433. *Some Heterocyclic Analogues of Stilbenes.*

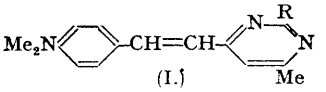
By Daniel M. Brown and George A. R. Kon.

Derivatives of 4-aminostilbene are known to be carcinogenic and also to exercise an inhibitory effect on the development of transplanted tumours in the rat. A number of analogous compounds, in which one benzene ring of the stilbene is replaced by a heterocyclic ring, are now described.

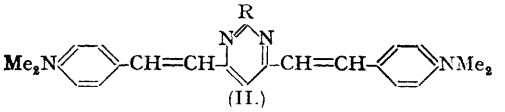
It has recently been found that a number of basically substituted stilbenes of the general type $NR_2 \cdot C_6H_4 \cdot CH{:}CH \cdot Ar$ are carcinogenic and possess the property common to many carcinogens of inhibiting the development of transplanted tumours in rats. A full account of this work has recently been published (*Phil. Trans.*, 1948, *A*, **241**, 147). It appeared of interest to prepare for tests certain analogues of the biologically active stilbene, containing heterocyclic in place of the homocyclic nuclei.

As a preparative method, advantage was taken of the well-known reactivity of the methyl groups in certain positions of a variety of heterocyclic compounds (pyridine, quinoline, pyrimidine, etc.), whereby styryl derivatives are produced by condensation with aromatic aldehydes (cf., *e.g.*, Gabriel and Colman, *Ber.*, 1903, **36**, 3383; Stark, *ibid.*, 1909, **42**, 702; Stark and Bögemann, *ibid.*, 1910, **43**, 1128).

Pyrimidine Derivatives.—4-Dimethylaminobenzaldehyde condenses smoothly with 4-methylpyrimidine in presence of zinc chloride, to give 4-(4-*dimethylaminostyryl*)*pyrimidine*. Stark and Bögemann (*loc. cit.*) have shown that 4-dimethylaminobenzaldehyde condenses with 2-hydroxy-4 : 6-dimethylpyrimidine in presence of catalytic amounts of piperidine in boiling ethanol to give 2-hydroxy-4-(4-dimethylaminostyryl)-6-methylpyrimidine (I; R = OH). We find that the reaction product also contains some 2-*hydroxy*-4 : 6-*bis*-(4-*dimethylaminostyryl*)*pyrimidine* (II; R = OH). Analysis figures for this compound are only approximate and are more in accord with those calculated for the hemihydrate. This condensation takes place more rapidly in aqueous ethanol in presence of either catalytic or molecular quantities of hydrochloric acid and again gives a mixture of the mono- and bis-compounds (I and II; R = OH). Owing to the insoluble nature of the hydroxy-compounds purification on a large scale is difficult, so that the crude preparation of I (R = OH) is used for the preparation of 2-*chloro*-4-(4-*dimethylaminostyryl*)-6-*methylpyrimidine* (I; R = Cl) together with some 2-*chloro*-4 : 6-*bis*-(4-*dimethylaminostyryl*)*pyrimidine* (II; R = Cl). The latter is also obtained from the pure bis-compound which is prepared from 2-hydroxy-4 : 6-dimethylpyrimidine and 2 molecules of 4-dimethylaminobenzaldehyde in presence of either piperidine or hydrochloric acid. The chloro-compounds are readily separated by chromatography on alumina; this also constitutes an excellent method of purification.



(I.)



(II.)

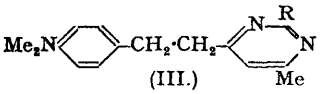
Heating 2-chloro-4-(4-dimethylaminostyryl)-6-methylpyrimidine (I; R = Cl) with a variety of amines affords 2-basically-substituted *pyrimidines* [I; R = piperidino-, morpholino-, *cyclo*hexylamino-, diethylamino-, 2-diethylaminoethylamino-, or bis-(2-hydroxyethyl)amino-] in high yield. No product can be isolated from the reaction with methanolic ammonia at 175°, and when this is carried out at 110° the starting material is recovered unchanged. However, 2-*acetamido*-4-(4-*dimethylaminostyryl*)-6-*methylpyrimidine* (I; R = NHAc) is obtained in small yield from 4-dimethylaminobenzaldehyde and 2-amino-4 : 6-dimethylpyrimidine in boiling acetic anhydride.

2-Chloro-4 : 6-bis-(4-dimethylaminostyryl)pyrimidine (II; R = Cl) reacts readily with piperidine to give 2-*piperidino*-4 : 6-*bis*-(4-*dimethylaminostyryl*)*pyrimidine* (II; R = piperidino-).

2-*Ethoxy*-4-(4-*dimethylaminostyryl*)-6-*methylpyrimidine* (I; R = OEt) is obtained from (I; R = Cl) with sodium ethoxide.

Attempts to dehalogenate (I; R = Cl) have not been successful. No reaction is observed on boiling a suspension of the chloro-compound with zinc dust in water (cf., *inter alia.*, Gabriel and Colman, *loc. cit.*) or in solution in aqueous dioxan. Hydrogenation at room temperature and pressure over 2% palladised strontium carbonate is rapid and gives only 2-*chloro*-4-[2-(4-*dimethylaminophenyl*)*ethyl*]-6-*methylpyrimidine* (III; R = Cl). This reacts with piperidine to give 2-*piperidino*-4-[2-(4-*dimethylaminophenyl*)*ethyl*]-6-*methylpyrimidine* (III; R = piperidino-)

identical with that prepared by hydrogenation over palladised strontium carbonate of 2-piperidino-4-(4-dimethylaminostyryl)-6-methylpyrimidine (I; R = piperidino-).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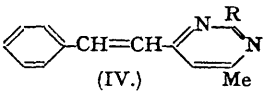
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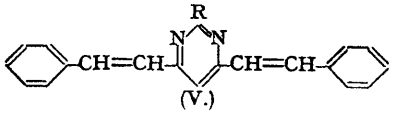

(V.)

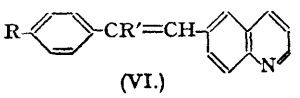
2-Hydroxy-4-styryl-6-methylpyrimidine (Stark and Bögemann, *loc. cit.*) gives 2-chloro-4-styryl-6-methylpyrimidine (IV; R = Cl) with phosphorus oxychloride. Treatment with piperidine affords *2-piperidino-4-styryl-6-methylpyrimidine* (IV; R = piperidino-). In the same way, from 2-hydroxy-4 : 6-distyrylpyrimidine (Stark and Bögemann, *loc. cit.*), *2-chloro-4 : 6-distyrylpyrimidine* (V; R = Cl) and *2-piperidino-4 : 6-distyrylpyrimidine* (V; R = piperidino-) are prepared.

2-Piperidino-4 : 6-dimethylpyrimidine and 2 : 6-dipiperidino-4-methylpyrimidine, prepared from the corresponding chloro-compounds, fail to react with 4-dimethylaminobenzaldehyde under a variety of conditions. However, further work in progress in these laboratories should shed light on the effect of substituents on the condensations of aldehyde with methylpyrimidines.

The results of the biological tests will be reported in detail elsewhere; the compounds (I; R = piperidino- or morpholino-) possess considerable growth-inhibitory action.

Styrylquinolines.—Condensation of 4-nitrophenylacetic acid with quinoline-6- and -8-aldehydes (Rodionov and Berkenheim, *J. Gen. Chem. Russia*, 1944, **14**, 330), by the method of Pfeiffer (*Ber.*, 1915, **48**, 179) leads to the formation of 6- and 8-(*4-nitrostyryl*)*quinoline* (VI; R = NO_2, R′ = H) and (VII; R = NO_2). Stannous chloride reduction (Pfeiffer and Seriewskaja, *Ber.*, 1911, **44**, 1110) gives the corresponding 6- and 8-(*4-aminostyryl*)*quinoline* (VI; R = NH_2, R′ = H), and (VII; R = NH_2).

Cook, Heilbron, and Steiger (*J.*, 1943, 413) failed to obtain *6-styrylquinoline* (VI; R = R′ = H) by the Meerwein reaction (Meerwein, Büchner, and van Emster, *J. pr. Chem.*, 1939, **152**, 237). In our hands the Grignard reaction between benzylmagnesium chloride and quinoline-6-aldehyde gives a very small yield of *2-phenyl-1-(6-quinolyl)ethanol* (VIII), together with unidentified resinous material. The condensation of quinoline-6-aldehyde with sodium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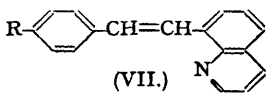
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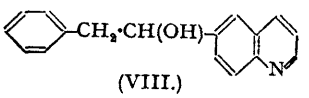
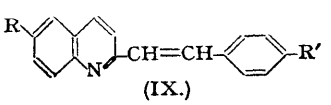

(VIII.)

phenylacetate and acetic anhydride gives *α-phenyl-β-(6-quinolyl)acrylic acid* (VI; R = H, R′ = CO_2H) quantitatively, but we have not succeeded in decarboxylating it. A Skraup synthesis using 4-aminostilbene gives no recognisable product. The styrylquinoline is obtained in poor yield, by deamination of 6-(4-aminostyryl)quinoline, by reduction of the diazonium salt with hypophosphorous acid (" Organic Reactions," Vol. II, 262).

The carcinogenicity of " styryl 430 " (Browning, Gulbransen, and Niven, *J. Path. Bact.*, 1936, **42**, 155), together with the tumour-inhibiting action of the closely related 6-acetamido-2-(4-aminostyryl)quinoline methoacetate (Badger, Elson, Haddow, Hewett, and Robinson, *Proc. Roy. Soc.*, 1942, *B*, **130**, 255), led us to synthesise some substituted 6-amino-2-styrylquinolines. 6-Nitro-2-styrylquinoline (Schmidt, *Ber.*, 1905, **38**, 3718) is reduced to *6-amino-2-styrylquinoline* (IX; R = NH_2, R′ = H) by stannous chloride in glacial acetic acid saturated with dry hydrogen chloride, and is characterised as the *acetyl* derivative (IX; R = NHAc, R′ = H). If tin and hydrochloric acid are used, 2-(2-phenylethyl)quinoline is obtained (Schmidt, *loc. cit.*).

Condensations of 6-nitroquinaldine (Hamer, *J.*, 1921, **119**, 1435) with 4-dimethylaminobenzaldehyde and 4-nitrobenzaldehyde in presence of zinc chloride give *6-nitro-2-(4-dimethylaminostyryl)quinoline* (IX; R = NO_2, R′ = NMe_2) and *6-nitro-2-(4-nitrostyryl)quinoline* (IX; R = R′ = NO_2) in almost quantitative yields. Reduction is best effected by stannous chloride in fuming hydrochloric acid, yielding *6-amino-2-(4-dimethylaminostyryl)quinoline* (IX; R = NH_2, R′ = NMe_2), characterised as the *acetyl* derivative (IX; R = NHAc, R′ = NMe_2) and 6-amino-2-(4-aminostyryl)quinoline (IX; R = R′ = NH_2), already prepared by Browning, Cohen, Cooper, and Gulbransen (*Proc. Roy. Soc.*, 1931, *B*, **109**, 51). The free amines are very sensitive to aerial oxidation.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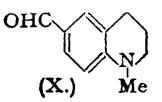
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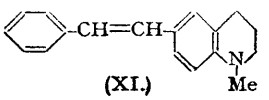
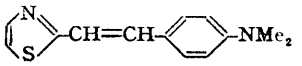

(XI.)

For the preparation of 6-*styryl*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (XI), 6-*formyl*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (X) was required. This is readily obtained by formylation of 1-methyltetrahydroquinoline (Feers and Koenigs, *Ber.*, 1885, **18**, 2389) by means of *N*-methylformanilide and phosphorus oxychloride in benzene (Vilsmeier and Haak, *Ber.*, 1927, **60**, 119). Quinoline fails to undergo a similar reaction (Cook, Heilbron, and Steiger, *loc. cit.*). The orientation of the formyl group is determined by Kishner–Wolff reduction to a dimethyltetrahydroquinoline and comparison of the picrate with that of the previously described 1 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoline (von Braun and Aust, *Ber.*, 1916, **49**, 509). The action of benzylmagnesium chloride on this aldehyde, followed by dehydration of the intermediate carbinol (not isolated), gives the required styryl compound.

Miscellaneous Styrylheterocycles.—Condensation of 2-methylthiazole with 4-dimethylaminobenzaldehyde in presence of zinc chloride gives 2-(4-*dimethylaminostyryl*)*thiazole* (XII). The yield of product in this condensation is very low and sometimes nil, and the analysis figures obtained are only approximate. Similarly, 2-methyl-β-naphthathiazole gives 2-(4-*dimethylaminostyryl*)-β-*naphthathiazole* (XIII). 2-Styrylbenzthiazole, previously prepared by Hofmann (*Ber.*, 1880, **13**, 1235) by heating cinnamic acid with *o*-aminothiophenol, and by Mills and Whitworth (*J.*, 1927, 2748) by the action of cinnamoyl chloride on the sodium salt of *o*-aminothiophenol, is made by heating 2-methylbenzthiazole with benzaldehyde in presence of concentrated hydrochloric acid (cf. Brooker and Sprague, *J. Amer. Chem. Soc.*, 1941, **63**, 3212). In the same way 2-(4-dimethylaminostyryl)-ββ′-naphthathiazole is prepared from its components; the condensation without catalyst described by Rupe and Schwarz (*Z. Farben u. Textil Chem.*, 1904, **3**, 397; *Chem. Zentr.*, 1905, I, 100) could not be repeated.



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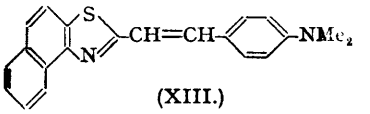
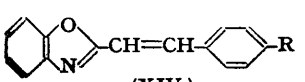


(XIII.)

2-(4-Dimethylaminostyryl)benziminazole (Rupe, Pedrini, and Collin, *Helv. Chim. Acta*, 1923, **15**, 1321) is readily prepared from *o*-phenylenediamine and 4-dimethylaminocinnamaldehyde in presence of cupric acetate by an extension of the method of Weidenhagen (*Ber.*, 1936, **69**, 2263).

There are many references to the condensation of quaternary salts of 2-methylbenzoxazole with aldehydes, in the preparation of cyanine-type dyes (*inter alia*, Brooker and White, *J. Amer. Chem. Soc.*, 1935, **57**, 2480). This, together with the fact that benzoxazole-2-carboxylic acid is readily decarboxylated (Skraup and Moser, *Ber.*, 1926, **59**, 1007), suggests that the 2-methyl group should be active and undergo condensation reactions. However, the condensation of the base itself has not been described. Skraup (*Annalen*, 1919, **419**, 85) prepared an oil, b. p. 325—335°, provisionally regarded as 2-styrylbenzoxazole (XIV; R = H), by heating *o*-aminophenol with cinnamamide. Subsequently Skraup and Moser (*loc. cit.*) attempted without success to condense 2-methylbenzoxazole with benzaldehyde in presence of piperidine at 250°. Dent (Thesis presented to the Graduate Faculty of the University of Cincinnati, 1942, 50, quoted from Bywater, Coleman, Kamm, and Merritt, *J. Amer. Chem. Soc.*, 1945, **67**, 905) obtained 2-styrylbenzoxazole (b. p. 193—194°/2 mm.; m. p. 79—80°). This publication is not available, so that the method of preparation is not known. Bywater *et al.* (*loc. cit.*) obtained the same compound (b. p. 220—221°/14 mm.; m. p. 83—84°) by heating together *o*-aminophenol and cinnamic acid; a by-product of unestablished structure isolated by these authors and characterised as the hydrochloride (m. p. 154—155°) was almost certainly 2-methylbenzoxazole. An authentic specimen of 2-*methylbenzoxazole hydrochloride* has m. p. 154°. We find that 2-methylbenzoxazole condenses readily with benzaldehyde in presence of zinc chloride to give 2-styrylbenzoxazole, m. p. 81—82° (*picrate*, m. p. 163—164°). Similarly condensation with 4-dimethylaminobenzaldehyde, under carefully controlled conditions, gives 2-(4-*dimethylaminostyryl*)*benzoxazole* (XIV; R = NMe_2).



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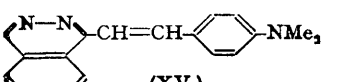
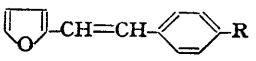


(XV.)

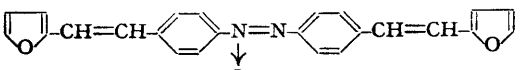
Heating 4-dimethylaminobenzaldehyde with 1-methylphthalazine in presence of zinc chloride affords 1-(4-*dimethylaminostyryl*)*phthalazine* (XV) in poor yield.

2-(4-*Nitrostyryl*)*furan* (XVI; R = NO_2) is prepared by condensation of furfuraldehyde and

4-nitrophenylacetic acid in presence of piperidine, and from diazotised *p*-nitroaniline and furylacrylic acid (Meerwein reaction). Reduction under acid conditions gives rise to resinous



(XVI.)



(XVII.)

products, while hydrogenation over Raney nickel at atmospheric pressure affords only the *azoxy*-compound (XVII). Reduction to 2-(*4-aminostyryl*)*furan* (XVI; R = NH_2) is readily accomplished by zinc dust and ammonium chloride in alcoholic solution, with evolution of heat. The amine darkens rapidly in the air, and gives an *acetyl* derivative (XVI; R = NHAc).

Experimental.

(Melting points are uncorrected.)

4-(*4-Dimethylaminostyryl*)*pyrimidine*.—4-Methylpyrimidine (1·0 g.; Gabriel and Colman, *Ber.*, 1899, **32**, 1525), 4-dimethylaminobenzaldehyde (1·5 g. = 1 mol.), and zinc chloride (fused; 0·5 g.) were heated in an oil-bath at 165° for 1·5 hours. The product was dissolved in dilute hydrochloric acid, the solution basified with ammonia, and the yellow precipitate collected and crystallised from ethanol. 4-(*4-Dimethylaminostyryl*)*pyrimidine* separated in yellow needles (1·2 g.), m. p. 179° (Found: C, 74·4; H, 6·6. $C_{14}H_{15}N_3$ requires C, 74·6; H, 6·7%). The *picrate* separated from methanol in purple, elongated prisms, m. p. 195—196° (transformation to long black needles at 175°) (Found: C, 53·0; H, 4·1. $C_{20}H_{18}O_7N_6$ requires C, 52·8; H, 4·0%).

Condensation of 2-*Hydroxy*-4 : 6-*dimethylpyrimidine and* 4-*Dimethylaminobenzaldehyde* (1 mol.).—(a) *Method of Stark and Bögemann* (loc. cit.). From the crude reaction product [m. p. 250—260° (decomp.)] was isolated, by several crystallisations from diethylene glycol (2 : 2′-dihydroxydiethyl ether), 2-*hydroxy*-4 : 6-*bis*-(*4-dimethylaminostytyl*)*pyrimidine*. It formed glistening purple leaflets, decomp. 316—318° (Found: C, 73·3, 73·0; H, 6·5, 6·4; N, 14·4. $C_{24}H_{26}ON_4$ requires C, 74·6; H, 6·8; N, 14·5. $C_{24}H_{26}ON_4,\frac{1}{2}H_2O$ requires C, 73·1; H, 6·9; N, 14·2%). Crystallisation of the more soluble fraction from 2-methoxyethanol yielded small scarlet platelets, m. p. 253° (decomp.) (Stark and Bögemann, *loc. cit.*, give m. p. 250—252° for the monostyryl compound). Attempts to separate the components of the reaction product by crystallisation of the hydrochloride or the sodium salt were unsuccessful.

(b) *Acid-catalysed condensation*. 4-Dimethylaminobenzaldehyde (1·5 g.), and 2-hydroxy-4 : 6-dimethylpyrimidine hydrochloride (1·5 g. = 1 mol.), dissolved in ethanol (20 c.c.) and water (10 c.c.), were heated at the boil for 4 hours, during which time a purple colour developed and solid material separated. After trituration with ammonia, the scarlet base was collected, washed well with water, ethanol, and ether, and dried; (1·4 g.), decomp. 313°, after softening and slow decomposition from 280°. Crystallisation from diethylene glycol yielded the characteristic purple leaflets of the bis-compound, decomp. 314—316°; the crude product, however, was a mixture of the hydroxy-mono- and -bis-compounds since treatment with phosphorus oxychloride gave both corresponding chloro-compounds (see below).

The same product was obtained when the reaction (12 hours) was catalysed by 1 drop of concentrated hydrochloric acid.

2-*Hydroxy*-4 : 6-*bis*-(*4-dimethylaminostyryl*)*pyrimidine*.—(*a*) 2-Hydroxy-4 : 6-dimethylpyrimidine (1·1 g.), 4-dimethylaminobenzaldehyde (3·0 g. = 2 mols.), and piperidine (10 drops) in ethanol (100 c.c.) were refluxed for 48 hours. After this time, small red platelets separated and were collected and crystallised from very much ethanol, forming small red platelets, decomp. 313—316°.

(*b*) 4-Dimethylaminobenzaldehyde (1·5 g.), 2-hydroxy-4 : 6-dimethylpyrimidine hydrochloride (0·75 g.), water (5 c.c.), and ethanol (20 c.c.) were heated, at the boil, overnight. Treatment with ammonia gave the free base as a red powder (1·22 g.). One crystallisation from diethylene glycol afforded glistening leaflets, decomp. 316—318° (Found: C, 73·1; H, 6·9%).

The crude product from the preparation of 2-hydroxy-4-(4-dimethylaminostyryl)-6-methylpyrimidine (I; R = OH) (2·0 g.) was refluxed with phosphorus oxychloride (10 c.c., freshly distilled) for 2 hours, or until all solid was in solution, excess of phosphorus oxychloride was removed under reduced pressure, and the residue was poured on ice. After making faintly alkaline with ammonia, the red precipitate was collected and dissolved in benzene–light petroleum, and the solution was dried (Na_2SO_4) and chromatographed on alumina. The orange band was eluted with the same solvent, and gave 2-*chloro*-4-(*4-dimethylaminostyryl*)-6-*methylpyrimidine*, which crystallised from benzene–light petroleum (b. p. 60—80°) in yellow leaflets (1·2 g.), m. p. 176—177° (Found: C, 65·9; H, 5·8. $C_{15}H_{16}N_3Cl$ requires C, 65·8; H, 5·9%). Further elution of the column with benzene–chloroform gave 2-*chloro*-4 : 6-*bis*-(*4-dimethylaminostyryl*)*pyrimidine*, also prepared from pure 2-hydroxy-4 : 6-bis-(4-dimethylaminostyryl)pyrimidine, separating from benzene in clusters of red platelets (0·1 g.), m. p. 223—224° (Found: C, 71·1; H, 6·2. $C_{24}H_{25}N_4Cl$ requires C, 71·3; H, 6·2%).

2-*Piperidino*-4 : 6-*bis*-(*4-dimethylaminostyryl*)*pyrimidine*.—2-Chloro-4 : 6-bis-(4-dimethylaminostyryl)pyrimidine (0·1 g.) was boiled with piperidine (1 c.c.) for 3 minutes. After addition of water (10 c.c.), the yellow *product* was collected and crystallised thrice from benzene–light petroleum (b. p. 60—80°). It separated in yellow prisms (0·025 g.), m. p. 223—224° (Found: C, 76·9; H, 7·6. $C_{23}H_{35}N_5$ requires C, 76·9; H, 7·8%).

2-*Piperidino*-4-(*4-dimethylaminostyryl*)-6-*methylpyrimidine*.—2-Chloro-4-(4-dimethylaminostyryl)-6-methylpyrimidine (0·52 g.) was boiled for 3 minutes with piperidine (2 c.c.), water (20 c.c.) added, and the *product* (0·6 g.) collected and dried. One crystallisation from light petroleum (b. p. 60—80°) gave light yellow platelets, m. p. 168—169° (Found: C, 74·5; H, 8·1. $C_{20}H_{26}N_4$ requires C, 74·3; H, 7·8%).

Boiling the chloro-compound with morpholine for 5 minutes and working up in the same way gave 2-*morpholino*-4-(4-*dimethylaminostyryl*)-6-*methylpyrimidine* (100%) which crystallised from light petroleum (b. p. 60—80°) as pale yellow needles, m. p. 155° (Found: C, 70·4; H, 7·3. $C_{19}H_{24}ON_4$ requires C, 70·4; H, 7·5%). Heating with *cyclo*hexylamine at 140—150° for 8 hours gave 2-cyclo*hexylamino*-4-(4-*dimethylaminostyryl*)-6-*methylpyrimidine* which separated from light petroleum (b. p. 60—80°) in bright yellow, flattened needles (82%), m. p. 142—143° (Found: C, 75·0; H, 8·4. $C_{21}H_{25}N_4$ requires C, 75·0; H, 8·4%).

2-Diethylaminoethylamine at 120° for 2½ hours gave 2-(2-*diethylaminoethylamino*)-4-(4-*dimethylaminostyryl*)-6-*methylpyrimidine* which crystallised from a little light petroleum (b. p. 60—80°) in clumps of yellow elongated prisms (65%), m. p. 80—81° (Found: C, 71·5; H, 8·8. $C_{21}H_{31}N_5$ requires C, 71·3; H, 8·8%). Diethylamine in a sealed tube at 130—140° for 5 hours gave 2-*diethylamino*-4-(4-*dimethylaminostyryl*)-6-*methylpyrimidine*, separating from a little light petroleum (b. p. 60—80°) in fine yellow needles (74%) or from aqueous ethanol in greenish-yellow laminae, m. p. 121—122° (Found: C, 73·4; H, 8·35. $C_{19}H_{26}N_4$ requires C, 73·5; H, 8·4%).

Diethanolamine at 140—150° for 3 hours gave 2-*bis*-(2-*hydroxyethyl*)*amino*-4-(4-*dimethylaminostyryl*)-6-*methylpyrimidine* which was recrystallised from aqueous ethanol to give small, bright yellow prisms, m. p. 116° (Found: C, 66·9; H, 7·7. $C_{19}H_{26}O_2N_4$ requires C, 66·7; H, 7·7%).

2-*Piperidino*-4-[2-(4-*dimethylaminophenyl*)*ethyl*]-6-*methylpyrimidine*.—2-Piperidino-4-(4-dimethylaminostyryl)-6-methylpyrimidine (1·0 g.) suspended in ethanol (50 c.c.) was rapidly hydrogenated at room temperature and pressure over 2% palladium–strontium carbonate catalyst. Removal of the catalyst by filtration through a layer of alumina and removal of solvent gave the *product* which crystallised from aqueous ethanol in colourless swords (0·8 g.), m. p. 70° (Found: C, 73·9; H, 8·4. $C_{20}H_{28}N_4$ requires C, 74·0; H, 8·7%).

2-*Ethoxy*-4-(4-*dimethylaminostyryl*)-6-*methylpyrimidine*.—The 2-chloro-compound (I; R = Cl) (1·0 g.), alcoholic sodium ethoxide [from sodium (0·085 g.) and dry ethanol (25 c.c.)], and benzene (10 c.c.) were refluxed on a steam-bath for 1½ hours. Sodium chloride was removed by filtration, and, after removal of solvent, the *product* (0·8 g.) was crystallised from light petroleum (b. p. 60—80°), affording orange leaflets, m. p. 120° (Found: C, 72·2; H, 7·2. $C_{17}H_{21}ON_3$ requires C, 72·0; H, 7·5%).

In attempts to dehalogenate 2-chloro-4-(4-dimethylaminostyryl)-6-methylpyrimidine, it (0·2 g.) was dissolved in dioxan (15 c.c.) and water (20 c.c.), and refluxed with zinc dust (2 g.) for 3 hours. Filtration and removal of solvent gave a residue which had m. p. 175° after crystallisation from ethanol, undepressed by admixture with the starting material.

The chloro-compound (0·2 g.) was hydrogenated in benzene–ethanol solution over 2% palladium–strontium carbonate. Removal of catalyst and solvent gave 2-*chloro*-4-[2-(4-*dimethylaminophenyl*)*ethyl*]-6-*methylpyrimidine*, separating from light petroleum (b. p. 40—60°) in colourless prisms, m. p. 59—60° (Found: C, 64·9; H, 6·7. $C_{15}H_{18}N_3Cl$ requires C, 64·9; H, 6·6%). It reacted exothermically with piperidine to give a product which separated from aqueous ethanol in colourless flattened needles, m. p. 69° alone and admixed with 2-piperidino-4-[2-(4-dimethylaminophenyl)ethyl]-6-methylpyrimidine prepared by the other route.

2-*Chloro*-4-*styryl*-6-*methylpyrimidine*.—2-Hydroxy-4-styryl-6-methylpyrimidine (1·1 g.; Stark, *loc. cit.*) and phosphorus oxychloride (6 c.c.) were refluxed for 1 hour. The clear solution was poured on ice, and the gum which separated was extracted with benzene, and the solution dried and percolated through a short column of alumina. Elution with the same solvent and evaporation gave the product which crystallised from light petroleum in long, colourless, prismatic needles (0·35 g.), m. p. 95° (Found: C, 67·95; H, 4·9. $C_{13}H_{11}N_2Cl$ requires C, 67·6; H, 4·8%).

The above *chloro*-compound was refluxed with piperidine for 3 minutes, water was added, and the product which separated was collected and crystallised from aqueous ethanol. 2-*Piperidino*-4-*styryl*-6-*methylpyrimidine* separated in light yellow leaflets, m. p. 94° (Found: C, 77·6; H, 7·6. $C_{18}H_{21}N_3$ requires C, 77·4; H, 7·6%).

2-*Chloro*-4 : 6-*distyrylpyrimidine*.—2-Hydroxy-4 : 6-distyrylpyrimidine (2·5 g.; Stark, *loc. cit.*) and phosphorus oxychloride (13 c.c.) were refluxed for 5 hours. The clear solution was poured on ice, and the product extracted with benzene after neutralisation with ammonia. Three crystallisations from much ethanol (charcoal) gave long, colourless needles, m. p. 177—178° (Found: C, 75·2; H, 4·75. $C_{20}H_{15}N_2Cl$ requires C, 75·4; H, 4·74%).

2-*Piperidino*-4 : 6-*distyrylpyrimidine* was prepared as usual from the above *chloro*-compound (0·5 g.) and piperidine (3 c.c.). It separated from light petroleum (b. p. 60—80°) in light yellow, flattened needles (0·4 g.), m. p. 133° [Found (after drying at 120° in a high vacuum): C, 81·9; H, 6·8. $C_{25}H_{25}N_3$ requires C, 81·7; H, 6·9%].

2-*Piperidino*-4 : 6-*dimethylpyrimidine*, prepared from 2-chloro-4 : 6-dimethylpyrimidine (St. Angerstein, *Ber.*, 1901, **34**, 3959) and excess of piperidine, separated from aqueous ethanol in long, colourless, prismatic needles, m. p. 60—61° (Found: C, 69·1; H, 9·0. $C_{11}H_{17}N_3$ requires C, 69·05; H, 9·0%).

2 : 6-*Dipiperidino*-4-*methylpyrimidine*, prepared from 2 : 6-dichloro-4-methylpyrimidine (Gabriel and Colman, *loc. cit.*) and excess of piperidine, crystallised from aqueous ethanol in long, colourless needles or irregular laminae, m. p. 118° (Found: C, 69·4; H, 9·1. $C_{15}H_{24}N_4$ requires C, 69·2; H, 9·3%).

2-*Acetamido*-4-(4-*dimethylaminostyryl*)-6-*methylpyrimidine*.—2-Amino-4 : 6-dimethylpyrimidine (5·0 g.; Combes and Combes, *Bull. Soc. chim.*, 1892, **7**, 791) was refluxed for 5 minutes with acetic anhydride (15 c.c.). 4-Dimethylaminobenzaldehyde (6 g.; 1 mol.) in acetic anhydride (5 c.c.) was added, and the whole refluxed for 1 hour and then poured into water. After basification with sodium hydroxide, the solution was left overnight; the tarry product which had then solidified was boiled with much water, and the solid material was collected and crystallised several times from benzene and then from ethanol. The *product* separated in yellow needles (0·2 g.), m. p. 218—219° (Found: C, 68·8; H, 6·9. $C_{17}H_{20}ON_4$ requires C, 68·9; H, 6·8%).

6-(4-*Nitrostyryl*)*quinoline*.—Quinoline-6-aldehyde (5·0 g.; Rodionov and Berkenheim, *loc. cit.*), 4-nitrophenylacetic acid (5·8 g. = 1 mol.), and piperidine (2 c.c.) were heated under an air-condenser at

130—140° for 1½ hours. Cooling and stirring with acetic acid caused crystallisation of the *product* which was collected and recrystallised from aqueous acetic acid. It separated in yellow micro-needles (3·0 g.) m. p. 199—200° (Found : C, 73·8; H, 4·6. $C_{17}H_{12}O_2N_2$ requires C, 73·9; H, 4·4%).

8-(4-*Nitrostyryl*)*quinoline*.—Quinoline-8-aldehyde (6·75 g.), 4-nitrophenylacetic acid (7·8 g.), and piperidine were heated to 140° in an oil-bath and kept at that temperature for 1½ hours. The dark product was dissolved in chloroform, washed with sodium carbonate solution, then with water, and dried. The solution was percolated down a column of alumina (the top inch containing 50% of Norit), and the yellow band eluted with the same solvent. Removal of the solvent and crystallisation of the residue from benzene–light petroleum gave the *product* as yellow needles (2·3 g.), m. p. 171° (Found : C, 73·8; H, 4·6. $C_{17}H_{12}O_2N_2$ requires C, 73·9; H, 4·4%).

6-(4-*Aminostyryl*)*quinoline*.—To a solution of crystalline stannous chloride (16 g.) in glacial acetic acid (40 c.c.) saturated with dry hydrogen chloride, was added 6-(4-nitrostyryl)quinoline (powdered; 2·0 g.), and the solution stirred at room temperature for several hours. After being warmed on the steam-bath for 4 hours, the solution was cooled and the flocculent precipitate collected and boiled with water (300 c.c.) for 3 hours. After filtration and basification of the solution, the *product* was collected. It crystallised from chloroform in clusters of yellow platelets (0·87 g.), m. p. 214—215° (Found : C, 83·3; H, 6·0. $C_{17}H_{14}N_2$ requires C, 82·9; H, 5·7%).

8-(4-*Aminostyryl*)*quinoline* was prepared as above from 8-(4-nitrostyryl)quinoline (0·5 g.). The tin complex was decomposed by boiling it with sodium carbonate solution. The *amine* crystallised from benzene–light petroleum in burrs of yellow, flattened needles (0·38 g.), m. p. 156° (Found : C, 82·9; H, 5·8. $C_{17}H_{14}N_2$ requires C, 82·9; H, 5·7%).

2-*Phenyl*-1-(6-*quinolyl*)*ethanol*.—Quinoline-6-aldehyde (3·64 g.) in benzene (25 c.c.) was added to the Grignard reagent prepared from benzyl chloride (3·3 g.) and magnesium (0·62 g.) in ether (50 c.c.). A deep red flocculent precipitate separated immediately. After 2 hours' refluxing the mixture was decomposed with an ice-cold solution of ammonium chloride. The aqueous layer was extracted with benzene and the combined organic layers evaporated. The dark residual oil was dissolved in concentrated hydrochloric acid and extracted with ether. The acid layer was made alkaline and extracted with benzene. After removal of solvent the residue was distilled at 203°/0·1 mm. The distillate crystallised after treatment with a little methanol, and the *compound* separated finally from benzene–light petroleum in colourless needles (0·25 g.), m. p. 129·5—130° (Found : C, 82·2; H, 6·45. $C_{17}H_{15}ON$ requires C, 81·9; H, 6·1%).

α-*Phenyl*-β-(6-*quinolyl*)*acrylic acid*.—Sodium phenylacetate (0·9 g.), quinoline-6-aldehyde (0·9 g.), acetic anhydride (5 c.c.), and zinc chloride (0·2 g.) were heated at 160° for 3 hours. The reaction mixture was poured into water and the colourless precipitate collected and dissolved in hot sodium carbonate solution. Undissolved oil was removed by extraction with benzene. The aqueous layer was acidified with acetic acid and the precipitate collected and dried (1·4 g.). One crystallisation from ethanol gave the pure *product* as a colourless crystalline powder, m. p. 265° (Found : C, 78·7; H, 4·9. $C_{18}H_{13}O_2N$ requires C, 78·5; H, 4·7%).

6-*Styrylquinoline*.—6-(4-Aminostyryl)quinoline (0·5 g.) dissolved in 5N-hydrochloric acid (2 c.c.) was diazotised at 0° with sodium nitrite (0·14 g.) in water (1 c.c.). The diazonium salt which separated was redissolved by adding water (3 c.c.) and, after addition of hypophosphorous acid (3 c.c. of 30% solution), the solution was left overnight at 0° and then at room temperature for 1 day. After basification with sodium hydroxide the product was extracted with benzene. It was purified by chromatography in light petroleum on alumina. 6-*Styrylquinoline* was eluted with benzene and crystallised from light petroleum, giving colourless platelets (10 mg.), m. p. 119° (Found : C, 88·3; H, 5·7. $C_{17}H_{13}N$ requires C, 87·8; H, 5·7%).

6-Nitroquinaldine was prepared by the method of Hamer (*loc. cit.*). Purification by chromatography in benzene on alumina and crystallisation from benzene–light petroleum gave colourless needles, m. p. 165° (described by Hamer, *loc. cit.*, as yellow needles, m. p. 164°).

6-*Amino*-2-*styrylquinoline* was prepared from 6-nitro-2-styrylquinoline (Schmidt, *loc. cit.*) by stannous chloride reduction as above. The tin complex was decomposed by hot sodium hydroxide solution and the amine extracted with chloroform. It separated from benzene–light petroleum in brown, sword-like prisms, m. p. 198—199° (Found : C, 82·8; H, 5·9. $C_{17}H_{14}N_2$ requires C, 82·9; H, 5·7%). The *acetyl* derivative separated from chloroform with 1 molecule of chloroform of crystallisation in large colourless prisms, m. p. 193° (Found : C, 58·7; H, 4·0. $C_{19}H_{16}ON_2,CHCl_3$ requires C, 58·9; H, 4·2%). Crystallisation from aqueous ethanol afforded small colourless platelets, m. p. 193° (Found, after drying at 120°/2 mm. : C, 79·0; H, 5·6. $C_{19}H_{16}ON_2$ requires C, 79·2; H, 5·6%).

6-*Nitro*-2-(4-*dimethylaminostyryl*)*quinoline*.—6-Nitroquinaldine (5·0 g.), 4-dimethylaminobenzaldehyde (4·0 g.), and fused zinc chloride (0·2 g.) were heated at 160° for ½ hour. After cooling, the residue was dissolved in concentrated hydrochloric acid, and the solution diluted and basified with ammonia. The *product* was collected and crystallised from chloroform, separating in deep purple prismatic needles (7·6 g.), m. p. 248—249° (Found : C, 71·8; H, 5·5. $C_{19}H_{17}O_2N_3$ requires C, 71·5; H, 5·4%).

6-*Nitro*-2-(4-*nitrostyryl*)*quinoline*.—6-Nitroquinaldine (2·1 g.), 4-nitrobenzaldehyde (1·7 g.), and a little fused zinc chloride were heated at 170°. The melt frothed and rapidly solidified to a yellow mass; this was almost insoluble in benzene or chloroform, but a sample crystallised from much glacial acetic acid in clusters of yellow needles, m. p. 278° (Found : C, 63·7; H, 3·6. $C_{17}H_{11}O_4N_3$ requires C, 63·5; H, 3·5%).

6-*Amino*-2-(4-*dimethylaminostyryl*)*quinoline*.—The corresponding nitro-compound (IX; R = NO_2, R′ = NMe_2) (2·0 g.), crystalline stannous chloride (10·0 g.), and fuming hydrochloric acid (15 c.c.) were warmed on a steam-bath for 1 hour. The tin complex was collected, dissolved in hot water, and decomposed with excess of 10N-sodium hydroxide. The yellow precipitate was collected, well washed with water, and crystallised from methanol. The *amine* separated in brown needles (1·15 g.), m. p. 251—252° (Found : C, 79·0; H, 6·7. $C_{19}H_{19}N_3$ requires C, 78·9; H, 6·6%). The *acetyl* derivative, prepared by heating the amine with acetic anhydride and 1 drop of sulphuric acid at 100° for ½ hour, separated from aqueous methanol in orange-yellow needles, m. p. 241—242° (Found : C, 76·0; H, 6·5. $C_{21}H_{21}ON_3$ requires C, 76·1; H, 6·4%).

6-Amino-2-(4-aminostyryl)quinoline was prepared as above from the corresponding dinitro-compound (IX; R = R' = NO_2) (1·0 g.). It crystallised from aqueous methanol in yellow needles (0·6 g.), m. p. 242—243° (Browning *et al.*, *loc. cit.*, give m. p. 241—242°) (Found: C, 77·9; H, 5·7. Calc. for $C_{17}H_{15}N_3$: C, 78·1; H, 5·8%).

6-*Formyl*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*.—Phosphorus oxychloride (10·5 g.; 6·5 c.c.) and *N*-methylformanilide (9·2 g.) were dissolved in benzene (10 c.c.), and the solution left at room temperature for 1 hour and cooled to 0°. *N*-Methyltetrahydroquinoline (10 g.) was added dropwise with shaking, and the solution left overnight at room temperature, then poured on ice, basified with sodium hydroxide, and steam distilled. The residue was extracted with ether and the *product* purified through the bisulphite compound. It distilled at 219—221°/15 mm., and crystallised on standing to form large colourless plates (5·5 g.), m. p. 28—29° (Found: C, 75·4; H, 7·5. $C_{11}H_{13}ON$ requires C, 75·4; H, 7·5%). The aldehyde (1 g.), hydrazine hydrate (100 c.c.; 2·25 c.c.), and ethanolic sodium ethoxide [16 c.c.; containing sodium (0·8 g.)] were heated in a sealed tube at 170—180° for 8 hours. Water (3 c.c.) was added to the contents of the tube, and most of the alcohol removed by distillation. The residue was diluted with water (20 c.c.) and extracted with ether (30 c.c.), and the ether extract washed (3 times) with water and dried. To a sample (2 c.c.) of this solution were added a few drops of saturated ethanolic picric acid. The picrate separated in light yellow plates, m. p. 150—152°. One recrystallisation from ethanol–ether gave yellow prisms, m. p. 152° (Found: N, 14·1. Calc. for $C_{17}H_{18}O_7N_4$: N, 14·4%). The picrate of authentic 1 : 6-dimethyltetrahydroquinoline has m. p. 152° (von Braun and Aust, *loc. cit.*).

6-*Styryl*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*.—To a Grignard reagent from benzyl chloride (1·23 g.) and magnesium (0·25 g.) in ether (30 c.c.) was added, dropwise and with shaking, a solution of formylmethyltetrahydroquinoline (1·53 g.) in benzene (25 c.c.). The solution was refluxed for 45 minutes on the water-bath, during which time a yellow complex separated. After standing at room temperature for 2 hours the reaction mixture was decomposed with saturated ammonium chloride solution and the organic layer separated. The aqueous layer was extracted with ether, and the combined organic layers evaporated to dryness. The residue was dissolved in benzene (25 c.c.) and refluxed with phosphoric oxide (2 g.) for 45 minutes. After decomposition with water and basification with 2N-sodium hydroxide, the benzene layer was separated, washed, dried, diluted with an equal volume of light petroleum, and chromatographed on alumina. Elution with the same solvent and crystallisation from light petroleum (b. p. 60—80°) gave the *product* as fine colourless needles (0·6 g.), m. p. 93—94° (Found: C, 86·6; H, 7·6. $C_{18}H_{19}N$ requires C, 86·7; H, 7·7%).

2-(4-*Dimethylaminostyryl*)*thiazole*.—2-Methylthiazole (1 c.c.), 4-dimethylaminobenzaldehyde (1·5 g.), and zinc chloride (fused; *ca.* 0·5 g.) were heated in a sealed tube at 160—170° for 14 hours. The product was dissolved in dilute hydrochloric acid, and the solution basified with ammonia and extracted with benzene. Chromatography of the extract on alumina and then two crystallisations from light petroleum (b. p. 40—60°) gave the *product* as yellow laminae (10 mg.), m. p. 124° (Found: C, 68·5; H, 6·0. $C_{13}H_{14}N_2S$ requires C, 67·8; H, 6·1%).

2-(4-*Dimethylaminostyryl*)-*β*-*naphthathiazole* was prepared as above by heating 2-methyl-*β*-naphthathiazole (0·5 g.), 4-dimethylaminobenzaldehyde (0·4 g.), and zinc chloride (0·5 g.) at 160—180° for 1½ hours. It crystallised from light petroleum (b. p. 60—80°) in the form of yellow swords (0·3 g.), m. p. 170—171° (Found: C, 76·6; H, 5·7. $C_{21}H_{18}N_2S$ requires C, 76·3; H, 5·5%).

2-*Styrylbenzthiazole*.—2-Methylbenzthiazole (1 g.), benzaldehyde (freshly distilled; 0·8 c.c.), and 2 drops of concentrated hydrochloric acid were heated overnight at 100° in a sealed tube. The product was worked up as above, and separated from ethanol in colourless needles (0·46 g.), m. p. 112°; Mills and Whitworth (*loc. cit.*) give m. p. 112—113°.

2-(4-Dimethylaminostyryl)-*ββ'*-naphthathiazole was prepared in the same way as 2-styrylbenzthiazole from 2-methyl-*ββ'*-naphthathiazole (0·5 g.). It crystallised from benzene–light petroleum (b. p. 60—80°) in yellow needles (0·33 g.), m. p. 217—218° (Rupe and Schwarz, *loc. cit.*, give m. p. 212°).

2-(4-*Dimethylaminostyryl*)*benziminazole*.—Solutions of *o*-phenylenediamine (2·2 g.) in methanol (50 c.c.), cupric acetate (8 g.) in water (100 c.c.), and 4-dimethylaminocinnamaldehyde (3·5 g.) in warm methanol (50 c.c.) were mixed and warmed on a steam-bath for 1 hour. After cooling, the brown precipitate was collected, washed with aqueous methanol, and suspended in 50% methanol (200 c.c.). Hydrogen sulphide was passed into the solution (2 hours). After filtration, the filtrate and washings were evaporated and the residue crystallised from methanol–ethanol. 2-(4-Dimethylaminostyryl)benziminazole separated in long orange prismatic needles (1·0 g.), m. p. 258° (Rupe *et al.*, *loc. cit.*, give m. p. 256°).

2-*Methylbenzoxazole hydrochloride*, prepared by passing dry hydrogen chloride into an ether solution of 2-methylbenzoxazole, separated from ethanol–ether in large colourless prisms, m. p. 154° (Found: C, 56·7; H, 4·8. C_8H_8ONCl requires C, 56·7; H, 4·8%).

2-*Styrylbenzoxazole*.—2-Methylbenzoxazole (2 c.c.), freshly distilled benzaldehyde (2 c.c.), and anhydrous zinc chloride (powdered; 1 g.) were heated in a sealed tube at 160° for 6 hours. The product was steam distilled until the distillate was clear, and the residue was made acid with hydrochloric acid and then basified with ammonia. The oil which separated rapidly solidified. It was purified by chromatography in benzene–light petroleum on alumina, and crystallised from light petroleum (b. p. 60—80°) in colourless needles (1 g.), m. p. 81—82° (Found: C, 81·8; H, 5·2. Calc. for $C_{15}H_{11}ON$: C, 81·5; H, 5·0%). The *picrate* separated from benzene–light petroleum in fine yellow needles, m. p. 163—164° (Found: C, 55·8; H, 3·2. $C_{15}H_{11}ON,C_6H_3O_7N_3$ requires C, 56·0; H, 3·1%).

2-(4-*Dimethylaminostyryl*)*benzoxazole* was obtained in the same way from 2-methylbenzoxazole (1·0 g.), 4-dimethylaminobenzaldehyde (1·12 g.), and fused zinc chloride (0·5 g.) overnight at 160°. It separated from benzene–light petroleum (b. p. 60—80°) in the form of yellow glistening leaflets (0·35 g.), m. p. 174—175° (Found: C, 77·2; H, 6·3. $C_{17}H_{16}ON_2$ requires C, 77·2; H, 6·1%).

1-(4-*Dimethylaminostyryl*)*phthalazine*.—1-Methylphthalazine (Gabriel and Eschenbach, *Ber.*, 1897, **30**, 3026) (2·5 g.), 4-dimethylaminobenzaldehyde (2·75 g.), and fused zinc chloride (0·75 g.) were heated in an oil-bath at 160° for 2 hours. After solution of the reaction mixture in dilute hydrochloric acid and basification with ammonia, the product was extracted with benzene. It was purified by percolation of the solution through a column of alumina (Savory and Moore, " Brockmann "; a more alkaline alumina

caused rapid decomposition of the product) and elution with benzene containing a few drops of methanol. 1-(4-*Dimethylaminostyryl*)*phthalazine* formed flattened orange needles (0·39 g.), m. p. 186—187° from benzene–light petroleum (Found: C, 78·3; H, 6·2. $C_{18}H_{17}N_3$ requires C, 78·5; H, 6·2%).

2-(4-*Nitrostyryl*)*furan* (Preparation by Dr. R. J. C. Harris).—(*a*) Furfuraldehyde (5·0 g.), 4-nitrophenylacetic acid (9·0 g.), and piperidine (1 c.c.) were heated at 130—140° for 5 hours. The black resinous product was extracted with hot benzene, and the extract washed with 2N-hydrochloric acid, sodium carbonate solution, and water, and dried. The solution was chromatographed on a column of alumina (75 g.), and the 2-(4-*nitrostyryl*)*furan* eluted with benzene. Evaporation of the eluate gave orange needles (2·0 g.), m. p. 130—131° from ethanol (Found: C, 66·95; H, 4·4. $C_{12}H_9O_3N$ requires C, 67·0; H, 4·2%).

(*b*) A mixture of *p*-nitroaniline (17·25 g.), 25% hydrochloric acid (50 g.), and ice (50 g.) was diazotised with a solution of sodium nitrite (9 g.) in water (15 c.c.). The diazonium salt solution was filtered and added to a solution of furylacrylic acid in acetone (150 c.c.). The solution was vigorously stirred, and sodium acetate (27·5 g.) and cupric chloride (5·35 g.) in water (15 c.c.) were added. After 2 hours the mixture was steam distilled, and the residue treated as in (*a*). Yield 5·0 g., m. p. 130—131°.

Reduction of 2-(4-*Nitrostyryl*)*furan*.—(*a*) The nitro-compound (0·5 g.) in ethyl acetate (30 c.c.) was shaken in hydrogen with Raney nickel (0·5 g.) at room temperature and pressure. After 1 hour, hydrogen uptake ceased and the catalyst and solvent were removed. The residue of brown needles was chromatographed in benzene on alumina, and the product crystallised from benzene. The *azoxy*-compound formed fine, orange needles, m. p. 231—232° (decomp.) (Found: C, 75·34; H, 4·9. $C_{24}H_{18}O_3N_2$ requires C, 75·36; H, 4·7%).

(*b*) The nitro-compound (1·0 g.), ammomium chloride (1·0 g.), zinc dust (4·0 g.) and ethanol (30 c.c.) containing water (3 c.c.) were refluxed on a steam-bath for 1 hour. The solution was filtered and diluted considerably with water; an almost colourless precipitate of fine needles then separated. This was collected and recrystallised from aqueous ethanol (charcoal), giving 2-(4-*aminostyryl*)*furan* in colourless needles, m. p. 104°. For analysis the compound crystallised from light petroleum in small colourless swords (Found: C, 77·8; H, 5·7. $C_{12}H_{11}ON$ requires C, 77·8; H, 6·0%). The *acetyl* derivative, prepared by boiling the amine for a few minutes with acetic anhydride, separated from aqueous ethanol in fine colourless needles, m. p. 201—202° (Found: C, 74·4; H, 6·0. $C_{14}H_{13}O_2N$ requires C, 74·0; H, 5·8%).

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