J. inorg. nucl. Chem., 1968, Vol. 30, pp. 668 to 669. Pergamon Press Ltd. Printed in Great Britain

The reactions of tris(dimethylamino)phosphine and tris(dimethylamino)arsine with nitrosobenzene

(Received 21 July 1967)

THE REACTIONS of tris(dimethylamino)phosphine and tris(dimethylamino)arsine with oxygen-containing organic molecules have been the subject of several studies in recent years [1-5]. All the reactions presently known can be classified as either ligand exchange[2] deoxygenation[1], dehydration[3] amination [2-5] or a combination of these. When similar products are formed the tris(dimethylamino) phosphine is usually found to be less reactive than the arsenic analog. Also, a divergence in their chemistry can often be interpreted by the formation of the stable hexamethylphosphoramide, $OP[N(CH_3)_2]_3$, which has no known arsenic analog. Indeed, this is found to be the case for the reactions under study. Hence, tris(dimethylamino)phosphine reacts with two moles of nitrosobenzene to yield the phosphoramide[6], and azoxybenzene.

With the arsenic analog, however, nitrosobenzene gives a new type of reaction, quite vigorous in solution after a short induction period but violent when neat, to give arsenic trioxide, dimethylamine and tetramethylmethylenediamine as the major products. This reaction may, therefore, be considered essentially as the oxidative degradation of the substituent methyl groups.

The highest yield of tetramethylmethylenediamine was obtained with 2 molar equivalents of nitrosobenzene; under these conditions up to 38 per cent[7] of the diamine could be detected by NMR analysis of sealed tube reactions. The yield of dimethylamine was in the order of 26 per cent[7] according to NMR measurement, which together with the yield of diamine accounted for approx 65 per cent of the total arsenical nitrogen. Loss of dimethyl environments and the failure to determine the stoichiometry of the reaction may, in part, be explained by the observation that both the products react vigorously with nitrosobenzene.

The formation of the phosphoramide in the reaction with the phosphorus analog suggests that the first step in the arsenic reaction may be formation of the presumably unstable $OAs[N(CH_3)_2]_3$ which rapidly decomposes. The necessary conversion of a N-methyl group to a diaminomethylene group probably takes place via the formation of N-methyl-imine, $CH_3N=CH_2$, or related intermediates. However, the formation of the diamine implies that species of the type $(>As-)_2N-CH_3$ and $(>As-)_3N$ would probably be present in the precipitated arsenic trioxide. Hydrolysis of this material followed by rapid scan mass spectral analysis of the resulting aqueous solution indicated the presence of ammonia and methylamine as expected if such species were indeed present.

The nitrosobenzene is converted to the usual collection of reduction products, principally azoxybenzene.

EXPERIMENTAL

Reaction of tris(dimethylamino)arsine with nitromethane

A solution of tris(dimethylamino)arsine (10.35 g, 0.05 mole) in 50 ml of ether was added to a solution of nitrosobenzene (10.7 g, 0.1 mole) in 50 ml of ether. After a short period the reaction proceeded quite vigorously (violently in the absence of solvent) with boiling of the solvent and evolution of dimethylamine (identified by mass spectral analysis). After the reaction was complete the deep

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6. The reaction was carried out in dioxane and benzene in an nmr tube. The phosphoramide was identified by its NMR spectrum which was identical to that of an authentic sample in the respective solvents.

7. The yields were calculated as a per cent of total arsenical nitrogen and do not represent the per cent of theoretical yield.

Notes

red reaction mixture was allowed to stand overnight. The arsenic trioxide (identified by X-ray diffraction) which precipitated was collected (4 g, 80 per cent). The solvent was removed from the filtrate and the resulting oil distilled to give 1.8 g (25 per cent)[7] tetramethylmethylenediamine. Its nmr spectrum exhibited singlets at τ 7.20 and τ 7.84[8] in the expected ratio 1:6 (neat, TMS internal standard) bp 36-37° (106 mm), its mol. wt. was 102 (mass spectral analysis) and its i.r. spectrum was identical to that of an authentic sample.

Ether extraction of the residue and chromatographic separation on a neutral Al_2O_3 column yielded 4 g (44 per cent) of azoxybenzene.

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