316. *Substitution in Compounds containing Two or More Phenyl Groups. Part II. The Nitration of 3-Methyldiphenyl.*

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CARNELLEY (J., 1876, **29**, 20) found that the mono-nitration of 4-methyldiphenyl gave a solid product, later shown by Gomberg and Pernert (*J. Amer. Chem. Soc.*, 1926, **48**, 1372) to be 4-nitro-4′-methyldiphenyl, and a yellow oil, which has been shown to contain mainly 2-nitro-4-methyldiphenyl together with 2-nitro-4′-methyldiphenyl (this vol., p. 1888). These results indicate that in 4-methyldiphenyl the substitution is primarily controlled by the strongly *op*-directive effects of the groups Ph and *p*-C_6H_4Me, which are superior to that of the methyl group. In the methylated nucleus of 4-methyldiphenyl the two radicals Ph and Me are acting in opposition with regard to their *op*-directive effects, whereas in the corresponding nucleus of 3-methyldiphenyl these effects of the two radicals co-operate. In the latter case predominating homonuclear substitution would be indicated and this has been borne out by experiment. In the nitration of 3-methyldiphenyl, unlike that of 4-methyldiphenyl, only 4-nitro-3-methyldiphenyl has so far been shown to be formed.

The nitration of 3-methyldiphenyl by concentrated nitric and glacial acetic acids gave a liquid product, from which on reduction and acetylation 4-*acetamido*-3-*methyldiphenyl* was obtained in good yield. Oxidation of this with neutral potassium permanganate gave 4-*acetamidodiphenyl*-3-*carboxylic acid*. This acetamidomethyldiphenyl is probably identical with that obtained by Pummerer, Binapfl, Bittner, and Schuegraf (*Ber.*, 1922, **55**, 3095) by a somewhat complicated reaction (compare also Pummerer and Binapfl, *ibid.*, 1921, **54**, 2768), but its structure is now definitely proved (a) by its synthesis, by the method of Gomberg and Bachmann (*J. Amer. Chem. Soc.*, 1924, **46**, 2339) and Gomberg and Pernert (*loc. cit.*), from 6-nitro-*m*-toluidine and benzene, and (b) by oxidation with chromic acid of the nitration product of 3-methyldiphenyl, which gave 4-nitro-3-methylbenzoic acid, identical with a specimen obtained from the oxidation of 4-nitro-*m*-xylene. Treatment of the nitration product of 3-methyldiphenyl with nitric acid (*d* 1·37) according to the method described in Vanino's " Handbuch der Präparativen Chemie " for the oxidation of *o*-nitrotoluene to *o*-nitrobenzoic acid produced 4 : *4'-dinitro-3-methyldiphenyl.*

Attempts to confirm the position of the nitro-group by reduction to the amine and subsequent titration with standard potassium bromate in the presence of acidified aqueous potassium bromide (compare Callan and Henderson, *J. Soc. Chem. Ind.*, 1922, **41**, 161T) were inconclusive, because the reaction was slow, no sharp end-point could be obtained, and a dark greenish indefinite oxidation product was precipitated. Such bases as *m*-4-xylidine, benzidine, and *o*-tolidine behave in this manner in the bromide–bromate reaction (Francis, *J. Amer. Chem. Soc.*, 1926, **48**, 1631), 4-aminodiphenyl also reacts abnormally to some extent, but with 2-aminodiphenyl the reaction proceeds quantitatively in the normal manner at room temperature to give 3 : 5-dibromo-2-aminodiphenyl.

The nitration of 4-methyldiphenyl at the 4'-position and of 3-methyldiphenyl at the 4-position shows a certain parallelism to the substitution reactions of 4- and 3-methylazobenzene respectively (Burns, McCombie, and Scarborough, J., 1928, 2928), although in 4-methyldiphenyl the high *op* ratios of the Ph and *p*-C_6H_4Me groups result in appreciable substitution at the 2- and 2'-positions as well.

EXPERIMENTAL.

Nitration of 3-Methyldiphenyl.—3-Methyldiphenyl (21·5 g.) in AcOH was warmed with conc. HNO_3 (100 c.c.; *d* 1·42) and AcOH (100 c.c.) on the water-bath for 10 mins., and the solution kept over-night at room temp. and poured into H_2O. An ethereal extract, washed with aq. alkali, dried, and evaporated, yielded a pale yellow oil, b. p. 195—200°/18 mm. (24 g.) (Found : N, 6·6. Calc. for mononitration : N, 6·6%).

Oxidation of the nitration product. The nitro-compound (5 g.) in AcOH was refluxed for 12 hrs., CrO_3 (30 g.) in 90% aq. AcOH being gradually added. When cold, the mixture was poured into H_2O and extracted with Et_2O, and this solvent evaporated, leaving an AcOH solution of the oxidation product, which was pptd. on addition of H_2O. Recrystn. from aq. EtOH gave 4-nitro-

3-methylbenzoic acid, m. p. 212° alone, and 213—214° when mixed with an authentic specimen prepared as described later (Found: C, 53·2; H, 4·0. Calc. for $C_8H_7O_4N$: C, 53·0; H, 3·9%). Hardly any oxidation could be effected by boiling the nitro-compound for 48 hrs. with alkaline $KMnO_4$ aq., or by heating it on the steam-bath for 1 day with HNO_3 (*d* 1·37). This treatment gradually produced a yellow cryst. solid, recrystn. of which from EtOH gave 4 : *4'-dinitro-3-methyldiphenyl* in fine, pale yellow needles, m. p. 197° (Found: C, 60·8; H, 3·9. $C_{13}H_{10}O_4N_2$ requires C, 60·5; H, 3·9%). Reduction of the dinitro-compound by $SnCl_2$ in EtOH and conc. HCl gave 3-methylbenzidine as a viscous oil [picrate, m. p. 204° (decomp.) (compare von Braun and Mintz, *Ber.*, 1917, **50**, 1651)].

4-Nitro-3-methylbenzoic acid was prepared from pure *m*-xylene by nitration with fuming HNO_3 at 15° (compare Beilstein and Kreusler, *Annalen*, 1867, **144**, 167); steam distillation of the water-washed product and extraction of the distillate with Et_2O gave, on evaporation of the solvent, crude 4-nitro-*m*-xylene (reduction and acetylation gave 4-aceto-*m*-xylidide, m. p. and mixed m. p. 120—122°). The residue in the flask contained 4 : 6-dinitro-*m*-xylene. Oxidation of the 4-nitro-*m*-xylene (6·5 g.) by 8 hrs.' heating with CrO_3 (13 g.) in AcOH and subsequent dilution with H_2O gave 4-nitro-3-methylbenzoic acid (2·5 g.), m. p. 214° after crystn. from aq. EtOH.

Reduction of the nitration product of 3-methyldiphenyl. The nitro-compound (6 g.) in EtOH (70 c.c.) was reduced with $SnCl_2$ (36 g.) in conc. HCl (80 c.c.) on the steam-bath for 2 hrs., and from the cooled solution, made alkaline, Et_2O extracted an oil, which was treated with Ac_2O. Crystn. from EtOH gave *4-acetamido-3-methyldiphenyl* in clusters of small needles, m. p. 166°; more was obtained on evaporation of the mother-liquor (Found: C, 80·0; H, 6·6; N, 6·2. $C_{15}H_{15}ON$ requires C, 80·0; H, 6·7; N, 6·2%).

Oxidation of 4-Acetamido-3-methyldiphenyl.—A suspension of 4-acetamido-3-methyldiphenyl (1·1 g.) in H_2O (100 c.c.) containing $KMnO_4$ (1·8 g.) and $MgSO_4$ (2·5 g.) was boiled for 30 hrs. When the hot filtered solution was treated with SO_2, *4-acetamidodiphenyl-3-carboxylic acid* was pptd.; microscopic crystals, m. p. 205—206°, after two crystns. from aq. EtOH (Found: C, 70·35; H, 5·5; N, 5·3. $C_{15}H_{13}O_3N$ requires C, 70·6; H, 5·1; N, 5·5%).

Synthesis of 4-Acetamido-3-methyldiphenyl.—A solution of crude 6-nitro-*m*-toluidine (Cohen and Dakin, J., 1903, **83**, 331; Noelting and Stoecklin, *Ber.*, 1891, **24**, 564) (41 g.) in conc. HCl (60 c.c., *d* 1·16) was diazotised at 10—15° with aq. $NaNO_2$ and after 2 hrs. was added slowly to C_6H_6 (300 c.c.) and aq. NaOH (40 g. in 120 c.c.) at 5—10°. After being stirred for 5 hrs. and left over-night, the mixture was heated on the water-bath for ½ hr. The C_6H_6 layer was washed with H_2O, conc. HCl, and again with H_2O, dried over $CaCl_2$, and evaporated, the residue distilled under reduced press. (not without some decomp.), and the oily distillate reduced in the same way as the nitration product of 3-methyldiphenyl. The base thus obtained, on acetylation with Ac_2O, gave 4-acetamido-3-methyldiphenyl, m. p. (after crystn. from 95% aq. EtOH) and mixed m. p. (with the prep. obtained from the nitration product of 3-methyldiphenyl by reduction and acetylation) 166°.

Grateful acknowledgment is made to the Chemical Society for a grant.

THE UNIVERSITY, MANCHESTER. [*Received, June 23rd*, 1932.]
