259. *Some Derivatives of 4 : 4′-Tetramethyldiaminodiphenylmethane.*

By D. C. Rhys Jones and Frederick A. Mason.

Little is known regarding the halogen-substitution products of 4 : 4′-tetramethyldiaminodiphenylmethane, $Me_2N{\cdot}C_6H_4{\cdot}CH_2{\cdot}C_6H_4{\cdot}NMe_2$ (referred to subsequently as the "methane base"). The 2 : 2′- and the 3 : 3′-dichloro-derivative were prepared by condensing *m*- and *o*-chlorodimethylaniline respectively with formaldehyde (von Braun and Kruber, *Ber.*, 1913, **46**, 3460, 3469). Direct chlorination of the methane base produces the 3 : 3′-dichloro-derivative. The 2-*chloro*- and 2-*bromo*-derivatives have now been obtained from the corresponding very unstable 2-diazonium compound by the Sandmeyer–Gattermann reaction. The 2 : 2′-dichloro- and the 2 : 2′-*dibromo*-derivative were obtained similarly from the 2 : 2′-bisdiazonium compound. Neither the mono- nor the di-iodo-derivative of the base could be obtained pure by similar means. The halogen atoms in the above products failed to react with activated magnesium (cf. von Baeyer, *Ber.*, 1905, **38**, 2759).

Sulphonation of the methane base with fuming sulphuric acid yields the 2-monosulphonic acid (Geigy & Co., G.P. 65017, 88085), but the hitherto unknown *disulphonic acid* has now been obtained by heating the base with chlorosulphonic acid in tetrachloroethane solution. Attempts to prepare the corresponding mono- or di-nitriles by distilling the sulphonic acids with potassium cyanide or ferricyanide were unsuccessful.

Diphenylmethane-3 : 3′-bistrimethylammonium iodide was obtained by methylation of 3 : 3′-diaminodiphenylmethane with methyl sulphate and precipitation with sodium iodide; it melted at 228°, whereas Scholl (*Monatsh.*, 1918, **39**, 236), by methylation with methyl iodide under pressure, obtained the same compound with m. p. 165°. Since our initial material was prepared from 3 : 3′-dinitrodiphenylmethane, and the m. p. of the corresponding diacetdiamido-compound (193°) agreed with that of Thorpe and Wildman (*J. Amer. Chem. Soc.*, 1915, **37**, 372), the identity of our compound is not open to doubt, and it would appear to exist in two modifications.

EXPERIMENTAL.

Action of Dilute Nitric Acid upon " Methane Base."—5 G. of the base, dissolved in 40% aqueous nitric acid (50 c.c.), were heated to 60° on a water-bath. A violent reaction occurred with evolution of nitric fumes; after cooling and neutralising the solution, an orange-yellow precipitate was obtained, crystallising from glacial acetic acid in yellow platelets, m. p. 163°. It was identified (mixed m. p.) as *p*-nitrodimethylaniline, so the methylene group was completely oxidised during the reaction.

2-*Chloro*-4 : 4′-*tetramethyldiaminodiphenylmethane.*—The corresponding 2-amino-derivative (11 g.), prepared by the method of Ullmann and Marié (*Ber.*, 1901, **34**, 4314), dissolved in concentrated hydrochloric acid (100 c.c.), was cooled to − 5° and a 25% solution of sodium nitrite (3 g. in 12 c.c.) was added slowly with stirring. The resultant diazonium solution was very unstable and rapidly decomposed either on dilution or on being very slightly warmed. The cold solution was stirred for ½ hour at − 5°, poured into a solution of cuprous chloride (5 g.) in concentrated hydrochloric acid (20 c.c.), and the mixture heated on a water-bath until evolution of nitrogen ceased. After dilution and neutralisation of the solution, the brown precipitate was freed from copper by washing with ammonia, and was then recrystallised successively from alcohol and light petroleum; pale yellow needles, m. p. 63° (Found : Cl, 12·4; N, 9·8. $C_{17}H_{21}N_2Cl$ requires Cl, 12·3; N, 9·7%). (In carrying out the halogen estimations it was necessary to allow the nitric acid to act upon the compounds before sealing off the capillary tube, since the action proceeds almost explosively even in the cold.)

2 : 2′-*Dichloro*-4 : 4′-*tetramethyldiaminodiphenylmethane.*—The corresponding 2 : 2′-diamino-compound (11 g.) was diazotised in concentrated hydrochloric acid, as described above, and the very unstable solution poured into a solution of cuprous chloride in concentrated hydrochloric acid. The product obtained after the usual procedure was uncrystallisable, but after distillation (b. p. 282—286°/20 mm.) it crystallised as pale yellow needles, m. p. 96° (cf. von Braun and Kruber, *loc. cit.*) (Found : Cl, 22·0. Calc. for $C_{17}H_{20}N_2Cl_2$: Cl, 22·0%).

3 : 3′-*Dichloro*-4 : 4′-*tetramethyldiaminodiphenylmethane.*—This substance was obtained by von Braun and Kruber (*loc. cit.*) as a yellow oil, b. p. 265°/20 mm. It may be obtained more conveniently by direct chlorination of the methane base : 10 g. of the latter and sodium acetate (10 g.) were dissolved in glacial acetic acid (150 c.c.) and rather more than the theoretical amount of chlorine was passed in. The blue solution became turbid, and an oil was precipitated. This was removed, and distilled under reduced pressure, the first fraction, containing unchlorinated base, coming over at 150—265°/20 mm., and the residue distilling constantly at 265° as an uncrystallisable oil (picrate, m. p. 173°) (Found : Cl, 21·4; N, 9·0. Calc. for $C_{17}H_{20}N_2Cl_2$: Cl, 22·0; N, 8·7%).

2-*Bromo*-4 : 4′-*tetramethyldiaminodiphenylmethane.*—6 G. of the 2-amino-compound were dissolved and diazotised in concentrated hydrobromic acid at − 5°, as described for the chloro-compound. The solution was added to a vigorously stirred suspension of copper powder (1·0 g.) in concentrated hydrobromic acid, and the mixture heated on the water-bath until evolution of nitrogen had ceased. The product, after extraction as for the chloro-compound, crystallised from light petroleum in pale, orange-yellow needles, m. p. 68° (Found : Br, 24·0; N, 8·8. $C_{17}H_{21}N_2Br$ requires Br, 24·0; N, 8·4%).

2 : 2′-*Dibromo*-4 : 4′-*tetramethyldiaminodiphenylmethane* was obtained in a similar manner from the corresponding 2 : 2′-diamino-compound. It crystallised from light petroleum as pale yellow needles, m. p. 103°; b. p. 265°/20 mm. (Found : Br, 38·8. $C_{17}H_{20}N_2Br_2$ requires Br, 38·8%).

3 : 3′-*Dibromo*-4 : 4′-*tetramethyldiaminodiphenylmethane.*—Bromine (2 equivs.) in 10% solution in glacial acetic acid was added slowly to a well-stirred solution of " methane base " (13 g.) in glacial acetic acid (100 c.c.). The blue coloration first produced disappeared, and a dark oil separated, which was washed, and then distilled under diminished pressure, the main fraction (16 g.) distilling at 274—279°/20 mm. as an uncrystallisable yellow oil (picrate, m. p. 188°) (Found : Br, 38·7. $C_{17}H_{20}N_2Br_2$ requires Br, 38·8%).

Attempts to monobrominate the methane base in solution in glacial acetic acid, chloroform, carbon tetrachloride, or tetrachloroethane resulted in all cases in the formation of a mixture of the dibromo-compound and unchanged base, fractionation of the mixture failing to reveal any monobromo-compound.

4 : 4′-*Tetramethyldiaminodiphenylmethane*-2 : 2′(?)-*disulphonic Acid.*—Chlorosulphonic acid (10 c.c.) was added to a solution of the " methane base " (10 g.) in tetrachloroethane (150 c.c.), the temperature raised gradually to the b. p. of the solvent, and the mixture stirred and boiled under reflux until evolution of hydrogen chloride had ceased. The sulphonic acid separated as a sticky transparent solid which was purified by dissolution in dilute aqueous sodium hydroxide and filtration from unsulphonated base. The sodium salt was obtained by evaporation to small volume and salting out with 20% brine. The free *acid* was obtained by adding the sodium salt to a solution of hydrochloric acid in absolute alcohol, and evaporating the filtered solution; large colourless crystals of the acid separated, containing alcohol of crystallisation which was lost on heating (Found : S, 15·6. $C_{17}H_{22}N_2S_2O_6$ requires S, 15·5%). From the aqueous solution the acid formed colourless crystals containing water of crystallisation; the barium salt is sparingly soluble in water.

Diphenylmethane-3 : 3′-*bistrimethylammonium Iodide.*—Methyl sulphate (25 g.) was added slowly to a suspension of 3 : 3′-diaminodiphenylmethane (5 g.) in a solution of sodium hydroxide (12·5 g.) in water (100 c.c.), and well stirred at room temperature until complete solution was effected. Solid sodium iodide was then added until no further precipitation of the white crystalline iodide occurred. After further recrystallisation from water, it melted at 228°; yield 9·5 g. (Found : N, 4·9; I, 46·9. Calc. for $C_{19}H_{28}N_2I_2$: N, 5·2; I, 47·2%).

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College of Technology, Manchester.
Headingley, Leeds.

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