

**935.** *The Direct Introduction of the Diazonium Group into Aromatic Nuclei. Part IX.*<sup>1</sup> *The Preparation of Diazonium Salts from Secondary Amines by the Fischer-Hepp Rearrangement.*

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Secondary aromatic amines have been converted into *p*-(*N*-alkyl-*N*-nitrosoamino)benzenediazonium salts by nitrosation, followed by Fischer-Hepp rearrangement and conversion of the *C*-nitroso-derivative so formed into the diazonium salt by treatment with more nitrous acid. *ortho*-Substituents do not interfere with the rearrangement but retard the conversion of the *C*-nitroso-compound into the diazonium salt; a *para*-substituent prevents the reaction from proceeding beyond the initial *N*-nitrosation.

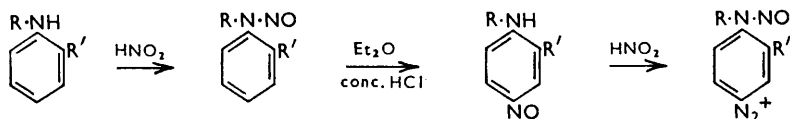
THE preceding paper describes the direct introduction of the diazonium group into tertiary aromatic amines. The present paper is concerned with extending this reaction to secondary aromatic amines. Fischer and Hepp were aware that, when an aromatic nitrosoamine was rearranged to an (alkylamino)nitrosobenzene, the *C*-nitroso-compound could react further to yield the alkylaminobenzenediazonium salt.<sup>2</sup> However, no attempts appear to have been made previously to use this reaction for preparative purposes.

In the present work the secondary amine was treated with aqueous nitrous acid, and

<sup>1</sup> Part VIII, preceding paper.

<sup>2</sup> Fischer and Hepp, *Ber.*, 1886, **19**, 2991; 1887, **20**, 2476.

the oily nitroso-compound was extracted with ether. The ether layer was treated with concentrated hydrochloric acid and, after thorough shaking, this acidic mixture was poured on a mixture of sodium nitrite (excess) and ice. The resultant two layers were shaken together and, when the colour had largely disappeared, the layers were separated and the ether layer was treated with more concentrated hydrochloric acid and then added



Yields (%) of azo-2-naphthol dyes from secondary aromatic amines.

<i>N</i> -Methylaniline .....	44	<i>N</i> -Ethyl- <i>o</i> -toluidine .....	2.5*
<i>N</i> -Ethylaniline .....	62	<i>N</i> -Ethyl- <i>p</i> -toluidine .....	0 †
Diphenylamine .....	58		

\* Ethyl-*o*-toluidine gave a 39% yield of *N*-ethyl-2-methyl-4-nitrosoaniline. † *N*-Ethyl-*p*-toluidine gave *N*-ethyl-*N*-nitroso-*p*-toluidine which remained unchanged by further treatment.

to a fresh mixture of sodium nitrite and ice. The ether layer was treated three times in this manner, and then the combined aqueous nitrous acid solutions were treated with sulphamic acid and coupled with 2-naphthol. The yields of azo-dye are listed in the Table. The reaction with *N*-methyl- and *N*-ethyl-aniline and with diphenylamine was straightforward and, as the Table shows, gave moderate yields of diazonium salt. *N*-Ethyl-*o*-toluidine was of particular interest because *NN*-dialkyl-*o*-toluidine is unreactive towards nitrous acid (see previous paper). However, it had been shown previously that *N*-ethyl-*N*-nitroso-*o*-toluidine undergoes a Fischer-Hepp rearrangement,<sup>2</sup> so a good yield of diazonium salt was expected. As the Table shows, although the *C*-nitroso-amine was formed, this was only partly converted into the diazonium salt; the reason for this slow reaction remains obscure.

*NN*-Dimethyl-*p*-toluidine and -*p*-anisidine are rapidly converted into *o*-nitro-derivatives by nitrous acid.<sup>1</sup> It was interesting to see if a similar reaction could be induced with *N*-ethyl-*p*-toluidine. If the 2-nitroso-amine were formed it might be expected to yield transiently the diazonium salt, which would react intramolecularly, giving the known *N*-alkyl-4,5-benzotriazole. However, in agreement with previous work, the *N*-ethyl-*N*-nitroso-*p*-toluidine failed to undergo a Fischer-Hepp rearrangement and treatment with further nitrous acid was also without effect.

#### EXPERIMENTAL

*N*-Methylaniline.—Sodium nitrite (4.14 g.) in water (20 c.c.) was added slowly to *N*-methylaniline (3.21 g.) in 2*N*-hydrochloric acid (75 c.c.) at <5° and stirring was continued for a further 0.5 hr. The mixture was made alkaline with sodium carbonate, and the *N*-methyl-*N*-nitrosoaniline was extracted in ether (no diazonium salt could be detected in the aqueous mother-liquor). The ether extract was dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated to 30 c.c., then shaken with concentrated hydrochloric acid (15 c.c.) for 20 min., and the whole was added to a solution of sodium nitrite (15 g.) in water and ice. After ½ hour's stirring, the excess of nitrous acid was destroyed by sulphamic acid, and the mixture rendered alkaline by sodium hydrogen carbonate. The mixture was thoroughly extracted with ether and the aqueous residue was coupled with alkaline β-naphthol. The ether layer was shaken with fresh concentrated hydrochloric acid (25 c.c. of ether solution with 45 c.c. of concentrated hydrochloric acid), and the whole process was repeated twice. The total yield of azo-dye, m. p. 176—178°, from the three treatments was 4.05 g. Recrystallisation from acetone gave 1-[*p*-(*N*-methyl-*N*-nitrosoamino)-phenylazo]-2-naphthol as red crystals, m. p. 179—180°<sup>3</sup> (Found: C, 66.4; H, 4.8; N, 18.0. Calc. for C<sub>17</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>: C, 66.7; H, 4.6; N, 18.3%), λ<sub>max.</sub> (in 95% EtOH) 480 mμ (ε 37,400).

<sup>3</sup> Hodgson and Marsden, *J.*, 1944, 400.

*N-Ethylaniline*.—Sodium nitrite (4.19 g.) in water (20 c.c.) was added slowly to *N*-ethylaniline (3.63 g.) in 2*N*-hydrochloric acid (125 c.c.). The reactants were stirred for a further  $\frac{1}{2}$  hr., still at  $<5^\circ$ . The mixture was neutralised with sodium hydrogen carbonate and extracted with ether (no diazonium salt could be detected in the aqueous phase). The ether extract was dried, concentrated to 30 c.c., and shaken with concentrated hydrochloric acid (45 c.c.) for 20 min. The subsequent treatment was similar to the previous experiment. The yield of crude azo-dye after four cycles was 5.88 g.; recrystallisation from acetone gave deep red 1-[*p*-(*N*-ethyl-*N*-nitrosoamino)phenylazo]-2-naphthol, m. p. 157—158° (Found: C, 67.4; H, 5.0; N, 17.4.  $C_{19}H_{16}N_4O_2$  requires C, 67.5; H, 5.0; N, 17.5%),  $\lambda_{max}$ . (in 95% ethanol) 458  $m\mu$  ( $\epsilon$  34,300).

*NN-Diphenylamine*.—2*N*-Hydrochloric acid (100 c.c.) was added to diphenylamine (3.38 g.) and sodium nitrite (78 g.) in acetone (225 c.c.) and water (75 c.c.) at 3—5°. The mixture was kept at 5° for 24 hr., then the acetone was evaporated under reduced pressure and the *N*-nitrosodiphenylamine separated as yellow-green plates (3.7 g.), 65—66°.<sup>4</sup> A solution of the nitroso-amine in ether (30 c.c.) was shaken with concentrated hydrochloric acid (45 c.c.) for 20 min., and mixture was added to a stirred solution of sodium nitrite (10 g.) in ice and water. Subsequent treatment was similar to the previous experiments and the yield of azo-dye from the first cycle was 3.84 g. (m. p. 150—155°). The ether solution was concentrated to 30 c.c. and recycled to yield a little more (0.1 g.) dye. The combined dye was recrystallised from aqueous ethanol, to give 1-(*p*-phenylaminophenylazo)-2-naphthol, m. p. 166—167° (lit.,<sup>4</sup> 168—170°) (Found: C, 76.2; H, 5.01; N, 11.6. Calc. for  $C_{22}H_{17}N_3O$ ,  $\frac{1}{2}H_2O$ : C, 75.9; H, 5.1; N, 12.1%),  $\lambda_{max}$ . (in 95% ethanol) 521  $m\mu$  ( $\epsilon$  38,200).

*N-Ethyl-o-toluidine*.—Sodium nitrite (4.14 g.) in water (20 c.c.) was added to a cold, stirred solution of *N*-ethyl-*o*-toluidine in 2*N*-hydrochloric acid (75 c.c.). After  $\frac{1}{2}$  hr. the solution was neutralised with sodium hydrogen carbonate and extracted with ether. The ether layer was dried, concentrated to 50 c.c., and shaken with concentrated hydrochloric acid (45 c.c.). This mixture was added to a stirred solution of sodium nitrite (10 g.) in ice and water. The mixture was stirred for  $\frac{1}{2}$  hr., then the nitrous acid was destroyed by sulphamic acid and the system neutralised with sodium carbonate. The mixture was extracted with ether, and the aqueous layer coupled with alkaline  $\beta$ -naphthol to give a poor yield (0.4 g.) of crude azo-dye. Recrystallisation from methanol yielded 1-[4-(*N*-ethyl-*N*-nitrosoamino)-*o*-tolylazo]-2-naphthol (0.25 g.), m. p. 131—132°, as an amorphous red solid (Found: C, 68.2; H, 5.4; N, 17.1.  $C_{17}H_{18}N_4O_2$  requires C, 68.8; H, 5.4; N, 16.8%),  $\lambda_{max}$ . (in 95% ethanol) 465  $m\mu$  ( $\epsilon$  15,900). The ether layer (see above) was dried and concentrated; green crystals (1.4 g.) separated. The filtrate was completely evaporated to give an oil (2.8 g.) which was redissolved in ether, shaken with fresh concentrated hydrochloric acid, and completely recycled. This treatment failed to yield further diazonium salt. Working up of the final ether solution gave further green crystals (0.5 g.) and unchanged *N*-nitroso-amine (1.13 g.). The two portions of green crystals were combined and recrystallised from benzene-light petroleum (b. p. 60—80°), to give *N*-ethyl-4-nitroso-*o*-toluidine, m. p. 136—137°<sup>2</sup> (Found: C, 65.8; H, 7.3; N, 16.9. Calc. for  $C_9H_{12}N_2O$ : C, 65.8; H, 7.3; N, 17.0%).

*N-Methyl-p-toluidine*.—A solution of sodium nitrite (4.14 g.) in water (15 c.c.) was added to a cold, stirred solution of *N*-methyl-*p*-toluidine (3.63 g.) in 2*N*-hydrochloric acid (125 c.c.). After  $\frac{1}{2}$  hr. *N*-methyl-*N*-nitroso-*p*-toluidine (8.2 g.) was collected by filtration. A portion, when recrystallised, had m. p. 48—49°.<sup>2</sup> A solution of this product (6.56 g.) in ether was shaken with concentrated hydrochloric acid (35 c.c.). When this mixture was poured on ice and sodium nitrite as in the previous experiments, no diazonium salt could be detected in the aqueous phase: the *N*-nitroso-*N*-methyl-*p*-toluidine was recovered unchanged from the ether layer.

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<sup>4</sup> Morgan and Micklethwait, *J.*, 1908, 613; Bamberger BÜsdorf, and Sand, *Ber.*, 1898, 31, 1516.