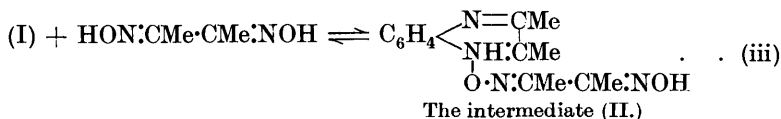
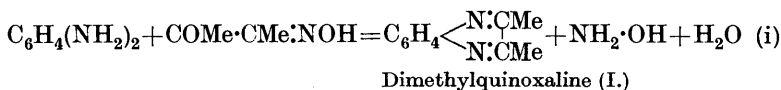


LXVI.—*The Quinoxaline Synthesis : Some Derivatives of 2 : 3-Dimethylquinoxaline.*

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THE synthesis of 2:3-dimethylquinoxaline from diacetylmonoxime and *o*-phenylenediamine (Gabriel and Sonn, *Ber.*, 1907, **40**, 4850) involves the formation of an intermediate substance, apparently not hitherto recognised as such. The reactions occurring are :



The *dimethylquinoxaline* derivative (II) of *dimethylglyoxime* is a definite compound which has also been prepared from the constituent base and dioxime; no such combination occurs, however, between dimethylglyoxime and quinoxaline itself, nor will *o*-phenylenediamine condense with the dioxime.

By the action of strong acid or alkali on (II) the base (I) is liberated, as in the normal preparative method (*loc. cit.*). In this method, however, the reactants are used in equimolecular proportion, and the maximum yield of (I) is about 70% on account of loss of diacetylmonoxime by reaction (ii) occurring simultaneously with

(i). The mother-liquor from the preparation, after removal of (I) by steam distillation in excess of alkali, consequently contains unattacked diamine which will react with more monoxime. It is evident that complete utilisation of the diamine can only be attained by adding 2 mols. of monoxime per mol. of diamine. Actually a 90% yield was thus obtained.

From 2 : 3-dimethylnaphthaquinoxaline a similar *compound* is formed, having two molecules of the base combined with one molecule of dimethylglyoxime.

Bromination of dimethylquinoxaline or of (II) in alcoholic solution gives 5 : 6 : 7 : 8-tetrabromo-2 : 3-dimethylquinoxaline, which has very feebly basic properties and considerable stability.

#### EXPERIMENTAL.

*The Intermediate (II).*—*o*-Phenylenediamine (1 mol.) in warm aqueous solution containing acetic acid (2 mols.) was treated slowly with a warm aqueous solution of diacetylmonoxime (1 mol.), whereby a mass of orange needle-shaped crystals was soon produced. This intermediate *substance* (II) was separated from the deep brown liquid and recrystallised from alcohol: more was obtained by further addition of the monoxime (1 mol.) to the mother-liquor.

Steam distillation of the original acid liquid with (II) in suspension slowly produced (I), but after addition of excess of alkali to the reaction liquid the base could be rapidly removed by this means or by extraction with ether. Acidification after removal of the base precipitated dimethylglyoxime.

The substance (II), on repeated crystallisation, formed lemon-yellow flakes, m. p. 182°. It also melted at 182° when mixed with the colourless product formed from dimethylglyoxime and dimethylquinoxaline in alcoholic solution. The "salts" prepared by the two different methods were of identical microscopic appearance. The temperature 182° was quite definite, but was only the initial m. p., the substance becoming completely liquid at about 215°. The initial m. p. was unaltered when the substance was mixed with dimethylglyoxime (m. p. 245°), but dimethylquinoxaline (m. p. 104°) lowered it to 103°: (II) evidently dissociates on heating (Found: C, 61.5, 61.6; H, 6.6, 6.7; N, 20.2, 20.4; *M*, by Rast's camphor method, 151.  $C_{14}H_{18}O_2N_4$  requires C, 61.3; H, 6.6; N, 20.4%; *M*, 274).

The substance (II) is insoluble in ether, ligroin, benzene, and chloroform and only slightly soluble in water. It is converted by the action of concentrated hydrochloric acid into diacetyl and a salt of dimethylquinoxaline, and by alkali into the base itself. In

alcoholic solution it shows as sensitive a colour reaction as dimethylglyoxime with nickel salts. A solution of (II) was used to estimate nickel by the usual procedure : the weights of precipitate obtained in two experiments were 0.1822 and 0.1832 g. Dimethylglyoxime gave 0.1809 and 0.1810 g. from the same quantity of nickel solution.

2 : 3-*Dimethylnaphthaquinoxaline*.—Equal weights (3 g.) of 1 : 2-naphthylenediamine and diacetylmonoxime, mixed in warm aqueous-alcoholic solution, produced an oil which soon crystallised in orange needles. Recrystallised from alcohol, these became lighter in colour. Melting began at 123° and was complete at about 200°. The nickel reaction was observed as above (Found : C, 72.0; H, 6.0; N, 15.6.  $C_{32}H_{32}O_2N_6$  requires C, 72.1; H, 6.1; N, 15.8%). The base, liberated by alkali, extracted with ether, and recrystallised from dilute alcohol, was pale yellow and melted at 101—102°. It combined with dimethylglyoxime to give the same intermediate "salt," initial m. p. 122°.

5 : 6 : 7 : 8-*Tetrabromo-2 : 3-dimethylquinoxaline*.—Dimethylquinoxaline (or the intermediate II), brominated in alcoholic solution on a water-bath with excess of bromine, gave a crystalline mass. After being washed with alcohol and water and recrystallised from absolute alcohol, glacial acetic acid, or benzene, the pale pink or colourless substance melted at 234° (decomp.). It was insoluble in water or ether, dissolved in concentrated sulphuric or nitric acid, and was reprecipitated unchanged on dilution several hours later. It was not appreciably attacked by boiling chromic and glacial acetic acids or by alkaline permanganate. Bromine was not removed by aqueous alkali or boiling alcoholic silver nitrate, but a mixture of chromic and sulphuric acids acted violently on the substance, bromine being evolved (Found : C, 25.5; H, 1.3; Br, 67.6.  $C_{10}H_6N_2Br_4$  requires C, 25.3; H, 1.3; Br, 67.5%).

Bromination of dimethylquinoxaline in chloroform solution gave the above substance, but the chief product was another faintly coloured substance, m. p. 150° after four recrystallisations from dilute alcohol. The bromine in this substance was partly removed by hot aqueous alkali (Found : Br, 51.6.  $C_6H_8N_2Br_2$  requires Br, 50.6%).

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