680. *The Structures of Some Supposed Azetid-2 : 4-diones. Part I. Derivatives of Malonic Acid.*

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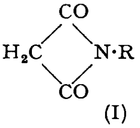
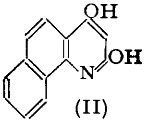
Evidence is given in support of the conclusions already published (*J.*, 1949, 1318) that the supposed *N*-(phenylamino)- and *N*-1-naphthyl-malonimide are respectively *N*-acetyl-*N'*-phenylhydrazine and 2 : 4-dihydroxy-7 : 8-benzoquinoline, and that malonylbenzidine is not a cyclic imide but a substance of polymeric nature.

A reinvestigation of several compounds hitherto formulated as malonimides has shown that they do not possess the constitutions formerly attributed to them (see King, *J.*, 1949, 1318). One of these is the so-called malonylphenylhydrazine (I; R = Ph·NH·), m. p. 128°, of E. Fischer and Passmore (*Ber.*, 1889, **22**, 2735), said to be a pyrolysis product of the phenylhydrazine salt of malonic acid monophenylhydrazide. This phenylhydrazine salt cannot, however, be prepared under the conditions apparently used by Fischer and Passmore, and the melting point (128°) of the product actually obtained led Biquard and Grammaticakis (*Bull. Soc. chim.*, 1940, **7**, 766) to regard it as identical with Fischer and Passmore's malonylphenylhydrazine. It is, in fact, *N*-acetyl-*N'*-phenylhydrazine, as also is the compound obtained on pyrolysis of the malonic acid monophenylhydrazide phenylhydrazine salt, the latter being synthesised without difficulty if the condensation of malonic acid and phenylhydrazine is performed without the addition of acetic acid.



(I)



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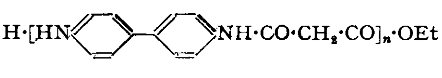

(III)

" N-1-*Naphthylmalonimide.*"—By the action of boiling ethyl malonate on α-naphthylamine, Baumgarten and Kärgel (*Ber.*, 1927, **60**, 841) prepared 2 : 4-dihydroxy-7 : 8-benzoquinoline (II); they were apparently unaware that under very similar conditions R. Meyer (*Annalen*, 1906, **347**, 23) had previously obtained a compound which he had described as α-naphthylmalonimide (I; R = α-$C_{10}H_7$). Repetition of both preparations has given products that are indistinguishable, both forming with nitrous acid the red hydroxyimino-derivative already described (Baumgarten and Kärgel, *loc. cit.*). Support for the dihydroxyquinoline structure (II) was found in the formation with diazomethane of an alkali-soluble monomethyl ether, and in the preparation, using phosphorus pentachloride, of 2 : 4-dichloro-7 : 8-benzoquinoline (Albert, Brown, and Duewell, *J.*, 1948, 1292). The latter product resisted catalytic hydrogenation but was partly reduced with hydriodic acid and phosphorus to 2(or 4)-iodo-7 : 8-benzoquinoline. Heating the dichlorobenzoquinoline with zinc dust gave 7 : 8-benzoquinoline, analysed as a picrate and identified by comparison of its sulphate and 2 : 4 : 6-trinitrobenzene derivative with those of a specimen obtained by the Skraup synthesis. Zinc dust distillation of 2 : 4-dihydroxy-7 : 8-benzoquinoline, believed by Baumgarten and Kärgel from the melting point of the product (51°) and of its sulphate (213°) to result in the formation of 7 : 8-benzoquinoline, has been found to give α-naphthylamine (m. p. 51°; sulphate, m. p. 220°).

Malonylbenzidine.—The foregoing identification indicated a possible alternative structure for "malonylbenzidine," a product formed under comparable conditions from ethyl malonate and benzidine and first prepared by Remfry (*J.*, 1911, **99**, 610). The compound was re-examined by Le Fèvre (*J.*, 1929, 733), and on the results of nitrogen analyses of an amorphous sulphate and of a crystalline derivative formed from salicylaldehyde in boiling phenol, Remfry's macro-ring formula of the Kaufler type was replaced by the structure (I; R = *p-p'*-$H_2N{\cdot}C_6H_4{\cdot}C_6H_4$). The supposed malonimide is said also to have been obtained by heating ethyl *N*-(4'-amino-4-diphenylyl)malonamate (Mehta and Thosar, *J. Indian Chem. Soc.*, 1938, **15**, 629). However, the product prepared by Remfry's method was shown not to be a dihydroxyquinoline from its insolubility in aqueous alkalis; moreover, heating it with 70% sulphuric acid resulted in a nearly quantitative recovery of benzidine. On the other hand, the properties of malonylbenzidine, which is amorphous and chars without melting when heated, are not those expected from the constitution (I; R = *p-p'*-$H_2N{\cdot}C_6H_4{\cdot}C_6H_4$). It is virtually non-basic, and analysis of the supposed sulphate, precipitated on pouring a concentrated sulphuric acid solution into water, revealed that the sulphur content varied from batch to batch and was only some 10% of that required by the formula $(C_{15}H_{12}O_2N_2)_2,H_2SO_4$. Re-examination of the salicylaldehyde reaction showed that the compound of m. p. *ca.* 300° formed after short heating is heterogeneous and contains disalicylidenebenzidine, m. p. 260°, which is the sole product after 1¾ hours' heating. In contrast, monoacetylbenzidine forms a crystalline acid sulphate and a salicylidene compound, and it can therefore be concluded that malonylbenzidine is a polycondensation product of type (III).

EXPERIMENTAL.

Malonic Acid Monophenylhydrazide Phenylhydrazine Salt.—Fischer and Passmore (*loc. cit.*) do not specify the acetic acid concentration, but from their other experiments on phenylhydrazides it is assumed to be 50%. By use of the recommended proportions, and heating on a steam-bath for 2 hours, a good yield of acetylphenylhydrazine was obtained, m. p. and mixed m. p. after recrystallisation from water, 128° (Found: C, 63·8; H, 6·6; N, 18·8. Calc. for $C_8H_{10}ON_2$: C, 64·1; H, 6·6; N, 18·7%). The identity of the product was confirmed by the formation of diacetylphenylhydrazine, m. p. 108°, on further acetylation. The required hydrazine salt was formed by heating under reflux for 2 hours a solution of malonic acid (20 g.) and phenylhydrazine (60 g.) in water (320 c.c.). Cooling precipitated a brownish solid which when crystallised from water gave the colourless compound (58 g.) described by Fischer and Passmore, having m. p. 142°—not, as recently stated (*J.*, 1949, 1326), 154°, which is the m. p. of the free malonic acid monophenylhydrazide (Found: C, 59·8; H, 5·6; N, 19·2. Calc. for $C_{15}H_{18}O_3N_4$: C, 59·6; H, 6·0; N, 18·5%).

The dried salt, in a flask fitted with a Bunsen valve, was heated in a bath at 200° and kept at this temperature for 15 minutes. The dark gummy residue was dissolved in hot ethyl acetate, and the colourless solid which separated from the cooled solution was identified by m. p. and mixed m. p. 128°, as acetylphenylhydrazine. On concentration of the residual ethyl acetate solution a further product separated which after recrystallisation from aqueous ethanol had m. p. 188°, alone or mixed with malonic bisphenylhydrazide (Found: C, 63·7; H, 5·1. Calc. for $C_{15}H_{16}O_2N_4$: C, 63·4; H, 5·6%).

2 : 4-*Dihydroxy*-7 : 8-*benzoquinoline.*—By repetition of Meyer's experiment, 2 : 4-dihydroxy-7 : 8-benzoquinoline (II) was obtained after crystallisation from ethanol–ethoxyethanol, as colourless needles, m. p. 326° (yield 25%). As lately reported by Albert, Brown, and Duewell (*loc. cit.*), Baumgarten and Kärgel's method is much less successful than has been claimed, but by heating equimolecular quantities of ethyl malonate and α-naphthylamine vigorously under reflux over a free flame until the mixture is almost solid (30—45 minutes) and working up in the usual way, yields of approx. 50% are readily obtained.

2(4)-*Hydroxy*-4(2)-*methoxy*-7 : 8-*benzoquinoline.*—The dihydroxyquinoline (II) (2 g.) was treated with excess of ethereal diazomethane, and the mixture occasionally shaken during 4 hours. Crystallisation of the insoluble bright yellow powder (2 g.), m. p. *ca.* 274°, from ethanol gave the *monomethyl* *ether* as yellow needles, m. p. 286° (Found : C, 74·1; H, 4·8; N, 6·3; OMe, 14·2. $C_{14}H_{11}O_2N$ requires C, 74·6; H, 4·9; N, 6·2; OMe, 13·8%). The derivative dissolved in hot aqueous sodium hydroxide, giving a sodium salt which separated from the cold solution as colourless plates. The ether was soluble also in hot concentrated hydrochloric acid, crystallising unchanged as the solution cooled.

2 : 4-*Dichloro*-7 : 8-*benzoquinoline.*—Before its preparation with phosphoryl chloride was described by Albert, Brown, and Duewell (*loc. cit.*), 2 : 4-dichloro-7 : 8-benzoquinoline was obtained by heating in an oil-bath at 135—140° for 2½ hours a mixture of the dihydroxybenzoquinoline (5 g.) and phosphorus pentachloride (30 g.) moistened with phosphoryl chloride. After removal of the phosphoryl chloride under reduced pressure the crude product was isolated by pouring the residue into a mixture of ice and aqueous ammonia. Repeated crystallisation of the dried yellow-brown solid (5 g.) from alcohol (charcoal) gave the dichlorobenzoquinoline in colourless needles, m. p. 132° (Found : C, 62·4; H, 2·4; N, 5·6; Cl, 28·1. Calc. for $C_{13}H_7NCl_2$: C, 62·9; H, 2·8; N, 5·7; Cl, 28·6%). Small specimens could be obtained pure by distillation in steam in which the compound is very slightly volatile.

2(or 4)-*Iodo*-7 : 8-*benzoquinoline.*—A mixture of 2 : 4-dichloro-7 : 8-benzoquinoline (2 g.) and red phosphorus (2 g.) was heated with hydriodic acid (45 c.c.; *d* 1·7) under reflux for 8 hours. The hot solution was then filtered and the light yellow solid which separated on cooling was collected and triturated with aqueous sodium hydroxide and ether. Evaporation of the ethereal solution gave pale yellow crystals (0·5 g.), m. p. *ca.* 120°, which on crystallisation from light petroleum formed very pale yellow rods, m. p. 120° (Found : C, 51·3; H, 2·6; N, 4·4; I, 40·2. $C_{13}H_8NI$ requires C, 51·2; H, 2·6; N, 4·6; I, 41·6%).

7 : 8-*Benzoquinoline.*—(i) The crude mixture of bases obtained from α-naphthylamine (50 g.) by the Skraup reaction (Bamberger and Stettenheimer, *Ber.*, 1891, **24**, 2472; Haid, *Monatsh.*, 1906, **27**, 318) was distilled at atmospheric pressure. The fraction, b. p. 320—340°, consisting of 7 : 8-benzoquinoline (18·5 g., 31%), readily solidified to a mass of prisms, m. p. 51° (cf. Haid, *loc. cit.*). It was shown by the diazotisation test to be free from α-naphthylamine, and when crystallised from alcohol gave colourless prisms, m. p. 51·5—52°. The hydrogen sulphate separated from alcohol as pale yellow needles, m. p. 210° (Found : C, 56·8; H, 4·0; N, 5·2. Calc. for $C_{13}H_9N,H_2SO_4$: C, 56·3; H, 4·0; N, 5·1%), and the 1 : 3 : 5-trinitrobenzene compound from aqueous ethanol as light yellow needles, m. p. 133°.

(ii) A mixture of 2 : 4-dichloro-7 : 8-benzoquinoline (5 g.) and zinc dust (20 g.) was heated in batches (5 g.) in a current of hydrogen. The distillate (0·75 g.) was purified through its hydrogen sulphate which was recrystallised from ethanol and was identified as 7 : 8-benzoquinoline by the m. p.s and mixed m. p.s of the sulphate and of the 1 : 3 : 5-trinitrobenzene compound. The base was further characterised by a picrate, yellow needles (from alcohol), m. p. 178° (Found : N, 13·2. Calc. for $C_{13}H_9N,C_6H_3O_7N_3$: N, 13·7%).

Zinc Dust Distillation of 2 : 4-*Dihydroxy*-7 : 8-*benzoquinoline.*—A mixture of the dihydroxybenzoquinoline (5 g.) and zinc dust (25 g.), heated in portions (6 g.) in a current of hydrogen, gave a low-melting base (0·65 g.) which responded to the diazotisation test for a primary amine. The acid-soluble portion of the product, m. p. 51°, formed a sulphate, m. p. 220° alone or mixed with α-naphthylamine sulphate, and a 1 : 3 : 5-trinitrobenzene compound, m. p. 212° undepressed by the corresponding α-naphthylamine derivative (Found : C, 54·2; H, 3·2. Calc. for $C_{10}H_9N,C_6H_3O_6N_3$: C, 53·9; H, 3·4%).

"*Malonylbenzidine.*"—Prepared by Remfry's method (*loc. cit.*), "malonylbenzidine" is a light brown amorphous powder insoluble in all organic solvents including phenol, camphor, and diphenylamine, thus precluding molecular-weight determinations. A specimen (2 g.) heated with sulphuric acid (20 c.c., 70%) at 150° for 2 hours gave a crystalline mass which, when triturated with water and dried, afforded benzidine sulphate (2·1 g., 95%).

Malonylbenzidine (2 g.) was ground in cold concentrated sulphuric acid (25 c.c.) and, after passing through a sintered-glass filter, the solution was poured into water. The gelatinous buff-coloured precipitate was washed by centrifuging it with water and then acetone and was dried at 100° [Found : C, 69·1, 68·8; H, 5·4, 5·5; N, 10·3, 10·6; S, 0·5. Calc. for $(C_{15}H_{12}O_2N_2)_2,H_2SO_4$: C, 59·8; H, 4·4; N, 9·3; S, 5·3%].

When a mixture of malonylbenzidine (2 g.), salicylaldehyde (6 c.c.), and phenol (20 g.) was heated under reflux for 30 minutes, a yellow solid was obtained which crystallised from phenol in plates, m. p. 298—300°. Treatment with boiling benzene in a Soxhlet apparatus left an insoluble amorphous material, m. p. 347° (decomp.), and gave disalicylidenebenzidine, m. p. 260° alone or mixed with an authentic specimen (Found : C, 79·5; H, 4·9; N, 7·1. Calc. for $C_{26}H_{20}O_2N_2$: C, 79·6; H, 5·1; N, 7·1%).

When the preparation was repeated with 1¾ hours' heating under reflux the product (90%) consisted of the salicylidene derivative, m. p. and mixed m. p. 260°.

N-*Acetylbenzidine.*—The monoacetylbenzidine, m. p. 199°, was prepared by Cain's method (*J.*, 1909, **95**, 717). Its alcoholic solution, treated with 2N-sulphuric acid, gave a gelatinous precipitate (cf. Schmidt and Schultz, *Ber.*, 1879, **12**, 489; *Annalen*, 1881, **207**, 332) which when dissolved in boiling water (400 c.c./g.) gave N-*acetylbenzidine sulphate* in shining plates, m. p. 312° (decomp.) with previous discoloration (Found : C, 58·8; H, 5·8; N, 9·6; S, 5·9. $C_{28}H_{28}O_2N_4,H_2SO_4,H_2O$ requires C, 59·1; H, 5·7; N, 9·8; S, 5·6. Found, after drying at 140° : C, 61·2; H, 5·1; N, 9·9; loss, 3·7. $C_{28}H_{28}O_2N_4,H_2SO_4$ requires C, 61·1; H, 5·5; N, 10·2; loss 3·2%). N-*Acetyl*-N′-*salicylidenebenzidine* crystallised from ethanol in yellow plates, m. p. 280—281° (Found : C, 76·0; H, 5·5; N, 8·3. $C_{21}H_{18}O_2N_2$ requires C, 76·3; H, 5·5; N, 8·5%).

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