

DEOXYGENATION OF DIMETHYLANILINE N-OXIDE WITH SODIUM
BROMIDE: A NOVEL PEROXIDE-CATALYSED REDUCTION

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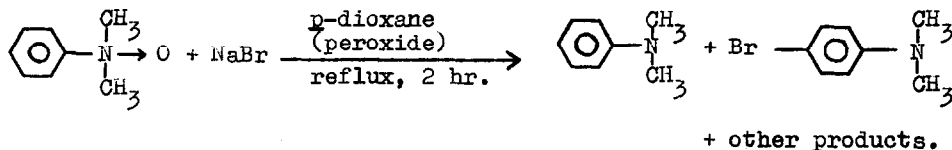
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Reactions of aliphatic tertiary amine N-oxides have attracted relatively little attention compared to aromatic heterocyclic N-oxides. One group of reactions which fall in this category is deoxygenation. Aliphatic N-oxides are comparatively less resistant to deoxygenation than aromatic N-oxides.¹ Deoxygenation of aliphatic N-oxides, e.g. dimethylaniline N-oxide, has been accomplished with a variety of reagents such as sulfurous acid¹, phosphorus trichloride², and sulfur in liquid ammonia³.

We report here a novel peroxide-catalysed deoxygenation of dimethylaniline N-oxide (DMAO) with sodium bromide in *p*-dioxane. Refluxing a stirred solution of DMAO in *p*-dioxane with an equal mole ratio of sodium bromide for two hours resulted in a mixture of products in which dimethylaniline was the major component, as shown by NMR, GLC, and TLC of the reaction mixture. Dimethylaniline was isolated in 53% yield (distilled) and characterized by comparison of its spectra (IR, NMR) with those of authentic sample. There was also obtained, from the same reaction, *p*-bromodimethylaniline in ~4% yield, m.p. 53.5-55°; its structure was confirmed by mixture melting point and comparison of its spectra (IR, NMR) with authentic sample.



This unexpected reaction between DMAO and sodium bromide was investigated further. It was found that a peroxide, which was present in the solvent used is essential for the deoxygenation. *p*-Dioxane is known to form peroxides readily.⁴ The *p*-dioxane (Matheson Coleman and Bell) used was shown to contain peroxides by reaction with acidified potassium iodide. If the peroxide was destroyed by treatment with sodium⁵ and the reaction was carried out under nitrogen using this purified solvent, deoxygenation did not take place and the DMAO was recovered unchanged quantitatively. However, addition of a small amount of solvent not purified in this way caused the reaction to proceed once more. Furthermore, the N-oxide was deoxygenated as before in purified solvent which had been re-peroxidised by exposure to oxygen and ultraviolet light. DMAO was unaffected by heavily peroxidised solvent in the absence of sodium bromide.

Further proof for the need of a peroxide for this reaction is shown by the fact that a small amount of dibenzoyl peroxide in purified dioxane (peroxide free) deoxygenates DMAO in the same manner, although not as efficiently as by the peroxides present in the solvent. A small amount of benzoic acid was isolated from the latter reaction. On the other hand, the reaction failed when tetrahydrofuran, which was free of peroxide, or acetonitrile were used as solvents. An example of a peroxide-catalysed deoxygenation of pyridine N-oxide with triethyl phosphite has been reported.⁶

The mechanism of this reaction is not known at present, but the need for a peroxide suggests a free-radical mechanism in spite of the polar nature of the N-oxide. Although little is known about the peroxides present in the dioxane, dibenzoyl peroxide is known to give benzoyl radicals upon heating which could initiate free-radical reactions. The fact that any *p*-bromodimethylaniline is observed indicates that some "positive" bromine (e.g. Br₂ or ROBr) is formed in

the course of the reaction. The possibility that bromine, which could have been formed by the oxidation of bromide ion by either the peroxide or the N-oxide, is responsible for the deoxygenation is ruled out for two reasons: Firstly, when the reaction was carried out in the presence of indene or cyclohexene, no addition of bromine to the alkene was observed. Secondly, if bromine were involved in the reaction it is expected that p-bromodimethylaniline would be the major product, since bromine in p-dioxane is known to selectively brominate dimethylaniline in the para-position in high yield.⁷ Indeed when bromine was used instead of sodium bromide (in purified p-dioxane under nitrogen), p-bromodimethylaniline was the major product and dimethylaniline was found in only small amounts.

The application of this reaction to other amine oxides, particularly of the hetero-aromatic series, and the mechanistic details are under investigation.

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References

1. (a) E. Ochiai, "Aromatic Amine Oxides", Elsevier Publishing Co., 1967, pp. 184-207.
(b) A. R. Katritsky, Quart. Rev. (London) 395 (1956).
2. Mosomoto Hamond, J. Pharm. Soc. Japan 75, 121 (1955); Chem. Abstr. 50, 18172 (1956).
3. Kenichi Takeda, J. Pharm. Soc. Japan 75, 620 (1955); Chem. Abstr. 50, 3443e (1956)(
4. J. B. Ramsey and F. T. Aldridge, J. Am. Chem. Soc. 77, 2561 (1955).
5. L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", John Wiley and Sons, Inc., New York, 1967, p. 333

6. T. R. Emerson and C. W. Rees, Proc. Chem. Soc. (1960) 418
7. (a) L. A. Yanovskaya, A. P. Terent'ev and L. I. Belen'Kii, J. Gen. Chem. 22, 1594 (1952); Chem. Abstr. 47, 8032 (1953)
(b) G. M. Kosolapoff, J. Am. Chem. Soc. 75, 3596 (1953)