

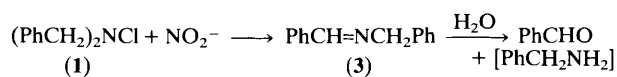
## ***N*-Nitrosamines from the Reaction of *N*-Chlorodialkylamines with Sodium Nitrite**

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The reaction of *N*-chlorodialkylamines with sodium nitrite leads to the corresponding *N*-nitrosamines in excellent yields.

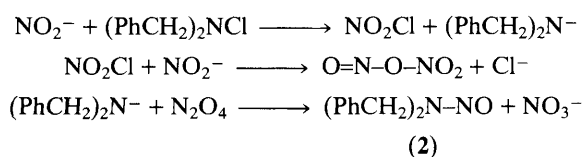
Over the last twenty five years, the generation and transformations of *N*-nitrosamines have become topics of major interest.<sup>1</sup> As a continuation of our investigations in this area,<sup>2</sup> we have studied the action of sodium nitrite on *N*-chlorodibenzylamine (**1**). Treatment of (**1**)<sup>3</sup> with *one* equivalent of sodium nitrite in acetonitrile at reflux resulted in a 50% yield of *N*-nitrosodibenzylamine (**2**). Although none of the starting material was recovered, an unknown solid, m.p. 189–191 °C (decomp.), was isolated; benzaldehyde was also formed as a by-product (as shown by n.m.r. spectroscopy). When this reaction was repeated with 1.5 equiv. of sodium nitrite, the



Scheme 1

yield of (**2**) increased with a concomitant decrease in the amount of the unknown solid.

The generation of benzaldehyde was rationalized in terms of elimination of the elements of hydrogen chloride from (**1**), perhaps induced by nitrite ion, to yield *N*-benzylbenzylideneamine (**3**) followed by *in situ* hydrolysis (Scheme 1). In



Scheme 2

contrast, the formation of (2) could not be explained *via* simple nitrite ion displacement *at nitrogen* as it would be difficult to envisage a reasonable path for the further transformation of the putative hydroxylamine nitrite intermediate into (2). This difficulty, coupled with the incomplete conversion of (1) into (2) prompted us to consider displacement by nitrite ion on the chlorine atom to yield nitryl chloride and dibenzylamine anion. Further reaction of nitrite ion would lead to dinitrogen tetroxide<sup>4</sup> which has been shown by White<sup>5</sup> to be an excellent nitrosating agent. The mechanism depicted in Scheme 2 would thus require the use of *two* equivalents of nitrite ion per equivalent of *N*-chlorodibenzylamine and the generation of nitrate ion as a by-product.

Indeed, when the reaction was carried out using this stoichiometry, *N*-nitrosodibenzylamine was obtained very cleanly in near quantitative yield and no benzaldehyde nor any other organic by-product could be detected; the inorganic salts which were removed prior to the isolation of (2), gave a positive test for nitrate ion.<sup>6</sup> This pathway was further supported by the characterization of the unknown solid isolated in reactions carried out with *less* than 2 equiv. of nitrite (*vide supra*), as the nitric acid salt of dibenzylamine.

This novel nitrosation procedure was equally successful with the purely aliphatic *N*-chlorodicyclohexylamine<sup>7</sup> which gave *N*-nitrosodicyclohexylamine, m.p. 107 °C,<sup>8</sup> in better than 90% yield. A general procedure is as follows. A mixture of 10 mmol *N*-chlorodialkylamine and 20 mmol sodium nitrite in *ca.* 40 ml dry acetonitrile was heated at reflux overnight. The cooled solution was filtered to remove the inorganic salts and the filtrate was evaporated *in vacuo* to yield the *N*-nitrosamine in 90–100% yields.

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