

## Reactions of 4-Methoxyppyrylium Salts with Secondary Amines

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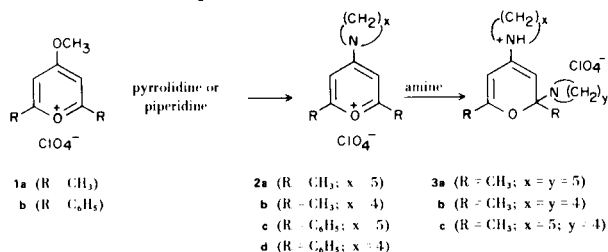
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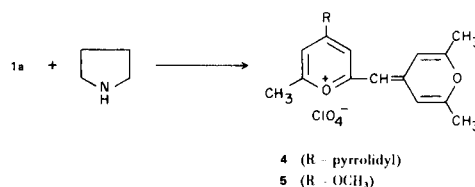
4-Aminopyrylium derivatives were prepared from secondary amines and 4-methoxy-2,6-dimethylpyrylium perchlorate (**1a**) and the corresponding 2,6-diphenyl derivative. Excess amine or elevated temperature resulted in the addition of two equivalents of amine to **1a**. The reactions of the aminopyrylium salts with hydroxide, ammonia, primary amines, hydrazines, cyanoacetamides, ethyl cyanoacetate, malononitrile, nitromethane, sodium sulfide, and a Grignard reagent are described.

The methoxy group of 4-methoxy-2,6-dimethylpyrylium perchlorate (**1a**) is displaced by nucleophiles such as active methylene compounds (1) and primary and secondary amines (2). We have investigated some reactions of **1a** and the corresponding 2,6-diphenyl derivative **1b** with secondary amines, and the present paper describes the products that are formed and certain transformations of these products.

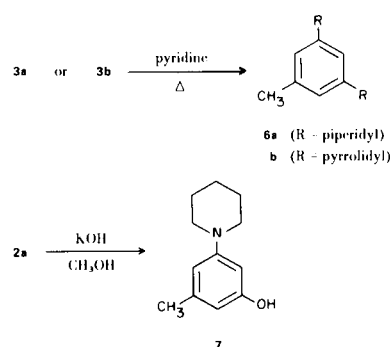
As previously reported (2), the methoxy group of **1a** is easily displaced by secondary amines to give the aminopyrylium derivatives **2a** and **2b**. We have found that excess amine or elevated temperature results in the formation of the bis-adducts **3a** and **3b**. Although **1b** gave the aminopyrylium salts **2c** and **2d**, the bis-adducts corresponding to **3a** and **3b** were not obtained with **1b**. It was also found that **2a** reacts with pyrrolidine to give the mixed bis-adduct **3c**. The nmr spectra for the bis-adducts **3a-3c**, which show absorption at  $\delta$  1.35 ppm (characteristic of  $-\dot{C}-CH_3$ ), are consistent with the assigned structures and not with the open-chain isomers.



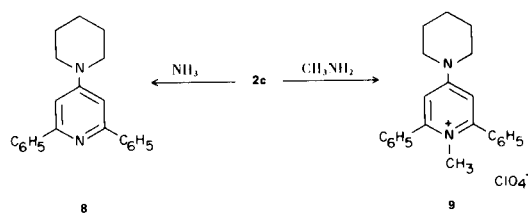
In one experiment using molecular equivalents of **1a** and pyrrolidine, a small amount of the dye **4** was isolated and was assigned the structure given because its electronic spectrum was similar to that of the known 4-methoxy analog **5**, which has been prepared from **1a** and sodium acetate (2).



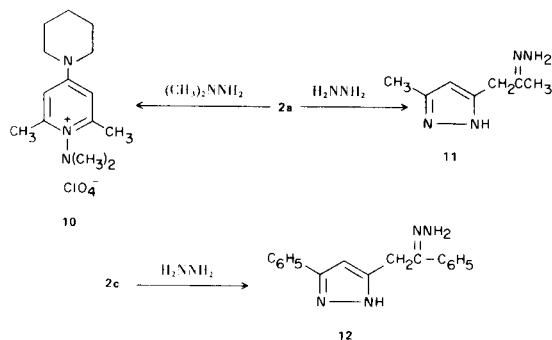
Heating a solution of **3a** or **3b** in pyridine results in the formation of the *m*-diaminobenzene derivatives **6a** and **6b**, respectively. The phenol **7** results from the action of methanolic potassium hydroxide on **2a**.



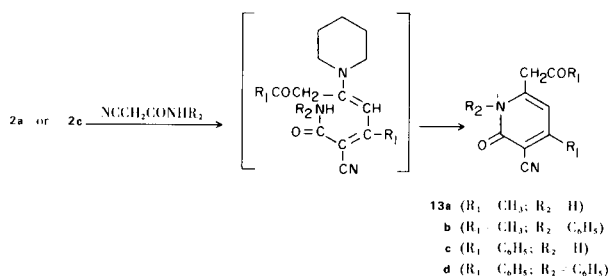
The piperidylpyrylium salt **2c** reacts with ammonia and primary amines to give the corresponding pyridine **8** and pyridinium salt **9**, as previously reported for **2a** (2). However, in the case of **2c**, the reactions had to be carried out in an autoclave at elevated temperatures.



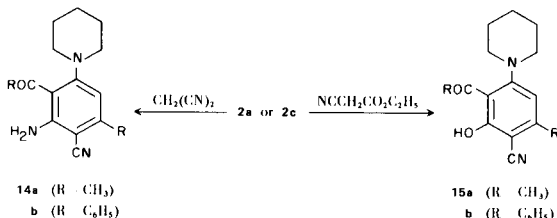
The reaction of **2a** with *N,N*-dimethylhydrazine takes a normal course to give *N*-dimethylamino-4-piperidino-2,6-dimethylpyridinium perchlorate (**10**), but with hydrazine, the pyrazole **11** is obtained and is identical with a sample prepared from 2,6-dimethyl-4-pyrone and hydrazine (3). The reaction of **2c** with hydrazine also gives the pyrazole derivative (**12**) which had been prepared previously from 2,6-diphenyl-4-pyrone and hydrazine (3).



Cyanoacetamide and cyanoacetanilide react with **2a** and **2c** under basic conditions to give the pyridones **13a-13c**, presumably by way of an intermediate which undergoes cyclization by the loss of the elements of piperidine.

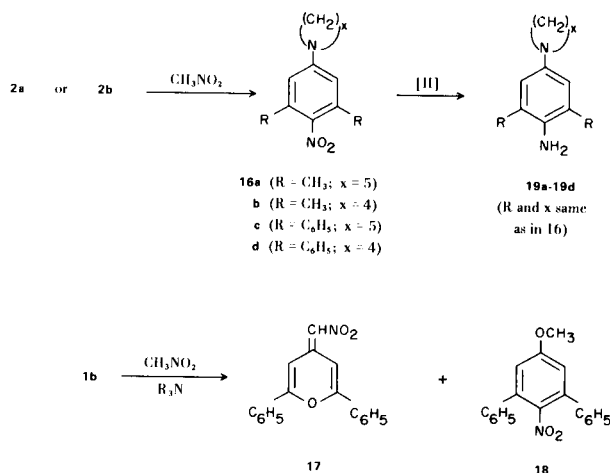


In contrast to the results obtained with the cyanoacetamides, **2a** and **2c** react with malononitrile and ethyl cyanoacetate with retention of the piperidyl moiety to give **14a**, **14b**, **15a**, and **15b**. The latter reactions are comparable to those of 2,4,6-trialkyl and triarylpyrylium salts with ethyl cyanoacetate and malononitrile (4).

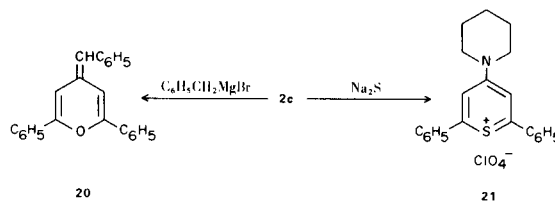


It is interesting to note that **2a-2d** react with nitromethane in the presence of a tertiary amine to give the substituted nitroaniline derivatives **16a-16d**; that 4-

methoxy-2,6-dimethylpyrylium perchlorate (**1a**) also gives the corresponding methoxy nitrobenzene derivative (4); but 4-methoxy-2,6-diphenylpyrylium perchlorate **1b** gives approximately equal amounts of 4-nitromethylene-2,6-diphenyl-4*H*-pyran **17** and the nitrobenzene derivative (**18**). The nitro compounds **16a-16d** have been catalytically reduced to the diamines **19a-19d**.



Benzylmagnesium bromide and **2c** give the pyran derivative **20**, and **2c** reacts with sodium sulfide to yield the corresponding thiapyrylium salt **21**.



## EXPERIMENTAL

The following compounds were prepared by published procedures: 4-methoxy-2,6-dimethylpyrylium perchlorate (**1a**) (2); 4-methoxy-2,6-diphenylpyrylium perchlorate (**1b**) (5); and 2,6-dimethyl-4-piperidylpyrylium perchlorate (**2a**) (2).

2,6-Dimethyl-4-pyrrolidylpyrylium Perchlorate (**2b**).

A mixture of 10 g. of **1a**, 3.4 ml. of pyrrolidine and 100 ml. of ethyl alcohol was stirred for 20 minutes, heated to boiling and chilled. The solid was collected and recrystallized from isopropyl alcohol to give 7 g. of **2b**, m.p. 157-158°. Compound **2b** shows absorption in acetonitrile,  $\lambda_{\text{max}}$  ( $\epsilon \times 10^{-3}$ ) at 225 (5.3), 282 (10.4), and 330  $\mu$  (14.5).

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_{16}\text{ClNO}_5$ : C, 47.6; H, 5.8; N, 5.0. Found: C, 47.7; H, 5.5; N, 5.0.

A run was made as described above except that the pyrrolidine was added to a boiling mixture of **1a** and alcohol; a lower yield (5 g.) of **2b** was obtained. In addition to this product, 2 g. of **3b** and 0.6 g. of **4**, m.p. 272-273° (from acetonitrile), were isolated. Product **4** shows absorption in acetonitrile,  $\lambda_{\text{max}}$  ( $\epsilon \times 10^{-3}$ ), at 254 (16.8), 294 (9.4), 425 (48.0), and 448  $\mu$  (46.5).

*Anal.* Calcd. for  $C_{18}H_{22}ClNO_6$ : C, 56.3; H, 5.8; N, 3.7. Found: C, 55.9; H, 5.7; N, 3.8.

#### 2,6-Diphenyl-4-piperidylpyrylium Perchlorate (2c).

To a solution of 6.8 g. of **1b** in 60 ml. of hot (about 60°) acetonitrile was added 4 ml. of piperidine. The solid was collected and washed with acetonitrile. The yield was 7 g. of product, m.p. 298-300°. The  $\lambda$  max ( $\epsilon \times 10^{-3}$ ) in acetonitrile were 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.

#### 2,6-Diphenyl-4-pyrrolidylpyrylium Perchlorate (2d).

This compound was prepared by the method described for **2c**; the yield was 5.5 g. of product, m.p. 294-295°. The  $\lambda$  max ( $\epsilon \times 10^{-3}$ ) in acetonitrile were 257 (19.7) and 314  $m\mu$  (39.3).

*Anal.* Calcd. for  $C_{21}H_{20}ClNO_5$ : C, 62.8; H, 5.0; N, 3.5. Found: C, 62.5; H, 5.2; N, 3.4.

#### 1-(2,6-Dimethyl-2-piperidyl-2H-pyran-4-yl)piperidinium Perchlorate (3a).

A solution of 1 g. of **2a** in 3 ml. of piperidine was stirred 1 hour, diluted with alcohol, and the solid was collected and recrystallized from alcohol yielding 0.8 g. of **3a**, m.p. 190-191°.

An alternative method of synthesis consisted in heating 5 g. of **1a** and 25 ml. of piperidine for ½ hour on a steam bath.

The nmr spectrum (6) in dimethylsulfoxide  $d_6$  (DMSO) shows absorption for  $CH_3-C-$  at  $\delta$  1.35 (S, 3H); piperidine protons 1.68 (broad S, 12H) and  $\delta$  3.7 (broad S, 8H);  $CH_3C = \delta$  2.7 (S, 3H); proton in 3-position of pyran  $\delta$  4.57 (broad S, 1H); and proton in 5-position of pyran at  $\delta$  5.78 ppm (S, 1H). The proton at  $\delta$  4.57 ppm exchanges with deuterium oxide showing that a small amount of the ring-opened ketone is in equilibrium with **3a**. The protonated piperidinium ring is tentatively assigned to the 4-position of the pyran on the basis of the chemical shift of the proton in the 3-position.

*Anal.* Calcd. for  $C_{17}H_{29}ClN_2O_5$ : C, 54.2; H, 7.8; N, 7.4. Found: C, 54.4; H, 7.7; N, 7.7.

#### 1-(2,6-Dimethyl-2-pyrrolidyl-2H-pyran-4-yl)pyrrolidinium Perchlorate (3b).

This compound was prepared by the procedures used to prepare **3a** and melted at 218-219°. The  $\lambda$  max ( $\epsilon \times 10^{-3}$ ) in acetonitrile were 212 (4.7) and 329  $m\mu$  (49.2). The nmr spectrum in DMSO is similar to that of **3a**.

*Anal.* Calcd. for  $C_{15}H_{25}ClN_2O_5$ : C, 51.6; H, 7.2; N, 8.1. Found: C, 51.5; H, 6.9; N, 8.0.

#### 1-(2,6-Dimethyl-2-pyrrolidyl-2H-pyran-4-yl)piperidinium Perchlorate (3c).

A solution of **2a** in pyrrolidine was allowed to react in the manner described for the preparation of **3a** to give **3c**, m.p. 170-171°.

*Anal.* Calcd. for  $C_{16}H_{27}ClN_2O_5$ : C, 52.9; H, 7.5; N, 7.7. Found: C, 52.8; H, 7.5; N, 7.5.

#### 3,5-Dipiperidyltoluene (6a).

A mixture of 3 g. of **3a** and 10 ml. of pyridine was refluxed for ½ hour, diluted with water, and the solid was crystallized from ligroin (b.p. 100-115°) yielding 1.8 g. of **6a**, m.p. 45-46°.

An alternative procedure consisted in heating a mixture of 5 g. of **2a** and 20 ml. of piperidine at reflux for ½ hour and precipitating the product by adding water.

The  $\lambda$  max ( $\epsilon \times 10^{-3}$ ) of **6a** in acetonitrile were at 242 (28.0) and 300  $m\mu$  (2.5).

The nmr spectrum in DMSO shows the piperidine protons at  $\delta$  1.6 (M, 6H) and  $\delta$  3.1 (M, 4H),  $CH_3-$  at  $\delta$  2.26 (S, 3H), and the aromatic protons at  $\delta$  6.3 ppm (broad S, 3H). The aromatic protons slowly exchange with deuterium oxide; this exchange is analogous to that reported for triaminobenzene (7).

*Anal.* Calcd. for  $C_{17}H_{26}N_2$ : C, 79.0; H, 10.1; N, 10.9. Found: C, 79.3; H, 9.8; N, 10.9.

#### 3,5-Dipyrrolidyltoluene (6b).

Compound **6b** was prepared by the procedure described for **6a**; the product melted at 80-81° after recrystallization from ligroin (b.p. 100-115°).

The nmr spectrum in DMSO shows the pyrrolidine protons at 1.91 (M, 8H) and  $\delta$  3.27 (M, 8H),  $CH_3-$  at  $\delta$  2.25 (S, 3H), and the aromatic protons at  $\delta$  5.82 (S, 2H) and  $\delta$  5.62 ppm (S, 1H). The two protons at  $\delta$  5.82 ppm exchange with deuterium oxide.

*Anal.* Calcd. for  $C_{15}H_{22}N_2$ : C, 78.2; H, 9.6; N, 12.2. Found: C, 78.3; H, 9.5; N, 12.0.

#### 5-Piperidyl-3-cresol (7).

A mixture of 3 g. of **2a**, 5.6 g. of potassium hydroxide and 75 ml. of methyl alcohol was refluxed for 1 hour, diluted with water, extracted with ether, and the aqueous phase was neutralized to pH 6 with hydrochloric acid. The solid was collected and crystallized from *n*-hexane yielding 1 g. of **7**, m.p. 89-90°.

The  $\lambda$  max ( $\epsilon \times 10^{-3}$ ) in acetonitrile was at 217 (2.28), 257 (1.1), and 287  $m\mu$  (0.244).

*Anal.* Calcd. for  $C_{12}H_{17}NO$ : C, 75.4; H, 9.0; N, 7.3. Found: C, 75.8; H, 9.0; N, 7.4.

#### 2,6-Diphenyl-4-piperidylpyridine (8).

A mixture of 5 g. of **2c**, 40 ml. of concentrated ammonium hydroxide and 40 ml. of acetonitrile was heated at 120° in an autoclave for 5 hours, and after cooling, the solid was separated and crystallized from acetonitrile giving 3.5 g. of **8**, m.p. 197-198°.

The  $\lambda$  max ( $\epsilon \times 10^{-3}$ ) in acetonitrile was 262  $m\mu$  (41.0).

*Anal.* Calcd. for  $C_{22}H_{22}N_2$ : C, 84.0; H, 7.1; N, 8.9. Found: C, 83.9; H, 7.3; N, 9.0.

#### 1-Methyl-2,6-diphenyl-4-piperidylpyridinium Perchlorate (9).

The procedure described for the preparation of **8** was employed except that 40% aqueous methylamine was substituted for ammonium hydroxide. The product melted at 279-280° after crystallization from acetonitrile and showed absorption in acetonitrile at 248 (19.0) and 298  $m\mu$  (23.5).

*Anal.* Calcd. for  $C_{23}H_{25}ClN_2O_4$ : C, 64.4; H, 5.9; N, 6.5. Found: C, 64.3; H, 6.1; N, 6.4.

#### 1-Dimethylamino-2,6-dimethyl-4-piperidylpyridinium Perchlorate (10).

A mixture of 1 g. of **2a**, 2 ml. of *N,N*-dimethylhydrazine and 4 ml. of alcohol was refluxed for 10 minutes, cooled, and the solid was collected and crystallized from alcohol, yielding 0.7 g. of **10**, m.p. 180-181°.

*Anal.* Calcd. for  $C_{14}H_{24}ClN_3O_4$ : C, 50.4; H, 7.2; N, 12.6. Found: C, 50.2; H, 6.9; N, 12.9.

#### 5-Acetyl-3-methylpyrazole Hydrazone (11).

A mixture of 2 g. of **2a** and 2 ml. of hydrazine hydrate was refluxed for ½ hour and evaporated to dryness. The product was an oil, as previously reported (3). The hydrazone was reduced

to 3-methyl-5- $\beta$ -aminopropylpyrazole which, in turn, was converted to the dihydrochloride, m.p. 184-185° (reported (3), m.p. 185°).

### 3-Phenyl-5-phenacylpyrazole Hydrazone (12).

A mixture of 2 g. of **2c**, 3 ml. of hydrazine hydrate and 10 ml. of alcohol was refluxed 1 hour, cooled and the solid was collected and crystallized from butyl alcohol, yielding 1.1 g. of **12**, m.p. 177-178° (reported (3), m.p. 178°).

*Anal.* Calcd. for  $C_{17}H_{16}N_4$ : C, 73.9; H, 5.8; N, 20.3. Found: C, 73.7; H, 6.1; N, 20.2.

### 6-Acetyl-3-cyano-4-methyl-2-pyridone (13a).

A mixture of 3 g. of **2a**, 2 g. of cyanoacetamide, 5 ml. of 10% methanolic potassium hydroxide and 15 ml. of acetonitrile was refluxed 1 hour, cooled, diluted with water and neutralized with acetic acid. The solid was removed by filtration and crystallized from acetonitrile yielding 1 g. of **13a**, m.p. 243-244°.

The  $\lambda$  max ( $\epsilon \times 10^{-3}$ ) in acetonitrile were 212 (19.8), 335 (10.3) and 410  $m\mu$  (4.1).

The nmr spectrum in DMSO showed absorption for  $CH_3$ - at  $\delta$  1.28 (S, 3H),  $COCH_3$  at  $\delta$  1.37 (S, 3H),  $COCH_2$  at  $\delta$  2.25 (S, 2H) and proton in 5-position at  $\delta$  3.68 ppm (S, 1H).

*Anal.* Calcd. for  $C_{10}H_{10}N_2O_2$ : C, 63.1; H, 5.3; N, 14.7. Found: C, 62.9; H, 5.2; N, 15.0.

### 6-Acetyl-3-cyano-4-methyl-1-phenyl-2-pyridone (13b).

This compound was prepared by the procedure described for **13a** using cyanoacetanilide; the yield of **13b** was 2 g., m.p. 216-217° (from alcohol).

The  $\lambda$  max ( $\epsilon \times 10^{-3}$ ) in acetonitrile were 210 (29.7) and 337  $m\mu$  (15.0).

*Anal.* Calcd. for  $C_{16}H_{14}N_2O_2$ : C, 72.2; H, 5.3; N, 10.5. Found: C, 71.9; H, 5.5; N, 10.6.

### 3-Cyano-6-phenacyl-4-phenyl-2-pyridone (13c).

This compound was prepared by the procedure described for **13a** using **2c**; the yield was 2.9 g. of **13c**, 224-225° (from alcohol). The product showed infrared and ultraviolet absorption curves which were identical with those of a sample prepared by another method (8).

### 3-Cyano-6-phenacyl-1,4-diphenyl-2-pyridone (13d).

Compound **13d** was prepared by the procedure described for **13a** using **2c** and cyanoacetanilide. The yield was 3 g., m.p. 179-180° and the absorption in acetonitrile was 243 (29.0), 278 (12.0), 352 (10.0), and 468  $m\mu$  (3.7).

The nmr spectrum in deuteriochloroform shows  $COCH_2$   $\delta$  4.12 (S, 2H), proton at 5-position  $\delta$  6.39 (S, 1H), and aromatic protons  $\delta$  7.2-7.8 ppm (M, 15H).

*Anal.* Calcd. for  $C_{26}H_{18}N_2O_2$ : C, 80.0; H, 4.7; N, 7.2. Found: C, 80.1; H, 4.8; N, 7.2.

### 2'-Amino-3'-cyano-4'-methyl-6'-piperidinoacetophenone (14a).

A mixture of 3 g. of **2a**, 3.4 g. of potassium *t*-butoxide, 2 g. of malononitrile and 25 ml. of *t*-butyl alcohol was refluxed 1 hour, cooled and neutralized to about pH 6 with dilute hydrochloric acid. Recrystallization of the solid from ligroin (b.p. 100-115°) afforded 1.9 g. of **14a**, m.p. 125-126°;  $\lambda$  max ( $\epsilon \times 10^{-3}$ ) in acetonitrile were 260 (19.3) and 362  $m\mu$  (7.7).

*Anal.* Calcd. for  $C_{15}H_{18}N_2O_2$ : C, 69.7; H, 7.0; N, 10.8. Found: C, 69.4; H, 7.1; N, 10.5.

### 2-Amino-3-cyano-4-phenyl-6-piperidylbenzophenone (14b).

This compound was prepared in 82% yield from **2c** and malono-

nitrile by the procedure described for the preparation of **14a**. The m.p. of **14b** was 189-190° (from butyl alcohol) and  $\lambda$  max ( $\epsilon \times 10^{-3}$ ) in acetonitrile were 250 (28.4) and 362  $m\mu$  (7.2).

*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.

### 3'-Cyano-2'-hydroxy-4'-methyl-5'-piperidylacetophenone (15a).

Compound **15a** was prepared in 45% yield by the procedure described for **14a** but using ethyl cyanoacetate rather than malononitrile. The m.p. of **15a** was 123-124° (from alcohol), and  $\lambda$  max ( $\epsilon \times 10^{-3}$ ) in acetonitrile were 270 (20.3) and 375  $m\mu$  (6.4).

*Anal.* Calcd. for  $C_{15}H_{18}N_2O_2$ : C, 69.7; H, 7.0; N, 10.8. Found: C, 69.4; H, 7.1; N, 10.5.

### 3-Cyano-2-hydroxy-4-phenyl-5-piperidylbenzophenone (15b).

The compound was prepared in 98% yield from **2c** and ethyl cyanoacetate by the procedure described for **14a**. The m.p. of **15b** was 224-225°.

*Anal.* Calcd. for  $C_{25}H_{22}N_2O_2$ : C, 78.5; H, 5.8; N, 7.3. Found: C, 78.4; H, 5.8; N, 7.1.

### 2,6-Dimethyl-4-piperidylnitrobenzene (16a).

A mixture of 2 g. of **2a**, 3 ml. of *N,N*-di-isopropylethylamine and 25 ml. of nitromethane was refluxed for 4 hours and evaporated to dryness. Crystallization of the residue from alcohol provided 1.5 g. of **16a**, m.p. 84-85°;  $\lambda$  max ( $\epsilon \times 10^{-3}$ ) in acetonitrile were 245 (2.78),  $\sim$  295 (8.3) and 385  $m\mu$  (1.68).

*Anal.* Calcd. for  $C_{13}H_{18}N_2O_2$ : C, 66.6; H, 7.7; N, 12.0. Found: C, 66.5; H, 7.8; N, 12.0.

In a similar manner, the following nitrobenzene derivatives were prepared from **2b-2d**.

### 2,6-Dimethyl-4-pyrrolidylnitrobenzene (16b).

M.p. 85-86° (from alcohol); yield 88%.

*Anal.* Calcd. for  $C_{12}H_{16}N_2O_2$ : C, 65.4; H, 7.3; N, 12.7. Found: C, 65.6; H, 7.5; N, 12.4.

### 2,6-Diphenyl-4-piperidylnitrobenzene (16c).

M.p. 188-189° (from nitromethane); yield 91%;  $\lambda$  max ( $\epsilon \times 10^{-3}$ ) in acetonitrile were 230 (35.6), 268 (12.1), and 400  $m\mu$  (4.16).

*Anal.* Calcd. for  $C_{23}H_{22}N_2O_2$ : C, 77.1; H, 6.2; N, 7.8. Found: C, 76.8; H, 6.2; N, 7.5.

### 2,6-Diphenyl-4-pyrrolidylnitrobenzene (16d).

M.p. 191-192° (from alcohol); yield 92%.

*Anal.* Calcd. for  $C_{22}H_{20}N_2O_2$ : C, 76.7; H, 5.9; N, 8.1. Found: C, 76.6; H, 6.1; N, 7.9.

### 4-(Nitromethylene)-2,6-diphenyl-4H-pyran (17).

A mixture of 3 g. of **1b**, 2 ml. of *N,N*-di-isopropylethylamine and 10 ml. of nitromethane was heated on a steam bath for 2 hours, evaporated to dryness, and the residue was recrystallized from alcohol yielding 1.1 g. of **17**, m.p. 169-170°. The filtrate was concentrated and the solid that separated was recrystallized from alcohol giving 0.8 g. of 4-methoxy-2,6-diphenylnitrobenzene (**18**), m.p. 121-122°.

The  $\lambda$  max ( $\epsilon \times 10^{-3}$ ) in acetonitrile for **17** were 235 (18.2), 247 (14.8), 325 (13.5), 415  $m\mu$  (29.3), and for **18** they were 226 (36.4), 320 (2.72), 415 (4.08), and 435  $m\mu$  (3.4).

Compound **17** showed a parent peak at 291 and **18** at 305 in the mass spectrometer.

*Anal.* Calcd. for **17** as  $C_{18}H_{13}NO_3$ : C, 74.2; H, 4.5; N, 4.8. Found: C, 73.9; H, 4.8; N, 4.8.

*Anal.* Calcd. for **18** as  $C_{19}H_{15}NO_3$ : C, 74.7; H, 5.0; N, 4.6. Found: C, 74.4; H, 4.8; N, 4.7.

#### 4-Piperidyl-2,6-dimethylaniline (**19a**).

A solution of 5 g. of **16a** in 100 ml. of alcohol was reduced using Raney nickel catalyst at 50 psi. The filtered reaction mixture was evaporated to dryness and the residue was recrystallized from petroleum ether (b.p. 35-60°) giving 2.8 g. of **19a**, m.p. 88-89°.

*Anal.* Calcd. for  $C_{13}H_{20}N_2$ : C, 76.4; H, 9.9; N, 13.7. Found: C, 76.0; H, 9.8; N, 13.6.

In a similar manner, the following aniline derivatives were prepared from **16b-16d**.

#### 2,6-Dimethyl-4-pyrrolidylaniline (**19b**).

This was an oil which was not further characterized.

#### 2,6-Diphenyl-4-piperidylaniline (**19c**).

M.p. 88-89° (from ligroin, b.p. 63-75°); yield 81%;  $\lambda$  max ( $\epsilon \times 10^{-3}$ ) in acetonitrile, 231 (33.4) and 243  $m\mu$  (4.1).

*Anal.* Calcd. for  $C_{23}H_{24}N_2$ : C, 84.1; H, 7.4; N, 8.5. Found: C, 84.2; H, 7.1; N, 8.5.

#### 2,6-Diphenyl-4-pyrrolidylaniline (**19d**).

M.p. 110-111° (from ligroin, b.p. 63-75°); yield 61%;  $\lambda$  max ( $\epsilon \times 10^{-3}$ ) in acetonitrile, 234 (35.0) and 366  $m\mu$  (7.0).

#### 4-Benzylidene-2,6-diphenyl-4H-pyran (**20**).

The Grignard reagent from 1.2 g. of magnesium and 6.4 g. of benzyl chloride was stirred with 3 g. of **2c** for 2 hours, aqueous ammonium chloride was added, and the solid was collected and crystallized from butyl alcohol yielding 1.9 g. of **20**, m.p. 140-141° (reported m.p. 140° (9)).

The  $\lambda$  max ( $\epsilon \times 10^{-3}$ ) in acetonitrile were 246 (21.2), ~270 (18.0) and 355  $m\mu$  (28.3).

#### 2,6-Diphenyl-4-piperidinothiapyrylium Perchlorate (**21**).

A solution of 2 g. of sodium sulfide in 50 ml. of water was added to 4.1 g. of **2c** in 200 ml. of acetone. The mixture was stirred for 1 hour, 6 ml. of 70% perchloric acid in 100 ml. of water was added, and after 15 minutes of stirring, the mixture was diluted with 100 ml. of water. The solid was collected and crystallized from acetonitrile giving 2.9 g. of **21**, m.p. 279-280°.

The  $\lambda$  max ( $\epsilon \times 10^{-3}$ ) in acetonitrile were 248 (14.5) and 340  $m\mu$  (26.0).

*Anal.* Calcd. for  $C_{22}H_{22}ClNO_4S$ : C, 61.2; H, 5.1; S, 7.4. Found: C, 60.9; H, 5.0; S, 7.2.

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