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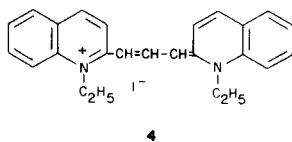
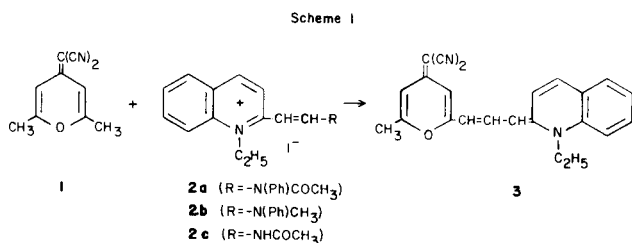
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Neutral dyes were prepared by reacting 1-ethyl-2[2-(*N*-methylanilino)vinyl]quinolinium iodide with 4-dicyanomethylene-2,6-dimethyl-4*H*-pyran and then condensing the resulting product with an aromatic aldehyde.

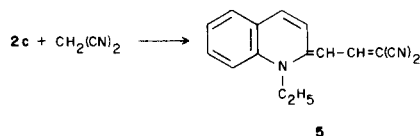
*J. Heterocyclic Chem.*, **17**, 1585 (1980).

We recently described a series of dyes derived from 4-dicyanomethylene-2,3-dimethyl-4*H*-pyran (**1**) (1). The published procedure (2) for preparing these dyes is not satisfactory due to low yields and purification problems. Since we required substantial amounts of certain of these dyes, we examined methods for their synthesis in more detail.

As an example, Brooker and Webster prepared **3** from **1** and **2a** in a refluxing mixture of pyridine, triethylamine, and acetic anhydride (2). We found that, under these conditions, pinacyanol (**4**) is also formed as a secondary product (15-20% of the product) and **3** is difficult to separate from **4**. Our best yields of **3** by this procedure under a variety of conditions were 40-50% after a tedious removal of the pinacyanol. We found that replacement of the

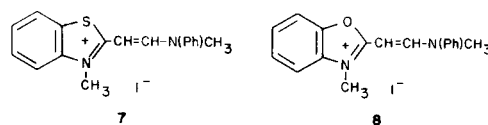


acetanilide group in **2a** by a methylanilino group (**2b**) resulted in the formation of **3** in 78% yield and no pinacyanol was present. Compound **2c** did not react with **1**, although it did give **5** with malononitrile.

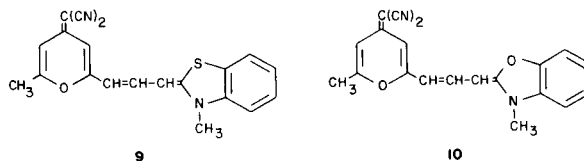


The preparation of **2b** from *N*-ethylquinaldinium iodide (**6**) and *N*-methylidiphenylformamidine in acetic anhydride has been described (3), but the compound was not

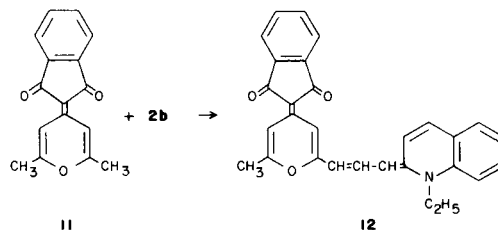
characterized and the yield was not given. We found that **2b** is conveniently prepared in 78% yield from **6**, *N*-methylaniline, and triethyl orthoformate. Several similar compounds (**7** and **8**) were prepared by this procedure.



Compounds **7** and **8** were allowed to react with **1** to give **9** and **10** in much higher yields than those obtained by the published procedure (2).



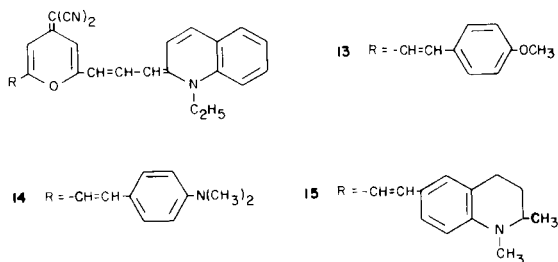
The pyran derivative **11** (4) and **2b** gave the dye **12** in good yield.



The methyl group in the 2-position of compound **3** readily condenses with aromatic aldehydes in pyridine with piperidine as a catalyst to give **13**, **14**, and **15**. The latter compounds are of interest as neutral dyes since they show absorption over most of the visible region of the spectrum.

Table I  
Physical Properties and Methods of Preparation

Compound	M.p. °C	Empirical Formula	Anal. C	Calcd. H	Found N	Yield %	Recrystallization Solvent	Method
<b>2b</b>	227-228	C <sub>20</sub> H <sub>21</sub> N <sub>2</sub> I	57.7 57.4	5.1 5.2	6.7 6.8	71	pyridine and methyl alcohol	I
<b>2c</b>	258-259 (5)							
<b>3</b>	284-285	C <sub>23</sub> H <sub>19</sub> N <sub>3</sub> O	78.2 77.9	5.4 5.5	11.9 11.9	78	pyridine and methyl alcohol	II
<b>5</b>	260-261	C <sub>16</sub> H <sub>13</sub> N <sub>3</sub>	77.7 77.4	5.3 5.6	17.0 17.4	83	pyridine and methyl alcohol	II
<b>7</b>	222-223	C <sub>17</sub> H <sub>17</sub> IN <sub>2</sub> S	50.0 49.9	4.2 4.1	6.9 6.9	77	methyl alcohol	I
<b>8</b>	228-230	C <sub>17</sub> H <sub>17</sub> OIN <sub>2</sub>	52.2 52.1	4.3 4.2	7.1 7.2	78	ethyl alcohol and water	I
<b>9</b>	271-272	C <sub>20</sub> H <sub>15</sub> N <sub>3</sub> OS	69.5 69.3	4.4 4.2	12.2 11.9	68	methyl alcohol	II
<b>10</b>	310-311	C <sub>20</sub> H <sub>15</sub> N <sub>3</sub> O	72.9 72.9	4.6 4.7	12.8 12.9	75	acetonitrile	II
<b>12</b>	203-204	C <sub>29</sub> H <sub>23</sub> NO <sub>3</sub>	80.3 80.2	5.3 4.9	3.2 3.2	50	pyridine and methyl alcohol	II
<b>13</b>	318-320	C <sub>31</sub> H <sub>25</sub> N <sub>3</sub> O <sub>2</sub>	79.0 78.9	5.3 5.1	8.9 9.1	68	pyridine and methyl alcohol	III
<b>14</b>	341-343	C <sub>32</sub> H <sub>28</sub> N <sub>4</sub> O	79.3 79.0	5.8 6.0	11.6 11.4	58	pyridine	III
<b>15</b>	282-283	C <sub>33</sub> H <sub>32</sub> N <sub>4</sub> O	79.6 79.3	6.0 6.1	11.2 11.2	76	pyridine	III



### EXPERIMENTAL

Compound **1** was prepared by the published procedure (5). The methods of preparation are described as general procedures for specific compounds, and other compounds that were prepared by these procedures are recorded in Table I.

Procedure I. 1-Ethyl-2[2-(*N*-methylanilino)vinyl]quinolinium Iodide (**2b**).

A mixture of 540 g. (1.181 moles) of 1-ethylquinolinium iodide, 396 ml. of *N*-methylaniline, 540 ml. of triethylorthoformate, and 2 l. of methoxyethanol was stirred at reflux for 2 hours. The solution was cooled, and the green solid was collected and slurried with 1.5 l. of refluxing acetone for

10 minutes. The solid was collected and washed with acetone.

Procedure II. 4-Dicyanomethylene-2-[3-(1-ethyl-1*H*-quinolin-2-ylidene)-1-propenyl]6-methyl-4*H*-pyran (**3**).

A mixture of 103.2 g. (0.6 mole) of **1**, 249.6 g. (0.6 mole) of **2b**, 1100 ml. of pyridine, and 240 ml. of triethylamine was stirred at reflux for 3 hours. The solution was cooled and diluted with 400 ml. of methyl alcohol, and the solid was collected and washed with 1 l. of methyl alcohol.

Procedure III. 4-Dicyanomethylene-2-[3-(1-ethyl-1*H*-quinolin-2-ylidene)-1-propenyl]6-(4-methoxystyryl)-4*H*-pyran (**14**).

A mixture of 3.5 g. (0.01 mole) of **3**, 2 ml. of anisaldehyde, 20 ml. of pyridine, and 25 ml. of piperidine was refluxed until the blue color had changed to black (~5 hours). The mixture was diluted with 30 ml. of methyl alcohol and the solid was collected.

### REFERENCES AND NOTES

- (1) J. A. Van Allan, F. G. Webster and G. A. Reynolds, U. S. Patent 4,145,215 (1979).
- (2) L. G. S. Brooker and F. B. Webster, U. S. Patent 2,965,486 (1960).
- (3) C. W. Johnson, British Patent 486,780 (1938).
- (4) J. Kelimen and R. Wizinger, *Helv. Chim. Acta*, **45**, 1980 (1962).
- (5) L. L. Woods, *J. Am. Chem. Soc.*, **80**, 1440 (1958).