

DEOXYGENATION OF AROMATIC N-OXIDES WITH SULPHUR MONOCHLORIDE

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(Received July 4, 1974; revised September 28, 1974)

Abstract. *N*-Oxides of pyridine, quinoline and their derivatives were prepared. The *N*-oxides were reduced with sulphur monochloride to give their parent bases. The yields of the deoxygenation are good.

N-Oxide groups in aromatic *N*-oxides are generally more stable towards reduction than those in aliphatic or alicyclic *N*-oxides.¹ Many reactions lead to the loss of *N*-oxide oxygen atom, but those in which the nucleophile is trivalent phosphorus compound are perhaps the best known.² A comprehensive survey of deoxygenation procedures for aromatic *N*-oxides has been published recently.^{2,3} In the present work, we have used sulphur monochloride as reducing agent for aromatic *N*-oxides. A number of pyridine and quinoline *N*-oxides were smoothly deoxygenated to their parent compounds in good yields. The compounds deoxygenated were the *N*-oxides of pyridine, quinoline, isoquinoline, 2-picoline and 4-picoline. It was observed that 4-chloro-, and 4-nitropyridine *N*-oxide were not reduced with sulphur monochloride even at higher temperatures which is in line with previous work⁴ where the authors get the 4-nitropyridine *N*-oxide unaltered from the reaction mixture of copper bronze in nitrobenzene at 140°. However, 4-nitropyridine *N*-oxide has been reduced⁵ though in poor yield with potassium nitrate in concentrated sulphuric acid at 160–170° and by phosphorus trichloride.⁷ It seems from the reaction mixtures that in these cases the free sulphur formed during the reduction further reacts with the compounds resulting in the resinification of the products. The work also reveals that in contrast with phosphorus trichloride and thionyl chloride which in addition to deoxygenation also chlorinate the aromatic *N*-oxides, sulphur monochloride does not act as chlorinating agent under similar reaction conditions. The reagent is readily available

in common laboratories. The results are recorded in Table I.

Experimental

The temperatures are in degrees centigrade.

Sulphur Monochloride. Pure sulphur monochloride (B.D.H.) was redistilled before use, b.p. 135–36° (lit. b.p. 135.6°)⁶ and stored in a well stoppered bottle in a dark place.

General Deoxygenation Procedure. The *N*-oxide (10 g) was dissolved in cold chloroform (150 ml) and added to sulphur monochloride (19 ml). The mixture was heated under reflux for 1 hr (70–80°). The reaction mixture was cooled, diluted with water (100 ml) and made alkaline with NaOH (15%), extracted with chloroform and dried (Na₂SO₄). After the removal of the solvent the product was distilled. The data of compounds studied are given in Table 2 and the yields of the products in Table 1.

TABLE 1. DEOXYGENATION OF AROMATIC *N*-OXIDES WITH SULPHUR MONOCHLORIDE.

Starting compound	Product	Yield %
Pyridine <i>N</i> -oxide	Pyridine	80
2-Picoline <i>N</i> -oxide	2-Picoline	79
4-Picoline <i>N</i> -oxide	4-Picoline	85
Quinoline <i>N</i> -oxide	Quinoline	79–82
Isoquinoline <i>N</i> -oxide	Isoquinoline	75

TABLE 2. PHYSICAL CONSTANTS OF THE COMPOUNDS STUDIED.

Starting compound	M.p./b.p.	Lit. (m.p./b.p.)	Product	M.p./b.p.	Lit. (m.p./b.p.)
Pyridine <i>N</i> -oxide	b.p. 137–140°/15 mm	b.p. ⁷ 138–141°/15 mm	Pyridine	b.p. 114.0°	b.p. ⁸ 115.5°
Quinoline <i>N</i> -oxide	m.p. 51.00°	m.p. ⁷ 60–62°	Quinoline	b.p. 237–239° and picrate m.p. 202.0°	b.p. ⁸ 238.0° picrate m.p. ⁸ 203–4°
4-Picoline <i>N</i> -oxide	m.p. 184–186°	m.p. ⁹ 185–186°	4-Picoline	b.p. 142–144° picrate m.p. 166.0°	b.p. 143.0° picrate m.p. ⁸ 167.0°
2-Picoline <i>N</i> -oxide	b.p. 122–128°/15 mm	b.p. ⁹ 123–124°/15 mm	2-Picoline	b.p. 128° picrate m.p. 169–172°	b.p. ⁸ 129.0° picrate m.p. 169–172°
4-Nitropyridine- <i>N</i> -oxide	m.p. 158.0°	m.p. ⁷ 158.0°	No identifiable	Product was obtained	—
4-Chloropyridine <i>N</i> -oxide	m.p. 168.0°	m.p. ⁷ 169.5°	„	„	—
Isoquinoline	m.p. 99.0°	m.p. ¹⁰ 100.0	Isoquinoline	b.p. 240–245° picrate m.p. 224.0°	b.p. ⁸ 242.0° picrate m.p. ⁸ 226.0°

Acknowledgement. We wish to thank Mr. Iftikhar Ahmad, Senior Research Officer of these Laboratories, for his useful suggestions and discussion during the course of this work.

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