

347. *Orientation Effects in the Diphenyl Series. Part XII. The Mono- and the Di-nitration of 4:4'-Dimethyldiphenyl.*

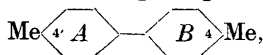
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THE conclusion drawn from a preliminary investigation (J., 1926, 476), that 4:4'-dimethyldiphenyl undergoes mononitration in position 2, further nitration producing the 2:3'-dinitro-compound, would if confirmed be of such importance from the point of view of the general problem of aromatic substitution that we have studied the nitration of ditolyl afresh. Harding's failure (*J. Soc. Chem. Ind.*, 1925, 44, 138T) to prepare a "di-saccharin" from ditolyl would be explained if 2:3'-disulphonation had occurred.

Under conditions in which diphenyl is only mononitrated, 4:4'-dimethyldiphenyl undergoes dinitration: from the product, only a single substance has been isolated, which is not the 2:2'- or the 3:3'-dinitro-4:4'-dimethyldiphenyl, and must therefore be the 2:3'-dinitro-compound, for otherwise it must contain two nitro-groups in one nucleus, which is inconceivable in view of the speed with which it is formed.

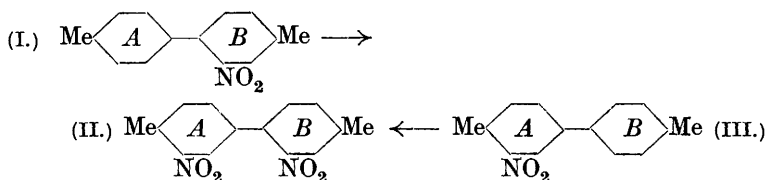
The product of mononitration of 4:4'-dimethyldiphenyl is practically a single substance, the only detectable impurity being the 2:3'-dinitro-compound. It is identical with 2-nitro-4:4'-dimethyldiphenyl synthesised from *p*-iodotoluene, 4-bromo-3-nitrotoluene, and copper-bronze, and is different from 3-nitro-4:4'-dimethyldiphenyl, prepared similarly from *p*-iodotoluene and 4-iodo-2-nitrotoluene. Both specimens of 2-nitroditolyl give 2:3'-dinitroditolyl when nitrated, and yield on reduction an aminoditolyl different from the "synthetic" 3-amino-compound.

Shaw and Turner (this vol., p. 1884), in discussing the results of mononitrating *p*-chloro- and *p*-bromo-toluene, concluded that activation not acquired by the *p*-positions became available at the *m*-positions. Application of this principle to ditolyl,



suggests that, mononitration being assumed to occur first in nucleus *B*, the 2-position would be markedly activated, even if nucleus *A* played no part. Actually, *A*, as our previous studies in this series have shown, has an activating effect on *B*; this activation is greatly enhanced owing to the presence of the methyl group in the 4'-position, and takes effect mainly in position 2. Therefore, a molecule of nitric acid which approaches near enough to *B* to react with it will react in the 2- rather than in the 3-position.

The dinitration stage is more difficult to explain, for although the 3'-nitration of 2-nitroditolyl may be regarded as normal, the same can hardly be said of the nitration of 3-nitroditolyl, which, as we now find, proceeds in position 2' :



It is possible to explain the 3'-nitration of 2-nitroditolyl (I \longrightarrow II), assuming that the nitro-group in *B* more than counteracts the activating effect of the methyl group (in *B*), so that nucleus *B* as a whole exerts a slightly deactivating effect on *A*. It would then appear to follow that when the nitro-group is *o* to the methyl group it cannot counteract the effect of that methyl group, since 3-nitroditolyl (III) is nitrated, as far as *B* is concerned, as if no nitro-group were present in *A*. That certain combinations (in the orientation sense) of nitro- and methyl groups have peculiar effects is known, though from a different aspect; *e.g.*, Lindemann and Pabst (*Annalen*, 1928, 462, 24) found that the relative positions of methyl and nitro-groups greatly affected the activation of halogen atoms by the latter. It is of course clear that the actual mechanisms are different in the two cases.

EXPERIMENTAL.

4:4'-Dimethyldiphenyl is most readily prepared by Krizewsky and Turner's method (*J.*, 1919, 115, 560). The Ullmann method of heating *p*-iodotoluene with copper-bronze is satisfactory if the latter is of good quality. A great deal of the copper-bronze we have purchased was entirely without action.

Mononitration of Ditolyl.—Ditolyl (33 g.) was kept in AcOH (600 c.c.) and HNO₃ (600 c.c.; *d* 1.42) at 50–55° until it dissolved. The cooled solution was poured into H₂O, and the ppt. (a solidifying oil) was melted several times under hot H₂O to remove traces of yellow phenolic compounds and then air-dried (40 g.). Of this, 37.9 g., distilled slowly in a Bennett vacuum fractionating apparatus, gave at 190–200°, 2.2 g., m. p. 66–67°; at 200–203°, 6.9 g., m. p. 67–68°; at 203–205°, 13.1 g., m. p. 67–68°; at 205–210°, 9.3 g., m. p. 66–67.5°; at 210°, 3.2 g., m. p. 64–66°; residue 2.8 g., loss 0.4 g.

Fractional crystn. of each fraction from MeOH showed that only one substance was present, except in the 5th fraction, which contained a very small quantity of an impurity. All the fractions melted at the same temp. whether mixed or not with synthetic 2-nitroditolyl (below), and the m. p.'s were all depressed when 3-nitroditolyl was added. From the residue in the distillation flask was obtained a small amount of a substance, m. p. about 110°, raised by addition of 2 : 3'-dinitroditolyl.

Synthesis of 2-Nitroditolyl.—*p*-Iodotoluene (25 g.) and 4-bromo-3-nitrotoluene (23 g.) were heated to 220°, and copper-bronze (40 g.) gradually added. The reaction occurred mainly at 225–230° and was completed at 260°. The whole was extracted with hot *o*-C₆H₄Cl₂, the extract steam-distilled, and the residue extracted with boiling light petroleum (b. p. 40–60°). The undissolved material was 2 : 2'-dinitroditolyl. The petroleum extract was distilled at ordinary press. and then in vac., ditolyl distilling first. The nitro-compound had b. p. 220–225°/29 mm., and crystallised from MeOH in bright yellow plates (3 g.), m. p. 69–70° (Found : N, 6.2. C₁₄H₁₃O₂N requires N, 6.2%).

2-Amino-4 : 4'-dimethyldiphenyl.—The nitro-compound was reduced with SnCl₂ in boiling AcOH and HCl aq. The base was isolated as the hydrochloride (7 g., m. p. 185–195°), which permitted of its separation from 1 g. of what was evidently 2 : 7-dimethylcarbazole. The free *2-aminoditolyl* separated from aq. EtOH in prisms, m. p. 62–63° (Found : N, 6.9. C₁₄H₁₅N requires N, 7.1%). The acetyl derivative formed needles, m. p. 118–119° (Found : N, 6.0. C₁₆H₁₇ON requires N, 5.9%). The benzoyl derivative formed needles, m. p. 95–96°.

Synthesis of 3-Nitro-4 : 4'-dimethyldiphenyl.—A mixture of *p*-iodotoluene (37 g.), 4-iodo-2-nitrotoluene (44 g.), and copper-bronze (35 g.) was heated at 230–250°, the product extracted with hot *o*-C₆H₄Cl₂, the solvent removed in steam, and the residue extracted with boiling EtOH. The cooled extract was filtered from 10 g. of 3 : 3'-dinitroditolyl and, after being evaporated, distilled in vac. Ditolyl distilled first, and the main bulk (6 g.) at 220–230°/20 mm. The latter crystallised from MeOH in scaly plates, m. p. 80–81° (Found : N, 6.2%). A mixture of this 3-nitroditolyl with the purified mononitration product (above) had m. p. 50–65°.

3-Amino-4 : 4'-dimethyldiphenyl was obtained by SnCl₂-AcOH-HCl reduction of the nitro-compound. No product corresponding to the carbazole was formed. The hydrochloride formed needles, m. p. about 230° (decomp.). The base separated from aq. EtOH in needles, m. p. 104–105° (Found : N, 7.0%); acetyl derivative, needles, m. p. 156–157° (Found : N, 6.1%); benzoyl derivative, m. p. 160–161°. A mixture of the base with the reduction product of the mononitration product melted at 57–70°, a mixture of the two acetyl derivatives at 95–110°, and one of the benzoyl derivatives at 75–94°.

Dinitration of 4 : 4'-Dimethyldiphenyl.—A solution of ditolyl (10 g.) in AcOH (200 c.c.) at 50–60° was treated with nitric acid (200 c.c.; *d* 1.47), the temp. raised to 95° for 5 mins., and the solution poured into H₂O. The ppt. had m. p. 99–106°, 104–108° after one crystn. from EtOH, 115–116° after a second, and 119–120° after one crystn. from BuOH. Almost colourless, hairy needles (Found : N, 10.4. Calc. : N, 10.3%). The m. p. was depressed when either 2 : 2'- or 3 : 3'-dinitroditolyl was added.

Mononitration of the Mononitration Product, of Synthetic 2-Nitro-, and of 3-Nitro-ditolyl.—These nitrations were effected under the conditions of the

last expt. The products in the first two cases were almost exactly similar to that obtained from ditolyl itself. That from the 3-nitro-compound required less purification before it showed the m. p. of the pure 2 : 3'-dinitro-compound. Identity of all four specimens of this compound was established by mixed m. p. determinations.

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