

CCCCXL.—*Nitro-derivatives of Naphthalene, Tetrahydronaphthalene, and Dinaphthyl.*

By WILLIAM MURDOCH CUMMING and GEORGE HOWIE.

CHUDOŽILOV (*Chem. Listy*, 1925, **19**, 187) has applied Ullmann's method (*Ber.*, 1901, **34**, 2174; *Annalen*, 1904, **332**, 38), *i.e.*, condensation of iodonitro-compounds by means of copper powder, to the preparation of numerous symmetrical nitrodinaphthyls. He found that only when the nitro-group is in the ortho-position to the halogen does the reaction proceed at all well. Thus 1:2- and 2:1-iodonitronaphthalenes react readily, whereas 1-iodo-3- and -4-nitronaphthalenes condense only above 200° and with much decomposition. In cases where the halogen and the nitro-group were in different nuclei nothing definite was isolated.

Although 1-iodo-3-nitronaphthalene condenses to give a small yield of the dinitrodinaphthyl, we have found that the reaction completely fails when 1-bromo-3-nitronaphthalene is employed. Schoepfle (*J. Amer. Chem. Soc.*, 1923, **45**, 1566) was able to condense 1-bromonaphthalene only at a high temperature, and the yield was barely 50% as compared with 74% when the iodo-compound was used (Ullmann, *loc. cit.*). Condensation of 2-iodo-4-nitro- and 4-iodo-2-nitro- α -naphthylamine and of the corresponding bromo-derivatives could not be effected.

In the course of this work, several iodonitro-*ar*-tetrahydronaphthalenes have been prepared. The *o*-compounds, *e.g.*, 2-iodo-1-nitro- and 2-iodo-3-nitro-tetrahydronaphthalenes, are again readily condensed, but the 3:1- and 1:3-derivatives do not react.

From the above results it is concluded that Ullmann's generalisations (*loc. cit.*) for the preparation of symmetrical diphenyls hold also in both the naphthalene and the tetrahydronaphthalene series, *viz.*, (1) the order of reactivity of the halogen is $I > Br > Cl$; (2) the halogen is activated by the presence of an acidic group (particularly NO_2) in the ortho-position to the halogen.

No condensation of the halogenitronaphthalenes could be effected by sodium, even in the case of ortho-compounds.

By the nitration of 2:2'-dinaphthyl, a mononitro-compound,

m. p. 179°, was obtained which on further nitration yielded a mixture of dinitro-isomerides, m. p. 198—208°. From the acid reduction product of the isomerides, 1 : 1'-imino-2 : 2'-dinaphthyl was isolated. The imine is formed from 1 : 1'-diamino-2 : 2'-dinaphthyl and hence the dinitro-isomerides contain 1 : 1'-dinitro-2 : 2'-dinaphthyl, from which it follows that the mononitrodinaphthyl is 1-nitro-2 : 2'-dinaphthyl.

The constitutions of the 2-iodo-4-nitro- and 4-iodo-2-nitro- α -naphthylamine described were established by elimination of the amino-groups.

EXPERIMENTAL.

4-Iodo-2-nitro- α -naphthylamine.—A solution of 2 g. of 2-nitro- α -naphthylamine (Lellmann and Remy, *Ber.*, 1886, **19**, 796; Morgan and Micklethwait, *J.*, 1905, **87**, 928) in 75 c.c. of glacial acetic acid was treated at room temperature with 1.8 g. of iodine monochloride in 20 c.c. of glacial acetic acid. After 18 hours, the crystals which had separated were washed with a little glacial acetic acid and finally with water and recrystallised from alcohol, 1.95 g. of the *iodo*-compound being obtained in bright orange needles, m. p. 192—193° (Found : I, 40.6. $C_{10}H_7O_2N_2I$ requires I, 40.45%).

2-Iodo-4-nitro- α -naphthylamine.—4-Nitro- α -naphthylamine (Lellmann and Remy; Morgan and Micklethwait, *loc. cit.*) (2 g.), iodinated as above, gave 2.1 g. of the *iodo*-compound, which formed yellowish-brown prisms, m. p. 234°, from alcohol (Found : I, 39.6%).

1-Iodo-3-nitrotetrahydronaphthalene.—A solution of 3.5 g. of 3-nitrotetrahydro- α -naphthylamine hydrochloride (Schroeter, *Annalen*, 1922, **426**, 43) in 100 c.c. of *N*/2-hydrochloric acid was diazotised with 1.3 g. of sodium nitrite in 30 c.c. of water and added to a solution of potassium iodide. After several hours, the precipitate was collected and extracted with alcohol, and the extract refluxed with decolorising carbon and filtered into dilute aqueous sodium hydroxide to remove free iodine. The precipitate, recrystallised from alcohol, gave 1.5 g. of the *iodo*-compound in colourless needles, m. p. 118—118.5° (Found : I, 42.0. $C_{10}H_{10}O_2NI$ requires I, 41.9%).

2-Iodo-1-nitrotetrahydronaphthalene.—3 G. of 1-nitrotetrahydro- β -naphthylamine (Schroeter, *loc. cit.*) in 20 c.c. of glacial acetic acid were precipitated with 40 c.c. of *N*/2-sulphuric acid. The fine precipitate, treated as above, gave 1.7 g. of the *iodo*-compound, which formed orange-red needles, m. p. 84°, from alcohol (Found : I, 41.7%).

2-Iodo-3-nitrotetrahydronaphthalene.—23.5 G. of 3-nitrotetrahydro- β -naphthylamine (Schroeter, *loc. cit.*) in 200 c.c. of 50% sulphuric acid, treated as above, gave 17 g. of the *iodo*-compound, which crystallised in long orange-yellow prisms, m. p. 76—76.5°, from alcohol (Found : I, 41.9%).

3-Iodo-1-nitrotetrahydronaphthalene.—20 G. of 4-nitrotetrahydroacet- β -naphthalide, prepared by the method of Schroeter (*loc. cit.*) by nitration at 15—20° instead of below 0°, were hydrolysed by refluxing for 2 hours with 200 c.c. of 25% sulphuric acid. The clear solution gave the sulphate of the base on cooling. 250 C.c. of 50% sulphuric acid were now added and the solution was treated as described above. The oily precipitate from the filtration into dilute sodium hydroxide solution was removed, washed with water and then with cold alcohol, and fractionated under reduced pressure. The fraction, b. p. 175—195°/8 mm., solidified on cooling and, recrystallised from alcohol, gave 7 g. of the iodo-compound in pale yellow needles, m. p. 64—65° (Found: I, 41.85%).

2-Iodo-3-nitronaphthalene.—1 G. of 2-iodo-3-nitrotetrahydronaphthalene was oxidised by bromine (Vesely and Dvořák, *Bull. Soc. chim.*, 1923, **33**, 326). The second stage in the oxidation commenced at 130—135° and was completed by keeping the temperature for 1 hour at 160°. Much decomposition, however, took place at the higher temperatures. The cold reaction product gave, after three recrystallisations from alcohol (charcoal), about 0.05 g. of the iodo-compound in greenish-yellow prisms, m. p. 89—89.5° (Found: I, 42.3. $C_{10}H_6O_2NI$ requires I, 42.5%).

3-Iodo-1-nitronaphthalene.—(1) 1 G. of 3-iodo-1-nitrotetrahydronaphthalene, oxidised by bromine as above, gave a small quantity of the iodo-compound, which formed pale yellow needles, m. p. 108°, from alcohol (Found: I, 41.5%). (2) 1 G. of 2-iodo-4-nitro- α -naphthylamine, treated as in preparation (2) of 1-iodo-3-nitronaphthalene, gave 0.05 g. of the iodo-compound, pale yellow needles, m. p. 108°, from alcohol. A mixed m. p. with that obtained above gave no depression.

1-Iodo-3-nitronaphthalene.—(1) *Attempted replacement of bromine in 1-bromo-3-nitronaphthalene.* When the bromo-compound (Meldola, J., 1885, **47**, 497) was refluxed in alcohol, or fused at 145°, with sodium iodide, no reaction took place.

(2) *Elimination of the amino-group in 4-iodo-2-nitro- α -naphthylamine.* 1 G. of the iodo-compound in 175 c.c. of absolute alcohol and 4 c.c. of concentrated sulphuric acid was treated with 1 g. of amyl nitrite in absolute alcohol and the whole boiled for 10 minutes. The addition of water gave a yellowish precipitate which, recrystallised from alcohol (charcoal), gave 0.2 g. of the iodo-compound in orange-yellow needles, m. p. 147°.

(3) *The method of Chudožilov.* Replacement of the amino-group in 3-nitro- α -naphthylamine gave a product, m. p. 147°, and not 142—143°.

1 : 1'-Dinitro-2 : 2'-bistetrahydronaphthyl.—1.7 G. of 2-iodo-1-

nitrotetrahydronaphthalene were fused with 1.5 g. of copper powder. The reaction began at about 135° and was complete at 190°. The fused mass was cooled, crushed, and extracted with benzene with addition of decolorising carbon. After removal of the benzene, the residue, recrystallised from glacial acetic acid, gave 0.2 g. of the *dinitro*-compound in irregular prisms, m. p. 187—188° (Found : N, 8.0. $C_{20}H_{20}O_4N_2$ requires N, 7.95%).

3 : 3'-*Dinitro*-2 : 2'-*bistetrahydronaphthyl*.—16 G. of 2-iodo-3-nitrotetrahydronaphthalene were heated to 110—120°, and 16 g. of copper powder gradually added. After $\frac{1}{2}$ hour at 140° the mass hardened. The reaction product, treated as above, gave 7 g. of the *dinitro*-compound, which formed yellow silky needles, m. p. 201°, from glacial acetic acid (Found : N, 8.1%).

4 : 4'-*Dinitro*-1 : 1'-*dinaphthyl*.—10 G. of 1 : 1'-dinaphthyl, nitrated according to the method of Schoepfle (*loc. cit.*), gave 8 g. of dinitro-compound. It was found much better to crystallise this from nitrobenzene; yellow prisms, m. p. 246°. Attempts to prepare the dinitro-compound by condensation of 4-nitronaphthalene-1-diazonium sulphate with copper paste failed.

3 : 3'-*Dinitro*-1 : 1'-*dinaphthyl*.—4 G. of 1-iodo-3-nitronaphthalene, condensed according to Chudožilov (*loc. cit.*), gave 0.8 g. of crude dinitrodinaphthyl, which, recrystallised twice from glacial acetic acid, gave 0.4 g. of golden-yellow plates, m. p. 281°. Chudožilov obtained a somewhat higher yield but describes his product as greenish-coloured crystals, m. p. 262—264°.

2 : 2'-*Dinitro*-1 : 1'-*dinaphthyl*.—Modification of the method of Chudožilov (*loc. cit.*), which we found did not give reliable results, was made as follows: 10 G. of 1-iodo-2-nitronaphthalene were fused at 120—130° and the copper powder was added in small quantities during 1 hour. After extraction and recrystallisation, 4 g. of dinitrodinaphthyl were obtained in light yellow needles, m. p. 187° (Chudožilov describes his product as greenish needles, m. p. 179—180°). When the condensation was carried out in nitrobenzene, 2 g. of idonitronaphthalene gave 0.1 g. of dinitrodinaphthyl, m. p. 187°. On keeping, the distillate from the steam distillation to remove the nitrobenzene deposited crystals, which, recrystallised from light petroleum, gave 2-nitronaphthalene, m. p. 79°.

1 : 1'-*Dinitro*-2 : 2'-*dinaphthyl*.—10 G. of 2-iodo-1-nitronaphthalene, fused by the above modified method of Chudožilov, gave 3 g. of dinitrodinaphthyl, which formed pale yellow plates, m. p. 284° (decomp.), from nitrobenzene. Chudožilov records m. p. 264—265°, and Vesely (*Ber.*, 1905, **38**, 136), 276° (decomp.).

3 : 3'-*Dinitro*-2 : 2'-*dinaphthyl*.—6 G. of 3 : 3'-dinitro-2 : 2'-bistetra-

hydronaphthyl were oxidised with 11 g. of bromine as described under 2-iodo-3-nitronaphthalene. The dark product was extracted with glacial acetic acid, and the extract decolorised and cooled. Recrystallisation from glacial acetic acid of the crystals which separated gave 0.5 g. of the *dinitrodinaphthyl* in golden-yellow needles, m. p. 257—258° (Found: N, 8.0. $C_{20}H_{12}O_4N_2$ requires N, 8.1%).

1-Nitro-2:2'-dinaphthyl.—2 G. of 2:2'-dinaphthyl, suspended in 40 c.c. of glacial acetic acid and 0.8 c.c. of nitric acid (d 1.42), were maintained at 100° for 1½ hours. The dinaphthyl disappeared and a light yellow compound separated. After cooling, the *nitro*-compound was collected, washed free of acid, and crystallised from glacial acetic acid, 2 g. of light yellow needles, m. p. 179°, being obtained (Found: N, 4.6. $C_{20}H_{13}O_2N$ requires N, 4.6%).

1:1'-Dinitro-2:2'-dinaphthyl and Isomerides.—5 G. of 1-nitro-2:2'-dinaphthyl in 45 c.c. of glacial acetic acid were treated with 10 c.c. of nitric acid (d 1.50) at 100°. After 1 hour, most of the dinitro-compounds had separated; the remainder crystallised on cooling. Recrystallised from glacial acetic acid, 3 g. of the dinitro-isomerides were obtained, m. p. 198—208° (Found: N, 8.1, 8.1. $C_{20}H_{12}O_4N_2$ requires N, 8.1%). The same mixture resulted on treatment of 2:2'-dinaphthyl, suspended in glacial acetic acid, with excess of fuming nitric acid at 100°. No separation of the isomerides could be effected by continued fractional recrystallisation.

Reduction of the Dinitro-2:2'-dinaphthyl Isomerides.—1 G. in the minimum quantity of boiling glacial acetic acid was reduced with zinc dust and 5 c.c. of concentrated hydrochloric acid. When the solution was gently refluxed, a white compound separated (6 hours). Recrystallised from glacial acetic acid, colourless leaflets, m. p. 221°, of 1:1'-imino-2:2'-dinaphthyl were obtained; a mixed m. p. with that obtained from dinaphthylene (1:1'-diamino-2:2'-dinaphthyl) gave no depression. The filtrate from the imine, on neutralisation with sodium hydroxide, yielded a mixture of diaminodinaphthyls which could not be separated by continued fractional recrystallisation.

1- and 2-Nitrotetrahydronaphthalenes.—The method of Schroeter (*loc. cit.*) was modified as follows: To 132 g. of tetrahydronaphthalene, b. p. 206—208°, maintained under efficient agitation and external cooling at 15—20°, was added, during 1 hour, a mixture of 100 g. of nitric acid (d 1.405) and 260 g. of concentrated sulphuric acid. The product, after being stirred for ½ hour at 20°, was poured into ice-water, and the brown emulsion treated as described by Schroeter; 125 g. of mixed isomerides were obtained. Schroeter claims an 80% yield, but under his conditions we recovered more

than half of the tetrahydronaphthalene unchanged. Moreover, his statement that tetrahydronaphthalene boils above $175^{\circ}/13$ mm. is incorrect; the b. p. was found to be $95-97^{\circ}/16$ mm.

ar-Tetrahydro- β -naphthylamine.—125 G. of mixed 1- and 2-nitro-tetrahydronaphthalenes were reduced according to Veselý and Chudožilov (*Rec. trav. chim.*, 1925, **44**, 352). These authors' long process for separating tetrahydro- β -naphthylamine from unchanged nitro-compounds was simplified by extracting the residue from the removal of the alcohol with ether, and precipitating the hydrochloride of the base by passing hydrogen chloride through the dried ethereal solution. The tetrahydro- β -naphthylamine hydrochloride formed colourless plates from dilute hydrochloric acid.

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THE ROYAL TECHNICAL COLLEGE,
GLASGOW.

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