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55. *The Condensation of* o-*Phenylenediamine with Ethyl Acetoacetate.*

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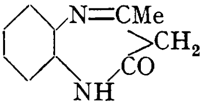
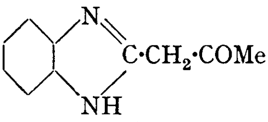
Under neutral or alkaline conditions *o*-phenylenediamine and ethyl acetoacetate afford a mixture of a *compound* having a seven-membered ring (I) and the isomeric *benziminazole-2-acetone* (II). Under acidic conditions ethyl β-2-aminoanilinocrotonate (III) is formed, and this cyclises to 2-methylbenziminazole.

It has been shown by Coffey, Thomson, and Wilson (J., 1936, 856) that the condensation of ethyl acetoacetate with arylamines to give esters of β-arylaminocrotonic acids is favoured by acid catalysts. It was therefore of interest to investigate the effect of catalysts on the condensation of *o*-phenylenediamine with ethyl acetoacetate. It has now been observed that the formation of ethyl β-2-aminoanilinocrotonate (Hinsberg and Koller, *Ber.*, 1896, **29**, 1500) is conditioned by the presence of an acid catalyst. This was probably provided in the work of these authors by the use of unpurified ester in the condensation. Ethyl β-2-aminoanilinocrotonate exists in two forms, and although several recrystallisations of freshly prepared material failed to change the lower-melting (needle) form into the higher-melting (plate) form (Hinsberg and Koller, *loc. cit.*), a change in melting point occurred after a week, and the plate form was then obtained by one crystallisation. This change is probably a *cis-trans* isomerisation and may have been brought about by light.

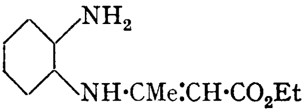
In a solvent under neutral conditions, condensation affords a mixture of two substances, water and alcohol being eliminated. The first *compound* ($C_{10}H_{10}ON_2$) was formed in 71—72% of the theoretical



(I.)



(II.)



(III.)

yield. It gave a sparingly soluble sodio-derivative, was precipitated unchanged from its alkaline solution by acetic acid, and failed to couple with diazotised amines. Boiling 20% sulphuric acid brought about hydrolysis to 2-hydroxybenziminazole and acetone. Its constitution is therefore considered to be (I). Similar compounds containing seven-membered rings have been described by Thiele and Steimmig (*Ber.*, 1907, **40**, 955) and by Phillips (J., 1928, 2393), who treated *o*-phenylenediamine with acetylacetone and with malonic acid respectively.

The second (isomeric) substance (yield, 12—13%) is characterised by ready solubility in dilute alkali or acid and ability to couple with diazotised amines. These properties lead to the belief that the substance is *benziminazole-2-acetone* (II).

Attempts to cyclise ethyl β-2-aminoanilinocrotonate afforded only 2-methylbenziminazole, with elimination of ethyl acetate, thus confirming the observation of Hinsberg and Koller (*loc. cit.*). It therefore seems improbable that formation of (I) proceeds by elimination of alcohol from (III). It is more likely that the condensation of ethyl acetoacetate with *o*-phenylenediamine proceeds through acetoacet-*o*-aminoanilide, which then cyclises under the conditions of the condensation to give (I) and (II). Reduction of *acetoacet-*o*-nitroanilide* with iron in fact gave (II), but formation of (I) in these circumstances was not detected.

Experimental.

Condensation of o-*Phenylenediamine with Ethyl Acetoacetate.*—(i) *Under acid conditions.* Powdered *o*-phenylenediamine (21·6 g.) was mixed with excess of ethyl acetoacetate purified as described by Coffey, Thomson, and Wilson (*loc. cit.*). After addition of three drops of hydrochloric acid the temperature rose to 35° and the mixture rapidly solidified. The ethyl β-2-aminoanilinocrotonate separated from light petroleum in white needle-shaped crystals (10·7 g.), m. p. 59—62°. After 8 days these had become yellow and melted at 85°. Recrystallisation from light petroleum then gave plates, m. p. 85°. Hinsberg and Koller (*loc. cit.*) give the m. p.'s of the two forms as 59° and 85°.

Unsuccessful attempts were made to cyclise the needle form of ethyl β-2-aminoanilinocrotonate to the compound (I) by (*a*) boiling in light petroleum solution in the presence of iodine, (*b*) heating to 100° either

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alone, with 2N-hydrochloric acid, or with a trace of iodine. The iodine catalysed the formation of 2-methylbenziminazole.

(ii) *Under neutral conditions.* Purified ethyl acetoacetate (29 c.c.), mixed with xylene (20 c.c.), was added during ½ hour to a boiling solution of *o*-phenylenediamine (21·6 g.) in xylene (200 c.c.). The liquid was boiled for 1 hour, during which 50—60 c.c. were removed. The distillate had a lower aqueous-alcoholic layer. On cooling, the *compound* (I) (11·5 g.) separated in almost colourless needles, m. p. 120°; it crystallised from ethyl alcohol in colourless rhombohedra, m. p. 121° (Found : C, 69·5; H, 5·8; N, 16·05. $C_{10}H_{10}ON_2$ requires C, 69·0; H, 5·8; N, 16·1%).

After the separation of (I) the xylene mother-liquors were extracted with 10% sodium hydroxide solution (300 c.c.) and the crystals which separated were dissolved in water and acidified. This gave a further 7·0 g. of (I). In a second experiment the total yield of (I) amounted to 71·3% of the theoretical.

From the alkaline liquid, after the separation of the sodium salt of (I), acidification afforded *benziminazole-2-acetone*, which crystallised from water in needles or from benzene in prisms, m. p. 148° (Found : C, 69·0; H, 5·8; N, 15·8. $C_{10}H_{10}ON_2$ requires C, 69·0; H, 5·8; N, 16·1%).

(iii) *Under alkaline conditions.* The conditions of (ii) were repeated except that (*a*) the ethyl acetoacetate was rendered slightly alkaline by standing over solid sodium carbonate and (*b*) N/2-alcoholic potash (1 c.c.) was added to the xylene solution of *o*-phenylenediamine before addition of the ester. After reaction was complete benziminazole-2-acetone separated on cooling in hexagonal prisms (22 g.; 63·5%), m. p. 147°. The mother-liquor was extracted with 10% sodium hydroxide solution, and the extracts saturated with sodium chloride to precipitate the sodio-derivative of (I), which was then converted into (I) by acidification (6·5 g.; 18·5%). A further quantity of (I) (4·2 g.; 12%) was recovered by acidification of the aqueous mother-liquor.

*Acetoacet-*o*-nitroanilide* was prepared by condensation of ethyl acetoacetate with *o*-nitroaniline, and was separated from contaminants by solution in 2N-alkali and salting-out of the sodio-derivative. Acidification of the sodio-derivative gave the product (19% yield), which was crystallised from alcohol and then from benzene–light petroleum. It formed yellow-red prisms, m. p. 65° (Found : N, 12·3. $C_{10}H_{10}O_4N_2$ requires N, 12·6%).

A solution of acetoacet-*o*-nitroanilide (26·5 g.) in alcohol (120 c.c.), after addition of 3·5% hydrochloric acid (13 c.c.), was reduced by boiling for 5 hours with iron filings (36 g.). The liquid was neutralised, separated hot from the iron oxide, and the oxide washed with hot alcohol (30 c.c.). On cooling, benziminazole-2-acetone (0·5 g.) separated. Concentration of the mother-liquor gave three successive crops (total 14 g.) of material, m. p. 135—138° approx., identified as benziminazole-2-acetone. The residue after evaporation to dryness (6·6 g.) had m. p. 128—130° after crystallisation from benzene. The m. p. was not depressed by benziminazole-2-acetone.

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