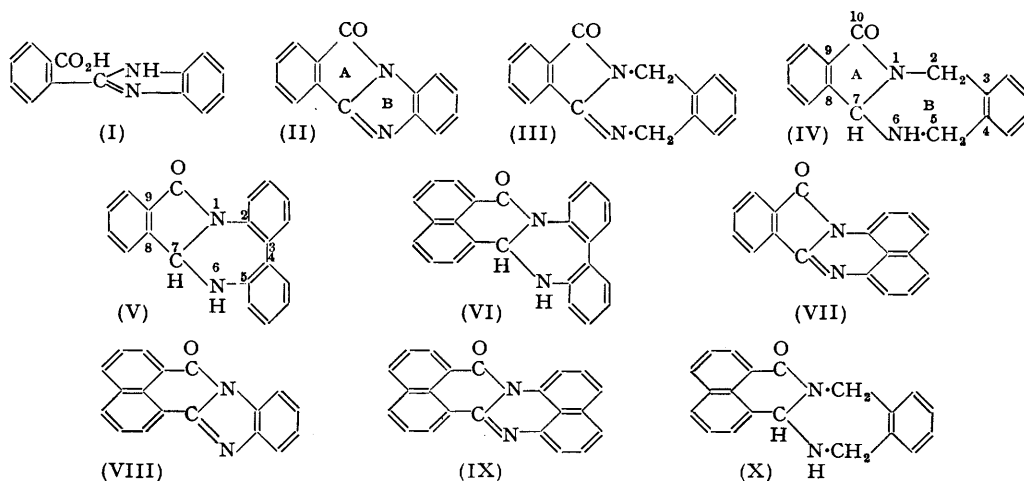


980. Heterocyclic Nitrogen Compounds. Part III.* The Condensation of Phthalaldehydic Acids and Diamines.

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The condensation of phthalaldehydic acid and 8-formyl-1-naphthoic acid with certain diamines has been studied. According to the pair of reagents used the reaction product is found to be analogous to Bistrzycki's "o-benzoylenebenzimidazole" (II) (*Ber.*, 1890, **23**, 1042; 1891, **24**, 627) containing a C:N bond or its reduction product containing a CH·NH system.

BISTRZYCKI (*Ber.*, 1890, **23**, 1042; 1891, **24**, 627) showed that phthalaldehydic acid and o-phenylenediamine produce the acid (I), one mol. of phthalaldehydic acid being reduced to phthalide. Hot acetic anhydride cyclises (I) to "o-benzoylenebenzimidazole" (II). If ωω'-diamino-o-xylene reacts similarly, then after cyclisation the product should be (III) and by reduction of the C:N linkage should yield (IV). This compound has already been prepared by another method and its structure established (Hatt and Stephenson, *J.*, 1952, 199). However, (IV) was produced directly and there was no evidence of the formation of the expected acid or its cyclisation product. Use of two molar proportions of phthalaldehydic acid did not increase the yield of (IV) and there was no evidence of the formation of phthalide.



Now, (I) and (II) are also produced by heating phthalic anhydride with o-phenylenediamine (for this and related examples see Bistrzycki and Fässler, *Helv. Chim. Acta*, 1923, **6**, 519; Bistrzycki and Lecco, *ibid.*, 1921, **4**, 425; Chakravarti, *J. Indian Chem. Soc.*, 1924, **1**, 19; 1925, **1**, 329; Betrabet and Chakravarti, *ibid.*, 1930, **7**, 191; Poraï-Koshits and Antoshul'skaya, *Chem. Abs.*, 1944, **38**, 1234) and analogous compounds are obtained from diphenic or naphthalic anhydride with o-phenylenediamine (Bistrzycki and Fässler, *loc. cit.*; Chakravarti, *loc. cit.*) and from naphthylene-1:8-diamine with phthalic or naphthalic anhydride (Sachs, *Annalen*, 1909, **365**, 117; cf. Sachs and Mosebach, *Ber.*, 1911, **44**, 2861). However, attempts to prepare (III) from phthalic anhydride and ωω'-diamino-o-xylene gave only the symmetrical diphtaloyl derivative of the diamine.

Further examples of the aldehydic acid condensation have now been studied such that the sizes of rings A and B differ from the system studied by Bistrzycki. Phthalaldehydic acid and 2:2'-diaminodiphenyl in acetic acid gave (V) smoothly, in good yield. Similarly, 8-formyl-1-naphthoic acid gave (VI). Both (V) and (VI) contain a CH·NH rather than a C:N group, since they can be nitrosated and acetylated and hydrolysis of the result-

* Part II, *J.*, 1952, 199.

ing derivatives regenerates the parent compounds. Compounds containing a C:N group are unstable to caustic alkalis, those containing a CH·NH group are stable. Both types are unstable in boiling 1 : 1 hydrochloric acid. However, other examples in which rings A and B were further varied did not yield CH·NH compounds. Thus, naphthylene-1 : 8-diamine with phthalaldehydic acid, and *o*-phenylenediamine with 8-formyl-1-naphthoic acid, gave (VII) and (VIII) in small yield, and no other pure materials. No pure product could be obtained from the condensation of naphthylene-1 : 8-diamine and 8-formyl-1-naphthoic acid although (IX) may have been formed in very small yield. No satisfactory results could be obtained from the condensation of diphenic anhydride and 2 : 2'-diaminodiphenyl.

From the above examples it seems that the CH·NH compounds may be first formed and that their conversion into C:N compounds depends on ability to reduce the aldehydic acid. Thus (VII) and (VIII), but not (III), would presumably be stabilised by resonance. However, the formation of a stable anil from naphthalic anhydride and 2 : 2'-diaminodiphenyl indicates that for (V) and (VI) steric factors are more important—Chakravarti (*loc. cit.*) reported that the anil from *o*-phenylenediamine and naphthalic anhydride is smoothly cyclised to (VIII). Preliminary results indicate that (IV) is stable to mild oxidising agents.

The compounds containing a C:N group are coloured, except for one reported by Bistrzycki and Fässler (*loc. cit.*). (IV) and (V) are white, but (VI) is bright yellow though its acetyl and nitroso-derivatives are colourless.

8-Formyl-1-naphthoic acid and $\omega\omega'$ -diamino-*o*-xylene in acetic acid gave a colourless product which formed the expected monoacetyl derivative but, unlike (IV), was decomposed by nitrous acid and did not yield a simple nitroso-derivative and has been assigned the provisional formula (X).

EXPERIMENTAL

M. p.s are corrected. The microanalyses were carried out in the Microanalytical Laboratory of the C.S.I.R.O. by Dr. W. Zimmermann and his staff.

10-Keto-1 : 6-diaza-3 : 4-8 : 9-dibenzobicyclo[5 : 3 : 0]deca-3 : 8-diene (IV).—Phthalaldehydic acid (0.075 g.), $\omega\omega'$ -diamino-*o*-xylene dihydrochloride hemihydrate (0.11 g.), hydrated sodium acetate (0.15 g.), and water (15 ml.) were refluxed for 9 hours. After 40 minutes, the amide (IV) began to separate. The mixture was cooled and the precipitate (55 mg.) collected. Crystallisation from ethanol gave colourless needles, m. p. 254—255° (decomp.) alone or mixed with the product prepared by Hatt and Stephenson (*loc. cit.*). A further 20 mg. were obtained by making the filtrate from the first precipitate strongly alkaline and keeping it for 24 hours. The acetyl derivative, m. p. 193.5—194°, gave no depression of m. p. with the acetyl derivative of (IV). When 2 molar proportions of phthalaldehydic acid were used, (IV) was again the only product isolated. The 6-methyl derivative was obtained by heating (IV) (0.5 g.), 90% formic acid (3 ml.), and 40% aqueous formaldehyde (3 ml.) on a water-bath for 1 hour, adding 4N-hydrochloric acid (10 ml.), and removing the solvents under reduced pressure. After dissolution of the residue in water the methyl derivative was liberated by excess of sodium hydroxide. After some hours the product (0.47 g.) was collected. It formed colourless crystals, m. p. 207—209° (decomp.), from aqueous ethanol (Found : C, 77.5; H, 6.3; N, 10.5. $C_{17}H_{16}ON_2$ requires C, 77.2; H, 6.1; N, 10.6%). Prolonged heating of (IV) with formic acid-formaldehyde caused decomposition products.

$\omega\omega'$ -Diphthalimido-*o*-xylene.—Phthalic anhydride (1 mol.), $\omega\omega'$ -diamino-*o*-xylene dihydrochloride hemihydrate (1 mol.), and the theoretical amount or an excess of sodium acetate were refluxed in ethanol for 3—10 hours. Only $\omega\omega'$ -diphthalimido-*o*-xylene was isolated, forming needles (from acetic acid or butanol), m. p. 266—267° (decomp.) alone or mixed with an authentic specimen (Gabriel and Pinkus, *Ber.*, 1893, 26, 2212) (Found : C, 72.9; H, 4.2; N, 7.1. Calc. for $C_{24}H_{16}O_4N_2$: C, 72.7; H, 4.1; N, 7.1%).

10-Keto-1 : 6-diaza-2 : 3-4 : 5-8 : 9-tribenzobicyclo[5 : 3 : 0]deca-2 : 4 : 8-triene (V).—2 : 2'-Diaminodiphenyl (1.76 g.), phthalaldehydic acid (1.35 g.), acetic acid (100 ml.), and water (50 ml.) were refluxed for 7 hours. Water (150 ml.) was then added to the hot solution and, after cooling, the white crystalline bicyclodecatriene (2.28 g.) was collected. Crystallisation from aqueous acetic acid or butanol gave colourless prisms, m. p. 245—247° (decomp.) (Found : C, 80.5; H, 4.7; N, 9.5. $C_{20}H_{14}ON_2$ requires C, 80.5; H, 4.7; N, 9.4%). The triene is stable in boiling alcoholic sodium ethoxide but is slowly attacked by boiling 1 : 1 hydrochloric acid. The

nitroso-derivative was obtained when (V) (0.75 g.) in acetic acid (40 ml.) and water (0.5 ml.) was cooled to 12° and treated with sodium nitrite (0.18 g.) in water (2 ml.). After 2 hours at room temperature the product (0.8 g.) was precipitated by water. Crystallisation from aqueous ethanol gave pale cream crystals, m. p. 198.5—200.5° (decomp.) (Found: C, 73.6; H, 4.3; N, 12.7. $C_{20}H_{13}O_2N_3$ requires C, 73.4; H, 4.0; N, 12.8%); it gave a positive Liebermann's nitroso-reaction. Hydrolysis with boiling aqueous-alcoholic potassium hydroxide caused regeneration of (V) plus unidentified by-products. The *acetyl* derivative, prepared by use of boiling acetic anhydride, formed prisms (from 40% ethanol), m. p. 221.5—222.0° (Found: C, 77.6; H, 4.8; N, 8.7. $C_{22}H_{16}O_2N_2$ requires C, 77.6; H, 4.7; N, 8.2%). Attempts to methylate (V) with formic acid-formaldehyde brought about its decomposition to unidentified products. Like (IV), (V) gives negative tests for the carbonyl group.

The Compound (VI).—To a solution of 8-formyl-1-naphthoic acid (1 g.) in hot acetic acid (25 ml.) 2:2'-diaminodiphenyl (0.92 g.) in acetic acid (10 ml.) was added, and the mixture refluxed for 5.5 hours, and poured into water (150 ml.), an emulsion being then formed. After partial neutralisation with sodium hydroxide the mixture was heated for 1 hour on the water-bath and kept overnight. The yellow solid (1.67 g.) was collected and chromatographed in benzene on alumina (B.D.H.; 2.5 × 11 cm.). The *compound* (VI) (*ca.* 1 g.) was eluted in benzene. Repeated crystallisation from butanol gave yellow prisms, m. p. 263.5—264.5° (Found: C, 82.7; H, 4.8; N, 8.0. $C_{24}H_{16}ON_2$ requires C, 82.7; H, 4.6; N, 8.0%). (VI) is stable to boiling alcoholic sodium ethoxide but is attacked by boiling 1:1 hydrochloric acid. The *nitroso*-derivative, obtained as above, formed cream-coloured prisms, m. p. 226—227° (decomp.), from butanol (Found: C, 76.7; H, 4.1; N, 11.1. $C_{24}H_{15}O_2N_3$ requires C, 76.4; H, 4.0; N, 11.1%) and gave a positive Liebermann reaction. It proved stable to boiling aqueous alcoholic potassium hydroxide. The *nitroso*-derivative (0.35 g.), potassium hydroxide (1.5 g.) in water (5 ml.) and ethanol (13 ml.) were refluxed with hydroxylamine hydrochloride (0.28 g.) in water (4 ml.) and ethanol (22 ml.) for 9 hours. (VI) (0.2 g.) was recovered from the resulting yellow solution by dilution with water and was identified by m. p. and mixed m. p. The *acetyl* derivative, formed in boiling acetic anhydride, comprised colourless prisms, m. p. 261—261.5° (decomp.) (from 50% ethanol) (Found: C, 80.4; H, 4.7; N, 7.5. $C_{26}H_{18}O_2N_2$ requires C, 80.0; H, 4.7; N, 7.2%).

The Compound (X).—8-Formyl-1-naphthoic acid (0.4 g.) and hydrated sodium acetate (0.6 g.) in warm acetic acid (15 ml.) and water (5 ml.) were refluxed with $\omega\omega'$ -diamino-*o*-xylene dihydrochloride hemihydrate (0.44 g.) in acetic acid (5 ml.) and water (5 ml.) for 6 hours. A small amount of a very sparingly soluble, high-melting precipitate soon separated. This substance melted at *ca.* 310° (decomp.) but was not obtained analytically pure. It may be the dinaphthoyl derivative of $\omega\omega'$ -diamino-*o*-xylene. Treatment of the filtrate with 30% aqueous sodium hydroxide (20 ml.; cooling) gave a dirty green precipitate (0.22 g.) (A). When the filtrate was basified and kept for 24 hours more precipitate (0.22 g.) (B) was obtained. The benzene solutions of (A) and (B) were chromatographed on alumina, coloured by-products being strongly adsorbed and (X) eluted as a colourless solution in benzene. Crystallisation from 50% ethanol gave a colourless *product* [(75 mg. and 95 mg. respectively from (A) and (B)]. Further crystallisation from 50% ethanol gave needles, m. p. 195—196° (decomp.) (Found: C, 80.0; H, 5.4; N, 8.7. $C_{20}H_{16}ON_2$ requires C, 80.0; H, 5.4; N, 9.3%). In the above chromatography elution with ethanol gave a yellow solid which, however, could not be completely freed from dark impurities. (X) is stable to boiling alcoholic sodium ethoxide and does not form a benzenesulphonyl derivative [cf. (IV); Hatt and Stephenson, *loc. cit.*]. The *acetyl* derivative had m. p. 215.5—216.5° (from 50% ethanol) (Found: C, 77.3; H, 5.3; N, 7.8. $C_{22}H_{18}O_2N_2$ requires C, 77.2; H, 5.3; N, 8.2%). Nitrosation gave needles, m. p. 237—238° from ethanol (Found: C, 79.7; H, 5.0; N, 4.9. $C_{19}H_{14}O_2N$ requires C, 79.2; H, 4.9; N, 4.9%).

N-2''-Amino-2'-diphenylnaphthalimide.—2:2'-Diaminodiphenyl (1.9 g.) in hot acetic acid (25 ml.) was added to naphthalic anhydride (1.98 g.) in boiling acetic acid (100 ml.) and after 7 hours' refluxing the clear yellow solution was set aside for 12 hours. Unchanged naphthalic anhydride (0.49 g.) was then removed. Treatment of the filtrate with water (200 ml.) and 30% aqueous sodium hydroxide (100 ml.) (cooling) gave a cream-coloured precipitate (2.6 g.), m. p. 225—237°. Purification was not achieved unless the crude material was first refluxed (7 hours) with potassium hydroxide (9 g.) in ethanol (25 ml.) and water (15 ml.). The resulting solution (in which a precipitate had sometimes separated) was diluted with water (250 ml.), digested on the water bath for 2—3 hours, and cooled and the bright yellow precipitate (2.07 g.) collected. Repeated crystallisation from butanol gave the *amil* as yellow prisms, m. p. 261—262.5° (decomp.) (Found: C, 79.1; H, 4.6; N, 7.9. $C_{24}H_{16}O_2N_2$ requires C, 79.1; H, 4.4; N, 7.7%).

The *acetyl* derivative, prepared in boiling acetic anhydride, formed white prisms, m. p. 252—254° (decomp.) (Found: C, 76.7; H, 4.4; N, 6.9. $C_{26}H_{18}O_3N_2$ requires C, 76.8; H, 4.5; N, 6.9%). The anil dissolves in hot 6*N*-hydrochloric acid and a colourless hydrochloride separates on cooling. On diazotisation and coupling with β -naphthol an orange-red azo-dye separates.

Diphenic Anhydride and 2 : 2'-Diaminodiphenyl.—Equimolar proportions were refluxed for 8 hours in acetic acid and also heated without solvent at 200—210°. No pure product was obtained

Naphthylene-1 : 8-diamine.—(a) *With 8-formyl-1-naphthoic acid*. Under conditions which were successful in the preparations of (II), (IV), (V), and (VI) no pure product was isolated, although it is possible that a trace of (IX) may have been formed.

(b) *With phthalaldehydic acid*. Under similar conditions a very poor yield of (VII) (isolated by vacuum-sublimation followed by crystallisation from acetic acid) was obtained. Identification was by m. p. and mixed m. p.

8-Formyl-1-naphthoic Acid and o-Phenylenediamine.—These reactants gave a poor yield of Chakravarti's "1 : 2-(1' : 8')-naphthoylene-1 : 3-benzodiazole," identified by m. p. and mixed m. p.

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