Cyclic Amidines. Part I. Derivatives of Phenhomazine (Dibenzo[b, f]-1 : 5-diazocine).

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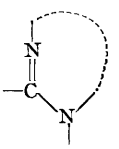
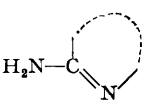
o-Cyanoanilinium toluene-*p*-sulphonate, on being heated, affords 6 : 12-diaminophenhomazine (III; X = Y = NH_2) and tricycloquinazoline (IV). Dianthranilide can be prepared by interaction of methyl anthranilate, a nitrile, and sodium. A generalised interpretation of this reaction, applicable to a number of analogous reactions, is suggested. The light-absorption characteristics of a number of phenhomazine derivatives are recorded.

The amidine group may form a fragment of a heterocyclic ring either as a chain of three atoms (I) or as a chain of two atoms with one nitrogen as a ring substituent (II). A variety of methods has been applied to the synthesis of both types of cyclic amidine. However, the reactions leading to the formation of semicyclic amidines are essentially of two types despite the wide range of heterocyclic rings which have been obtained by these methods. In the first type, ring formation has involved, at an appropriate stage, the addition of the group :NH to the group ·C:N; for example, in compounds containing one heterocyclic nitrogen atom, this addition has been exploited in the synthesis of pyrrolidines (Best and Thorpe, *J.*, 1909, **95**, 1506), pyridines (von Meyer, *J. pr. Chem.*, 1914, **90**, 29), and indoles (Pschorr and Hoppe, *Ber.*, 1910, **43**, 2543). In the second type of synthesis, the exocyclic nitrogen is introduced into the preformed heterocyclic ring either by an addition to the ammono-aldehyde system ·N:CH· (*e.g.*, Tschitschibabin and Zeide, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1216) or by replacement of halogen in a cyclic analogue of an imidoyl halide ·N:CHal· (*e.g.*, den Hertog and Wibaut, *Rec. Trav. chim.*, 1932, **51**, 381).

(I)   (II)

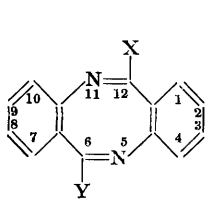
This series of communications deals with the application to the synthesis of semicyclic and cyclic amidines of the methods recently developed for the preparation of open-chain amidines, especially those involving the addition of :NH to ·C:N (Oxley and Short, *J.*, 1946, 147; Cooper and Partridge, *J.*, 1953, 255).

A simple example of the addition of :NH to ·C:N to form a semicyclic amidine is provided by the polymerisation of a salt of *o*-cyanoaniline. The rigidity with which the two *ortho*-substituents are held renders this reaction capable of affording a product containing an 8-membered ring, namely, 6 : 12-diaminophenhomazine (III; X = Y = NH_2). By analogy of this reaction with the anhydrisation of salicylic acid (Baker, Ollis, and Zealley, *J.*, 1951, 201), the simultaneous formation of products resulting from a higher degree of polymerisation would be expected.

In agreement with these speculations, we find that the isolable products from the material formed when *o*-cyanoanilinium toluene-*p*-sulphonate is heated for a short time are 6 : 12-diaminophenhomazine monotoluene-*p*-sulphonate (III; X = NH_2; Y = NH_3^+}$C_7H_7O_3S^-$ or a tautomeride) and tricycloquinazoline (IV). Tricycloquinazoline is apparently formed in this reaction by condensation of the trimer (V) of the *o*-cyanoanilinium cation. A compound isomeric with tricycloquinazoline formed when indazole (VI) is heated with copper powder was tentatively assigned the constitution (VII) (Jacobson and Huber, *Ber.*, 1908, **41**, 660). We find that the compound obtained in this way is identical in melting point and light-absorption characteristics with tricycloquinazoline prepared by heating *o*-aminobenzaldehyde with ammonium chloride (Kozak and Kalmus, *Bull. Acad. polonaise*, 1933, **10**, *A*, 532). Since indazole and *o*-cyanoaniline are isomeric, it is not unexpected that they could both yield tricycloquinazoline under appropriate conditions.

The constitution of the 6 : 12-diaminophenhomazine prepared from *o*-cyanoanilinium toluene-*p*-sulphonate was confirmed by comparison as the base, dihydrochloride, monohydrochloride, monotoluene-*p*-sulphonate, and picrate with specimens prepared by heating 6 : 12-dichlorophenhomazine (III; X = Y = Cl) (Schroeter, *Ber.*, 1919, **52**, 2224) with methanolic ammonia at 150°.

Derivatives of phenhomazine have hitherto received little attention. Contrary to the statement of Morton, " The Chemistry of Heterocyclic Compounds," McGraw-Hill, New York,



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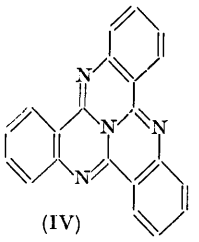

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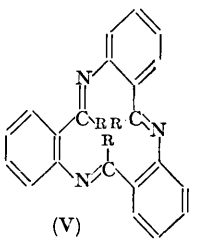

(R = NH_3^+)

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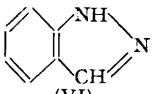

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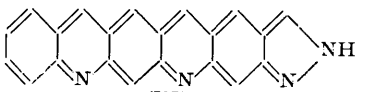


(VII)

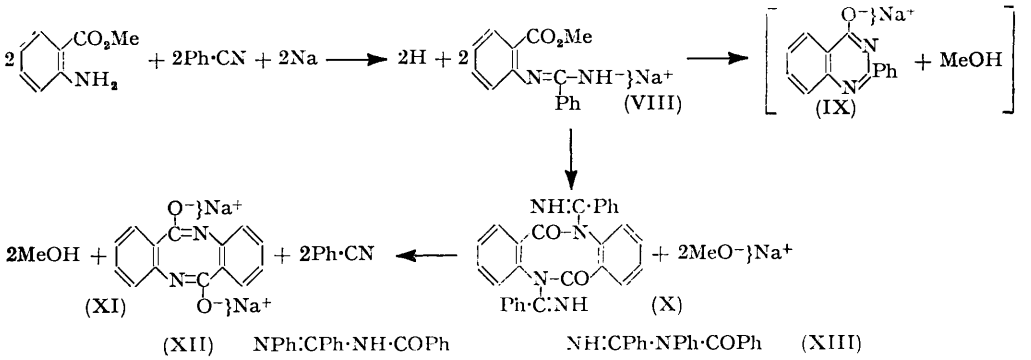
1946, p. 271, phenhomazine itself is not formed when *o*-aminobenzaldehyde is kept at pH 3 (cf. Schöpf and Lehmann, *Annalen*, 1932, **497**, 7; Bamberger, *Ber.*, 1927, **60**, 314). The most readily accessible derivative of phenhomazine, namely, dianthranilide (III; X = Y = OH or its tautomeride), was prepared by hydrolysis of the product of acetolysis of an *NN'*-diarylsulphonyldianthranilide which is itself formed when an *o*-arylsulphonamidobenzoyl chloride undergoes condensation in pyridine (Schroeter and Eisleb, *Annalen*, 1909, **367**, 101; Schroeter, *loc. cit.*).

In an attempt to extend an open-chain amidine synthesis (Cooper and Partridge, *loc. cit.*) to the preparation of 2-amino-4-hydroxyquinolines, we examined the reaction of acetonitrile with methyl anthranilate in the presence of " powdered " sodium in boiling benzene. The main product formed was dianthranilide. The same compound can be obtained more simply and in better yield by the use of benzonitrile instead of acetonitrile. Dianthranilide prepared in this way afforded *NN'*-dimethyl (Schroeter and Eisleb, *loc. cit.*) and *NN'*-diethyl derivatives by treatment with the appropriate dialkyl sulphate in the presence of alkali. The corresponding ethers (III; X = Y = OMe and X = Y = OEt) were obtained by boiling 6 : 12-dichlorophenhomazine with alcoholic solutions of the respective alkoxides.

We suggest that the foregoing reactions resulting in the production of dianthranilide may be interpreted as in the annexed scheme. Evidence in support of the formation of a substituted amidine (VIII) in the first stage of the reaction was provided by the isolation of 4-hydroxy-2-phenylquinazoline (cf. IX) as a by-product. Collateral evidence for the condensation of the sodioamidine (VIII) to yield *NN'*-dibenzimidoyldianthranilide (X) was obtained by demonstrating that *N*-phenylbenzamidine is benzoylated by boiling together its sodio-derivative and ethyl benzoate in benzene; the main product isolated was *N*-benzoyl-*N'*-phenylbenzamidine (XII). The formation of benzoic acid, dibenzoylamine, and benzanilide, isolated as by-products, can be accounted for in several ways. It is known that on benzoylation at a low temperature *N*-phenylbenzamidine affords *N*-benzoyl-*N*-phenylbenzamidine (XIII) (Wheeler, Johnson, and McFarland, *J. Amer. Chem. Soc.*, 1903, **25**, 787) which rearranges with great facility to the more stable *N*-benzoyl-*N'*-phenylbenzamidine (XII). The constitution of the main product of the benzoylation of *N*-phenylbenzamidine with ethyl benzoate is therefore in accordance with expectation. An analogous rearrangement in the case of *NN'*-dibenzimidoyldianthranilide appears to be extremely unlikely since this would involve fission of the 8-membered ring and formation of a 12-membered ring.

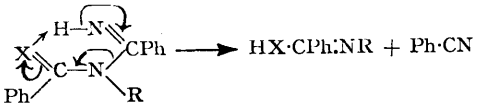
The postulated decomposition of *NN'*-dibenzimidoyldianthranilide (X) to dianthranilide

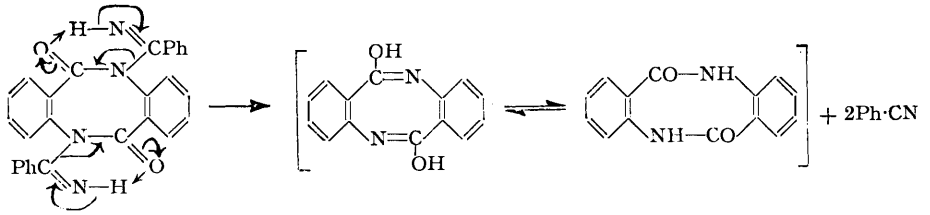
(cf. XI) and benzonitrile is similar to that observed in a number of open-chain analogues having the structure NH:CPh·NR·CPh:X; *N*-benzoyl-*N*-phenylbenzamidine (R = Ph, X = O; see below), 2 : 4-diphenyl- (R = H, X = NH) (Peak, *J.*, 1952, 215), 1 : 2 : 4-triphenyl- (R = H; X = NPh), and 1 : 2 : 3 : 4-tetraphenyl-1 : 3 : 5-triazapenta-1 : 4-diene (R = Ph;



(XII) NPh:CPh·NH·COPh NH:CPh·NPh·COPh (XIII)

X = NPh) (Cooper, Partridge, and Short, *J.*, 1951, 391) all afford benzonitrile and a second product varying according to the nature of R and X. It is probable that the decomposition is initiated by the formation of a hydrogen bond which governs the subsequent electron drifts :





The process then becomes consistent not only with the foregoing decompositions but also with the fission of diamidides and triamidides with acids (Cooper, Partridge, and Short, *loc. cit.*) and with the formation of cyanides by the decomposition of imidic esters (Wislicenus and Goldschmidt, *Ber.*, 1900, **33**, 1467), of amidines (Oxley, Partridge, and Short, *J.*, 1948, 303), of imidoyl sulphonates (Oxley, Partridge, Robson, and Short, *J.*, 1946, 763; Oxley, Peak, and Short, *J.*, 1948, 1618), and of cyanamides by the decomposition of *O*-arylsulphonylureas (Oxley, Partridge, Peak, and Short, *Chem. and Ind.*, 1949, 419; Partridge and Turner, *J. Pharm. Pharmacol.*, 1953, **5**, 103).

The suggestion that the reaction is simply a base-catalysed condensation of methyl anthranilate cannot be sustained since when this compound was boiled with " powdered " sodium in benzene, sodium ethoxide in benzene, or sodium ethoxide in ethanol, the maximum yield of dianthranilide was 4%. It may appear from the suggested interpretation of the reaction leading to the formation of dianthranilide that not more than a catalytic quantity of benzonitrile would be required. However, benzonitrile is consumed in reactions of this kind not only in the formation of the quinazolone (cf. IX) but also by reduction to benzene and a number of other products (Cooper and Partridge, *loc. cit.*; Anker and Cook, *J.*, 1941, 323).

The light-absorption characteristics of a number of phenhomazine derivatives are summarised in the Table. It is clear from the absence of absorption at long wave-lengths that the eight-membered ring in dianthranilide and its dialkyl ethers is not in cyclic conjugation with the aromatic rings and in this respect these compounds resemble 1 : 2 : 5 : 6-

dibenzo*cyclo*octatetraene (Fieser and Pechet, *J. Amer. Chem. Soc.*, 1946, **68**, 2577). Indeed, it is apparent that even the simple co-planar conjugated structure of the chromophoric systems of ethyl benzimidoate, benzamide, or *NN'*-dimethylbenzamide, which absorb at 225—228 mμ (Ley and Specker, *Ber.*, 1939, **72**, 192), cannot be assumed. The partial chromophore of dianthranilide in neutral or in acid solution appears to be similar to that of its *NN'*-dialkyl derivatives rather than its dialkyl ethers.

Compound	Solvent	Light absorption (mμ; ε in parentheses)
Dianthranilide	EtOH	214 (28,500)
,,	N/10-HCl–EtOH	214 (28,800)
,,	N/10-NaOH–EtOH	230 (20,400)
NN'-Dimethyldianthranilide	EtOH	212 (24,800)
NN'-Diethyldianthranilide	EtOH	213 (20,900)
6 : 12-Dimethoxyphenhomazine	EtOH	208 (8,700); 251 (950)
6 : 12-Diethoxyphenhomazine	EtOH	209 (13,700); *ca. 260* (2,200)
6 : 12-Diaminophenhomazine	EtOH	*206* (10,700); 223 (29,100); 235 (31,100) *262* (17,500); 301 (9,000); 330 (7,900)
,,	N/100-HCl–EtOH	208 (39,600); 242 (30,500); 280 (25,200) 314 (10,700); *330* (7,300); 415 (9,400)
,, monohydrochloride	Water	206 (33,400); 234 (29,500); *275* (15,300) 315 (9,000); *ca. 360* (4,200)
,, dihydrochloride	Water	205 (34,200); 230 (28,900); 274 (17,300) 313 (9,100); 360 (4,600)
,, ,,	4N-HCl	210 (25,900); 261 (33,600); 322 (9,700)

Figures in italics denote inflexions. The solvent EtOH refers to ethanol (95%).

No simple interpretation of the bright yellow colour of the monohydrochloride of 6 : 12-diaminophenhomazine is apparent. Some similarities to 9-aminophenanthridine might be expected, but this forms a colourless solution in acid (Morgan and Walls, *J.*, 1932, 2225). The colour of the singly charged cation may be a manifestation of charge resonance of forms having the proton donated to the ring nitrogen (cf. Craig and Short, *J.*, 1945, 419) and strained planar structures. On the other hand, the band at 415 mμ, observed with a solution of the base in N/100-ethanolic hydrogen chloride, is similar in position and intensity to that reported for 5-aminoacridine (Craig and Short, *loc. cit.*). In alcoholic solution, the base exhibits absorption characteristics resembling 2-aminoquinoline and 1-amino*iso*-quinoline (Steck and Ewing, *J. Amer. Chem. Soc.*, 1948, **70**, 3397). In strong acid solution the absorption at longer wave-lengths disappears; this is in agreement with the suggestion that charge resonance would then be suppressed.

Experimental

o-*Cyanoanilinium Toluene*-p-*sulphonate*.—Interaction of *o*-chloronitrobenzene (52·5 g., 0·33 mole), cuprous cyanide (32·9 g., 0·37 mole), and pyridine (29·0 g., 0·37 mole) at 160° for 4 hr., then at 180° for 1 hr., and addition of the melt to hydrochloric acid (350 ml.) afforded crude *o*-cyanonitrobenzene (32·0 g., 65%), m. p. 103—106°, raised to 107·5—108·5° after crystallisation from acetic acid (Bogert and Hand, *J. Amer. Chem. Soc.*, 1902, **24**, 1031, record m. p. 109·5°). *o*-Cyanoaniline (Bogert and Hand, *loc. cit.*) (15 g.) was warmed with toluene-*p*-sulphonic acid (25 g.) in water (40 ml.) until homogeneous; on cooling, the solution deposited o-*cyanoanilinium toluene*-p-*sulphonate* (27·7 g., 94%) as prisms, m. p. 170—171°, unchanged by crystallisation from *iso*propyl alcohol (Found: C, 57·8; H, 4·75. $C_{14}H_{14}O_3N_2S$ requires C, 57·9; H, 4·85%). The *picrate*, red prisms from water, had m. p. 109—110° (Found: C, 45·0; H, 2·6. $C_{13}H_9O_7N_5$ requires C, 45·0; H, 2·6%).

Action of Heat on o-*Cyanoanilinium Toluene*-p-*sulphonate*.—When *o*-cyanoanilinium toluene-*p*-sulphonate (20 g.) was heated in a refluxing nitrobenzene vapour-bath for 15 min., the temperature of the melt rose to 230° after 5 min., and then rapidly dropped to 210°, while the clear liquid became pasty. The cooled melt was powdered and extracted successively with hot water (4 × 150 ml.) and hot 1·5N-hydrochloric acid (250 ml.). The orange residue (2·4 g.), m. p. 317—320°, was crystallised from xylene and gave 1·9 g. (26%) of tricycloquinazoline as fluffy yellow needles, m. p. 322—323°, not depressed by an authentic specimen (see below) (Found: C, 79·1; H, 3·6; N, 17·7. Calc. for $C_{21}H_{12}N_4$: C, 78·75; H, 3·75; N, 17·5%). When kept for 10 days the aqueous extract deposited an orange solid (2·2 g.), which was fractionally crystallised from ethanol and afforded 6 : 12-*diaminophenhomazine monotoluene*-p-*sulphonate* (0·25 g., 2%) as

small orange needles, m. p. 280—282° (Found : C, 61·5; H, 4·9; N, 13·3; S, 7·9. $C_{21}H_{20}O_3N_4S$ requires C, 61·75; H, 4·95; N, 13·7; S, 7·85%); it was characterised by conversion into the monopicrate (see below), which had m. p. 225—227° and mixed m. p. 226—228°. Another toluene-*p*-sulphonate (0·95 g.), m. p. 228—229°, separated during this fractional crystallisation but was not identified. The aqueous filtrate and acid extract were combined and made alkaline with ammonia, and the resulting precipitate (4·0 g.) was crystallised from 4N-hydrochloric acid, affording 6 : 12-diaminophenhomazine dihydrochloride monohydrate (2·55 g., 18%), m. p. and mixed m. p. 285—287° (decomp.). Samples of the base, monohydrochloride, and monopicrate made from this dihydrochloride had m. p. and mixed m. p. identical with those described below.

Tricycloquinazoline.—(i) *o*-Aminobenzaldehyde (4 g.) and ammonium chloride (10 g.), treated according to the directions of Kozak and Kalmus (*loc. cit.*), gave 0·6 g. (17%) of tricycloquinazoline as fluffy yellow needles, m. p. 322—323° after crystallisation from toluene. Kozak and Kalmus state that this compound melts at 308—310°.

(ii) When indazole (1 g.) and copper powder (1 g.) were heated together as described by Jacobson and Huber (*loc. cit.*), 0·15 g. (17%) of tricycloquinazoline, m. p. and mixed m. p. 322—323°, was obtained. Jacobson and Huber record m. p. 318—319° for a compound made in this way.

Absorption spectra of the compound made in various ways are recorded in the Table.

Light absorption of tricycloquinazoline in chloroform.

From *o*-cyanoaniline	$\lambda_{max.}$	252	284	296	310	378	400	424	452 mμ
	$\varepsilon_{max.}$	40,900	23,500	32,600	29,200	23,800	23,000	8200	2600
From *o*-aminobenzaldehyde	$\lambda_{max.}$	252	284	296	310	378	400	424	450 mμ
	$\varepsilon_{max.}$	42,300	23,100	31,600	28,400	23,000	22,400	8000	2500
From indazole	$\lambda_{max.}$	252	284	296	310	380	400	424	450 mμ
	$\varepsilon_{max.}$	45,100	25,400	34,500	31,300	25,100	24,500	8700	2700

Dianthranilide.—(i) When methyl anthranilate (45·4 g., 0·3 mole), powdered sodium (13·8 g., 0·6 g.-atom), and acetonitrile (24·6 g., 0·6 mole) were mixed in dry benzene (170 ml.) at room temperature, the initial exothermic reaction caused the mixture to boil vigorously and much light brown solid separated; the mixture was then refluxed for 24 hr. The cooled mixture was shaken with water (150 ml.) and with 2N-sodium hydroxide (70 ml.), and the mixed aqueous solutions, after charcoal treatment, were added to excess of hydrochloric acid, affording crude dianthranilide (17·1 g., 48%), m. p. 320—327°, which, after crystallisation from ethanol, had m. p. 335—337°, not depressed by an authentic specimen (see below) (Found : C, 70·6; H, 3·8; N, 12·1. Calc. for $C_{14}H_{10}O_2N_2$: C, 70·6; H, 4·25; N, 11·75%). With periods of refluxing of 0, 0·5, and 21 hr., the yields of crude dianthranilide were 30, 31, and 40% respectively. With twice the above proportion of acetonitrile and with 3·5 hours' refluxing, the yield was 38%. With double the proportion of both acetonitrile and of sodium and with 20 hours' refluxing, the yield was 44%; after removal of the dianthranilide the mother-liquors were neutralised with ammonia and the precipitated solid was crystallised from benzene, affording 0·4 g. of an amphoteric compound, possibly 2-*anthraniloylmethyl*-4-*hydroxyquinazoline*, as small, pale yellow needles, m. p. 176—177° [Found : C, 68·5; H, 4·65; N, 15·3%; *M* (Rast), 268. $C_{16}H_{13}O_2N_3$ requires C, 68·8; H, 4·7; N, 15·05%; *M*, 279].

(ii) There was no reaction when methyl anthranilate (22·7 g., 0·15 mole), powdered sodium (6·9 g., 0·3 g.-atom), and benzonitrile (30·9 g., 0·3 mole) were mixed in benzene (70 ml.) at room temperature. After the vigorous exothermic reaction which was initiated by warming had subsided, the mixture was refluxed for 2 hr. and cooled. The resulting suspension was extracted with water (70 ml.) and then with 2N-sodium hydroxide (40 ml.); this extract, after treatment with charcoal, afforded, on the addition of hydrochloric acid, dianthranilide (8·8 g., 49%), m. p. 332—335°, raised by crystallisation from ethanol to 335—337°, not depressed by an authentic specimen. Neutralisation of the filtrate with ammonia gave a solid (1·9 g.), m. p. 220—228°, which, when crystallised from ethanol (charcoal), gave 4-hydroxy-2-phenylquinazoline (1·5 g., 4·5%), as needles, m. p. 235—236° (Bischler and Lang, *Ber.*, 1895, **28**, 279, give m. p. 235—236°) (Found : C, 75·5; H, 4·7. Calc. for $C_{14}H_{10}ON_2$: C, 75·65; H, 4·55%). Distillation of the extracted benzene solution afforded benzonitrile (7·25 g., 0·07 mole), b. p. 74—76°/16 mm., n_D^{19} 1·5289.

Repetition of the foregoing experiment but with the proportion of benzonitrile reduced to 0·23 mole and with refluxing for 3 and 4 hr. gave 55 and 56% respectively of dianthranilide.

(iii) Interaction of methyl anthranilate (0·1 mole) and sodium (0·1 g.-atom) in refluxing

benzene for 8 hr. afforded a 4% yield of dianthranilide : similarly, interaction in boiling ethanol for 12 hr. gave a 3% yield. No dianthranilide was isolated when methyl anthranilate (0·1 mole), sodium (0·3 g.-atom), and ethanol (0·1 mole) were boiled together for 22 hr. in benzene.

(iv) Dianthranilide, prepared by Schroeter and Eisleb's method (*loc. cit.*), had m. p. 335—337°; Schroeter and Eisleb record m. p. about 330°. *NN'*-Ditoluene-*p*-sulphonyldianthranilide, an intermediate in this synthesis, had m. p. 252—253° which rose on storage to 271—272°. Schroeter and Eisleb give m. p. 240° for this compound (Found : C, 61·7; H, 4·1. Calc. for $C_{28}H_{22}O_6N_2S_2$: C, 61·5; H, 4·05%).

6 : 12-*Dichlorophenhomazine*.—Made by Schroeter's method (*loc. cit.*), this had m. p. 219—220° : (Found : C, 61·2; H, 3·25. Calc. for $C_{14}H_8N_2Cl_2$: C, 61·15; H, 2·95%). Schroeter gives m. p. 220°.

NN'-*Dimethyldianthranilide*.—This, prepared by Schroeter and Eisleb's method (*loc. cit.*), had m. p. 205—207° : Schroeter and Eisleb record m. p. 207°.

NN'-*Diethyldianthranilide* was prepared in 60% yield by shaking together dianthranilide (1·0 g.) and diethyl sulphate (1·3 g.) in 0·5N-sodium hydroxide (17 ml.) frequently during 6 hr. It crystallised from benzene–light petroleum (b. p. 80—100°) as prisms, m. p. 192—193° (Found : C, 73·4; H, 6·3. $C_{18}H_{18}O_2N_2$ requires C, 73·5; H, 6·15%).

6 : 12-*Dimethoxyphenhomazine*.—6 : 12-Dichlorophenhomazine (2·0 g.) was added to sodium (0·35 g.) dissolved in methanol (100 ml.), and the solution was refluxed for 26 hr. The residue obtained by evaporating the solution to dryness was stirred with water, and the resultant solid (1·8 g., 93%), m. p. 161—162°, afforded 6 : 12-*dimethoxyphenhomazine* as prisms, m. p. 161—162°, on crystallisation from light petroleum (b. p. 100—120°) (Found : C, 72·5; H, 5·45. $C_{16}H_{14}O_2N_2$ requires C, 72·15; H, 5·3%). This compound was soluble in concentrated hydrochloric acid but was precipitated by the addition of water. The *monopicrate*, made by interaction of the base and picric acid in benzene, crystallised as slender yellow prisms, m. p. 144—155°, from benzene–light petroleum (b. p. 60—80°) (Found : C, 53·5; H, 3·55; N, 14·2. $C_{22}H_{17}O_9N_5$ requires C, 53·3; H, 3·45; N, 14·15%). Attempts to crystallise the picrate from methanol, ethanol, or *iso*propyl alcohol yielded the base.

6 : 12-*Diethoxyphenhomazine*, formed as above in 98% yield from 6 : 12-dichlorophenhomazine, sodium, and ethanol, crystallised as prisms, m. p. 146—147°, from light petroleum (b. p. 100—120°) (Found : C, 73·9; H, 6·25. $C_{18}H_{18}O_2N_2$ requires C, 73·5; H, 6·15%).

6 : 12-*Diaminophenhomazine*.—A suspension of finely powdered 6 : 12-dichlorophenhomazine (5 g.) in 14% w/w methanolic ammonia (200 g.) was heated in a rotary autoclave at 120—150° for 6 hr. The resultant solution was evaporated to dryness, the residue dissolved by warming with 50 ml. of 1·5N-hydrochloric acid, and the solution filtered from a trace of insoluble matter. 20 ml. of this solution were added to excess of aqueous ammonia and afforded 6 : 12-*diaminophenhomazine* (1·7 g., 39%), which crystallised from aqueous ethanol as small colourless cubes, m. p. 127—128° (Found : C, 71·1; H, 5·25; N, 23·4. $C_{14}H_{12}N_4$ requires C, 71·2; H, 5·1; N, 23·7%). The base crystallised from benzene as very small, pale yellow rods, m. p. 92—93° with effervescence, containing solvent of crystallisation which was lost on prolonged storage (Found : C, 76·3; H, 5·75; N, 18·3. $C_{14}H_{12}N_4, C_6H_6$ requires C, 76·4; H, 5·8; N, 17·8%). The remaining 30 ml. of acid solution, on cooling, deposited 6 : 12-*diaminophenhomazine dihydrochloride monohydrate* (3·2 g., 54%) as pale yellow needles, m. p. 283—286° (decomp.), changed to 285—287° (decomp.) by crystallisation from 4N-hydrochloric acid [Found : C, 51·2; H, 5·2; N, 16·8; Cl, 22·1; H_2O (Karl Fischer), 6·3. $C_{14}H_{12}N_4,2HCl,H_2O$ requires C, 51·4; H, 4·95; N, 17·1; Cl, 21·65; H_2O, 5·5%]. When a solution of the dihydrochloride in hot water was cooled, slender orange needles of the *monohydrochloride* were deposited, having m. p. 283—287° (decomp.), unchanged by recrystallisation from water [Found : C, 61·6; H, 5·1; N, 20·4; Cl, 13·0; H_2O (Karl Fischer), Nil. $C_{14}H_{12}N_4,HCl$ requires C, 61·65; H, 4·8; N, 20·55; Cl, 13·0%]. The *monopicrate*, prepared by interaction of the base and sodium picrate in aqueous lactic acid, crystallised from glacial acetic acid as solvated brownish-red needles, m. p. 227—228° (decomp.) when slowly heated from 120° but melting immediately with effervescence when inserted into a bath at 210° (Found : loss at 150°/vac., 10·2. Found, on dried material : C, 51·4; H, 3·35; N, 21·0. $C_{20}H_{15}O_7N_7,C_2H_4O_2$ requires $C_2H_4O_2$, 11·4. $C_{20}H_{15}O_7N_7$ requires C, 51·6; H, 3·25; N, 21·05%).

6 : 12-Dichlorophenhomazine failed to give any recognisable basic product when treated with ethanolic ammonia for 3 weeks at room temperature or with sodamide for 22 hr. in refluxing benzene : 42% and 80% respectively of starting material was recovered. No recognisable products were isolated when 6 : 12-dichlorophenhomazine was heated at 120—130° with ammonium carbonate in phenol or at 210° with urea.

Interaction of N-Phenylbenzamidine, Sodium, and Ethyl Benzoate.—To a suspension of sodio-*N*-phenylbenzamidine made by refluxing *N*-phenylbenzamidine (9·8 g., 0·05 mole) and sodium (1·15 g., 0·05 g.-atom) in dry benzene (150 ml.) for 24 hr. was added ethyl benzoate (7·5 g., 0·05 mole); the mixture was refluxed for a further 8 hr., during which nearly all the solid dissolved. The resulting mixture afforded benzoic acid (0·9 g.), dibenzoylamine (0·4 g.), and *N*-phenylbenzamidine (2·7 g.) by extraction first with water and then with acid; benzanilide (0·15 g.) and *N*-benzoyl-*N'*-phenylbenzamidine (3·4 g.) were isolated from the benzene-soluble products by fractional crystallisation from ethanol.

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