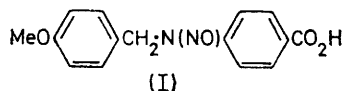


## Reduction of Nitrosamines to Hydrazines

By **B. T. Hayes** and **T. S. Stevens**,\* Department of Chemistry, The University of Sheffield, and Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow C.1

The reduction of nitrosamines to hydrazines can be effected advantageously by zinc-ammonia-ammonium carbonate

ATTEMPTS to reduce the nitroso-compound (I) to the related hydrazine by the usual methods<sup>1</sup> failed, but satisfactory results were obtained by use of zinc-ammonia-ammonium carbonate. Experiments on the general applicability of the method are summarised in the Table. The procedure failed with 2-*N*-nitroso-anilino-2-phenylpropane and, surprisingly, with the methyl ester of the acid (I), giving in each case the parent secondary amine.



Reduction of nitrosamines, NR<sup>1</sup>R<sup>2</sup>NO

	R <sup>1</sup>	R <sup>2</sup>	Yield of hydrazine (%)
(1) <sup>2</sup>	Me	Me	38
(2) <sup>3</sup>	Ph	Me	70
(3) <sup>4</sup>	Ph	Ph	82
(4) <sup>5</sup>	Ph	CH <sub>2</sub> Ph	72
(5) <sup>6</sup>	CH <sub>2</sub> Ph	CH <sub>2</sub> Ph	67
(6)	Compound (I)		63

### EXPERIMENTAL

**4-[4-Methoxybenzyl(nitroso)amino]benzoic Acid (I).**—Magnesium turnings (6 g.) were added to a solution of 4-(4-methoxybenzylideneamino)benzoic acid<sup>7</sup> (10 g.) in methanol (100 ml.), followed by a crystal of mercury(II) chloride. When the vigorous reaction subsided, the mixture was poured into ice-water containing acetic acid; the precipitated 4-(4-methoxybenzylamino)benzoic acid crystallised from methanol in prisms, m.p. 204—205° (Found: C, 70.0; H, 5.7; N, 5.7. C<sub>15</sub>H<sub>15</sub>NO<sub>3</sub> requires C, 70.0; H, 5.8; N, 5.4%). Sodium nitrite (1.4 g.) and sulphuric acid (2.5 g.) were added to the acid (5.1 g.) in ethanol (100 ml.) at 0—5°. After 2 hr. the mixture was poured into ice-water; the precipitated nitroso-compound (I) crystallised from ethanol

as needles, m.p. 201—202° (decomp.) (Found: C, 62.6; H, 4.7; N, 10.1. C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub> requires C, 62.9; H, 4.9; N, 9.8%).

Methyl 4-(4-methoxybenzylideneamino)benzoate,<sup>8</sup> treated in the same way as the free acid, gave methyl 4-(4-methoxybenzylamino)benzoate, plates from methanol-water, m.p. 122—123° (Found: N, 4.9. C<sub>16</sub>H<sub>17</sub>NO<sub>3</sub> requires N, 5.2%); and methyl 4-[4-methoxybenzyl(nitroso)amino]benzoate, prisms from ethanol, m.p. 130—131° (Found: C, 64.0; H, 5.4; N, 9.3. C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub> requires C, 64.0; H, 5.4; N, 9.3%).

**2-Anilino-2-phenylpropane.**—Aniline (9.3 g.) and crude 2-chloro-2-phenylpropane<sup>9</sup> (7.7 g.) in ether were set aside for 36 hr. Aqueous sodium hydroxide was then added, and the dried ethereal layer was distilled, giving the secondary base (8.0 g.), b.p. 108—110°/0.6 mm., needles, m.p. 48—49° (from light petroleum) (Found: C, 85.0; H, 8.1; N, 6.5. C<sub>15</sub>H<sub>17</sub>N requires C, 85.3; H, 8.0; N, 6.6%). 2-*N*-Nitroso-anilino-2-phenylpropane, prepared as in the foregoing experiments, crystallised from ethanol in needles, m.p. 87—88° (Found: C, 75.2; H, 6.4; N, 11.5. C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O requires C, 75.0; H, 6.6; N, 11.6%).

All nitrosamines were obtained in yields of 80% or more; nos. (1)—(4) in the Table by the methods of the references cited and no. (5) in the same way as no. (4). All had the properties recorded in the literature.

**Reduction of Nitrosamines.**—The nitrosamine (0.04 mole) in ethanol (25 ml.), with ammonium carbonate (16 g.) in the minimum volume of water, and zinc dust (8 g.) were stirred at 0° with gradual addition of aqueous ammonia (*d* 0.88; 40 ml.). After 1 hr. zinc dust (8 g.) was added and stirring was continued for 3 hr. The mixture was filtered, the solid residue was washed with dilute hydrochloric acid and the filtrate and washings were treated as follows (numbers refer to compounds listed in the Table).

(1). The mixture, strongly basified with sodium hydroxide was distilled in steam until a sample of distillate showed little reduction of Fehling's solution. The distillate,

<sup>1</sup> E. Enders in Houben-Weyl, 'Methoden der organischen Chemie,' 1967, 10/2, 224.

<sup>2</sup> H. H. Hatt, *Org. Synth.*, 1936, **16**, 22.

<sup>3</sup> W. W. Hartman and L. J. Roll, *Org. Synth.*, 1933, **13**, 82.

<sup>4</sup> A. Lachman, *Ber.*, 1900, **33**, 1026.

<sup>5</sup> O. Antrick, *Annalen*, 1885, **227**, 360.

<sup>6</sup> F. Walder, *Ber.*, 1886, **19**, 3288.

<sup>7</sup> A. Senier and R. B. Forster, *J. Chem. Soc.*, 1915, **107**, 1172.

<sup>8</sup> J. S. Dave, P. R. Patel, and K. L. Vasanth, *Indian J. Chem.*, 1966, **4**, 505.

<sup>9</sup> A. Klages, *Ber.*, 1902, **35**, 2638.

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acidified with hydrochloric acid, was evaporated to a syrup which became crystalline after repeated evaporation with ethanol; ethanol then extracted *NN*-dimethylhydrazine hydrochloride, m.p. 80—82°; picrate, m.p. and mixed m.p. 141—142°.<sup>10</sup>

(3) and (4). Ethanol was removed under reduced pressure, sodium hydroxide was added until the zinc hydroxide had dissolved, and the hydrazine was extracted with ether, giving (3) *NN*-diphenylhydrazine, b.p. 212°/30 mm., and (4) *N*-benzyl-*N*-phenylhydrazine, b.p. 202—204°/5 mm., which yielded benzaldehyde benzylphenylhydrazone, m.p. 108—109°.

(2) and (5). Zinc was precipitated from the partially neutralised solution with hydrogen sulphide, and the basic

product was separated from the filtrate to give *N*-methyl-*N*-phenylhydrazine, b.p. 105—109°/13 mm., or *NN*-dibenzylhydrazine, m.p. 62—64°.

(6). The mixture was freed from zinc as just described, ethanol was removed under reduced pressure, and hydrochloric acid was added until the white precipitate almost redissolved. The filtered solution was treated carefully with aqueous sodium hydroxide and the precipitate was crystallised from ethanol. *N*-4-Carboxyphenyl-*N*-4-methoxybenzylhydrazine formed fine needles, m.p. 190—191° (Found: C, 65.9; H, 5.9; N, 10.1.  $C_{15}H_{16}N_2O_3$  requires C, 66.2; H, 5.9; N, 10.3%).

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<sup>10</sup> D. Todd, *J. Amer. Chem. Soc.*, 1949, **71**, 1354.

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