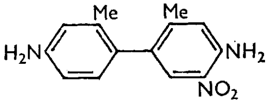
887. *Orientation Effects in the Diphenyl [Biphenyl] Series. Part XV.*[1] *Derivatives of 2,2'-Bitolyl and of 2,4,2',4'-Tetramethylbiphenyl.*

By Pauline M. Everitt, Shiu May Loh, and E. E. Turner.

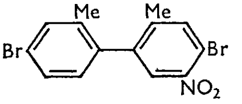
Nitration of *m*-tolidine in presence of excess of concentrated sulphuric acid occurs in position 5. 5-Nitro-2,2'-bitolyl and 2,4,2',4'-tetramethyl-6-nitrobiphenyl have been made and reduced to the corresponding amines.

Since 2-nitrobenzidine is readily obtained by nitrating benzidine in concentrated sulphuric acid solution, it appeared possible that the main product of nitrating *m*-tolidine under similar conditions would be the 6-derivative. In fact, however, the 5-nitro-compound (I) is formed in over 60% yield, the de-activating effect of the amine sulphate group evidently being unable to outweigh the effect of the methyl group, which might be reinforced by steric opposition to reaction in the 2-position.

The structure of the 5-nitro-*m*-tolidine has been proved as follows: (1) Replacement of both amino-groups by bromine atoms gave a 4,4'-dibromonitro-2,2'-bitolyl (II) in which only one bromine atom reacted with warm piperidine.



(I)



(II)

(2) Deamination gave 5-nitro-2,2'-bitolyl, which was converted by simple stages into the known 5-nitrobiphenic acid[2] and 3-nitrobiphenyl.

m-Tolidine as prepared by us usually melted at 87—88°, as recorded by Schultz and Rohde,[3] but one sample melted at 104—105° (cf. Carlin and Foltz[4] and other authors[5,6]). The re-solidified material, however, melted at 87—88°. The identity of our *m*-tolidine was established by deamination, 2,2'-bitolyl being obtained.

6-Nitro-2,2'-bitolyl,[7,8] which it had originally been hoped to derive from 6-nitro-*m*-tolidine, was prepared from 6,6'-dinitro-2,2'-bitolyl[4] by partial reduction with sodium sulphide,[9] followed by deamination by the diazo-hypophosphorous acid method. Reduction gave 6-amino-2,2'-bitolyl, m. p. 27° (Mascarelli and Angeletti[8] recorded m. p.

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[1] Part XIV, *J.*, 1955, 1274.
[2] Schmidt and Austin, *Ber.*, 1903, **36**, 3730.
[3] Schultz and Rohde, *Z. Farben- u. Textilchemie*, 1902, I, 567.
[4] Carlin and Foltz, *J. Amer. Chem. Soc.*, 1956, **78**, 1997.
[5] Jacobsen and Fabian, *Ber.*, 1895, **28**, 2541.
[6] Buchka and Schachbeck, *Ber.*, 1889, **22**, 834.
[7] Ritchie, *J. Proc. Roy. Soc., N.S.W.*, 1945, **78**, 159.
[8] Mascarelli and Angeletti, *Gazzetta*, 1938, **68**, 29.
[9] Sako, *Bull. Soc. Japan*, 1934, **9**, 393.

105°; Ritchie[7] described the base as an oil). The 5-amino-compound, m. p. 59—60°, was obtained by reduction of 5-nitro-2,2′-bitolyl.

2,4,2′,4′-Tetramethyl-6,6′-dinitrobiphenyl was prepared by an Ullmann reaction on 2-iodo-1,5-dimethyl-3-nitrobenzene[10] and was reduced to 6-amino-2,4,2′4′-tetramethyl-6′-nitrobiphenyl. This by deamination gave 2,4,2′4′-tetramethyl-6-nitrobiphenyl. The corresponding amino-compound was converted by common processes into 9-*p*-aminophenyl-2,4,5,7-tetramethylphenanthridine.

EXPERIMENTAL

m-Tolidine was prepared from *m*-nitrotoluene in 55% yield by reduction in ethanol with zinc dust and sodium hydroxide solution, followed by rearrangement in acid; it formed plates, m. p. 87—88°, from benzene (Found: C, 79·3; H, 7·4; N, 13·3. Calc. for $C_{14}H_{16}N_2$: C, 79·2; H, 7·6; N, 13·2%). Schultz and Rohde[3] give m. p. 87—88°; other workers have recorded higher m. p.s: 106—107°,[5] 108—109°,[6] 105—106°.[4]

Deamination of m-*Tolidine.*—*m*-Tolidine was diazotised at 0° to −5° in hydrochloric acid and then treated with 50% hypophosphorous acid. After 15 hr. the products (red oil and aqueous layer) were together extracted with ether. The ethereal extract, after being shaken with aqueous alkali, dried, and distilled, gave a 52% yield of 2,2′-bitolyl, b. p. 110—113°/1—5 mm., m. p. 18° alone or mixed with pure 2,2′-bitolyl.

5-*Nitro*-m-*tolidine.*—A solution of *m*-tolidine (106 g., 1 mol.) in sulphuric acid (700 c.c.; *d* 1·84) was stirred and treated at 0° to −5° with finely ground potassium nitrate (50·5 g., 1 mol.). The addition took 2 hr. and the solution was poured on to crushed ice (6 l.), after being stirred for a further hour. The precipitated sulphate was filtered off and ground with 30% sodium hydroxide solution. The *base* liberated was crystallised from ethanol (2½ l.), giving a first crop 48 g., m. p. 170—173°, and a second crop 35 g., m. p. 168—171°. These were sufficiently pure for use in the next stage. Several crystallisations raised the m. p. to 173—175°. A total of 364 g. of mononitrated product (62% yield) was obtained from 483 g. of *m*-tolidine (Found: C, 64·5; H, 5·8; N, 16·4. $C_{14}H_{15}N_3O_2$ requires C, 65·35; H, 5·9; N, 16·3%).

4,4′-*Dibromo*-5-*nitro*-2,2′-*bitolyl.*—5-Nitro-*m*-tolidine was diazotised in hydrobromic acid at 0° to −5°, and the diazo-solution added slowly to a cold suspension of cuprous bromide in hydrobromic acid. The reaction was complete at 100° in 1 hr. The sticky solid obtained was washed with alkali and water and crystallised several times from ethanol. The *dibromo-compound* had m. p. 100—101° (Found: Br, 41·8. $C_{14}H_{11}Br_2NO_2$ requires Br, 41·5%).

4-*Bromo*-5′-*nitro*-4′-*piperidino*-2,2′-*bitolyl.*—A solution of the above dibromo-compound (0·4 g.) in piperidine (1 c.c.) was warmed on a water-bath for 5 min. The *piperidino-compound* obtained on cooling crystallised from ethanol in orange needles, m. p. 105—107° (Found: N, 6·9. $C_{19}H_{21}BrN_2O_2$ requires N, 7·2%).

5-*Nitro*-2,2′-*bitolyl.*—5-Nitro-*m*-tolidine (85·7 g., 1 mol.) was diazotised in hydrochloric acid and the diazo-solution treated with hypophosphorous acid. After some hours the product was dissolved in ether, washed, and dried. The residue obtained after evaporation of the ether was distilled in a vacuum: it then crystallised from ethanol in yellow needles, m. p. 65—66°. A total of 340 g. of nitrotolidine was converted into 133·5 g. of 5-*nitro*-2,2′-*ditolyl* (yield 45%) (Found: C, 73·4; H, 5·8. $C_{14}H_{13}NO_2$ requires C, 74·0; H, 5·8%). Catalytic reduction (platinic oxide) in ethanol, followed by purification through the hydrochloride, gave a 70% yield of 5-*amino*-2,2′-*bitolyl*, which crystallised from dilute ethanol in flakes, m. p. 59—60° (Found: C, 84·9; H, 7·1; N, 7·2. $C_{14}H_{15}N$ requires C, 85·2; H, 7·7; N, 7·1%).

The *benzoyl derivative* formed needles, m. p. 129—130°, from dilute ethanol (Found: N, 5·1. $C_{21}H_{19}NO$ requires N, 4·7%). The p-*nitrobenzoyl derivative* of the base crystallised from aqueous alcohol in pale yellow plates, m. p. 160—161° (Found: C, 72·2; H, 5·2. $C_{21}H_{18}N_2O_3$ requires C, 72·8; H, 5·2%). The *formyl derivative* crystallised from light petroleum (b. p. 60—80°) and had m. p. 124—126° (Found: C, 80·0; H, 6·2; N, 6·2. $C_{15}H_{15}NO$ requires C, 80·0; H, 6·7; N, 6·2%). The *acetyl derivative* formed needles, m. p. 131—133°, from light petroleum (b. p. 60—80°) (Found: C, 80·2; H, 7·2; N, 5·9. $C_{16}H_{17}NO$ requires C, 80·3; H, 7·1; N, 5·9%).

5-*Dimethylamino*-2,2′-*bitolyl* was obtained by gradually adding dimethyl sulphate to a hot mixture of benzene, aqueous alkali, and 5-aminobitolyl, and working up the mixture normally.

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[10] Blanksma, *Rec. Trav. chim.*, 1906, **25**, 168.

The base, isolated in 61% yield, had b. p. 146—148°/7 mm. (Found: C, 84·8; H, 8·4. $C_{16}H_{19}N$ requires C, 85·3; H, 8·5%). The dimethylaminobitolyl combined readily with methyl iodide at room temperature to give the *quaternary iodide*, which crystallised from water in needles, m. p. 177—178° (Found: C, 55·8; H, 6·1; I, 34·1. $C_{17}H_{22}NI$ requires C, 55·6; H, 6·0; I, 34·6%).

Oxidation of 5-nitro-2,2′-bitolyl by boiling with alkaline potassium permanganate for 6 hr. gave a 29% yield of 5-nitrobiphenic acid,[2] m. p. 266—267° (from dilute ethanol) (Found: N, 4·9. Calc. for $C_{14}H_9NO_6$: N, 4·9%). The anhydride [11] was obtained after boiling the acid with acetic anhydride for 1 hr. It crystallised from the reaction mixture in needles, m. p. 194—195°. The acid (0·9 g.) was decarboxylated by boiling its solution in quinoline in the presence of copper powder for 1 hr. The product was poured into acid, and the mixture extracted with ether. After evaporation of the ether the residue was steam-distilled, and the solid product filtered off and crystallised from light petroleum; it had m. p. and mixed m. p. with authentic 3-nitrobiphenyl, 63—64°.

6-*Amino*-2,2′-*bitolyl*.—Sodium sulphide reduction of 6,6′-dinitro-2,2′-bitolyl gave a 66% yield of 6-amino-6′-nitro-2,2′-bitolyl, m. p. 123—124° (Sako [9] gave m. p. 121—123°). This nitro-amine (4·8 g., 1 mol.) was dissolved in hot concentrated hydrochloric acid (5 c.c., 2·5 mol.) and water (20 c.c.). It was diazotised at 0—5° with sodium nitrite solution (1·52 g., 1·1 mol., in the minimum amount of water). After 30 min. hypophosphorous acid, pre-cooled to 0°, was added. A vigorous reaction resulted. The product, after being left at 0° overnight, was extracted with ether, and the ethereal solution washed with water. The ether layer was evaporated, and the residue steam-distilled from alkaline solution. 6-Nitro-2,2′-bitolyl distilled as a pale yellow oil which solidified. It crystallised from ethanol in flakes, m. p. 42—43° (2·3 g., 51%) (Ritchie [7] gives m. p. 45°, and Mascarelli and Angeletti [8] m. p. 42—43°). Catalytic reduction (platinic oxide) in ethanol and purification through the hydrochloride gave 6-amino-2,2′-bitolyl, m. p. 27°, needles from light petroleum (b. p. 40—60°) (yield 73%) (Found: N, 6·9. Calc. for $C_{14}H_{15}N$: N, 7·1%).

2,4,2′,4′-*Tetramethyl*-6,6′-*dinitrobiphenyl*.—2-Iodo-1,5-dimethyl-3-nitrobenzene [10] (50 g.) at 130—135° was gradually treated with copper powder (50 g.). The reaction was very vigorous and the scale could not be increased. After the addition of copper (1 hr.) the mixture was heated at 155—160° for 30 min. and the product was extracted with chlorobenzene. The *dinitro-compound* forms pale yellow prisms, m. p. 136—137° (85%), from ethanol or benzene (Found: C, 63·5; H, 4·7; N, 9·6. $C_{16}H_{16}N_2O_4$ requires C, 64·0; H, 5·4; N, 9·3%).

6-*Amino*-2,4,2′,4′-*tetramethyl*-6′-*nitrobiphenyl*.—The above dinitro-compound (60 g., 1 mol.) was dissolved in boiling ethanol (600 c.c.) in a 2-l. 3-necked flask fitted with a stirrer. A solution of sodium sulphide nonahydrate (57·6 g., 1·2 mol.) and sulphur (15·4 g., 2·4 mol.) in water (150 c.c.) was added during 15 min., and the mixture boiled for 3 hr. It was then concentrated to about 400 c.c. and cooled in ice with stirring. The solid was filtered off and extracted several times with boiling dilute hydrochloric acid. The hydrochloride is readily hydrolysed by water, liberating the amine as a bright yellow solid. 6-*Amino*-2,4,2′,4′-*tetramethyl*-6′-*nitrobiphenyl* crystallised from ethanol in needles, m. p. 117—118° (Found: C, 71·7; H, 6·9; N, 10·3. $C_{16}H_{18}N_2O_2$ requires C, 71·1; H, 6·7; N, 10·4%).

2,4,2′,4′-*Tetramethyl*-6-*nitrobiphenyl*.—The last-mentioned amine was diazotised in dilute hydrochloric acid. The diazo-solution was treated with hypophosphorous acid. Addition of copper powder accelerated the reaction, which was complete in 1 hr. at 15—20°. The solid was filtered off and then steam-distilled from alkaline solution. The *nitro-compound* crystallised from ethanol in pale yellow rhombs, m. p. 107—108° (54%) (Found: C, 75·2; H, 6·6; N, 5·6. $C_{16}H_{17}NO_2$ requires C, 75·3; H, 6·7; N, 5·5%).

6-*Amino*-2,4,2′,4′-*tetramethylbiphenyl*.—The above nitro-compound was reduced either catalytically (platinic oxide, ethanol) or by stannous chloride and hydrochloric acid. Catalytic reduction was preferred, since working up was more rapid and the yield was nearly quantitative. In the catalytic reduction of the nitro-compound (10 g.), the residue, after evaporation of the ethanol, was treated with concentrated hydrochloric acid, and the solid *hydrochloride* filtered off and crystallised from dilute hydrochloric acid (Found: C, 72·9; H, 7·5; N, 4·9. $C_{16}H_{20}ClN$ requires C, 73·4; H, 7·7; N, 5·4%). The amine was liberated by ammonia and extracted into ether. After evaporation of the ether the residue eventually solidified (yield 96%), having m. p. 50—51°. The amine was very soluble in all usual solvents and could not be recrystallised.

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[11] Bell and Robinson, *J.*, 1927, 2237.

2,4,2′4′-*Tetramethyl*-6-p-*nitrobenzamidobiphenyl* was prepared from the amine by using pyridine and *p*-nitrobenzoyl chloride. It crystallised from ethanol in pale yellow prisms or needles, m. p. 140—141° (75%) (Found: N, 7·2. $C_{23}H_{22}N_2O_3$ requires N, 7·5%).

2,4,5,7-*Tetramethyl*-9-p-*nitrophenylphenanthridine*.—2,4,2′4′-Tetramethyl-6-*p*-nitrobenzamidobiphenyl (8 g.) and phosphoryl chloride (16 g., 9·3 c.c.) in nitrobenzene (25 c.c.) were heated at 175—180° for 12 hr. The product was poured into alkali and steam-distilled to remove nitrobenzene. The residue crystallised from ethanol in bright yellow rhombs (78%). It melted partly at 160° and then completely at 177—178°. In different crystallisations flat needles, m. p. 159—160°, or rhombs, m. p. 177—178°, were obtained. The ultravolet absorption spectra of the two kinds of crystal were identical (Found: C, 77·8; H, 5·9; N, 8·0. $C_{23}H_{20}N_2O_2$ requires C, 77·5; H, 5·7; N, 7·9%).

9-p-*Aminophenyl*-2,4,5,7-*tetramethylphenanthridine*.—A solution of 2,4,5,7-tetramethyl-9-*p*-nitrophenylphenanthridine (7·3 g., 1 mol.) in hot acetic acid (40 c.c.) was treated at 70° with a solution of stannous chloride dihydrate (15 g., 3 mol.) in concentrated hydrochloric acid (18 c.c., 9 mol.). The solution was boiled under reflux for 15 min., and the reaction completed by heating on a boiling-water bath for 45 min. Pouring into excess of 10% sodium hydroxide solution precipitated a pale yellow solid, which was filtered off and washed with water. It dissolved in dilute hydrochloric acid to give an orange-red solution, which was filtered from a trace of impurity. The amine was then reprecipitated with alkali, filtered off, and dried. It was treated with boiling benzene (100 c.c.) and filtered from insoluble tin salts, the filtrate being concentrated to about 40 c.c. Light petroleum (b. p. 60—80°) was added until a slight turbidity was produced. The solution was boiled until a clear solution was obtained and then, on cooling, the *phenanthridine* crystallised in pale yellow prisms, m. p. 195—196° (77%) (Found: C, 84·3; H, 6·5; N, 9·2. $C_{23}H_{22}N_2$ requires C, 84·6; H, 6·8; N, 8·6%).

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