

Reactions of Some 4-Dicyanomethylenepyran Derivatives
with Malononitrile and Hydrazines

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4-Dicyanomethylene-2-phenyl-4*H*-benzo[*b*]pyran, the corresponding thiapyran, and 4-dicyanomethylene-2,6-diphenyl-4*H*-pyran react with malononitrile under basic conditions to give 5-amino-4-cyano-2-phenylbenzo[*b*]pyrano[4,3,2-*de*][1,6]naphthyridine, the corresponding thiapyranonaphthyridine derivative, and 5-amino-6-cyano-2,8-diphenylpyrano[4,3,2-*de*][1,6]naphthyridine, respectively. Certain other related reactions were studied in the course of investigating the above reactions. Hydrazine hydrate and 4-dicyanomethylene-2-phenyl-4*H*-benzo[*b*]pyran gave 5-(2-hydroxyphenyl)-3-phenylpyrazole, and phenylhydrazine gave 5-(2-hydroxyphenyl)-1,3-diphenylpyrazole.

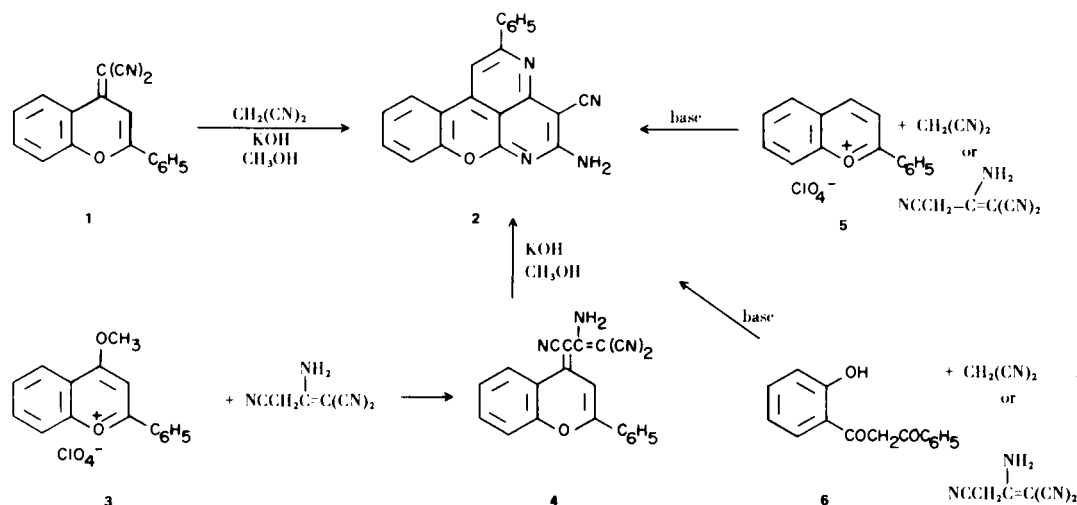
The reactions of some 4-dicyanomethylene derivatives of pyran and benzo[*b*]pyran with amines and several other nucleophiles have been described (1,2). We now report the reactions of these pyran derivatives as well as 4-dicyanomethylene-2-phenyl-4*H*-benzo[*b*]thiapyran with malononitrile (in the presence of bases) and of a benzo[*b*]pyran derivative with hydrazine and phenylhydrazine.

4-Dicyanomethylene-2-phenyl-4*H*-benzo[*b*]pyran (1) reacts with malononitrile in methanolic potassium hydroxide to give a product which has been assigned structure 2. Compound 2 is also obtained by (a) treatment with base of compound 4, which is formed from 4-methoxyflavylium perchlorate (3) and malononitrile dimer (3); (b) reaction of flavylium perchlorate (5) with either malononitrile or malononitrile dimer under basic conditions; (c) reaction of 1-(2-hydroxyphenyl)-3-phenylpropane-1,3-dione (6) with malononitrile or malononitrile dimer under alkaline conditions. These methods are shown in Scheme I.

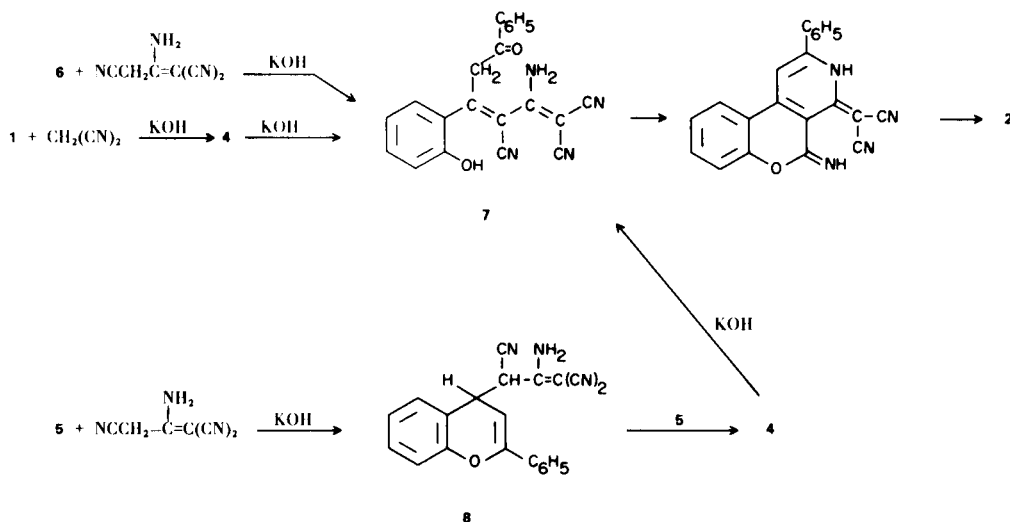
There are several routes which could lead to the formation of 2 by these different procedures, but we will present only one. In Scheme II, a reaction sequence is shown which assumes that a common intermediate, 7, is formed by the different procedures, and that this intermediate cyclizes to the product 2. The formation of 2 by the reaction of 5 with malononitrile dimer probably involves the formation of an adduct, 8, which is dehydrogenated to 4 by means of 5, since 5 is a known dehydrogenating agent (4).

Support for the structure 2, in addition to the four methods of preparation, was derived from the fact that the mass spectrum shows the parent ion at *m/e* 336 with very little fragmentation, as is characteristic of many aromatic compounds. The ir spectrum of 2 shows absorptions at 3.0 and 3.1 μ and at 4.5 μ , which are assigned to the amino and nitrile functions. The nmr spectrum shows only aromatic protons. Related compounds, which are

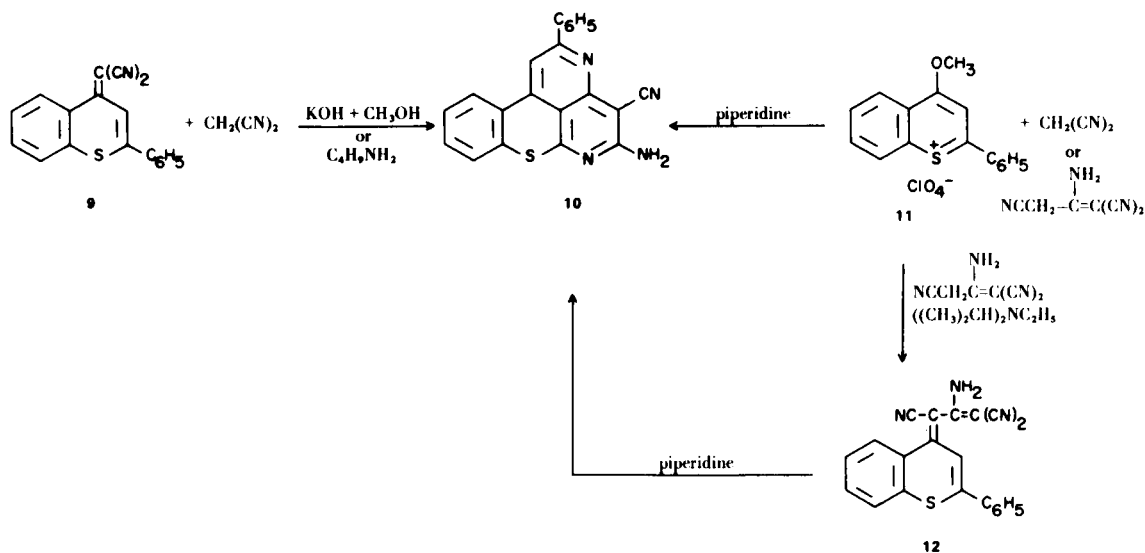
Scheme I



Scheme II



Scheme III



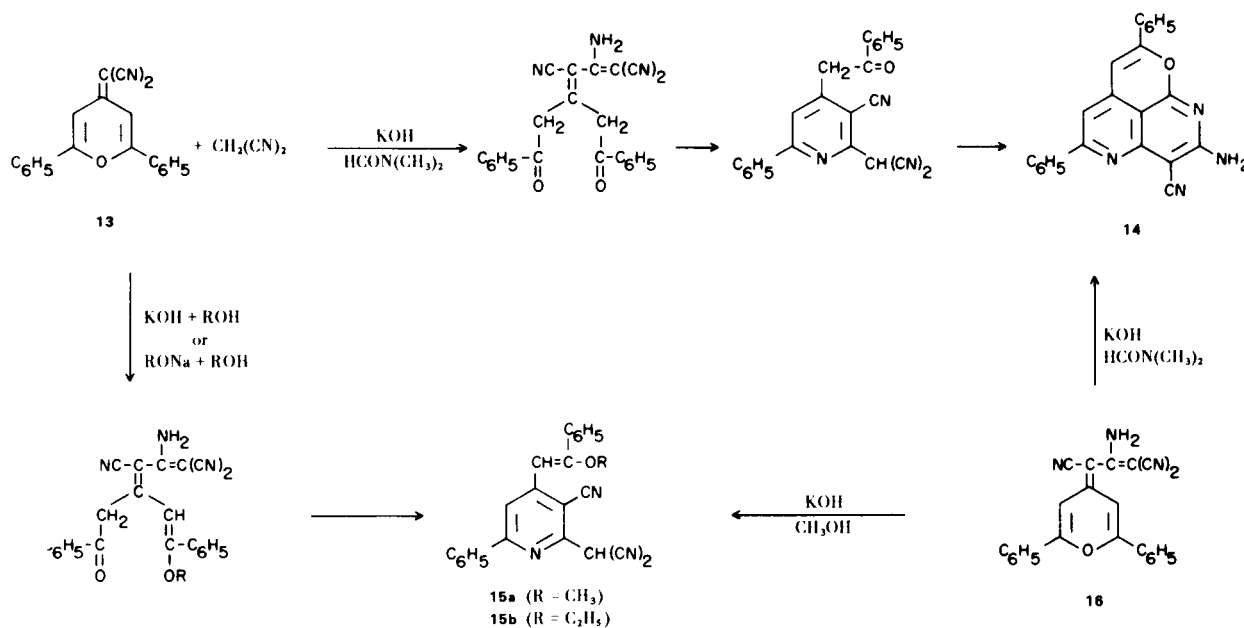
described later in the paper (particularly 14), gave more useful nmr spectra.

Some of the reactions shown in Scheme I have been extended to 4-dicyanomethylene-2-phenyl-4H-benzo[*b*]thiapyran (9) (Scheme III). For example, 9 reacts with malononitrile in the presence of either methanolic potassium hydroxide or butylamine to give 10. Compound 10 also can be prepared from the thiapyrylium salt 11 and malononitrile or malononitrile dimer using piperidine as the basic reagent; if diisopropylethylamine is used as the base, the intermediate 12 is obtained. Compound 12 is cyclized to 10 by heating with piperidine. It was interesting to find that 9 was converted to 10 in boiling butylamine. This fact suggests that under these conditions the

dicyanomethylene group is displaced to give 4-butylimino-2-phenyl-4H-benzothiazopyran and malononitrile, which in turn react to give 12 and finally 10. This postulate is supported by the formation of 10 by the reaction of 4-butylimino-2-phenyl-4H-benzo[*b*]thiapyrylium perchlorate and malononitrile in the presence of butylamine. The reaction paths leading to the formation of 10 should be similar to those proposed for 7.

4-Dicyanomethylene-2,6-diphenyl-4H-pyran (13) reacts with malononitrile in a slightly different manner than 1 does in that the basic reagent can change the course of the reaction. Thus 13 and malononitrile in the presence of potassium hydroxide in dimethylformamide gave 14, but in the presence of methanolic potassium hydroxide, the

Scheme IV



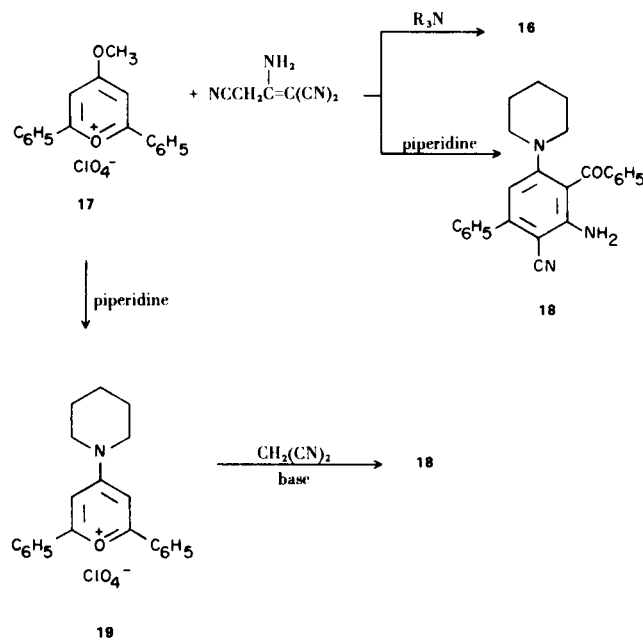
product was **15a** and with ethanolic potassium hydroxide it was **15b**. The products **14** and **15a** were also obtained from **16** with potassium hydroxide in dimethylformamide and in methanol, respectively. A plausible explanation for the change in the reaction course is presented in Scheme IV.

Compound **16** was prepared from 4-methoxy-2,6-diphenylpyrylium perchlorate (**17**) and malononitrile dimer using a tertiary amine as the base. An attempt to use piperidine as the base led to the formation of **18**, rather than **16**. Compound **18** is also formed from **17**, malononitrile and piperidine or from 2,6-diphenyl-4-piperidinopyrylium perchlorate (**19**) with malononitrile and a base. These facts suggest that **17** first reacts with piperidine to give **19**, which in turn is converted to **18**.

Several derivatives of **14** were prepared in order to substantiate the structural assignment. For example, treatment of **14** with 80% sulfuric acid gives 5-amino-2,8-diphenylpyrano[4,3,2-de][1,6]naphthyridine (**20**), which in turn was benzoylated to give **21**. The reaction of **14** with nitrous acid in the presence of hydrochloric acid gives the chloro derivative **22**.

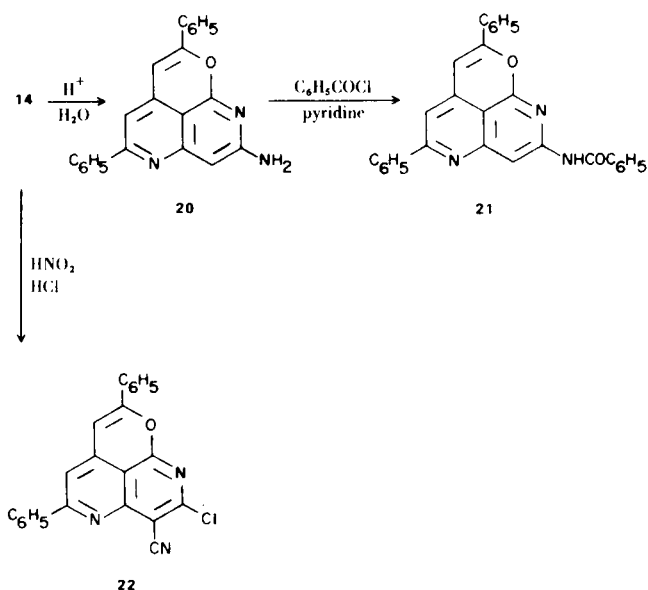
Hydrazine hydrate reacts with **1** or **4** to give 5-(2-hydroxyphenyl)-3-phenylpyrazole (**23**), which had been obtained previously (**5**) from the diketone **6** and hydrazine hydrate. Phenylhydrazine reacts with **1** to give 5-(2-hydroxyphenyl)-1,3-diphenylpyrazole (**24**). Structure **24** was assigned since the product differs from the known

Scheme V

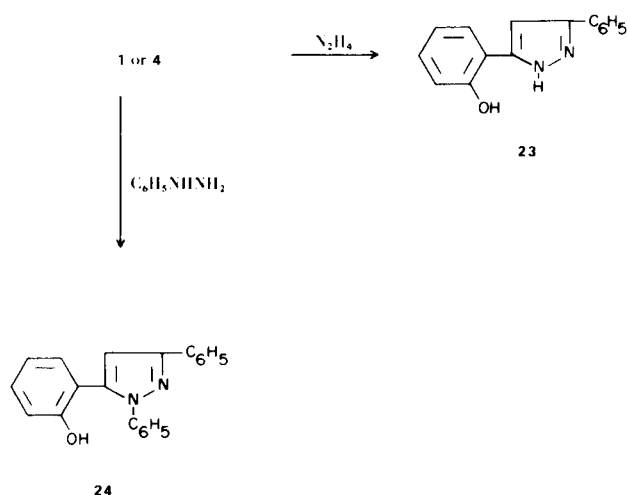


isomeric 3-(2-hydroxyphenyl)-1,5-diphenylpyrazole (**5**) and the phenylhydrazone of 4-flavone (**6**). Support for structure **24** was obtained from the mass spectrum, which shows a m/e for the parent minus $\text{C}_6\text{H}_5\text{N}=\text{CH}^+$, while the isomeric 3-hydroxyphenyl compound shows a m/e for the parent minus *o*-hydroxybenzoyl.

Scheme VI



Scheme VII



EXPERIMENTAL (7)

4-Dicyanomethylene-2-phenyl-4*H*-benzo[*b*]pyran (1).

Compound 1 was prepared as described previously (2).

5-Amino-4-cyano-2-phenylbenzo[*b*]pyrano[4,3,2-*de*][1,6]naphthyridine (2).

(a) A mixture of 2.7 g. of 1, 1.5 g. of malononitrile, 20 ml. of pyridine, and 10 ml. of 10% methanolic potassium hydroxide was heated for 2 hours on a steam bath, cooled and the solid was crystallized from dimethylformamide yielding 3 g. of 2, m.p. 370-371°.

(b) A mixture of 0.5 g. of 4, 1 g. of potassium hydroxide and 50 ml. of methanol was refluxed for 1 hour, cooled and the solid was collected, yield 0.35 g., m.p. 369-371°.

(c) A mixture of 3.1 g. of flavylum perchlorate, 2 g. of malononitrile dimer and 10 ml. of pyridine was heated on a steam bath for 2 hours, chilled and the solid, after crystallization, weighed 1.6 g., m.p. 368-371°.

(d) Flavylum perchlorate (3 g.) and 2 g. of malononitrile in 25 ml. of pyridine were allowed to react as described in method (c) giving 1.3 g. of 2, m.p. 369-371°.

(e) A mixture of 4.4 g. of 6, 3 g. of malononitrile, 4 ml. of diisopropylethylamine and 20 ml. of acetonitrile was refluxed for 3 hours and on chilling, 3.1 g. of 2 separated, m.p. 370-371°.

(f) Procedure (e) was repeated using 2.7 g. of malononitrile dimer in place of malononitrile. The yield of 2 was 3.9 g., m.p. 372-373°.

The mass spectrum shows a parent peak (M^+) at m/e 336, another peak at 335, and very little fragmentation. The λ max ($\epsilon \times 10^{-3}$) (in dimethylformamide) are 292 (55.7) and 408 $m\mu$ (8.3). The nmr spectrum shows absorption at δ 7.42-8.7 ppm. (complex multiplet) and exchangeable protons could not be determined owing to the precipitation of the compound on addition of deuterium oxide.

Anal. Calcd. for $C_{21}H_{12}N_4O$: C, 75.0; H, 3.6; N, 16.7. Found: C, 74.9; H, 3.8; N, 16.7.

4-(2-Amino-1,3,3-tricyanoallylidene)-2-phenyl-4*H*-benzo[*b*]pyran (4).

A mixture of 3.5 g. of 4-methoxyflavylum perchlorate (3), 2 g. of malononitrile dimer and 2 ml. of diisopropylethylamine in 25 ml. of alcohol (10 ml. of pyridine can be substituted for the tertiary amine and alcohol) was heated on a steam bath for 20 hours, cooled and the solid was crystallized from alcohol, giving 1.1 g. of 4 and 0.1 g. of insoluble 2. The m.p. of 4 was 268-270°. The mass spectrum shows a parent peak (M^+) at m/e 336 and numerous fragments such as 335 (M^+-H); 310 (M^+-CN); 309 (M^+-HCN); 270 ($M^+-CH_2(CN)_2$); 105 ($C_6H_5CO^+$); and 102 ($C_6H_5\equiv CH$). The λ max ($\epsilon \times 10^{-3}$) are 242 (23.5), 280 (18.5), 296 (18.0), and 385 $m\mu$ (20.0). The nmr spectrum shows absorption at δ 6.95-9.0 ppm.

Anal. Calcd. for $C_{21}H_{12}N_4O$: C, 75.0; H, 3.6; N, 16.7. Found: C, 74.8; H, 3.6; N, 16.7.

4-Dicyanomethylene-2-phenyl-4*H*-benzo[*b*]thiapyran (9).

This compound was prepared from 4-thiaflavone and malononitrile in the usual manner (2) and melted at 195-196°.

Anal. Calcd. for $C_{18}H_{10}N_2S$: C, 75.5; H, 3.5; N, 9.8. Found: C, 75.3; H, 3.6; N, 9.6.

5-Amino-4-cyano-2-phenylbenzo[*b*]thiapyrano[4,3,2-*de*][1,6]naphthyridine (10).

(a) A mixture of 2 g. of 9, 1 g. of malononitrile, 10 ml. of 10% methanolic potassium hydroxide and 15 ml. of pyridine (10 ml. of butylamine can be substituted for the potassium hydroxide and solvents) was heated on a steam bath for 0.5 hour, cooled and the solid was collected and crystallized from dimethylsulfoxide, giving 1.2 and 1.8 g., respectively, of 10, m.p. 363-365°.

(b) A mixture of 5.3 g. of 4-methoxythiaflavylum perchlorate (11), 2.6 g. of malononitrile (or 2.5 g. of malononitrile dimer), and 25 ml. of piperidine was refluxed for 15 minutes, cooled and the solid treated as in (a), giving 1.5 g. and 1.4 g., respectively, of 10.

(c) A mixture of 0.5 g. of 12 and 5 ml. of piperidine was refluxed for 5 minutes and cooled, giving 0.3 g. of 10.

(d) When a solution of 2 g. of 9 in 10 ml. of butylamine was heated on a steam bath for 10 minutes, 0.5 g. of 10 was obtained.

(e) A solution of 0.2 g. of 4-butylaminothiaflavylium perchlorate, 0.2 g. of malononitrile and 2 ml. of butylamine was heated for 5 minutes on a steam bath, giving 0.1 g. of **10**.

The λ max (ϵ not given because of limited solubility) are 249, 304, and 426 $m\mu$. The nmr spectrum shows absorption at δ 7.2-8.15 ppm. (M) for the aromatic protons and a broad singlet, which may be the amino protons, at δ 6.35 ppm. The assignment of the latter absorption to the amino protons could not be verified because the sample precipitated on addition of deuterium oxide.

Anal. Calcd. for $C_{21}H_{12}N_4S$: C, 71.6; H, 3.5; N, 15.9; S, 9.1. Found: C, 71.7; H, 3.5; N, 15.7; S, 9.4.

4-(2-Amino-1,3,3-tricyanoallylidene)-2-phenyl-4H-benzo[*b*]thiapyran (**12**).

A solution of 2.6 g. of 4-methoxythiaflavylium perchlorate (**11**), 0.9 g. of malononitrile dimer, 1 ml. of diisopropylethylamine and 25 ml. of alcohol was refluxed for 4 hours, diluted with aqueous acetic acid and the sticky solid was crystallized from aqueous alcohol, giving 1 g. of **12**, m.p. 240-242°. The λ max ($\epsilon \times 10^{-3}$) are 258 (29.4) and 409 $m\mu$ (17.9). The nmr spectrum shows absorption at δ 7.0 (S, 1H) for the proton in the 3-position, at δ 7.37-7.6 (M, 9H) for the aromatic protons, and at δ 9.0 ppm. (broad S, 2H, exchangeable) for the amino protons.

Anal. Calcd. for $C_{21}H_{12}N_4S$: C, 71.6; H, 3.4; N, 15.9. Found: C, 71.2; H, 3.5; N, 16.2.

4-Dicyanomethylene-2,6-diphenyl-4H-pyran (**13**).

This compound was prepared as previously described (2). 5-Amino-6-cyano-2,8-diphenylpyrano[4,3,2-*de*][1,6]naphthyridine (**14**).

(a) A mixture of 15 ml. of dimethylformamide, 1.5 g. of **13**, 0.4 g. of malononitrile and 0.4 g. of potassium hydroxide dissolved in 2 ml. of water was refluxed for 1 hour, and after chilling, the solid was collected and crystallized from ethoxyethanol giving 0.7 g. of **14**, m.p. 348-349°.

(b) A mixture of 1.5 g. of **16**, 15 ml. of dimethylformamide and 0.5 g. of potassium hydroxide was allowed to react as described in (a) giving 0.5 g. of **14**, m.p. 348-350°.

The λ max ($\epsilon \times 10^{-3}$) are 235 (20.9), 272 (46.1) and 408 $m\mu$ (9.0). The nmr spectrum shows absorption at δ 6.39 (broad S, 2H) for the amino protons, δ 6.95 (S, 1H) for the proton in the 1-position, δ 7.17 (S, 1H) for the proton in the 9-position, and δ 7.1-7.95 ppm. (M, 10H) for the aromatic protons. Addition of deuterium oxide to the solution causes the sample to precipitate.

Anal. Calcd. for $C_{23}H_{14}N_4O$: C, 76.2; H, 3.9; N, 15.5. Found: C, 75.9; H, 4.2; N, 15.2.

3-Cyano-2-dicyanomethyl-4-(2-methoxystyryl)-6-phenylpyridine (**15a**).

A solution of 1 g. of **16** (or 1 g. of **13** plus 0.5 g. of malononitrile) in 0.4 g. of potassium hydroxide and 15 ml. of methyl alcohol was refluxed for 5 hours, diluted with 1 ml. of acetic acid in 10 ml. of water, and the solid was crystallized from acetic acid, giving 0.5 g. of **15a**, m.p. 218-220°. The λ max ($\epsilon \times 10^{-3}$) are 280 (30.9), 338 (46.3), and 460 $m\mu$ (5.9). The nmr spectrum shows absorption at δ 3.75 and δ 3.93 (S, combined=3H). These two absorptions are considered to be due to the methoxy protons in *cis* and *trans* forms of the styryl group and the signal at higher field is approximately three times greater than the other. Absorption occurs at δ 6.02 and δ 6.09 (S, combined=1H) for the *cis* and *trans* vinyl protons with the low field signal the larger. The aromatic protons absorb at δ 7.4-7.75 ppm. (M, 11H). There was

no signal for the dicyanomethyl proton but this could be due to a rapid exchange.

Anal. Calcd. for $C_{24}H_{16}N_4O$: C, 76.6; H, 4.3; N, 14.9. Found: C, 76.2; H, 4.4; N, 15.2.

3-Cyano-2-dicyanomethyl-4-(2-ethoxystyryl)-6-phenylpyridine (**15b**).

This compound was prepared by the procedure described for **15a** except that ethyl alcohol was used as the solvent. The product was obtained in 91% yield and melted at 202-203°. The λ max ($\epsilon \times 10^{-3}$) are 280 (28.2), 338 (44.1), and 455 $m\mu$ (5.88). The nmr spectrum again shows that *cis* and *trans* forms of the styryl group are present. The CH_3CO- shows absorption at δ 1.3-1.63 (two T, 3H). The $C-CH_2O$ shows absorption at δ 4.0-4.34 (two Q, 2H), the vinyl proton at δ 6.03 and δ 6.14 (two S, 1H), and the aromatic protons at δ 7.27-7.78 ppm. (M, 10H). The dicyanomethyl proton again did not show up.

Anal. Calcd. for $C_{25}H_{18}N_4O$: C, 76.9; H, 4.6; N, 14.4. Found: C, 76.9; H, 4.6; N, 14.4.

4-(2-Amino-1,3,3-tricyanoallylidene)-2,6-diphenyl-4H-pyran (**16**).

A mixture of 3.6 g. of 4-methoxy-2,6-diphenylpyrylium perchlorate, 2 g. of malononitrile dimer, 3 ml. of diisopropylethylamine, and 25 ml. of alcohol was refluxed for 6 hours, chilled and the solid was crystallized from ethoxyethanol, giving 3 g. of **16**, m.p. 310-311°. The λ max ($\epsilon \times 10^{-3}$) are 225 (17.2), ~292 (18.6), 315 (21.3), and 398 $m\mu$ (24.2). The nmr spectrum shows absorption for the vinyl proton on the 3- (or 5-) position at δ 6.96 (S, 1H), for the other vinyl proton at δ 7.08 (S, 1H), and for the aromatic protons at δ 7.45-8.06 ppm. (M, 10H).

Anal. Calcd. for $C_{23}H_{14}N_4O$: C, 76.2; H, 3.9; N, 15.5. Found: C, 76.3; H, 4.2; N, 15.7.

2-Amino-3-benzoyl-5-phenyl-4-piperidinobenzonitrile (**18**).

(a) A mixture of 5.2 g. of 4-methoxy-2,6-diphenylpyrylium perchlorate (**17**), 2.6 g. of malononitrile dimer and 20 ml. of piperidine was refluxed for 15 minutes, diluted with aqueous methyl alcohol, and the solid was crystallized from alcohol, giving 1.5 g. of **18**, m.p. 196-197°.

(b) The procedure described in (a) was repeated using 2.5 g. of malononitrile instead of the dimer. The yield of product was 3.2 g., m.p. 195-197°.

(c) A solution of 2 g. of **19**, 0.5 g. of malononitrile, 1 ml. of diisopropylethylamine and 20 ml. of alcohol was refluxed for 0.5 hour, cooled and the solid worked up as described in (a) to give 1.1 g. of **18**.

The λ max ($\epsilon \times 10^{-3}$) are 250 (28.4) and 362 $m\mu$ (7.2). The nmr in deuteriochloroform shows absorption at δ 0.83-1.33 (M, 6H) and δ 2.76-3.07 (M, 4H) for the piperidine protons, at δ 5.8 (broad S, 2H) for $-NH_2$, at δ 6.38 (S, 1H) for the proton in the 5-position, and δ 7.25-7.86 ppm. (M, 10H) for the aromatic protons.

Anal. Calcd. for $C_{25}H_{23}N_3O$: C, 78.7; H, 6.1; N, 11.0. Found: C, 78.5; H, 6.2; N, 11.0.

2,6-Diphenyl-4-piperidinopyrylium Perchlorate (**19**).

To a solution of 6.8 g. of 4-methoxy-2,6-diphenylpyrylium perchlorate (**17**) in 60 ml. of hot (about 60°) acetonitrile was added 4 ml. of piperidine. The mixture was stirred for ten minutes, and the solid was collected and washed with acetonitrile. The yield of **19** was 7 g., m.p. 298-300° (reported (8) m.p. 294-295°).

The λ max ($\epsilon \times 10^{-3}$) are 258 (16.7) and 316 $m\mu$ (36.6).

Anal. Calcd. for $C_{22}H_{22}ClNO_5$: C, 63.5; H, 5.3; N, 3.4. Found: C, 63.2; H, 5.4; N, 3.3.

5-Amino-2,8-diphenylpyrano[4,3,2-*de*][1,6]naphthyridine (**20**).

A solution of 2 g. of **14** in 5 ml. of 80% sulfuric acid was heated on a steam bath for 1 hour, poured into dilute ammonium hydroxide, and the solid was crystallized from butyl alcohol, yielding 1.6 g. of **20**, m.p. 256-258°. The λ max ($\epsilon \times 10^{-3}$) are 235 (32.1), 266 (65.2), \sim 285 (45.4), and 415 m μ (9.3). The nmr spectrum shows absorption for the proton in the 1-position at δ 6.26 (S, 1H), for protons in the 6- and 9-positions at δ 7.13 (S, 1H) and δ 7.17 (S, 1H), and for the aromatic protons at δ 7.3-8.3 ppm. (M, 10H).

Anal. Calcd. for C₂₂H₁₅N₃O: C, 78.3; H, 4.5; N, 12.5. Found: C, 78.4; H, 4.6; N, 12.3.

5-Benzamido-2,8-diphenylpyrano[4,3,2-*de*][1,6]naphthyridine (**21**).

A mixture of 0.5 g. of **20**, 1 ml. of benzoyl chloride and 15 ml. of pyridine was heated for 0.5 hour on a steam bath, diluted with water, and the solid was crystallized from butyl alcohol; yield 0.3 g., m.p. 249-250°. The λ max ($\epsilon \times 10^{-3}$) are 260 (52.4), 292 (53.2), and 395 m μ (10.2).

Anal. Calcd. for C₂₉H₁₉N₃O₂: C, 78.9; H, 4.3; N, 9.5. Found: C, 79.0; H, 4.1; N, 9.3.

5-Chloro-6-cyano-2,8-diphenylpyrano[4,3,2-*de*][1,6]naphthyridine (**22**).

Sodium nitrite (1.2 g.) in 5 ml. of water was added to a solution of 1 g. of **14** in 50 ml. of acetic acid and 10 ml. of hydrochloric acid, and the mixture was stirred for 2 hours. The solid was crystallized from *N*-methylpyrrolidone; yield 0.6 g., m.p. 342-344°. The λ max (ϵ not given because of incomplete solubility) are 232, \sim 250, 287, 375, 392, and 414 m μ .

Anal. Calcd. for C₂₃H₁₂ClN₃O: C, 72.4; H, 3.2; Cl, 9.3. Found: C, 72.9; H, 3.2; Cl, 9.0.

5-(2-Hydroxyphenyl)-3-phenylpyrazole (**23**).

(a) A mixture of 2.7 g. of **1** and 10 ml. of hydrazine hydrate was heated on a steam bath for 2 hours and then diluted with water and acetic acid. The solid was dissolved in hot methyl alcohol, a trace of insoluble material was removed by filtration, and the filtrate was evaporated to dryness. The residue was crystallized from ligroin (b.p. 100-115°), giving 0.8 g. of **23**, m.p. 142-143°.

(b) Procedure (a) was repeated using 0.5 g. of **4** and 5 ml. of

hydrazine hydrate; 0.2 g. of **23** was obtained.

The reported m.p. for **23** was 144° (5) and a sample prepared by the published procedure showed its absorption which was identical with those of the samples described above.

The λ max ($\epsilon \times 10^{-3}$) are 209 (50.8), 255 (34.7), 292 (9.88), and 305 m μ (8.98).

5-(2-Hydroxyphenyl)-1,3-diphenylpyrazole (**24**).

Procedure (a), described for the preparation of **23**, was used except that phenylhydrazine replaced hydrazine hydrate. The product was crystallized from ligroin (b.p. 100-115°), yielding 1.2 g. of **24**, m.p. 166-167°. The λ max ($\epsilon \times 10^{-3}$) are 250 (21.9), 256 (21.8), and 272 m μ (24.2).

Anal. Calcd. for C₂₁H₁₆N₂O: C, 80.7; H, 5.2; N, 9.0. Found: C, 80.3; H, 5.2; N, 9.4.

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- (7) The nmr spectra were measured at 60 MHz on a Varian A-60 spectrometer in dimethylsulfoxide-d₆ with tetramethylsilane as an internal standard. The mass spectra of all compounds were determined and are consistent with the proposed structures, but the results are reported only for a few significant examples. The electronic spectra were determined in acetonitrile unless noted otherwise.
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