The Preparation of Some N-*Alkyl- and* NN-*Dialkyl*-p-*nitrosoanilines.*

By J. WILLENZ.

[Reprint Order No. 6066.]

Preparation of a number of *N*-alkyl- and *NN*-dialkyl-*p*-nitrosoanilines is described. Attempted Fischer–Hepp rearrangement of *N*-nitroso-*N*-*n*-octadecylaniline results in denitrosation. No difficulty was experienced in direct introduction of a *p*-nitroso-group into any dialkylanilines, even those with bulky substituents.

A SERIES of *p*-nitrosoanilines has been prepared after the observation that *p*-nitrosoaniline and a number of its derivatives in which the amino-group is alkylated with very small alkyl groups showed high activities *in vitro* as fungicides and as bactericides against a wide range of test organisms. These biological results will be reported elsewhere.

As expected, nitrosation of *N*-*iso*propylaniline followed by Fischer–Hepp rearrangement of the *N*-nitroso-derivative (*Ber.*, 1886, **19**, 2991) gave the *p*-nitroso-compound, *via* the hydrochloride, without difficulty. *N*-*n*-Hexylaniline, which was preferably obtained in a pure state by a one-stage process from excess of aniline and hexyl bromide (cf. Hickinbottom, *J.*, 1937, 1119), readily gave the *N*-nitroso-compound, but rearrangement gave poor yields of *N*-*n*-hexyl-*p*-nitrosoaniline.

3 : 5 : 5-Trimethylhexylaniline was prepared pure by prolonged treatment of a large excess of aniline with 3 : 5 : 5-trimethylhexyl iodide in light petroleum. The autoclave method of Reilly and Hickinbottom (*J.*, 1918, **113**, 99) using aniline hydrochloride and 3 : 5 : 5-trimethylhexanol gave no material corresponding to either mono- or di-alkylated aniline. Nitrosation of the base in the usual way gave *N*-nitroso-*N*-(3 : 5 : 5-trimethylhexyl)aniline in good yield which was rearranged to the corresponding *p*-nitroso-compound in 33% yield.

N-*n*-Octadecylaniline was described by Adler, Haskelberg, and Bergmann (*J.*, 1940, 576). Nitrosation of the pure base gave the *N*-nitroso-derivative, but attempts to rearrange the latter always resulted in denitrosation to *N*-*n*-octadecylaniline hydrochloride. Steric hindrance could be the explanation for the failure of the Fischer–Hepp rearrangement here. Inspection of the Stuart model shows that the aliphatic chain is sufficiently long to coil around the aromatic ring in such a way as to block not only the *para*-position but also any position of the benzene nucleus. Hickinbottom (*J.*, 1933, 946) similarly made unsuccessful attempts to prepare *N*-*tert.*-butyl-*p*-nitrosoaniline by the action of solutions of hydrogen chloride in alcohol or acetic acid on the *N*-nitroso-amine, the hydrochloride of *tert.*-butylaniline being the principal product.

Crossley, Turner, Hofmann, Dreisbach, and Parker (*J. Amer. Chem. Soc.*, 1952, **74**, 578) failed to prepare *p*-nitroso-*NN*-di*iso*propylaniline and explained this on steric grounds, citing Hickinbottom's reports of an unsuccessful attempt (*J.*, 1933, 946) to nitrosate *N*-methyl-*N*-*tert.*-butylaniline. It has also been claimed that the reaction fails if the alkyl groups are large (see Sidgwick, "The Organic Chemistry of Nitrogen," Clarendon Press, Oxford, 1942, p. 218). However, in the present work *NN*-dialkyl-*p*-nitrosoanilines were successfully prepared by the direct introduction of the *p*-nitroso-group into the appropriate dialkylaniline and no difficulty has been experienced in the preparation of several heavily substituted dialkyl-*p*-nitrosoanilines.

NN-Di-*n*-hexylaniline (orginally prepared by Slotta and Franke, *Ber.*, 1933, **66**, 104) was obtained by prolonged heating of 2 mols. of *n*-hexylaniline and 1 mol. of hexyl bromide in light petroleum. Nitrosation gave *NN*-di-*n*-hexyl-*p*-nitrosoaniline, which was characterised by reduction to the corresponding *p*-phenylenediamine and this with 1-chloro-2 : 4-dinitrobenzene gave 4-di-*n*-hexylamino-2′ : 4′-dinitrodiphenylamine.

N-*n*-Hexyl-*N*-methylaniline was obtained in good yield from *N*-methylaniline and *n*-hexyl bromide. This gave *N*-*n*-hexyl-*N*-methyl-*p*-nitrosoaniline, and thence the corresponding diamine.

Prolonged refluxing of 2 mols. of *N*-3 : 5 : 5-trimethylhexylaniline with 1 mol. of 3 : 5 : 5-trimethylhexyl iodide in light petroleum gave the dialkylaniline in good yield. This readily gave the *p*-nitroso-compound, the diamine, and 4-*NN*-bis-(3 : 5 : 5-trimethylhexyl)amino-2′ : 4′-dinitrodiphenylamine.

A superior synthesis of *N*-methyl-*N*-3 : 5 : 5-trimethylhexylaniline was devised (see de Benneville and Macartney, *J. Amer. Soc.*, 1950, **72**, 3073). Conditions for nitrosating this compound were critical. The *p*-nitroso-compound gave a derivative with picrolonic acid that although of sharp m. p. gave unsatisfactory analytical data. Reduction of the hydrochloride of the *p*-nitroso-compound, however, gave the corresponding *p*-phenylenediamine which led to 4-(*N*-methyl-*N*-3 : 5 : 5-trimethylhexylamino)-2′ : 4′-dinitrodiphenylamine. Analogously, the *N*-ethyl-*N*-3 : 5 : 5-trimethylhexylaniline was prepared, but, whereas the *N*-methyl compound gave a stable and well-defined picrolonate, this compound gave an ill-informed adduct with picrolonic acid for which analytical results were never satisfactory. Nitrosation of the *N*-ethyl analogue was carried out normally, and the product reduced and converted into the dinitrodiphenylamine derivative.

EXPERIMENTAL

p-*Nitroso*-N-iso*propylaniline*.—*N*-*iso*Propylaniline (b. p. 204—207°; 10 g.) in concentrated hydrochloric acid (10·75 c.c.) was nitrosated in the usual way with a solution of sodium nitrite (5·33 g.) in water (18·5 c.c.). Ether-extraction and evaporation of the dried extract gave *N*-nitroso-*N*-*iso*propylaniline as a yellow oil; it was dissolved in dry ether (25 c.c.) and absolute alcohol (60 c.c.) which was saturated with hydrogen chloride. The mixture was set aside for *ca.* 1½ hr. at room temperature and the hydrochloride of *p*-nitroso-*N*-*iso*propylaniline was then precipitated on addition of more ether. It was collected and treated with an excess of aqueous ammonia, and the free base extracted with ether. Evaporation of the dried ether extract gave pure p-*nitroso*-N-iso*propylaniline*, bluish-green crystals of metallic lustre (3·1 g., 25·4%), m. p. 82·5° (decomp.), not increased after recrystallization from light petroleum (b. p. 60—80°) (Found: C, 65·6; H, 7·7; N, 17·0. $C_9H_{12}ON_2$ requires C, 65·8; H, 7·33; N, 17·1%).

While this work was in progress Crossley *et al.* (*loc. cit.*) reported the preparation of *p*-nitroso-*N*-*iso*propylaniline as a green solid, m. p. 53·3—53·7°. Independent preparation of this compound in these laboratories by Dr. C. Wickham Jones gave greenish-blue crystals (from ethyl acetate and light petroleum, b. p. 40—60°), m. p. 86°. The mixed m. p. of the latter sample with a sample described above (m. p. 82·5°) was 84—85°.

N-n-*Hexylaniline*.—Aniline (100 g.) was refluxed with *n*-hexyl bromide (55 g.) in light petroleum (b. p. 60—80°; 30 c.c.) for 39 hr. The mixture was poured into water, treated with an excess of aqueous ammonia, and extracted with ether. The washed (H_2O) and dried (Na_2SO_4) ether extract was filtered, the solvent evaporated, and the residual oil fractionally distilled *in vacuo*. *N*-*n*-Hexylaniline was obtained as a pale yellow oil, b. p. 94—101°/0·7—1 mm., n_D^{20} 1·5223 [Found: C, 81·3; H, 10·7; N, 7·9%; *M* (cryoscopic in benzene), 172 ± 5. Calc. for $C_{12}H_{19}N$: C, 81·4; H, 10·7; N, 7·8%; *M*, 177]. The toluene-*p*-sulphonyl derivative had m. p. 63—64° (Hickinbottom, *J.*, 1937, 1119, gives 67—68°) (Found: C, 68·8; H, 7·6; N, 4·5. Calc. for $C_{19}H_{25}O_2NS$: C, 68·9; H; 7·6; N, 4·2%). The pale yellow *picrolonate* had m. p. 160—161·5° (from ether) (Found: C, 60·0; H, 6·0; N, 15·7. $C_{22}H_{27}O_5N_5$ requires C, 59·8; H, 6·1; N, 15·9%). *N*-*n*-Hexylaniline did not give a solid hydrochloride in dry ether or light petroleum (b. p. 40—60°).

N-n-*Hexyl*-N-*nitrosoaniline*.—*N*-*n*-Hexylaniline (10 g.) did not dissolve in concentrated hydrochloric acid (33 c.c.) at 0°; even when hydrogen chloride was bubbled through the mixture, complete dissolution was not obtained. The mixture was nitrosated with an aqueous solution (14·2 c.c.) of sodium nitrite (4·07 g.) in the usual way and worked up as described for *N*-nitroso-*N*-*iso*propylaniline. N-n-*Hexyl*-N-*nitrosoaniline* (9·27 g., 80%) was obtained as an amber-coloured, viscous oil, b. p. 127—130°/1·5 mm. [Found: C, 69·8; H, 8·6; N, 13·5%; *M*, 198 (cryoscopic in benzene). $C_{12}H_{18}ON_2$ requires C, 69·9; H, 8·75; N, 13·6%; *M*, 206].

N-n-*Hexyl*-p-*nitrosoaniline*.—(*a*) *N*-*n*-Hexyl-*N*-nitrosoaniline (7·95 g.) in dry ether was treated with dry pure methanol (60 c.c.) which was saturated with dry hydrogen chloride. Adding a very large amount of dry ether and passing further dry hydrogen chloride through the solution precipitated a solid after several hours' storage. This was collected, dissolved in aqueous ammonia, and extracted with ether, and the dried extract evaporated. Three recrystallisations of the residual material from benzene–light petroleum (b. p. 40—60°) gave N-n-*hexyl*-p-*nitrosoaniline* as blue crystals with a metallic lustre, m, p. 47—48° (0·58 g., 7·2%) (Found: C, 69·8; H, 9·1; N, 13·1%; *M*, 202 ± 10. $C_{12}H_{18}ON_2$ requires C, 69·9; H, 8·8; N, 13·6%; *M*, 206). (*b*) Methanol (12 c.c.) and ether (30 c.c.), both saturated in the cold with dry hydrogen chloride, were added to *N*-*n*-hexyl-*N*-nitrosoaniline (*ca.* 8 g.), and the solution kept a room temperature for 2 hr. No solid was precipitated; the solution was evaporated *in vacuo* (water-bath). The residual orange-coloured, viscous oil was treated with an excess of aqueous potassium carbonate and extracted with ether, and the washed and dried (Na_2SO_4) extract evaporated. The residual oil was extracted with boiling light petroleum (b. p. 40—60°, or 60—80°) from which *N*-*n*-hexyl-*p*-nitrosoaniline was obtained on cooling (1·19 g., *ca.* 15%; crude, m. p. 41—42°). The *picrolonate*, m. p. 133·5° (decomp.), was obtained from ether as a light brown powder. Although this was sparingly soluble in ether, the ether solution had to be evaporated to very small bulk before crystallisation occurred (Found: C, 55·8; H, 5·4; N, 17·7. $C_{22}H_{26}O_6N_6$ requires C, 56·2; H, 5·5; N, 17·9%).

N-3 : 5 : 5-*Trimethylhexylaniline*.—3 : 5 : 5-Trimethylhexyl iodide [freshly prepared (cf. Jones and Whitfield, *J.*, 1953, 2795); b. p. 62°/2 mm., 50·8 g.] and aniline (freshly distilled; 60 g.) in light petroleum (b. p. 60—80°; 25 c.c.) were refluxed for 30 hr. and the product was worked up as described for *N*-*n*-hexylaniline. N-3 : 5 : 5-*Trimethylhexylaniline* (b. p. 108—112°/0·5 mm., 310°/760 mm., n_D^{20} 1·5110; 32·8 g., 75%) was obtained as a colourless oil (Found, for material of b. p. 110°/0·5 mm.: C, 82·1; H, 11·5; N, 6·4. $C_{15}H_{25}N$ requires C, 82·2; H, 11·4; N, 6·4%).

N-*Nitroso*-N-3 : 5 : 5-*trimethylhexylaniline*.—Nitrosation of *N*-3 : 5 : 5-trimethylhexylaniline, carried out in the usual way with a 25% excess of aqueous sodium nitrite, gave after distillation of the washed and dried ether extract N-*nitroso*-N-3 : 5 : 5-*trimethylhexylaniline* as a yellow oil,

b. p. 126—128°/0·7 mm., n_D^{20} 1·5164 in a yield of 86% (Found: C, 72·7; H, 9·8; N, 11·7. $C_{15}H_{24}ON_2$ requires C, 72·6; H, 9·7; N, 11·3%).

p-*Nitroso*-N-3 : 5 : 5-*trimethylhexylaniline*.—*N*-Nitroso-*N*-3 : 5 : 5-trimethylhexylaniline (b. p. 142—145°/1 mm.; 35·76 g.) in dry ether (70 c.c.), treated with pure methanol (50 c.c.) which had been previously saturated with dry hydrochloric acid, was kept for 4 hr. at room temperature. Subsequent addition of a large amount of dry ether precipitated the yellow hydrochloride of *p*-nitroso-*N*-3 : 5 : 5-trimethylhexylaniline. This was filtered off and suspended in aqueous ammonia which gave the crude blue p-*nitroso*-N-3 : 5 : 5-*trimethylhexylaniline* (11·7 g., 33% yield), which was collected and purified by several recrystallisations from light petroleum (b. p. 40—60°), to give green crystals, m. p. 93—94° (Found: C, 72·6; H, 9·8; N, 11·6. $C_{15}H_{24}ON_2$ requires C, 72·6; H, 9·7; N, 11·3%). It gave a yellowish-green *picrate*, m. p. 93·5° (Found: C, 52·4; H, 5·7; N, 14·3. $C_{21}H_{27}O_8N_5$ requires C, 52·8; H, 5·7; N, 14·7%). On admixture with *p*-nitroso-*N*-3 : 5 : 5-trimethylhexylaniline, the m. p. was depressed to 59°. The crude addition compound obtained from the *p*-nitroso-compound with 2 : 4-dinitrophenol in ethanol had m. p. 70—74°; the m. p. was lowered after each subsequent crystallisation from ethanol, giving 68·5°, 60—62°, 52—58° successively.

N-n-*Octadecylaniline*.—*n*-Octadecyl bromide (66·6 g.) and aniline (47 g.) in light petroleum (b. p. 60—80°; 30 c.c.) were refluxed for 40 hr. The product was poured into aqueous ammonia and extracted with ether. The washed (H_2O) extract was dried ($MgSO_4$), filtered, and concentrated. The residual brown oil was distilled to give *N*-*n*-octadecylaniline (35·3 g., 51%), m. p. 51—51·5°, b. p. 215—220°/1 mm. Recrystallisation from acetone gave m. p. 51·5° (Bergmann *et al.*, *loc. cit.*, gave m. p. 42°, b. p. 196°/0·6 mm.) (Found: C, 83·5; H, 12·3; N, 4·1. Calc. for $C_{24}H_{43}N$: C, 83·5; H, 12·4; N, 4·1%).

N-*Nitroso*-N-n-*octadecylaniline*.—*N*-*n*-Octadecylaniline (5 g.) in glacial acetic acid (75 c.c.) was nitrosated in suspension at about 5° with vigorous stirring with sodium nitrite (5 g.) in water (8 c.c.). Crystallisation of the crude product (m. p. 48·5—49·5°), obtained in theoretical yield, from methanol gave N-*nitroso*-N-n-*octadecylaniline*, m. p. 50°, as pale yellow needles (Found: C, 77·0; H, 11·2; N, 7·6. $C_{24}H_{42}ON_2$ requires C, 77·0; H, 11·2; N, 7·5%). Admixture with pure *N*-*n*-octadecylaniline (m. p. 51·5°) depressed the m. p. to 41—46°.

Attempted Fischer–Hepp rearrangement. (*a*) The *N*-nitroso-compound (5 g.) in dry ether (20 c.c.) was treated with methanol (10 c.c.) which had been saturated with dry hydrogen chloride. A yellow solid (5·3 g.), the *hydrochloride* of *N*-*n*-octadecylaniline, was immediately precipitated (m. p. 103—103·5°). The m. p. was not raised by recrystallisation from methanol which gave pale yellow, lustrous plates (Found: C, 75·6; H, 11·4; N, 3·8; Cl, 9·2. $C_{24}H_{44}NCl$ requires C, 75·5; H, 11·5; N, 3·7; Cl, 9·3%). The m. p. was not depressed on admixture with a specimen (m. p. 103°) obtained by treating a light petroleum (b. p. 60—80°) solution of *n*-octadecylaniline with dry hydrogen chloride.

(*b*) The hydrochloride was also obtained when *N*-nitroso-*n*-octadecylaniline (2 g.) in glacial acetic acid (15 c.c.) was treated with glacial acetic acid (20 c.c.) saturated with dry hydrogen chloride. Some solid was precipitated immediately and more came down in a few minutes (total, 1·8 g.).

(*c*) *N*-Nitroso-*n*-octadecylaniline (2·5 g.) was dissolved in toluene (40 c.c.) which was saturated with hydrogen chloride. After 4 hr. the brown solution deposited a yellow solid (0·15 g.; m. p. 90°), and adding ether precipitated more material (2 g.; m. p. 89°) which, after recrystallisation from methanol, gave the pure hydrochloride, m. p. 103°.

NN-*Di*-n-*hexylaniline*.—*N*-*n*-Hexylaniline (50 g.) was refluxed with *n*-hexyl bromide (23·3 g.) in light petroleum (b. p. 60—80°) for 48 hr. and worked up as described for the preparation of *N*-*n*-hexylaniline. *NN*-Di-*n*-hexylaniline (21·83 g., 59·3% calc. on hexyl bromide), b. p. 130—135°/0·5 mm. (Slotta and Franke, *loc. cit.*, give b. p. 300—301°/755 mm., 172—173°/15 mm.), n_D^{20} 1·5067 (Found: C, 82·7; H, 12·0; N, 5·6. Calc. for $C_{18}H_{31}N$: C, 82·7; H, 11·9; N, 5·4%), did not give a solid hydrochloride in dry ether when dry hydrogen chloride was passed through it. On evaporation of the solvent a viscous oil was obtained which solidified to a colourless solid, m. p. 101—109°, which was not further purified. A picrate could not be obtained, and the *picrolonate* only could be obtained pure by treating equimolecular proportions of the aniline and picrolonic acid; it formed yellow crystals (from ether), m. p. 108—110° (Found: C, 63·9; H, 7·4; N, 13·2. $C_{28}H_{39}O_5N_5$ requires C, 64·0; H, 7·4; N, 13·3%).

NN-*Di*-n-*hexyl*-p-*nitrosoaniline*.—*NN*-Di-*n*-hexylaniline (4 g.), dissolved in glacial acetic acid (40 c.c.) and concentrated hydrochloric acid (5 c.c.), was nitrosated with stirring with aqueous (5 c.c.) sodium nitrite (1·41 g.) within 8 min. at 2·5—6°. The mixture was treated immediately with an excess of aqueous potassium carbonate and extracted with light petroleum

(b. p. 40—60°), and the dried (Na_2SO_4) extract was evaporated. The residue solidified to a green crystalline mass on strong cooling (solid carbon dioxide–methanol) and scratching but liquefied again at room temperature. NN-*Di*-n-*hexyl*-p-*nitrosoaniline* was purified by repeatedly freezing out from its light petroleum (b. p. 40—60°) solution. At room temperature it is a very viscous oil with a greenish-blue sheen [Found, for material dried at 50° in a high vacuum: C, 74·3; H, 10·2; N, 9·8%; *M* (cryoscopic in benzene), 336 ± 20. $C_{18}H_{30}ON_2$ requires C, 74·5; H, 10·3; N, 9·7%; *M*, 290].

4-*Di*-n-*hexylamino*-2′ : 4′-*dinitrodiphenylamine*.—Reduction of *NN*-di-*n*-hexyl-*p*-nitrosoaniline (1·19 g.) with zinc dust and hydrochloric acid (cf. Reilly and Hickinbottom, *loc. cit.*) gave the corresponding crude *p*-phenylenediamine (0·8 g.) which was condensed in hot alcohol with 1-chloro-2 : 4-dinitrobenzene (0·59 g.) to give, after crystallisation from alcohol and subsequently light petroleum, orange crystals of 4-*di*-n-*hexylamino*-2′ : 4′-*dinitrodiphenylamine*, m. p. 74·5—75° (Found: C, 65·0; H, 7·7; N, 12·7. $C_{24}H_{34}O_4N_4$ requires C, 65·2; H, 7·7; N, 12·7%).

N-n-*Hexyl*-N-*methylaniline*.—*N*-Methylaniline (71·2 g.) was refluxed in light petroleum (b. p. 60—80°; 25 c.c.) with *n*-hexyl bromide (55 g.) for 3 days and the product worked up as described under *N*-*n*-hexylaniline, to give N-n-*hexyl*-N-*methylaniline* (44·6 g., 70·5%), as a practically colourless oil, b. p. 94—98°/0·3 mm., n_D^{20} 1·5229 (Found: C, 81·9; H, 10·8; N, 7·5%; *M*, 181 ± 6. $C_{13}H_{21}N$ requires C, 81·7; H, 11·0; N, 7·3%; *M*, 191).

N-n-*Hexyl*-N-*methyl*-p-*nitrosoaniline*.—*N*-Hexyl-*N*-methylaniline (3·64 g.) in acetic acid (36·5 c.c.) and concentrated hydrochloric acid (4 c.c.) was nitrosated at 3—4° by adding saturated aqueous sodium nitrite (4·5 c.c.) during 7 min. The mixture was then kept for 4—5 min.; its temperature rose to 7°. It was worked up as described under *NN*-di-*n*-hexyl-*p*-nitrosoaniline to give 3·79 g. (90·5%) of a greenish-blue oil which solidified on cooling (solid carbon dioxide–methanol). After freezing out from the dried (Na_2SO_4) light petroleum solution (b. p. 40—60°), N-n-*hexyl*-N-*methyl*-p-*nitrosoaniline* was obtained as bright green needles, m. p. 33·5—34° (Found: C, 70·5; H, 9·1; N, 12·7. $C_{13}H_{20}ON_2$ requires C, 70·9; H, 9·1; N, 12·7%). The *picrolonate*, m. p. 108—109° (decomp.), was obtained as a pale brown solid from aqueous methanol (Found: C, 56·4; H, 6·2; N, 17·4. $C_{23}H_{28}O_6N_6$ requires C, 57·0; H, 5·8; N, 17·4%). Reduction of the *p*-nitroso-compound with zinc dust in hydrochloric acid (cf. Reilly and Hickinbottom, *loc. cit.*) gave the crude *N*-*n*-hexyl-*N*-methyl-*p*-phenylenediamine which was converted into the yellow *picrolonate*, m. p. 141—142° (decomp.) (from chloroform and light petroleum) (Found: C, 58·7; H, 6·6; N, 17·9. $C_{23}H_{30}O_5N_6$ requires C, 58·7; H, 6·7; N, 17·9%).

NN-*Bis*-(3 : 5 : 5-*trimethylhexyl*)*aniline*.—Refluxing *N*-3 : 5 : 5-trimethylhexylaniline (2 equivs.) with 3 : 5 : 5-trimethylhexyl iodide (1 equiv.) in light petroleum and working up as described in the preparation of *N*-*n*-hexylaniline gave NN-*bis*-(3 : 5 : 5-*trimethylhexyl*)*aniline* (77·5%), b. p. 150°/0·5 mm., n_D^{20} 1·4961, as a straw-coloured, moderately viscous oil (Found: C, 83·4; H, 12·6; N, 4·2. $C_{24}H_{43}N$ requires C, 83·5; H, 12·5; N, 4·1%). The *monopicrate* was obtained as yellow needles [from light petroleum (b. p. 40—60°)], m. p. 109° (Found: C, 62·5; H, 8·1; N, 10·1. $C_{30}H_{46}O_7N_4$ requires C, 62·7; H, 8·0; N, 9·8%).

p-*Nitroso*-NN-*bis*-(3 : 5 : 5-*trimethylhexyl*)*aniline*.—Nitrosation of *NN*-bis-(3 : 5 : 5-trimethylhexyl)aniline (5 g.) in acetic acid (25 c.c.) and concentrated hydrochloric acid (5 c.c.) with sodium nitrite (3 g.) in water (7 c.c.) gave after basification with sodium carbonate solution a green oil. This solidified after extraction with light petroleum, washing, drying, and evaporation of the extract (m. p. 44—46°; 2·8 g., 52%). After final purification from light petroleum (b. p. 40—60°), the p-*nitroso-compound* was obtained as green crystals, m. p. 48—48·5° (Found: C, 76·8; H, 11·1; N, 7·7. $C_{24}H_{42}ON_2$ requires C, 77·0; H, 11·2; N, 7·5%). A picrate or a picrolonate could not be obtained.

4-*Bis*-(3 : 5 : 5-*trimethylhexyl*)*amino*-2′ : 4′-*dinitrodiphenylamine*.—Reduction of the preceding compound as above gave *NN*-bis-(3 : 5 : 5-trimethylhexyl)-*p*-phenylenediamine as a brown oil in theoretical yield. This was coupled in alcohol with an equimolecular amount of 1-chloro-2 : 4-dinitrobenzene, to give after recrystallisation from alcohol crimson needles, m. p. 91·5° of 4-*bis*-(3 : 5 : 5-*trimethylhexyl*)*amino*-2′ : 4′-*dinitrodiphenylamine* (Found: C, 68·0; H, 8·6; N, 10·9. $C_{30}H_{46}O_4N_4$ requires C, 68·5; H, 8·7; N, 10·6%).

N-*Methyl*-N-3 : 5 : 5-*trimethylhexylaniline*.—This was prepared from methylaniline (45 g.) and 3 : 5 : 5-trimethylhexyl iodide (50·8 g.) in light petroleum (b. p. 60—80°; 15 c.c.) and worked up as described for the preparation of *N*-*n*-hexylaniline, giving N-*methyl*-N-3 : 5 : 5-*trimethylhexylaniline* as a yellow oil, b. p. 136—140°/2—2·5 mm. (40·7 g., 88%) (Found, for material, b. p. 138°/2 mm., n_D^{20} 1·5108: C, 82·4; H, 11·7; N, 6·1. $C_{16}H_{27}N$ requires C, 82·4;

H, 11·6; N, 6·0%). The *picrolonate* was obtained as canary-yellow crystals, m. p. 133·5—135°, after several recrystallisations from ether (Found: C, 62·7; H, 7·3; N, 13·9. $C_{26}H_{35}O_5N_5$ requires C, 62·8; H, 7·0; N, 14·1%).

N-*Methyl*-p-*nitroso*-N-3 : 5 : 5-*trimethylhexylaniline*.—*N*-Methyl-*N*-3 : 5 : 5-trimethylhexylaniline (8·7 g.) in concentrated hydrochloric acid (10 c.c.), water (10 c.c.), and glacial acetic acid (20 c.c.) was nitrosated at 0° (±2°) with sodium nitrite (3·5 g., theor., 2·58 g.) in water (10 c.c.) during 20 min. with stirring. The nitrite solution was run under the surface of the liquid. Stirring was continued for a further 20 min. The dark red solution was made alkaline with potassium carbonate and the green viscous oil which separated immediately extracted with ether. The ether extract was washed with water, dried (Na_2SO_4), filtered, and evaporated. The residual oil gave, on strong cooling and scratching, a solid, m. p. 41—44° (7·5 g., 77%); after several crystallisations from light petroleum (b. p. 40—60°), green crystals, m. p. 48° (*ca.* 45—50%) of N-*methyl*-p-*nitroso*-N-3 : 5 : 5-*trimethylhexylaniline* were obtained (Found: C, 73·2; H, 9·7; N, 10·8. $C_{16}H_{26}ON_2$ requires C, 73·3; H, 9·9; N, 10·7%).

Other attempted nitrosation procedures gave incomplete reaction. Rapidity of working-up of the nitrosated material is essential.

The yellow *hydrochloride* was obtained from light petroleum (b. p. 60—80°) solution; purified from alcohol–ether, it had m. p. 134° (decomp.) (Found: C, 64·0; H, 9·0; N, 9·6; Cl, 12·4. $C_{16}H_{27}ON_2Cl$ requires C, 64·3; H, 9·0; N, 9·4; Cl, 11·9%). On reduction with zinc dust in aqueous hydrochloric acid (1 : 1) it gave the crude diamine as a violet oil which with 1-chloro-2 : 4-dinitrobenzene in very concentrated alcoholic solution gave, after recrystallisation from alcohol, 4-(N-*methyl*-N-3 : 5 : 5-*trimethylhexylamino*)-2′ : 4′-*dinitrodiphenylamine hydrochloride*, m. p. 205°, which darkened in air (Found: C, 58·7; H, 6·9; N, 12·7; Cl, 7·9. $C_{22}H_{31}O_4N_4Cl$ requires C, 58·6; H, 6·9; N, 12·4; Cl, 7·9%). With aqueous potassium carbonate this gave, after crystallisation of the products from ethanol and then from light petroleum (b. p. 60—80°), reddish-brown 4-(N-*methyl*-N-3 : 5 : 5-*trimethylhexylamino*)-2′ : 4′-*dinitrodiphenylamine*, m. p. 65·5° (Found: C, 63·8; H, 7·4; N, 13·5. $C_{22}H_{30}O_4N_4$ requires C, 63·8; H, 7·3; N, 13·5%).

N-*Ethyl*-N-3 : 5 : 5-*trimethylhexylaniline*.—This was prepared in the same way as the corresponding *N*-methyl compound [*N*-ethylaniline (48·4 g.) replacing methylaniline], in 85% yield. The *base* was straw-coloured and had b. p. 140°/2·5 mm., n_D^{20} 1·5091 (Found: C, 82·1; H, 11·9; N, 5·7. $C_{17}H_{29}N$ requires C, 82·5; H, 11·7; N, 5·7%). The addition compound with picrolonic acid was unstable in ether.

N-*Ethyl*-p-*nitroso*-N-3 : 5 : 5-*trimethylhexylaniline*.—The base (10 g.) in acetic acid (60 c.c.) and concentrated hydrochloric acid (12·5 c.c.) was nitrosated with stirring at 0° with sodium nitrite (3·6 g., *ca.* 30% excess) in water within 5 min. After a further 5 minutes' stirring the solution was made alkaline with potassium carbonate and extracted with light petroleum (b. p. 40—60°), and the washed (water) and dried ($MgSO_4$) extract was filtered and evaporated. The residual dark green oil did not solidify. In light petroleum (b. p. 60—80°) it gave N-*ethyl*-p-*nitroso*-N-3 : 5 : 5-*trimethylhexylaniline hydrochloride* (7·4 g., 59%) as a flocculent, yellow precipitate (crude m. p. 122°). Crystallisation from ethanol–ether gave yellow crystals, m. p. 129° (decomp.) (Found: C, 65·4; H, 9·3; N, 8·7; Cl, 11·4. $C_{17}H_{29}ON_2Cl$ requires C, 65·2; H, 9·2; N, 9·0; Cl, 11·4%). Aqueous sodium hydroxide liberated the base which was extracted with light petroleum (b. p. 40—60°); the washed (water), dried ($MgSO_4$), and filtered extract was evaporated, giving N-*ethyl*-p-*nitroso*-N-3 : 5 : 5-*trimethylhexylaniline* as a green oil (Found: C, 74·1; H, 10·1; N, 10·3. $C_{17}H_{28}ON_2$ requires C, 74·0; H, 10·1; N, 10·1%). Reduction of the hydrochloride (3 g.) with zinc dust in aqueous-alcoholic hydrochloric acid gave the diamine as a violet oil (2 g.). Condensation with 1-chloro-2 : 4-dinitrobenzene in alcohol, treatment of the solid obtained with aqueous 1% sodium hydroxide, extraction with light petroleum (b. p. 60—80°), and concentration of the dried extract gave 4-(N-*ethyl*-N-3 : 5 : 5-*trimethylhexylamino*)-2′ : 4′-*dinitrodiphenylamine* as brick-red crystals, which, after further purification from light petroleum (b. p. 60—80°), melted at 80·5° (Found: C, 64·2; H, 7·3; N, 13·3. $C_{13}H_{32}O_4N_4$ requires C, 64·5; H, 7·5; N, 13·1%).

RESEARCH DEPARTMENT, IMPERIAL CHEMICAL INDUSTRIES LIMITED,
BILLINGHAM DIVISION, BILLINGHAM, CO. DURHAM.

[*Received, January 25th,* 1955.]