2 : 3-*Derivatives of Naphthalene. Part II.** *Preparation of 2 : 3-Dinitronaphthalene and 3-Nitro-2-naphthylamine.*

By E. R. Ward and T. M. Coulson.

[Reprint Order No. 5607.]

Improved syntheses of 2 : 3-dinitronaphthalene and 3-nitro-2-naphthylamine are described.

Van Rij, Verkade, and Wepster (*Rec. Trav. chim.*, 1951, **70**, 236) obtained 2 : 3-dinitronaphthalene and 3-nitro-2-naphthylamine by the route: 6-acetyl-1 : 2 : 3 : 4-tetrahydronaphthalene ⟶ 6-acetamido-1 : 2 : 3 : 4-tetrahydronaphthalene (by Beckmann rearrangement of the oxime) ⟶ 6-acetamido-1 : 2 : 3 : 4-tetrahydro-7-nitronaphthalene (nitration and separation from attendant 5-nitro-compound) ⟶ 6-amino-1 : 2 : 3 : 4-tetrahydro-7-nitronaphthalene ⟶ 1 : 2 : 3 : 4-tetrahydro-6-nitro-7-nitrosonaphthalene (oxidation with persulphuric acid) ⟶ 1 : 2 : 3 : 4-tetrahydro-6 : 7-dinitronaphthalene (oxidation with hydrogen peroxide and nitric acid) ⟶ 2 : 3-dinitronaphthalene (bromination, dehydrobromination) ⟶ 3-nitro-2-naphthylamine (reduction with sodium disulphide in methanol). The overall yield of dinitronaphthalene was 3·55%, and of nitro-

---

* Part I, preceding paper.

naphthylamine, 1·56%. By simplifying and modifying this route, we have increased these overall yields to 14·2% and 10·0% respectively, the latter representing a six-fold increase in the overall yield of the most inaccessible of the fourteen nitronaphthylamines.

The Beckmann rearrangement of the oxime we carried out with polyphosphoric acid (Horning *et al.*, *J. Amer. Chem. Soc.*, 1952, **74**, 2680, 5151, 5153); one-third of the amount of polyphosphoric acid prescribed by these authors gave a 95—99% yield. Using benzenesulphonyl chloride in pyridine for the rearrangement, Verkade *et al.* (*loc. cit.*) obtained a yield of 75%. We confirmed that 6-acetamido-1 : 2 : 3 : 4-tetrahydronaphthalene, prepared by catalytic hydrogenation of 2-naphthylamine, behaved less satisfactorily in the subsequent nitration: this reaction, described by Schroeter (*Annalen*, 1922, **426**, 65) has been used, apparently satisfactorily, by several other investigators, including Verkade *et al.*, but we were unable to obtain the yield claimed or to get a good granular crude product. Acetyl nitrate in acetic anhydride was more efficient but still not entirely satisfactory.

We converted 6-amino-1 : 2 : 3 : 4-tetrahydro-7-nitronaphthalene into 1 : 2 : 3 : 4-tetrahydro-6 : 7-dinitronaphthalene in one stage by diazotisation and replacement of the diazonium by the nitro-group, by an extension of the method of Hodgson, Mahadevan, and Ward (*J.*, 1947, 1392; cf. Hodgson and Mahadevan, *J.*, 1947, 325) (see p. 4547). We have applied this modification satisfactorily to other amines. Our yield was 55%, which compares favourably with 35% for the original two-stage conversion. Chudozilov (*Coll. Czech. Chem. Comm.*, 1929, **1**, 302) obtained a 3% yield by a direct diazo-decomposition.

In the dehydrogenation of 1 : 2 : 3 : 4-tetrahydro-6 : 7-dinitronaphthalene by bromination–dehydrobromination, we have increased the yield from 10% (Chudozilov, *loc. cit.*) or 43% (Verkade *et al.*, *loc. cit.*) to 74%.

In the last stage Verkade *et al.* obtained a 44% yield in 7 hours. We obtained a 70% yield in 30 minutes by using sodium hydrogen sulphide in methanol (Hodgson and Ward, *J.*, 1949, 1187).

EXPERIMENTAL

Preparation and Beckmann Rearrangement of Methyl 5 : 6 : 7 : 8-*Tetrahydro*-2-*naphthyl Ketoxime*.—To a solution of sodium hydroxide (120 g.) in water (800 c.c.), containing ice (700 g.), was added hydroxylamine hydrochloride (100 g.). After dissolution, 6-acetyl-1 : 2 : 3 : 4-tetrahydronaphthalene (50 g.) was added, followed by sufficient ethanol (*ca.* 1300 c.c.) to give a clear solution. After 2 days, the mixture was neutralised to phenolphthalein with hydrochloric acid and diluted with water (to 10 l.), and the product collected and dried (52 g., 95%). This had m. p. 101—104°, raised to 106° by recrystallisation from aqueous ethanol (Verkade *et al.*, *loc. cit.*, give 105—106°).

The oxime (100 g.) was heated with tetraphosphoric acid (1 kg.) at 105° for 10 min. with stirring, then poured into warm water (8 l.). Stirring was continued until the product became granular; this was separated, triturated with water, filtered at the pump, and washed repeatedly with water (yield, 96 g., 96%; m. p. 104—106°; Verkade *et al.*, *loc. cit.*, give 106—107°).

Nitration of 6-*Acetamido*-1 : 2 : 3 : 4-*tetrahydronaphthalene*.—To a suspension of the amide (5 g.) in acetic anhydride (5 c.c.) was added dropwise a 1 : 1 (v/v) mixture (4·5 c.c.) of acetic anhydride and nitric acid (*d* 1·42) with stirring, the temperature being allowed to rise to, but not to exceed, 40°. Stirring was continued for a further hour, and the precipitate which appeared overnight was collected, washed with ether, and dried (1·38 g.). The filtrate was poured into water (200 c.c.), and after 2 days the precipitate was filtered off, washed with water, dried, and recrystallised from ethanol (20 c.c.). The combined yield of 6-acetamido-1 : 2 : 3 : 4-tetrahydro-7-nitronaphthalene, m. p. 133—135° (Verkade *et al.*, *loc. cit.*, give 134—135°), was 2·35 g. (38%). The yield decreased on working with larger amounts. Nitration in acetic acid containing boron trifluoride proceeded at a lower temperature and gave a similar yield, but gave a greatly reduced yield on the large scale. *Note Added in Proof.*—The direct conversion of 1 : 2 : 3 : 4-tetrahydro-7-nitronaphthalene into 2-acetamido-3-nitronaphthalene by bromination and dehydrobromination has now been reported (Curtis and Viswanath, *Chem. and Ind.*, 1954, 1174).

6-*Amino*-1 : 2 : 3 : 4-*tetrahydro*-7-*nitronaphthalene*.—The acetyl compound (60 g.) was refluxed (30 min.) with ethanol (300 c.c.) and aqueous sulphuric acid (50% v/v; 300 c.c.).

The mixture was cooled, poured into ice-water (6 l.), and basified with ammonia at 0°, and the precipitate collected. The product was purified by dissolving it in boiling aqueous hydrochloric acid (10% w/v), filtering, and basifying the filtrate with ammonia at 0°. It was collected, washed with water, and dried (yield, almost quantitative), and then had m. p. 124—127° (Verkade *et al.*, *loc. cit.*, give 126—127°).

1 : 2 : 3 : 4-*Tetrahydro*-6 : 7-*dinitronaphthalene.*—The foregoing amine (10 g.) was stirred into a solution of sodium nitrite (4·2 g.) in sulphuric acid (*d* 1·84; 21 c.c.) below 20°, and this solution was added, below 30°, to acetic acid (42 c.c.). After 30 min., ether (250 c.c., dried over sodium) was stirred in, and the mixture cooled at 0° for 1 hr. The supernatant liquor was decanted from the pasty precipitate, and the latter twice washed with ether by decantation. Residual ether was removed with a jet of air. The paste was dissolved in ice-water (100 g.), and the solution added dropwise, below the surface, to the decomposition mixture with vigorous stirring. [The decomposition mixture was prepared by adding a solution of crystalline sodium sulphite (65 g.) in water (250 c.c.) to one of crystalline copper sulphate (65 g.) in water (500 c.c.), then adding, immediately before use, a solution of sodium nitrite (130 g.) in water (500 c.c.).] After 1 hour's stirring the mixture was set aside until evolution of gas had ceased (1—2 days), and the solids were filtered off, washed with water, dried, and extracted several times with boiling methanol (350 c.c. in all). The extract was refluxed with charcoal, filtered, and concentrated to 25 c.c. On cooling, crude material (6·5 g.) was obtained, which, on recrystallisation from hot methanol (60 c.c.) gave a pure product (5·1 g.), m. p. 107—108° (Kuhn and van Klaveren, *Ber.*, 1938, **71**, 779, give 108°). Evaporation of the combined mother-liquors to dryness gave a paste, from which the oil was separated by filtration. On recrystallisation of the residue from methanol, a further quantity of pure product was obtained (total yield, 6·3 g., 55%). By the method of Hodgson, Heyworth, and Ward (*J.*, 1948, 1512), the yield was 52%; a modification of Hodgson and Ward's method (*J.*, 1947, 127) gave a 40% yield. In this the amine was diazotised in 60% sulphuric acid and neutralised by chalk, sodium cobaltinitrite solution was stirred into the resultant slurry, and the mixture, without filtration at any stage, was used for the decomposition in the ordinary way.

2 : 3-*Dinitronaphthalene.*—1 : 2 : 3 : 4-Tetrahydro-2 : 3-dinitronaphthalene (10 g.) was treated dropwise (shaking) with bromine (4·6 c.c.) under a reflux water-condenser. The mixture was then heated on the boiling-water bath until evolution of hydrogen bromide ceased, and then further heated at 170—190°, again until no more hydrogen bromide was evolved. After cooling, the solid cake was loosened by boiling with ethanol, then crushed and repeatedly extracted with ethanol under reflux. The combined extracts (500 c.c.) were filtered, refluxed with charcoal, filtered, concentrated to 200 c.c., and cooled, the precipitate was collected, and the mother-liquor further concentrated to obtain more product. The total yield was 7·24 g. (74%), and the m. p. 172—174° (Verkade *et al.*, *loc cit.*, give 174·5—175°).

3-*Nitro*-2-*naphthylamine.*—The procedure followed was that of Hodgson and Ward (*J.*, 1949, 1187; cf. Ward, Coulson, and Hawkins, *J.*, 1954, 2974). After purification by dissolution in boiling hydrochloric acid (10% w/v) and basification with ammonia at 0°, the product (yield, 70%) had m. p. 109—113°, raised to 115—116° by crystallisation from light petroleum (b. p. 100—120°; charcoal). Verkade *et al.*, *loc cit.*, give 115—116°. The filtrate after removal of the crude product was purple, but attempts to obtain from it a nitronaphthyl sulphide (by acidification), or a di(nitronaphthyl) disulphide (by oxidation) failed.

The authors are indebted to the Department of Scientific and Industrial Research for a maintenance grant (to T. M. C.), to Professor P. E. Verkade for providing authentic specimens of 2 : 3-dinitronaphthalene and 3-nitro-2-naphthylamine, and to Imperial Chemical Industries Limited, Dyestuffs Division, for gifts of chemicals.

LEICESTER COLLEGE OF TECHNOLOGY AND COMMERCE,
LEICESTER.

[*Received, July* 30*th*, 1954.]