26. *The Application of Ullmann's Reaction to the Preparation of Dinaphthyls.*

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CHUDOŽILOV (*Chem. Listy*, 1925, **19**, 187) applied Ullmann's method (*Ber.*, 1901, **34**, 2174; *Annalen*, 1904, **332**, 38) of heating aromatic halogeno-compounds with finely divided copper to form diaryls to the iodonitronaphthalenes, and reported that only the homonuclear derivatives afforded dinaphthyls. Further, from a study of the 1-iodo-2-, -3-, and -4-nitronaphthalenes and of 2-iodo-1-nitronaphthalene, Chudožilov concluded that the iodine should preferentially be in the ortho-position to the nitro-group for satisfactory results. Cumming and Howie (J., 1931, 3176) supported Chudožilov's generalisations after an investigation of substituted tetrahydronaphthalenes. The effect of the unsubstituted nucleus on the iodine atom and its configuration with respect to the nitro-group appears, however, to have been overlooked, and the present investigation has established the very considerable influence of the adjacent nucleus.

Dinaphthyl formation by Ullmann's method appears to depend on the ability of the copper to form covalent cuprous iodide with the substituted iodine, since sodium has been found by Cumming and Howie (*loc. cit.*) not to effect condensation even in the case of the ortho-compounds. This reaction thus differs from the Fittig mechanism in that copper does not release one of its electrons to the carbon and so enable ionic iodine to separate, as sodium would do whether acting as metal or in sodium alkoxide, and consequently radical formation will depend upon the ease of detachment of neutral iodine from neutral carbon as depicted: $2RI + 2Cu \longrightarrow 2R^{\cdot} + Cu_2I_2 \longrightarrow R{:}R + Cu_2I_2$. Now the unsubstituted nucleus has been found to exert a restraining (electron-attracting) influence in numerous naphthalene derivatives, the most familiar example, perhaps, being the fact that β-naphthylamine is a stronger base than its α-isomeride; the easier detachment of iodine from 3-iodo-1-nitronaphthalene than from 1-iodo-3-nitronaphthalene (cf. Chudožilov; Cumming and Howie, *locc. cit.*) provides additional evidence of this kationoid effect. Consequently Chudožilov's ortho-generalisation must be modified by taking into account the effect of the unsubstituted nucleus, which will depend on the position of the iodine. A test case for this effect would appear to be furnished by the fact that in a relatively inert medium such as nitrobenzene, the 4-iodine (*i.e.*, meta to the nitro-group) was removed by copper from 1 : 4-*di-iodo*-2-*nitronaphthalene* instead of the 1-iodine as would be expected from Chudožilov's generalisation, with the formation of 4 : 4′-*di-iodo*-3 : 3′-*dinitro*-1 : 1′-*dinaphthyl*. The constitution of the last-named product was established by the production from it on heating of 3 : 3′-dinitro-1 : 1′-dinaphthyl and iodine.

The more severe operation of the dry heating of copper with 1 : 4-di-iodo-2-nitronaphthalene resulted mainly in the formation of 1-iodo-3-nitronaphthalene, though a little 1-iodo-2-nitronaphthalene was detected; the production and preservation of both the previous compounds in such drastic reactions testify to the strength of the bond between the iodine and the α-carbon atom, *i.e.*, to the restraining effect of the adjacent nucleus. With 1 : 2-di-iodo-4-nitronaphthalene, only α-nitronaphthalene could be isolated from the Ullmann reaction product, owing probably to the accommodation of the 2-iodine in relieving the strain on the 1-iodine, and thereby promoting ultimately the hydrogenation of both positions in the destructive decomposition which arises.

Cumming and Howie (*loc. cit.*) have reported the preparation of 3 : 3'-dinitro-2 : 2'-dinaphthyl in microscopic yield by the oxidation with bromine of the 3 : 3'-dinitro-2 : 2'-bistetrahydronaphthyl obtained from Ullmann's reaction with 2-iodo-3-nitrotetrahydronaphthalene. The present authors, however, could only obtain 2-nitronaphthalene when the reaction was applied to 3-iodo-2-nitronaphthalene itself, with no indication of dinaphthyl formation, a result entirely in harmony with the recorded instability of the 2 : 3-halogenonitronaphthalenes (Hodgson and Elliott, J., 1936, 1151), and in contradiction to Chudožilov's ortho-generalisation.

In marked contrast to 3-iodo-2-nitronaphthalene, which is non-volatile in steam, 3-iodo-1-nitro- and 1-iodo-3-nitro-naphthalene are volatile to the extent of 0·35 g. and 0·08 g., respectively, per litre of distillate.

EXPERIMENTAL.

Preparation of 4 : 4'-*Dinitro*-2 : 2'-*dinaphthyl*.—3-Iodo-1-nitronaphthalene (4 g.) (Hodgson and Elliott, J., 1934, 1706) was intimately mixed with precipitated copper powder (7 g.), and refluxed for 5 hours with freshly distilled and carefully dried nitrobenzene (25 c.c.); the liquid was filtered hot, 10 c.c. of nitrobenzene were removed by distillation, and the remainder was kept for 36 hours; deep brown, lustrous plates of 4 : 4'-*dinitro*-2 : 2'-*dinaphthyl* (0·2 g.) separated, m. p. 316° after recrystallisation from nitrobenzene (Found: N, 8·3. $C_{20}H_{12}O_4N_2$ requires N, 8·1%). After removal of the nitrobenzene from the mother-liquor by steam distillation and extraction of the residue with boiling glacial acetic acid, 1·75 g. of unchanged 3-iodo-1-nitronaphthalene were obtained. The residue from the first filtration (above), consisting mainly of copper powder and cuprous iodide, was extracted with boiling nitrobenzene, a further 0·15 g. of crude (m. p. 306°) 4 : 4'-dinitro-2 : 2'-dinaphthyl being obtained; total yield, 31·5%. Prolonged refluxing, for periods up to 10 hours, removed the iodine, but the product was mainly tar and the yields of the dinaphthyl were decreased.

Ullmann's Reaction with 2-*Iodo*-3-*nitronaphthalene*.—Copper powder (3 g.) and 2-iodo-3-nitronaphthalene (2 g.) (Hodgson and Elliott, *loc. cit.*) were refluxed for 5 hours with nitrobenzene (20 c.c.), this was then removed from the hot filtered liquid by steam distillation, and the residue was extracted with boiling glacial acetic acid. From this extract, only β-nitronaphthalene (0·3 g., m. p. 79°) could be obtained; the steam distillate afforded a further 0·08 g. No product of higher m. p. indicative of dinaphthyl formation could be identified in the copper residues.

Preparation of 1 : 4-*Di-iodo*-2-*nitronaphthalene*.—4-Iodo-2-nitronaphthylamine (20 g.) (Hodgson and Elliott, J., 1935, 1850), suspended in glacial acetic acid, was slowly added to a solution of sodium nitrite (6 g.) in concentrated sulphuric acid (100 c.c.) kept below 20°. The excess of nitrous acid was destroyed by urea, and the diazo-solution added rapidly to a saturated aqueous solution of potassium iodide (300 c.c.) at 15°, the temperature being allowed to reach 75°; much iodine and hydrogen iodide were evolved. After 1 hour, the mixture was stirred into cold water (1 l.); the precipitated 1 : 4-*di-iodo*-2-*nitronaphthalene* was extracted repeatedly with 10% aqueous potassium iodide (500 c.c.) and then with 90% alcohol (300 c.c.) to remove iodine; it was finally recrystallised three times from glacial acetic acid and obtained in dark brown scales, m. p. 126° (Found: I, 59·5. $C_{10}H_5O_2NI_2$ requires I, 59·8%).

1 : 2-*Di-iodo*-4-*nitronaphthalene*, obtained from 2-iodo-4-nitro-1-naphthylamine (Hodgson and Elliott, J., 1934, 1705) in like manner, crystallised from glacial acetic acid in deep chocolate-brown needles, m. p. 172° (Found: I, 59·6. $C_{10}H_5O_2NI_2$ requires I, 59·8%).

4 : 4'-*Di-iodo*-3 : 3'-*dinitro*-1 : 1'-*dinaphthyl*.—1 : 4-Di-iodo-2-nitronaphthalene (2 g.) and copper powder (2 g.) were refluxed for 5 hours with nitrobenzene (25 c.c.), and the residue remaining after steam distillation was extracted with boiling glacial acetic acid. After 24 hours, 4 : 4'-*di-iodo*-3 : 3'-*dinitro*-1 : 1'-*dinaphthyl* separated as a light brown, micro-crystalline powder, which softened with apparent decomposition at 220° and sublimation of iodine, fused at 275—280°, and decomposed completely at 375° (Found: I, 42·3. $C_{20}H_{10}O_4N_2I_2$ requires I, 42·6%). A larger amount, heated slowly above 220°, lost iodine and became 3 : 3'-dinitro-1 : 1'-dinaphthyl, the residue on crystallisation from glacial acetic acid affording golden-yellow plates of this compound, m. p. 281° (Cumming and Howie, *loc. cit.*, give m. p. 281°) (Found: N, 8·2. Calc. for $C_{20}H_{12}O_4N_2$: N, 8·1%). The acetic acid mother-liquor above, from which the 4 : 4'-di-iodo-3 : 3'-dinitro-1 : 1'-dinaphthyl had crystallised, was poured into water; 1-iodo-2-nitronaphtha-

lene was precipitated (0·15 g.) and after two crystallisations from glacial acetic acid it had m. p. and mixed m. p. with an authentic specimen (Hodgson and Kilner, J., 1926, 9) 111° (Found : I, 42·1. Calc. for $C_{10}H_6O_2NI$: I, 42·4%).

Action of Copper Powder alone on 1 : 4-*Di-iodo-*2-*nitronaphthalene.*—During the dry fusion of 1 : 4-di-iodo-2-nitronaphthalene (2 g.) with precipitated copper powder (2 g.), no reaction took place below 180—190°, but a glacial acetic acid extract of the reaction product after 2 hours' heating at 180—210°, when poured into water, afforded a brick-red precipitate (m. p. 112°) which, recrystallised once from glacial acetic acid and once from alcohol, gave orange-yellow needles (0·3 g.) of 1-iodo-3-nitronaphthalene, m. p. and mixed m. p. with an authentic specimen, 147° (Found : I, 42·3. Calc. for $C_{10}H_6O_2NI$: I, 42·4%). A trace of 1-iodo-2-nitronaphthalene (0·05 g.) was also identified (m. p. and mixed m. p.) in the acetic acid extract.

Action of Copper on 1 : 2-*Di-iodo-*4-*naphthalene.*—After 5 hours' refluxing with nitrobenzene and the procedure described above for the isomeride, this substance was recovered unchanged, but the iodine was completely removed after 10 hours' boiling, with formation of much tar, from which only α-nitronaphthalene could be extracted. Dry fusion, as above, produced complete decomposition at 200°.

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