES

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Nitrile oxides are known to be easily reduced to nitriles with zinc and acetic acid[1)] or with stannous chloride and acids[2)]; still more convenient seems the recently discovered reduction with phosphines or phosphites[3-5)].

We now wish to report that isonitriles react easily with benzonitrile oxide to form isocyanates and benzonitrile according to the following equation:

$$C_6H_5CNO + RNC \longrightarrow C_6H_5CN + RNCO$$

This oxygen exchange is not so immediate as in the case of the reaction between benzonitrile oxide and triphenylphosphine or triethylphosphite[3)]: here some unchanged isonitrile was always recovered and some diphenylfuroxan, the product of benzonitrile oxide dimerization, was isolated. Sometimes a small quantity of 3, 5-diphenyl-1, 2, 4-oxadiazole, formed by condensation of benzonitrile oxide with benzonitrile[6)], could also be detected.

When an ethereal solution of benzonitrile oxide[7)] was treated with an equimolecular amount of cyclohexylisonitrile, heat was evolved. After solvent evaporation the residue was distilled fractionally, giving unchanged isonitrile, cyclohexylisocyanate and benzonitrile, whereas in the residue some diphenylfuroxan crystallized. Since the separation of the several reaction products in a pure state resulted rather troublesome and wasteful, identification of benzonitrile as benzoic acid and of isocyanate as symmetrically disubstituted ureas was routinely undertaken.

Following procedure is typical: 6. 8 g of cyclohexylisocyanide were refluxed for 5 hrs. with an ethereal solution of benzonitrile oxide, prepared from 14.9 g of benzohydroxamic chloride[7]. After removal of the solvent, the oily residue was refluxed for 3 hrs. with 150 ml of water. The mixture was extracted thrice with diethyl ether and the insoluble product filtered and washed with chloroform, thus obtaining 4.3 g (62 % yield) of N,N'-dicyclohexylurea. The oily residue from the ethereal extracts was stirred at room temperature for 5 hrs. with HCl 1:9 and again extracted with ether. Neutralization of the acidic solution gave 0.8 g (10 % yield) of N-cyclohexylformamide. The residue obtained from the ethereal extracts after careful removal of the solvent was refluxed for 4 hrs. with 10 % aqueous NaOH: acidification of the alkaline solution gave 3.0 g (43 % yield) of benzoic acid, whereas the neutral fraction (1.4 g) was recognized as a mixture of diphenylfuroxan and 3,5-diphenyl-1,2,4-oxadiazole, separated with the aid of column chromatography.

Analogous results could be achieved on reaction of benzonitrile oxide with the following isocyanides: phenyl-, p.chlorophenyl-, p.bromophenyl-, tert.butyl-isocyanides. Benzoic acid was obtained in 37-56 % and diaryl- (or dialkyl-)ureas $(RNH)_2CO$ in 28-53 % yields.

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