248. 2 : 4-*Diamino*-1-*methylnaphthalene.*

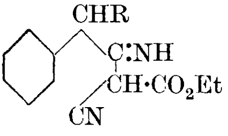
By HENRY WILLIAM THOMPSON.

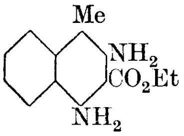
2 : 4-DIAMINO-1-METHYLNAPHTHALENE has been synthesised by the methods outlined below, in order that it should serve as a standard in connexion with the orientation of the products of nitration of 1-methylnaphthalene.

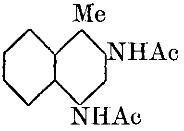
Following the procedure of Atkinson and Thorpe (J., 1906, **89**, 1906) for the lower homologue, phenylmethylacetonitrile was condensed with ethyl sodiocyanoacetate to give ethyl α-cyano-β-imino-γ-phenylvalerate (I; R = Me). This ester was converted by treatment with sulphuric acid into ethyl 2 : 4-diamino-1-methylnaphthalene-3-carboxylate (II). After removal of the carbethoxyl group, acetylation of the resultant diamine furnished 2 : 4-diacetamido-1-methylnaphthalene (III), identical with the compound obtainable from authentic 2 : 4-dinitro-1-methylnaphthalene.

Atkinson and Thorpe considered that methylation of ethyl α-cyano-β-imino-γ-phenylbutyrate (I; R = H) occurred at the γ-carbon atom to give the substituted *n*-valerate (I; R = Me); but the compound which has been obtained by following their prescription is different from this ester. Moreover, the derived ring compounds and diaminohydrocarbons are different in the two series. As there can be no doubt about the position of the methyl group in the new compounds (I, R = Me, and derivatives), the position assigned to the methyl group by Atkinson and Thorpe in the product of methylation of ethyl α-cyano-β-imino-γ-phenylbutyrate would appear to be incorrect. Certain compounds in this series, however, are subject to a peculiar form of isomerism, the nature of which has not yet been completely elucidated (compare Lees and Thorpe, J., 1907, **91**, 1296; Gibson, Kentish, and Simonsen, J., 1928, 2131; Kentish, J., 1929, 1169; Lesslie and Turner, *ibid.*, p. 1512), and

Professor Thorpe suggests that the present discrepancy may be explicable on similar lines : he intends to repeat the work of Atkinson and Thorpe and further investigate the structure of the products.


(I.)


(II.)


(III.)

EXPERIMENTAL.

Ethyl α-Cyano-β-imino-γ-phenylvalerate (I; R = Me).—To a well-cooled mixture of ethyl cyanoacetate (43 g.) and a solution of sodium ethoxide (9 g. of sodium and 105 g. of alcohol), phenylmethylacetonitrile (50 g.) (V. Meyer, *Annalen*, 1889, **250**, 123) was added, and the whole refluxed for 15 hours; the white paste slowly changed into a thick red jelly. A slight excess of dilute hydrochloric acid having been added, ether extracted a substance, which was washed with sodium carbonate solution and steam-distilled to remove unchanged cyano-compounds (50 g.). The non-volatile red oil, twice crystallised from a little alcohol, gave the *ester* (2—3 g.) in colourless needles, m. p. 107° (Found : C, 68·9; H, 6·7; N, 11·2. $C_{14}H_{16}O_2N_2$ requires C, 68·7; H, 6·6; N, 11·5%), and m. p. 80° when mixed with the substance, m. p. 93°, obtained by the methylation of ethyl α-cyano-β-imino-γ-phenylbutyrate (Atkinson and Thorpe, *loc. cit.*).

Ethyl 2 : 4-*Diamino*-1-*methylnaphthalene*-3-*carboxylate* (II).—The pale green solution obtained by stirring the finely powdered valerate (2 g.) into ice-cooled sulphuric acid (4 c.c.) was after 3 minutes poured into cold alcohol (20 c.c.), a little dry ether added, the crystalline sulphate collected, washed with a little alcohol and with much ether, air-dried for a short time (surface discoloration), and dissolved in cold water, and excess of ammonia added to the yellow solution. The precipitate crystallised from alcohol in canary-yellow micro-needles (1·2 g.), m. p. 115° (Found : C, 68·8; H, 6·3; N, 11·3. $C_{14}H_{16}O_2N_2$ requires C, 68·7; H, 6·56; N, 11·5%). Even in the dark, this *compound* changed into a black resinous mass.

The corresponding compound prepared by Atkinson and Thorpe's method (*loc. cit.*, 1925) had m. p. 75° (these authors give m. p. 74°).

2 : 4-*Diacetamido*-1-*methylnaphthalene* (III).—The carbethoxy-compound (0·5 g.) was heated on the steam-bath with alcoholic potash for 15 minutes, the alcohol distilled, concentrated hydrochloric acid (50 c.c.) added to the residue, and the solution filtered

from potassium chloride and evaporated to dryness on the steam-bath under 30 mm. An aqueous solution of the yellow residue was mixed with sodium acetate, the amine removed in ether, in which it was very sparingly soluble, recovered, and shaken with hot water, the emulsion cooled, and a few drops of acetic anhydride added. The brown powder obtained, crystallised from acetic acid, had m. p. 302°, and 303° when mixed with authentic 2 : 4-diacetamido-1-methylnaphthalene (see below).

2 : 4-*Diamino*-1-*methylnaphthalene*.—Water (20 c.c.) was added to a mixture of 2 : 4-dinitro-1-methylnaphthalene (2 g.) (Veselý and Pastak, *Bull. Soc. chim.*, 1925, **37**, 1444) and phosphorus tri-iodide (25 g.). Slight warming initiated a violent reaction, which was completed by heating on the steam-bath for 1 hour. Excess of ammonia was added to the cold yellow solution; the sticky red precipitate, extracted with ether and crystallised from light petroleum–benzene, afforded a pale yellow micro-crystalline substance, m. p. 93° (Found : C, 76·5; H, 7·1; N, 15·4. $C_{11}H_{12}N_2$ requires C, 76·7; H, 6·98; N, 16·3%). This compound darkens considerably in the air. Atkinson and Thorpe (*loc. cit.*, 1926) record m. p. 65° for their diamino-compound. The *diacetyl* compound (III), prepared by treating the amine with cold water and acetic anhydride, crystallised from alcohol (very sparingly soluble) in white flakes, m. p. 303° (Found : C, 69·9; H, 6·3; N, 10·5. $C_{15}H_{16}O_2N_2$ requires C, 70·3; H, 6·25; N, 11·0%).

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