609. *The Phenylation of Some Diazines.*

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Phenylations have been carried out with benzoyl peroxide, benzenediazonium salts, and *N*-nitrosoacetanilide. There is no evidence that phenylation of pyridazine has occurred at positions adjacent to the ring-nitrogen atoms. Quinoxaline yields 2-, 5-, and 6-phenylquinoxaline in the approximate ratio of 40 : 10 : 1. Phthalazine has given only 5-phenylphthalazine, but phenylation of cinnoline is more complex: 4 : 4′-dicinnolyl is the main product, 4-phenylcinnoline and an isomer have been isolated in much lower yield, and smaller amounts of four other products have been obtained.

Phenylation of nitrogen-heterocyclic compounds, by reactions involving free radicals, has received relatively little attention compared with the carbocyclic field. The results of the phenylation of pyridine, quinoline and benzothiazole have been summarised,[1] and further examination by Pausacker [2] of the phenylation of quinoline has shown the formation of 2 : 2′-diquinolyl as well as each of the monophenylquinolines; Hey and Walker [3] had already identified 4- and 5-phenylquinoline and indicated the presence of other products.

For the present work, pyridazine was prepared in excellent yield by a modification of a known method,[4] and quinoxaline was also readily available; [5] these compounds were used to select the most reliable and convenient phenylating agent for use with the less accessible heterocycles, cinnoline and phthalazine. The former has been prepared from methyl anthranilate in about 48% overall yield [6] and, in 22% overall yield, from *o*-aminoacetophenone *via* 4-hydroxycinnoline and 4-cinnolylhydrazine or its toluene-*p*-sulphonyl derivative.[7] However, reduction of 4-hydroxycinnoline with lithium aluminium hydride (*J.*, 1959, 2858) gave cinnoline in a yield of 52% (based on *o*-aminoacetophenone). Phthalazine was prepared by reduction of 1-chlorophthalazine with phosphorus and hydriodic acid (55% yield obtained; cf. 75% claimed [8]); lithium aluminium hydride reduction of tetra-*N*-methylphthalamide [9] was convenient only on the small scale. 1 : 4-Dichlorophthalazine,

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[1] Dermer and Edmison, *Chem. Rev.*, 1957, **57**, 77.
[2] Pausacker, *Austral. J. Chem.*, 1958, 200.
[3] Hey and Walker, *J.*, 1948, 2213.
[4] Mizzoni and Spoerri, *J. Amer. Chem. Soc.*, 1951, **73**, 1873.
[5] Landquist, *J.*, 1953, 2817.
[6] Jacobs, Winstein, Henderson, and Spaeth, *J. Amer. Chem. Soc.*, 1946, **68**, 1310.
[7] Schofield and Swain, *J.*, 1950, 392; Alford and Schofield, *J.*, 1953, 609.
[8] Paul, *Ber.*, 1899, **32**, 2014.
[9] Weygand and Tietjen, *Ber.*, 1951, **84**, 625.

readily available[10] from the 1 : 4-dihydroxy-compound, gave with phosphorus and hydriodic acid about 35% of phthalazine, but variable amounts of 1-hydroxyphthalazine were also produced; reaction with toluene-*p*-sulphonhydrazide gave no useful product.

Yield (%) * *of phenylquinoxalines and* 4-*phenylpyridazine.*

Reagent	Quinoxalines 2-Phenyl	5-Phenyl	6-Phenyl	4-Phenylpyridazine
N-Nitrosoacetanilide	15·5	2·3	0·35	26 †
PhN_2·OH	1·9	0·45	0·05	2·3
Benzoyl peroxide	17·4	5·4	0·35	14
PhN_2Cl	0	0	0	7·2
PhN_2·OAc	0·4	0	0 ‡	

* Yields are based on the phenylating agent and on reaction (*a*) or (*b*), as appropriate:

$$(a)\ \mathrm{Ph{\cdot}N_2X + RH \longrightarrow PhR + N_2 + HX}$$
$$(b)\ \mathrm{(Ph{\cdot}CO{\cdot}O)_2 + RH \longrightarrow PhR + CO_2 + Ph{\cdot}CO_2H}$$

† A diphenylpyridazine (0·6%), m. p. 160—161°, was also isolated.

‡ 80% of the reagent was accounted for as *p*-hydroxyazobenzene or phenol.

The annexed Table shows our phenylation results. If allowance is made for losses inherent in the separation of isomers by chromatography and fractional crystallisation, the isomer ratios are quite consistent. The trends are, in general, those which would be expected from consideration of the behaviour of pyridine and naphthalene towards free-radicals. Thus, in pyridine, the rate factors for phenylation at positions *o*-, *m*-, and *p*- to the ring-nitrogen atom are F_o (1·81), F_m (0·87), F_p (0·87),[11] while in naphthalene the additional fused ring results in greater activation than is conferred by any other substituent and phenylation gives α- and β-isomers in the ratio 5 : 1.[12] Benzoylation of some 1-substituted naphthalenes has revealed enhanced reactivity *para* to the substituent and the effects of the substituent and the fused ring are to some extent additive.[13] The isolation of 2-, 5-, and 6-phenylquinoxaline in an approximate ratio of 40 : 10 : 1, respectively, reflects the powerful activation of the ring-nitrogen atoms on the *ortho*-position, and the greater activity of the α- over the β-position in the *Bz*-ring. In the case of pyridazine, if the effect of two ring-nitrogen atoms may be calculated, from the pyridine data, by the method normally applied to two substituents in benzene,[14] then phenylation at $C_{(3)}$ in pyridazine should be more than twice that at $C_{(4)}$. In fact, no 3-phenylpyridazine was detected. The diphenylpyridazine, m. p. 160—161°, is probably the 4 : 5-compound since the 3 : 4-, 3 : 5-, and 3 : 6-isomers have been described[15] and the low concentration of 4-phenylpyridazine in the reaction precludes further phenylation to a diphenylyl derivative.

Only one pure compound (6% yield) was isolated from reaction between phthalazine and *N*-nitrosoacetanilide; this differed from 6-phenylphthalazine (*J.*, 1959, 2858), and from the 1-phenyl-isomer;[16] the compound, m. p. 174—175°, described as 1-phenylphthalazine[17] is probably dibenzaldazine;[18] our product is therefore represented as 5-phenylphthalazine. Since the majority of the products could not be separated, no conclusions can be drawn about the course of phenylation.

Phenylation of cinnoline with *N*-nitrosoacetanilide yielded a complex mixture: equal amounts of 4-phenylcinnoline and 5(or 8)-phenylcinnoline, were isolated. Fractionation of a mixture of picrates yielded another four products but in yields about one-tenth those

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[10] Drew and Hatt, *J.*, 1937, 16.

[11] Hey *et al.*, *J.*, 1955, 3963; 1952, 2094.

[12] Huisgen and Sorge, *Annalen*, 1950, **566**, 162.

[13] Dannley and Gippin, *J. Amer. Chem. Soc.*, 1952, **74**, 332.

[14] Augood, Hey, and Williams, *J.*, 1953, 44.

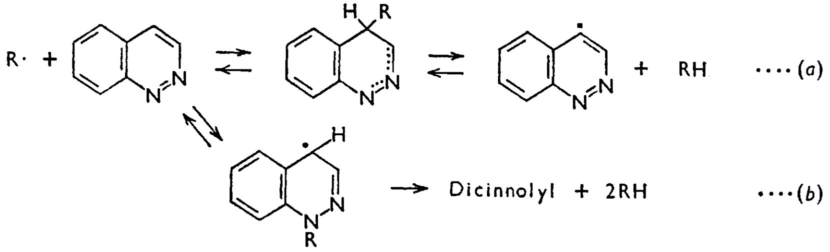
[15] Almström, *Annalen*, 1913, **400**, 131; Paal and Schulze, *Ber.*, 1900, **33**, 3798, 3789.

[16] Liek, *Ber.*, 1905, **38**, 3922.

[17] Aggarwal, Darbari, and Ray, *J.*, 1929, 1941.

[18] Kochetkov and Varotnikova, *J. Gen. Chem.* (*U.S.S.R.*), 1956, **26**, 1927 (U.S. translation); Ikeda and Kanahara, *Ann. Rep. Fac. Pharm., Kanazawa Univ.*, 1955, **5**, 5.

of the monophenylcinnolines, which were insufficient to permit identification. The possibility of recycling the unchanged cinnoline to obtain more of these products could not be realised since each run yielded ten times as much 4 : 4′-dicinnolyl as all the other products combined. Thus it appears that substitution is more difficult to achieve than hydrogen-abstraction from $C_{(4)}$. Two mechanisms (*a*) and (*b*), for this process are possible.



The mechanism involving the σ-complex (*a*) has been discussed by Augood and Williams [19] and is supported by the isolation of methane on reaction of toluene with atomic hydrogen.[20] The alternative (*b*), involving a quinonoid intermediate, is similar to that postulated for the formation of diaryls in the reaction between chlorobenzene and methyl [21] or phenyl [14] radicals. The ready formation of dicinnolyl is reminiscent of its formation, as the major product, on catalytic hydrogenation of 4-chlorocinnoline, and, as the minor product on decarboxylation of cinnoline-4-carboxylic acid: [22] although the latter formation has been regarded as arising from a protonised cinnolyl anion the obvious activity of a cinnolyl free-radical supports the possibility of decarboxylation by a free-radical mechanism. Comment on the phenylated derivatives must await identification of the four minor components, but at least one of these must be an anomalous product.

EXPERIMENTAL

Light petroleum had b. p. 40—60° unless otherwise stated. Solvents used for chromatography were dried (over sodium where possible) and redistilled.

Pyridazine.—3 : 6-Dichloropyridazine (29·6 g.), alcohol (70 ml.), aqueous ammonia (*d* 0·880; 32 ml.), and 5% palladised charcoal (2 g.) were shaken with hydrogen at 3—5 atm. for 65 min., then combined with two other batches (from 29·6 and 30·1 g. of dichloropyridazine) and filtered, and the catalyst was washed with benzene (200 ml.). The filtrate and washings were evaporated, and the residual benzene solution was made up to 600 ml. with benzene, and dried azeotropically (Dean and Stark apparatus). The solution was cooled, shaken with solid potassium hydroxide, and filtered from inorganic material. The filtrate was first evaporated to 100 ml. under slightly reduced pressure, the last traces of solvent being removed at 1 mm. (it is important that air should not be admitted to the apparatus at this stage as the crude pyridazine is liable to inflame); pyridazine distilled as a very pale yellow liquid (42·6 g., 89%), b. p. 50—51°/1 mm.

Phthalazine.—(*a*) 1-Chlorophthalazine (18 g.) and toluene-*p*-sulphonhydrazide (42 g.) were heated under reflux in dry chloroform (420 ml.) for 2 hr. The product (30·2 g.), m. p. 217° (decomp.), was collected when cold, washed with a little chloroform and then with light petroleum, and dried in air. Trituration with acetone and recrystallisation from glacial acetic acid gave 1-N′-(*toluene*-p-*sulphonyl*)*hydrazinophthalazine hydrochloride*, m. p. 220° (decomp.) (Found: C, 51·7; H, 5·0; N, 15·3; Cl, 11·4. $C_{15}H_{15}O_2N_4SCl$ requires C, 51·4; H, 4·3; N, 15·9; Cl, 10·1%). The crude salt (30·2 g.) was added portionwise during 1 hr. to N-sodium hydroxide (435 ml.) at 90—95° with stirring and heated on the water-bath for a further 1 hr. Continuous extraction with benzene provided phthalazine (7·8 g., 55%) as a pale yellow solid, m. p. 89—91° (lit., 91°).

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[19] Augood and Williams, *Chem. Reviews*, 1957, **57**, 123.
[20] Szwarc, *Nature*, 1948, **161**, 890.
[21] Beckwith and Waters, *J.*, 1957, 1665.
[22] Morley, *J.*, 1951, 1971.

(*b*) 1 : 4-Dichlorophthalazine (10 g.), red phosphorus (5 g.), and hydriodic acid (*d* 1·7; 165 ml.) were heated under reflux for 80 min. The solution was diluted with water (150 ml.), cooled, filtered, made alkaline with concentrated potassium hydroxide solution, and extracted continuously with benzene. On concentration of the extract to 50 ml., 1-hydroxyphthalazine (1·0 g.), m. p. 183—184°, separated, and complete removal of solvent from the mother-liquors yielded phthalazine (1·95 g., 35%), m. p. 90—91°, b. p. 134°/1·5 mm.

The potassium hydroxide solution was evaporated to dryness on the water-bath, and the residue boiled with chloroform (750 ml.) and filtered. The residue after evaporation of the filtrate was dissolved in 3N-sodium hydroxide from which 1-hydroxyphthalazine (3 g.), m. p. 183—184°, was precipitated on acidification.

Phenylation of Quinoxaline.—The phenylquinoxalines and their picrates were identified by mixed-melting-point determinations with authentic samples.

(a) *With* N-*nitrosoacetanilide*. *N*-Nitrosoacetanilide (8·2 g., 0·05 mole) was added portionwise during 1 hr. to stirred molten quinoxaline (75 g., 0·5 mole) at 38—40° and the mixture was stirred at 40° until gas evolution ceased (3 hr.). Ether (*ca.* 250 ml.) was added and the solution was extracted with 3N-sodium hydroxide (150 ml. in all). The washed and dried ($MgSO_4$) ether layer was evaporated, finally under reduced pressure, and the excess of quinoxaline was recovered by distillation at 70—75°/2—3 mm. A further small quantity of quinoxaline was recovered as its picrate (m. p. 160—161°) from methanol washings of the apparatus (total recovery, 63·1 g.).

Eluant * (ml.)	Recryst. from *	Product Quinoxaline	Wt. (g.)	M. p.
	TABLE A			
Pet (400)	Pet	2-Ph	0·8	78°
1 : 1-C_6H_6–Pet (400)	Pet, aq. MeOH	2-Ph	0·41	78
C_6H_6 (160)	Pet	2-Ph †	<0·01	98—101
1 : 3-$CHCl_3$–C_6H_6 (280)	—	†	—	—
MeOH–Et_2O	—	Tar	—	—
	TABLE B			
Pet (200)	—	2-Ph	0·36	78
	—	Picrate	0·06	122
1 : 2-C_6H_6–Pet (200)	—	5-Ph	0·1	124
2 : 1- ,, (200)	—	Picrate	0·08	148
C_6H_6 (200)	—	6-Ph picrate	0·07	170

* Pet = light petroleum (b. p. 40—60°). † Impure.

The residue in the distillation flask was digested with warm 5N-hydrochloric acid (150 ml.) and filtered from a black solid (3·2 g.), m. p. 230°. The acid extract was made alkaline with concentrated aqueous potassium hydroxide and extracted with ether. Some black intractable tar, which was sparingly soluble in ether, was rejected. The basic fraction (7·6 g.), a brown oil obtained by evaporation of the dried ($MgSO_4$) ether-extract, was transferred in benzene (40 ml.)-light petroleum (10 ml.) to a column of alumina (100 g., type H). Table A shows the fractionation thus achieved. The crystallisation mother-liquors from these fractions were combined, evaporated, and chromatographed again on alumina (35 g.) with the results shown in Table B.

(b) *With benzenediazohydroxide*. Aniline (9·3 g.) in concentrated hydrochloric acid (35 ml.) and water (10 ml.) was diazotised at 0—5° with sodium nitrite (7·1 g.) in water (30 ml.). Quinoxaline (78 g.) was added and the mixture was stirred at 0—5° during the addition, in 1½ hr., of sodium hydroxide (16 g.) in water (60 ml.), and then for a further 1 hr. After being stirred overnight at room temperature, the solution was made strongly alkaline with 6N-sodium hydroxide and extracted with ether. The dried ($MgSO_4$) extract yielded, by distillation, quinoxaline (68·4 g.), b. p. 70—75°/2—3 mm. The high-boiling residues from three such experiments were taken up in ether and extracted with 5N-hydrochloric acid, and the extract was washed with ether, made alkaline with 6N-sodium hydroxide, and extracted with ether. The basic fraction so obtained, a dark brown oil (8·2 g.), was separated as in (a).

(c) *With benzenediazonium chloride*. Aniline (2 g.) in concentrated hydrochloric acid (3·8 ml.) and water (1 ml.) was diazotised in the usual way and added during 1 hr. to quinoxaline (28 g.) stirred at 40°. Stirring was continued for ½ hr. (no further gas evolution) and the mixture was treated as in (b). Apart from quinoxaline (92%) and phenol, no recognisable product was obtained.

(d) *With benzenediazonium acetate.* Aniline (4·65 g.) in concentrated hydrochloric acid (17·5 ml.) and water (5 ml.) was diazotised as usual, and powdered quinoxaline (36 g.) was added. The mixture was stirred at 0° ± 2° during the addition, in 1 hr., of aqueous sodium acetate (8 g. in 20 ml.), and for another 2 hr.; stirring was continued at room temperature for for 24 hr. (no further gas evolution). Isolation as in (b) yielded 4-hydroxyazobenzene (2·9 g.), phenol (0·9 g.), 2-phenylquinoxaline picrate (0·09 g.), and quinoxaline (95%).

(e) *With dibenzoyl peroxide.* A mixture of quinoxaline (78·2 g.) and dry dibenzoyl peroxide (12·1 g.) was stirred at 80—85° for 72 hr. Separation by the method employed in (b) gave an acidic fraction which consisted of benzoic acid (6·93 g.) and a brown oil (1·15 g.) which resisted attempts at purification. The basic fraction yielded quinoxaline (61·9 g.), three monophenylquinoxalines, a small quantity of a mixture, m. p. 180—280°, and residual tar.

Phenylation of Pyridazine.—4-Phenylpyridazine (m. p. 86°) and its picrate (m. p. 166°) were identified by mixed m. p. determinations.

(a) *With* N-*nitrosoacetanilide.* Pyridazine (40 g.) was stirred at 40—45° during the portionwise addition, in 1¼ hr., of *N*-nitrosoacetanilide (8·2 g.). The cold-water bath was removed and the temperature was kept at 40° for a further ½ hr. Distillation at 48—50°/0·8 mm. gave pyridazine contaminated with some acetic acid (39 g., *i.e.*, a minimum recovery of 36 g. of pyridazine).

The residue in the distillation flask was digested with hot 5N-hydrochloric acid, filtered, cooled, and made alkaline with solid potassium hydroxide. Extraction with benzene yielded a brown sticky solid (4·1 g.), unchanged by chromatography on an alumina column. This fraction was distilled through a 5″ column and yielded a yellow solid (2·72 g.), m. p. 74—84°, b. p. 100—120°/0·1—0·5 mm., from which 4-phenylpyridazine (1·82 g.) was obtained by recrystallisation from ligroin. The mother-liquors gave a residue which was converted into 4-phenylpyridazine picrate (0·24 g.). The remaining distillate (0·71 g.), b. p. 120°/0·1 mm., was a yellow oil from which, by recrystallisation from ligroin, then digestion with hot water, there was obtained a colourless product, presumably, 4 : 5-diphenylpyridazine (65 mg.), m. p. 160—161°. This gave a picrate which crystallised as yellow needles, m. p. 193°, from methanol or aqueous ethanol (Found: C, 57·4; H, 3·2; N, 15·2. $C_{22}H_{15}O_7N_5$ requires C, 57·25; H, 3·3; N, 15·2%). The ligroin and aqueous mother-liquors, on evaporation, gave a further 0·25 g. of 4-phenylpyridazine picrate.

(b) *With benzenediazohydroxide.* A diazotised solution of aniline (9·3 g.) was cooled to −10°, pyridazine (42·4 g.) was added, and the mixture stirred at −10° to −5° during addition, in 1½ hr., of a concentrated solution of sodium hydroxide. After a further 2 hr., the cooling-bath was removed and stirring was continued overnight. The mixture was acidified with concentrated hydrochloric acid, and after ½ hour's stirring the black tar (2·9 g.) which remained undissolved was removed. No pure compound could be obtained from the tar by chromatography on alumina.

The acid solution was washed with ether from which phenol (0·4 g.) was obtained, and the cooled aqueous layer was made alkaline with solid potassium hydroxide. Tar (2·5 g.) was removed, and the solution was concentrated *in vacuo* over sodium hydroxide, the last traces of water being removed by azeotropic distillation with benzene. Inorganic material was filtered from the benzene solution (250 ml.) and was washed with benzene, and the filtrate was distilled, finally under reduced pressure. The fraction of b. p. 74—78°/4 mm. was redistilled to yield pyridazine (27·4 g.), b. p. 78°/5 mm. The residue in the distillation flask yielded on digestion with ether an oily, brown solid (4·4 g.), which was chromatographed in benzene (15 ml.) and light petroleum (b. p. 40—60°; 5 ml.) on alumina (60 g., type H) with elution with benzene (400 ml.). Evaporation of the eluate and successive recrystallisation of the residue from light petroleum (b. p. 80—100°) and water yielded 4-phenylpyridazine (0·36 g.), m. p. 86·5°. The residues from the mother-liquors, on treatment with methanolic picric acid, gave only 4-phenylpyridazine picrate.

(c) *With benzenediazonium chloride.* Aniline (2 g.) was diazotised as usual and the solution was added dropwise, during 1 hr. with stirring, to pyridazine (20 g.), at 40°. After a further 45 min., the solution was cooled, made alkaline with 6N-potassium hydroxide, mixed with benzene, and dried azeotropically; after removal of inorganic material, the benzene solution was evaporated, finally under reduced pressure. Pyridazine was distilled from the residue and redistilled (16·1 g.; b. p. 78°/5 mm.); pyridazine picrate (2·8 g.; m. p. 172°) was obtained from mother-liquors and washings. A solution of the high-boiling residue in benzene

(250 ml.) was extracted with 5N-hydrochloric acid (4 × 55 ml.), washed with water, and, on evaporation, yielded only phenol (0·3 g.). The basic fraction (1·2 g.), a brown, sticky solid obtained by the procedure used in (a), yielded on distillation through a 5″ column a white solid (0·76 g.), m. p. 58—72°, b. p. 130—160°/1—2 mm. Three recrystallisations from light petroleum (b. p. 80—100°) gave 4-phenylpyridazine (0·24 g.), m. p. 80—83°, and the mother-liquors, yielded a mixture of picrates (140 mg.), m. p. 120—155°, which could not be separated.

(d) *With dibenzoyl peroxide.* Dry dibenzoyl peroxide (11·1 g.) was dissolved in pyridazine (35·9 g.) and warmed gently. At 30° a vigorous reaction set in, and the temperature rose rapidly to 180° despite water-cooling. The dark solution was stirred at 40° for 1 hr., then worked up as (a). Pyridazine (28 g.) was recovered and the less volatile distillate (1·08 g.), b. p. 100—130°/0·5 mm., gave 4-phenylpyridazine (1·01 g.), m. p. 86°, by recrystallisation from ligroin.

Phenylation of Phthalazine.—Phthalazine (26 g.; m. p. 91°) was stirred at 95—100° and this temperature was maintained initially by portionwise addition of *N*-nitrosoacetanilide (3·3 g.) in 30 min., and later, for 2 hr., by external heating. Distillation yielded phthalazine (20·2 g.), m. p. 89—91°, b. p. 112°/0·5 mm., and acetic acid (collected in a trap at about −40°), but no detectable quantity of benzene. Cold-water washing of the high-boiling residue provided phthalazine (2·3 g.). The water-insoluble residue was warmed with benzene (300 ml.), filtered from insoluble tar, and extracted with 6N-hydrochloric acid (5 × 30 ml.). The benzene solution yielded a brown oil (0·45 g.), from which no pure compound could be obtained. The aqueous solution was made alkaline with 6N-potassium hydroxide and extracted with chloroform, to provide a basic fraction (2·7 g.) which was transferred in benzene (10 ml.) to a column of alumina (27 g.; type H). Fractions obtained by elution with light petroleum and benzene–light petroleum were yellow or brown oils or sticky solids; these crystallised with difficulty from ligroin, giving the same yellow solid, m. p. 100—106°. Sublimation of the crude solid at 130°/0·5 mm. gave 5-*phenylphthalazine* (0·33 g.), m. p. 104—106°, which crystallised in colourless plates, m. p. 106°, from ligroin (Found: C, 81·6; H, 5·15; N, 13·45. $C_{14}H_{10}N_2$ requires C, 81·5; H, 4·9; N, 13·6%). Further elution of the column with benzene and with 1 : 1 chloroform–benzene gave dark oils which yielded no identifiable products.

Phenylation of Cinnoline.—Cinnoline (45 g.) was stirred at 55—60° during portionwise addition of *N*-nitrosoacetanilide (5·7 g.) during 50 min. Stirring was continued at 60° for 2 hr. and the mixture was distilled, a fraction of b. p. 124—126°/1 mm. being collected. This distillate was dissolved in benzene, treated with anhydrous sodium carbonate, filtered, and evaporated. The resultant green solid (42 g.), m. p. 30°, was distilled to yield yellow material (38·8 g.), m. p. 35°, b. p. 124°/1 mm.; residues and washings yielded cinnoline picrate (4·6 g.), m. p. 196°.

The fraction of b. p. 124°/1 mm. was digested with water (850 ml.) on the steam-bath for ¾ hr., and the insoluble portion (6·75 g.), m. p. 144—186°, was collected from the cooled mixture, washed with water, and dried *in vacuo*. This product (5·1 g.) was recrystallised from alcohol, and, after filtration from a less-soluble orange residue (0·7 g.), m. p. 210—225°, gave yellow needles (4·0 g.), m. p. 232—237°. Further recrystallisation from methanol and benzene gave yellow needles of 4 : 4′-dicinnolyl, m. p. and mixed m. p. 238° (Found: C, 74·7; H, 4·0; N, 21·5. Calc. for $C_{16}H_{10}N_4$: C, 74·5; H, 3·9; N, 21·7%).

The residue from the original distillation was extracted with 5N-hydrochloric acid (3 × 40 ml.), and the extract was filtered and washed with ether (the ether washings contained only a small quantity of tar). The aqueous layer was made alkaline with 6N-sodium hydroxide and extracted with benzene to yield the basic fraction (4·0 g.), a brown oil, which was transferred in benzene (10 ml.) and light petroleum (5 ml.) to alumina (40 g.; type H). Elution with light petroleum gave oils, which were converted into picrates and yielded, after several recrystallisations from water and dilute methanol, 4-phenylcinnoline picrate (0·43 g.), m. p. and mixed m. p. 158°, and another picrate (130 mg.), m. p. 138—140°. The remaining picrates could not be separated and were decomposed by hot 3N-sodium hydroxide from which chloroform-extraction yielded a green oil.

Elution with benzene–light petroleum gave oils which, after several recrystallisations from light petroleum (b. p. 60—80° and b. p. 80—100°) and from ligroin, gave pale yellow plates of a *phenylcinnoline* (0·45 g.), m. p. 131° (Found: C, 80·5; H, 5·2; N, 14·7. $C_{14}H_{10}N_2$ requires C, 81·5; H, 4·9; N, 13·6%). The picrate of this compound crystallised from benzene in deep yellow plates, m. p. 208°.

Elution with benzene and with 1 : 1 benzene–chloroform gave oils; these were chromatographed again on alumina. Residues from mother-liquors and from decomposed picrates were rechromatographed separately. Some of the residual oils gave picrates, fractional crystallisation of which gave yellow solids (50 mg.), having m. p.s 158°, 172°, and 154° severally. These were distinguished from one another and from 4-phenylcinnoline picrate by mixed-m. p. determinations.

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