

ATTEMPTS TO PREPARE THE PHTHALOYL DERIVATIVE OF TETRAKISAMINOMETHYLMETHANE*

By J. A. LAMBERTON†

Although the tetra-*p*-toluenesulphonyl and other derivatives of tetrakisaminomethylmethane (I) have been successfully prepared (van Alphen 1938; Litherland and Mann 1938) consideration of molecular models makes the formation of a tetraphthaloyl derivative seem unlikely on steric grounds. Two methods have been tried for the preparation of this tetraphthaloyl derivative.

When a solution of pentaerythrityl tetrabromide or tetraiodide, phthalimide, and potassium carbonate in dimethylformamide is heated under the conditions of the modified Gabriel synthesis (Billmann and Cash 1953), carbon dioxide and ammonia are evolved and only a low yield of a diphtalimido compound, $C_{20}H_{14}O_4N_2$, is obtained. As pentaerythrityl tetrabromide may be regarded as a substituted *neopentyl* compound (Dostrovsky, Hughes, and Ingold 1946) it is not surprising that the reaction in this instance should be accompanied by rearrangement, but the method seemed worth attempting because Litherland and Mann obtained the tetra-*p*-toluene sulphonyl derivative of I by heating pentaerythrityl tetrabromide with the sodium salt of *p*-toluene sulphonamide.

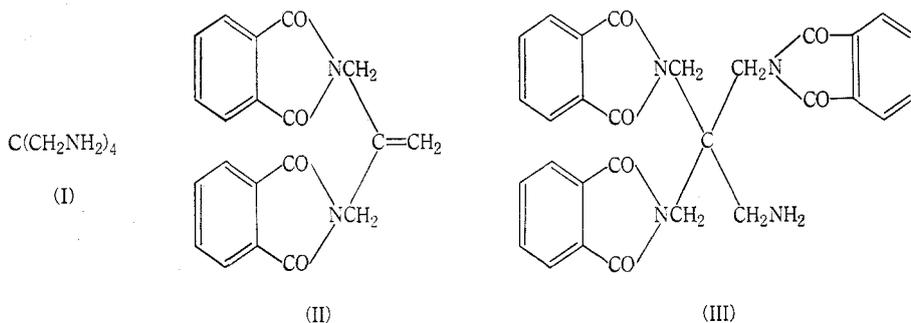
To explain the analytical results a formula such as II was considered for the resulting diphtalimido compound because of the observation by Issidorides and Mator (1955) that pentaerythrityl monobromide under alkaline conditions yields some 2-methylene-1,3-propane diol with the elimination of formaldehyde. This must be excluded because the diphtalimido compound shows no unsaturation and a cyclic structure is probable.

When the tetramine (I), prepared by the method of Litherland and Mann, is fused with phthalic anhydride or heated with phthalic anhydride and sodium

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† Organic Chemistry Section, C.S.I.R.O. Chemical Research Laboratories, Melbourne.

acetate in acetic acid, the triphthaloyl compound (III) is obtained. Evidently steric effects prevent introduction of a fourth group, but the free-amino group, although shielded by the phthalimido groups, still possesses salt-forming properties.



Experimental

Melting points are corrected. Microanalyses were carried out in the C.S.I.R.O. Micro-analytical Laboratory at the University of Melbourne.

(a) *Diphthalimido Compound*.—In a typical experiment pentaerythrityl tetraiodide (5.9 g), phthalimide (6.1 g), anhydrous potassium carbonate (3.6 g), and dimethylformamide (30 ml) were heated at 140 °C for 7 hr. The reaction mixture was poured into water and the sticky mass which separated was washed several times by stirring with water and with 1% aqueous sodium hydroxide solution to remove phthalimide. After warming with ethanol (30 ml) the crude product (1.0–1.1 g) was filtered and crystallized several times from glacial acetic acid. The purified compound (0.6–0.7 g) was obtained as colourless needles, m.p. 224–225 °C. The same product was obtained when pentaerythrityl tetrabromide was used. During the course of the reaction both ammonia and carbon dioxide were evolved and ammonium carbonate deposited in the condenser. The yield of the compound, m.p. 224–225 °C, was never high, and was approximately the same whether the reaction mixture was heated for 2–3 hr or for 20 hr, but with the shorter period of heating it had to be separated from unreacted iodo compound. A lower reaction temperature (e.g. 100 °C for 8 hr) gave much unreacted tetraiodide (Found: C, 69.2; H, 4.0; N, 8.4% after repeated crystallization from acetic acid. The same material after further crystallization from chloroform–ethanol gave C, 69.1; H, 4.2; N, 8.4%; mol. wt., 330 (Rast) and 343 (Signer). Calc. for $C_{20}H_{14}O_4N_2$: C, 69.4; H, 4.1; N, 8.1%; mol. wt., 346). With hydrazine in methanol this compound readily gave phthaloylhydrazine and a base which was converted into a *p*-toluenesulphonyl derivative, m.p. 170 °C. The infra-red absorption spectrum of the diphthalimido compound had strong bands at 1715 and 1774 cm^{-1} , and strongly resembled the infra-red spectrum of 1,4-diphthalimido butane. There were no bands at 3080 or 1645 cm^{-1} where an ethylenic bond such as that in II would be expected to absorb. The compound was recovered unchanged after attempted hydrogenation over platinum oxide in acetic acid containing perchloric acid, and only slowly decolorized a solution of bromine in carbon tetrachloride.

(b) *Triphthaloyl Compound (III)*.—A sample of tetrakisaminomethylmethane prepared by the method of Litherland and Mann was fused with excess of phthalic anhydride. The fusion mixture was heated with ethanol and the insoluble portion crystallized from aqueous acetic acid. This gave the triphthaloyl derivative (III) as colourless needles, m.p. 284–285 °C, which were readily soluble in glacial acetic acid and dilute hydrochloric acid (Found: C, 66.9; H, 4.5; N, 10.7%. Calc. for $C_{22}H_{22}O_6N_4$: C, 66.7; H, 4.2; N, 10.7%). The same compound, m.p. 284–285 °C, was obtained by heating the tetramine with phthalic anhydride and fused sodium acetate in glacial acetic acid.

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