

Preparation of Pyrylium Salts from 2-Phenyl-5*H*-phenaleno
[1,9-*bc*]pyran-5-one

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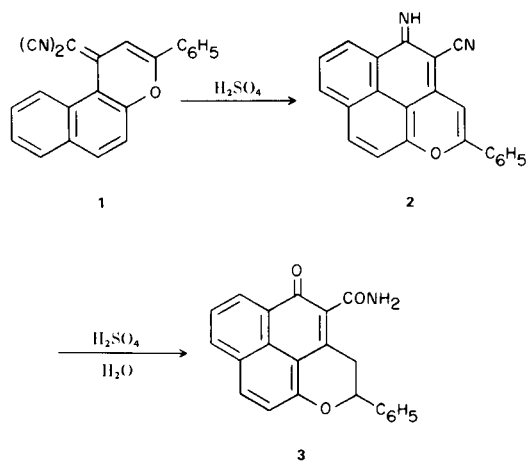
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The preparation of 2-phenyl-5*H*-phenaleno[1,9-*bc*]pyran-5-one (**7**) is described. Compound **7** undergoes reactions typical of pyrones and was therefore a useful intermediate for the preparation of pyrylium salts. Several pyrylium dyes were prepared from **7** and the long-wavelength absorptions of these dyes were compared with those of the corresponding flavylum dyes.

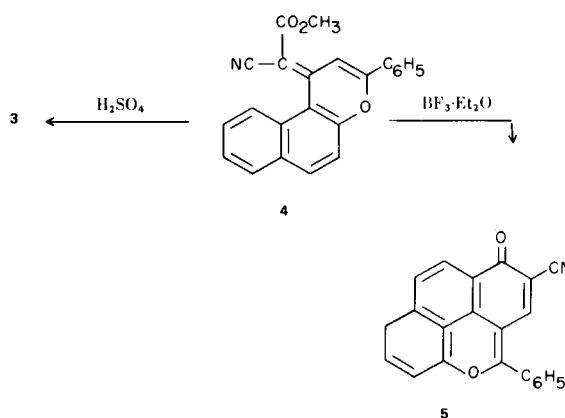
One class of compounds that is useful for preparing pyrylium salts, particularly pyrylium dyes, is the 4-pyrone derivatives (**1**). We thought it would be of interest to prepare a vinylogue of a 4-pyrone and determine the effect of increasing conjugation on the absorption spectra of the derived pyrylium salts. The present paper describes the preparation and reactions of the vinylogous 4-pyrone, compound **7**.

The work of Campaigne (**2**) suggested that **1** could serve as a convenient entry into the 6-pyrone series, and it was found that the dicyanomethylene derivative **1** cyclized in sulfuric acid at 25-30° to give the imino derivative **2**, which was in turn hydrolyzed to 4-carbamoyl-2-phenyl-5*H*-phenaleno[1,9-*bc*]pyran-5-one (**3**). Compound **3** could not be converted to pyrylium salts, and attempts to hydrolyze **3** to the acid were unsuccessful.



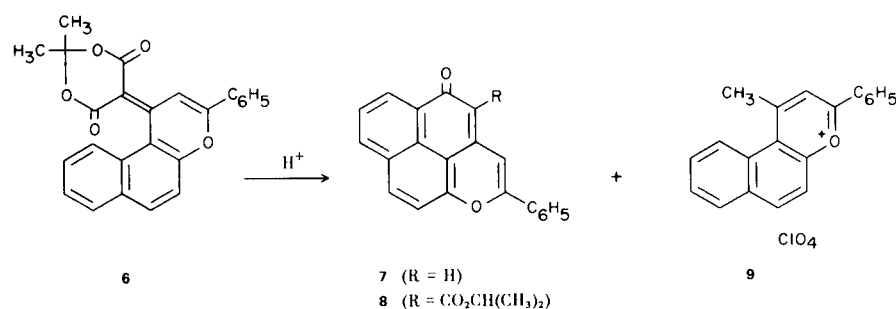
Since we thought that 2-phenyl-5*H*-phenaleno[1,9-*bc*]pyran-5-one (**7**) would form pyrylium salts, other routes to this compound were investigated. We found that the cyano ester **4** underwent cyclization through the ester group to

give **3** in the presence of sulfuric acid and the corresponding 4-cyano derivative (**5**) with boron trifluoride etherate.



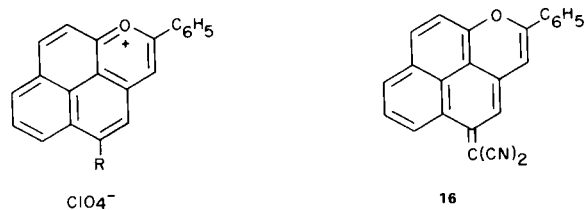
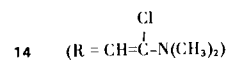
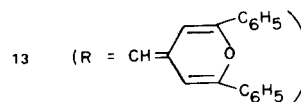
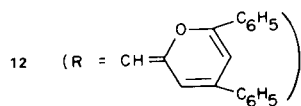
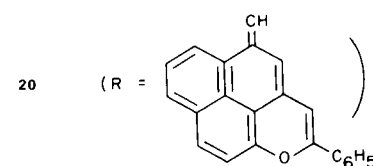
Since the ester group showed a greater tendency to cyclize than the cyano group, the bis-ester **6** was prepared and cyclized with sulfuric acid or preferably with trifluoroacetic acid to give **7** along with some of the ester **8** and a small amount of 1-methyl-3-phenyl-naphtho[2,1-*b*]pyrylium salt, which was isolated as the perchlorate (**9**). The latter compound was presumably formed by the acid catalyzed hydrolysis of **6** followed by decarboxylation.

In its chemical behavior, **7** acts as a typical pyrone as demonstrated by the following reactions. Oxygen methylation of **7** gave the methoxypyrylium salt **10**, which in turn reacted with butylamine to form **11**. Methylpyrylium salts reacted with **7** in acetic anhydride to give cyanine-like dyes such as **12** and **13**. With *N,N*-dimethylacetamide in the presence of phosphorus oxychloride, **7** gave the Vilsmeier adduct **14**, which was hydrolyzed to **15**. Attempts to prepare 5-methyl-2-phenylphenaleno[1,9-*bd*]pyrylium perchlorate (**18**) via **7** and methylmagnesium bromide gave a product that we have not identified. However, **7** reacted with malononitrile in acetic anhydride



to give the dicyanomethylene compound **16**, which was hydrolyzed with sulfuric acid to give **17** (after conversion to the perchlorate salt). The latter underwent decarboxylation to form **18** on recrystallization from benzonitrile. 4-Dimethylaminobenzaldehyde reacted with **18** in acetic anhydride to give the styryl dye **19**. The symmetrical dye **20** was prepared from **10** and **18**. The pyrylium salts that were prepared from **7** are listed in Chart I.

CHART I

10 (R = OCH₃)11 (R = NHC₆H₅)15 (R = CH₂CON(CH₃)₂)17 (R = CH₂CO₂H)18 (R = CH₃)19 (R = CH=CHC₆H₄-(4)-N(CH₃)₂)

The long-wavelength absorptions of the dyes derived from **7** are compared with those of the corresponding flavylium dyes **21-24** in Table I. It is seen that the additional conjugation gives rise to about a 135-m μ bathochromic shift for the cyanine-like dyes and 50 m μ for the styryl dye. The dye **20** was of interest, not only because it absorbed 295 m μ toward the red in comparison with the flavylium dye, but also because the long-wavelength absorption was extremely broad (from about 600 to 1100 m μ). Attempts to prepare higher methylene homologs of **20** were unsuccessful. The dyes prepared from **7**, in particular **20**, are very insoluble in most organic solvents, and the extinction coefficients are not reported for samples which obviously were not completely dissolved.

The dyes derived from **7** provide useful pyrylium salt sensitizers for organic photoconductive compositions as described previously (3).

EXPERIMENTAL (4)

1-Dicyanomethylene-3-phenyl-1H-naphtho[2,1-b]pyran (**1**).

A mixture of 6 g. of 5,6-benzoflavone, 4 g. of malononitrile and 20 ml. of phosphorus oxychloride was heated on a steam bath for 4 hours, cooled, and the solid was collected and crystallized from pyridine giving 5 g. of **1**, m.p. 270-271°. The λ max $\epsilon \times 10^{-3}$ are 241 (40.5), 286 (11.2), 359 (23.0) and 400 m μ (17.4).

Anal. Calcd. for C₂₂H₁₂N₂O: C, 82.5; H, 3.8; N, 8.8. Found: C, 82.6; H, 3.6; N, 9.0.

4-Cyano-2-phenyl-5-imino-5H-phenaleno[1,9-bc]pyran (**2**).

A solution of 2 g. of **1** in 5 ml. of sulfuric acid was allowed to stand overnight, poured into ice water, the solid was stirred with dilute ammonium hydroxide and crystallized from dimethylformamide, yielding bright red crystals of **2**, 1.1 g., m.p. 224-225°.

Anal. Calcd. for C₂₂H₁₂N₂O: C, 82.5; H, 3.8; N, 8.8. Found: C, 82.1; H, 3.7; N, 8.8.

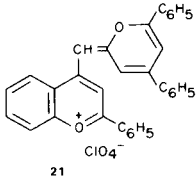
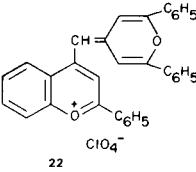
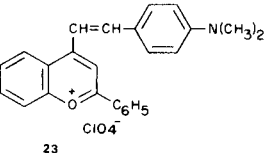
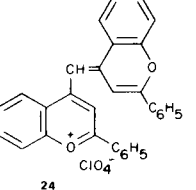
4-Carbamoyl-2-phenyl-5H-phenaleno[1,9-bc]pyran-5-one (**3**).

(A) A mixture of 1 g. of **2** and 15 ml. of 50% aqueous sulfuric acid was refluxed for 3 hours and poured into water. The solid was crystallized from dimethylformamide, yielding 0.3 g. of bright yellow **3**, m.p. 278-280°.

Anal. Calcd. for C₂₂H₁₃NO₃: C, 77.9; H, 3.9; N, 4.1. Found: C, 77.6; H, 3.9; N, 4.0.

(B) A solution of 4.3 g. of **4** in 10 ml. of sulfuric acid was

Table I
Comparison of λ max in Acetonitrile

| Dye | λ max ($\epsilon \times 10^{-3}$) | Dye | λ max ($\epsilon \times 10^{-3}$) |
|-----|---|---|---|
| 12 | 740 (74.0) |  | 602 (66.0) |
| 13 | 695 (58) |  | 570 (105) |
| 19 | 720 (—) |  | 670 (80.0) |
| 20 | 895 (—) |  | 600 (67.8) |

heated on a steam bath for 2 hours, poured into water, and the solid was crystallized from dimethylformamide, yielding 3 g. of **3**, m.p. 279-280° (ir identical with that of the product obtained by method A).

1-Cyanomethoxycarbonylmethylene-3-phenyl-1*H*-naphtho[2,1-*b*]pyran (**4**).

A solution of 4 g. of 1-methoxy-3-phenyl-naphtho[2,1-*b*]pyrylium perchlorate (prepared from 5,6-benzoflavone and methyl sulfate, m.p. 240-241°), 3 ml. of methyl cyanoacetate, 4 ml. of diisopropylethylamine and 30 ml. of acetonitrile was heated on a steam bath for 2 hours, chilled, and the solid was crystallized from acetonitrile, giving 3.5 g. of **4**, m.p. 191-192°. The λ max ($\epsilon \times 10^{-3}$) are 235 (41.7), 353 (21.1) and 398 $m\mu$ (17.3).

Anal. Calcd. for $C_{23}H_{15}NO_3$: C, 78.2; H, 4.3; N, 4.0. Found: C, 77.9; H, 4.4; N, 4.1.

4-Cyano-2-phenyl-5*H*-phenaleno[1,9-*bd*]pyran-5-one (**5**).

A mixture of 1.5 g. of **4** and 10 ml. of borontrifluoride etherate was heated on a steam bath for 3 hours. The solid was collected, washed with alcohol, and crystallized from a large amount of acetonitrile, giving 0.9 g. of **5**, m.p. 314-315°.

A sample of **5** was hydrolyzed to the amide **3** by heating with

80% sulfuric acid.

Anal. Calcd. for $C_{22}H_{11}NO_2$: C, 82.2; H, 3.5; N, 4.4. Found: C, 81.9; H, 3.6; N, 4.3.

1-(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-3-phenyl-4*H*-naphtho[2,1-*b*]pyran (**6**).

A mixture of 2.6 g. of 1-methoxy-3-phenyl-naphtho[2,1-*b*]pyrylium perchlorate, 1.2 g. of 2,2-dimethyl-4,6-dioxo-1,3-dioxan, 2 ml. of diisopropylethylamine and 15 ml. of acetonitrile was refluxed for 3 hours, and after chilling, the red solid was collected and crystallized from dimethylformamide, giving 2.5 g. of **6**, m.p. 224-225°. The λ max ($\epsilon \times 10^{-3}$) are 212 (22.0), 235 (19.0), 295 (11.6), 383 (21.2), and 430 $m\mu$ (15.7).

Anal. Calcd. for $C_{25}H_{18}O_5$: C, 75.4; H, 4.6. Found: C, 75.0; H, 4.7.

2-Phenyl-5*H*-phenaleno[1,9-*bc*]pyran-5-one (**7**).

(A) A mixture of 25 g. of **6** and 75 ml. of trifluoroacetic acid was heated on a steam bath for 24 hours, cooled, and 20 ml. of 70% perchloric acid was added. The 5-hydroxy-2-phenylphenaleno[1,9-*bc*]pyrylium perchlorate which precipitated was collected and crystallized from formic acid; m.p. 319-320°; yield 20 g. The pyrylium salt was dissolved in 100 ml. of boiling pyridine, and on

chilling, 14.2 g. of **7** separated, m.p. 231-232°. The λ max ($\epsilon \times 10^{-3}$) are 266 (35.2), ~240 (21.8), 352 (24.0), ~407 (14.1), 425 (16.5), and ~445 m μ (10.9).

Anal. Calcd. for C₂₁H₁₂O₂: C, 85.1; H, 4.1. Found: C, 84.8; H, 4.3.

(b) A mixture of 5 g. of **6** and 10 ml. of sulfuric acid was heated on a steam bath for 2 hours and poured into water. The solid that separated was a mixture of 5-hydroxy-2-phenylphenaleno[1,9-*bd*]pyrylium bisulfate and 4-isopropoxycarbonyl-2-phenyl-5*H*-phenaleno[1,9-*bd*]pyran-5-one (**8**).

4-Isopropoxycarbonyl-2-phenyl-5*H*-phenaleno[1,9-*bd*]pyran-5-one (**8**).

The crude product isolated from the method B for the preparation of **7** was crystallized from *N*-methylpyrrolidone, giving 1.1 g. of **8**, m.p. 277-278°.

Anal. Calcd. for C₂₅H₁₈O₄: C, 78.5; H, 4.7. Found: C, 78.7; H, 4.3.

1-Methyl-3-phenylnaphtho[2,1-*b*]pyrylium Perchlorate (**9**).

The formic acid filtrate from procedure A for the preparation of **7** was diluted with ether, and the solid was crystallized from acetonitrile, giving 3 g. of **9**, m.p. 254-255°. The ir absorption **9** was identical with that of a sample of **9** that was prepared from 5,6-benzoflavone and methylmagnesium bromide.

Anal. Calcd. for C₂₀H₁₅ClO₅: C, 64.8; H, 4.1; Cl, 9.6. Found: C, 64.4; H, 4.4; Cl, 9.5.

5-Methoxy-2-phenylphenaleno[1,9-*bc*]pyrylium Perchlorate (**10**).

A mixture of 3.3 g. of **7** and 20 ml. of dimethyl sulfate was heated on a steam bath for 4 hours, cooled, diluted with ether and the solid was collected and dissolved in hot alcohol. Addition of 3 ml. of 70% perchloric acid produced 3.8 g. of **10**, m.p. 283-285°.

Anal. Calcd. for C₂₂H₁₅ClO₆: C, 64.3; H, 3.7; Cl, 8.6. Found: C, 64.0; H, 3.8; Cl, 8.9.

5-Butylamino-2-phenylphenaleno[1,9-*bc*]pyrylium Perchlorate (**11**).

A mixture of 2 g. of **10**, 0.5 ml. of butylamine and 25 ml. of acetonitrile was heated on a steam bath for 15 minutes, and the solid was crystallized from acetonitrile, giving 1.9 g. of **11**, m.p. 319-320°. The λ max ($\epsilon \times 10^{-3}$) are 232 (18.6), 274 (38.5), 393 (33.1), 447 (28.1), and 471 m μ (30.0).

Anal. Calcd. for C₂₅H₂₂ClNO₅: C, 66.4; H, 4.9; N, 3.1. Found: C, 66.7; H, 5.2; N, 3.0.

2-Phenyl-5-[(2,4-diphenyl-6*H*-pyran-6-ylidene)methyl]phenaleno[1,9-*bc*]pyrylium Perchlorate (**12**).

A mixture of 1 g. of **7**, 0.9 g. of 2-methyl-4,6-diphenylpyrylium perchlorate, 0.5 ml. of pyridine and 25 ml. of acetic anhydride was refluxed 0.5 hour, chilled, and the solid was crystallized from acetic anhydride, yielding 0.6 g. of **12**, m.p. 289-290°. The λ max ($\epsilon \times 10^{-3}$) are 258 (45.5), 278 (42.0), 340 (27.0), 448 (35.0), 675 (46.0), and 740 m μ (74.0).

Anal. Calcd. for C₃₉H₂₅ClO₆: C, 74.9; H, 4.0; Cl, 5.7. Found: C, 74.9; H, 4.2; Cl, 5.6.

2-Phenyl-5-[(2,6-diphenyl-4*H*-pyran-4-ylidene)methyl]phenaleno[1,9-*bc*]pyrylium Perchlorate (**13**).

The procedure described for the preparation of **12** was followed using 4-methyl-2,6-diphenylpyrylium perchlorate to give 0.7 g. of **13**, m.p. 329-330° (from acetonitrile). The λ max ($\epsilon \times 10^{-3}$) are 258 (46.3); ~270 (40.0), 338 (16.0), 380 (19.0), 452 (38.3), and 695 m μ (58.0).

Anal. Calcd. for C₃₉H₂₅ClO₆: C, 74.9; H, 4.0; Cl, 5.7. Found: C, 74.7; H, 3.8; Cl, 6.0.

2-Phenyl-5-(2-chloro-2-dimethylaminovinyl)phenaleno[1,9-*bc*]pyrylium Perchlorate (**14**).

A mixture of 2 g. of **7**, 2 g. of *N,N*-dimethylacetamide and 5 ml. of phosphorus oxychloride was heated on a steam bath for 1 hour, cooled, diluted with ether, and the solid was dissolved in methyl alcohol. The solution was mixed with 2 ml. of 70% perchloric acid and the solid that formed was crystallized from a mixture of dimethylformamide and methyl alcohol, giving 2.5 g. of **14**, m.p. 258-259°.

Anal. Calcd. for C₂₅H₁₉Cl₂NO₅: C, 62.0; H, 4.0; Cl, 14.6. Found: C, 61.6; H, 3.7; Cl, 14.7.

2-Phenyl-5-(*N,N*-dimethylcarbamoylmethyl)phenaleno[1,9-*bc*]pyrylium Perchlorate (**15**).

A mixture of 0.5 g. of **14** and 10 ml. of 90% pyridine-water was boiled for 10 minutes, diluted with methyl alcohol, and the solid was crystallized from dimethylformamide, yielding 0.3 g. of **15**, m.p. 319-320°.

Anal. Calcd. for C₂₅H₂₀ClNO₆: C, 64.4; H, 4.3; N, 3.0. Found: C, 64.4; H, 4.6; N, 2.9.

5-Dicyanomethylene-2-phenyl-5*H*-phenaleno[1,9-*bc*]pyran (**16**).

A mixture of 5 g. of **7**, 3 g. of malononitrile and 60 ml. of acetic anhydride was refluxed for 1 hour, chilled and the solid was collected and crystallized from *N*-methylpyrrolidone, giving 5.4 g. of **16**, m.p. 297-298°. The λ max ($\epsilon \times 10^{-3}$) in dimethylformamide are ~305 (28.4), 395 (24.4), ~510 (18.2), 542 (29.4), and 585 m μ (27.4).

Anal. Calcd. for C₂₄H₁₂N₂O: C, 83.7; H, 3.5; N, 8.1. Found: C, 83.7; H, 3.8; N, 8.4.

5-Carboxymethyl-2-phenylphenaleno[1,9-*bc*]pyrylium Perchlorate (**17**).

A solution of 5 g. of **16** in 10 ml. of 70% aqueous sulfuric acid was heated on a steam bath for 2 hours and then refluxed for 10 minutes. After cooling, 2 ml. of 70% perchloric acid was added and the solid was collected, m.p. 235-238°.

Anal. Calcd. for C₂₃H₁₅ClO₇: C, 63.0; H, 3.4; Cl, 8.1. Found: C, 63.4; H, 3.3; Cl, 8.0.

5-Methyl-2-phenylphenaleno[1,9-*bc*]pyrylium Perchlorate (**18**).

A solution of 1 g. of **17** in 7 ml. of benzonitrile was boiled for 10 minutes, cooled, and the solid was crystallized from a mixture of formic acid and acetic acid, yielding 0.7 g. of **18**, m.p. 288-289°.

Anal. Calcd. for C₂₂H₁₅ClO₅: C, 66.9; H, 3.8; Cl, 9.0. Found: C, 66.8; H, 3.7; Cl, 8.8.

5-(4-Dimethylaminostyryl)-2-phenylphenaleno[1,9-*bc*]pyrylium Perchlorate (**19**).

A mixture of 0.4 g. of **18**, 0.3 g. of dimethylaminobenzaldehyde and 12 ml. of acetic anhydride was refluxed for 15 minutes, cooled and the solid was crystallized by extracting in a Soxhlet extractor with acetonitrile for 3 days. The yield of **19** was 0.35 g., m.p. 290-291°.

The insolubility of the dye precluded the determination of accurate extinction coefficients, but it was found that the λ max are 460 and 720 m μ .

Anal. Calcd. for C₃₁H₂₄ClNO₅: C, 70.8; H, 4.6; N, 2.7. Found: C, 71.3; H, 4.5; N, 2.4.

2-Phenyl-5-[(2-phenyl-5-phenaleno[1,9-*bc*]pyranylidene)methyl]-phenaleno[1,9-*bc*]pyrylium Perchlorate (**20**).

A solution of 0.5 g. of **10** and 0.5 g. of **18** in 150 ml. of acetic anhydride was heated to boiling and 0.1 g. of sodium acetate was added. The heating was continued for 5 minutes and after cooling, the solid was collected and washed with water; yield 0.7 g. and m.p. 300-301°. The λ max (ϵ not given because of dye insolubility) are 265, ~350, 468, ~730, 790, and 895 m μ .

Anal. Calcd. for C₄₃H₂₅ClO₆: C, 76.7; H, 3.7; Cl, 5.3. Found: C, 76.2; H, 3.8; Cl, 5.1.

4-[(4,6-Diphenyl-2*H*-pyran-2-ylidene)methyl]flavylium Perchlorate (**21**).

A mixture of 3 g. of flavylium perchlorate, 3.5 g. of 2-methyl-4,6-diphenylpyrylium perchlorate, 4 ml. of pyridine, and 100 ml. of acetic acid was refluxed for 4 hours, cooled, and the solid was crystallized from acetonitrile giving 2.8 g. of **21**, m.p. 280-281°. The λ max ($\epsilon \times 10^{-3}$) are 243 (30.8), 357 (54.7), ~570 (46.0), and 602 m μ (66.3).

Anal. Calcd. for C₃₃H₂₃ClO₆: C, 71.9; H, 4.2; Cl, 6.4. Found: C, 71.6; H, 4.4; Cl, 6.2.

4-[(2,6-Diphenyl-4*H*-pyran-4-ylidene)methyl]flavylium Perchlorate (**22**).

A mixture of 3 g. of flavone, 3.5 g. of 4-methyl-2,6-diphenylpyrylium perchlorate and 50 ml. of acetic anhydride was refluxed for 1 hour, cooled, and the solid was crystallized from acetonitrile giving 4 g. of **22**, m.p. 294-295°. The λ max ($\epsilon \times 10^{-3}$) are 238 (28.1), 267 (26.7), 383 (26.0), and 570 m μ (105).

Anal. Calcd. for C₃₃H₂₃ClO₆: C, 71.9; H, 4.2; Cl, 6.4. Found: C, 71.7; H, 4.2; Cl, 6.4.

4-(4-Dimethylaminostyryl)flavylium Perchlorate (**23**).

Compound **23** was prepared as described previously (5); m.p. 259-260° from acetonitrile (reported m.p. 243°). The λ max

($\epsilon \times 10^{-3}$) are 360 (15.0), 400 (8.0), and 670 m μ (75.0).

Anal. Calcd. for C₂₅H₂₂ClNO₅: C, 66.4; H, 4.9; N, 3.1. Found: C, 66.6; H, 5.1; N, 3.0.

4-[(2-Phenyl-4*H*-benzo[*b*]pyran-4-ylidene)methyl]flavylium Perchlorate (**24**).

A mixture of 6.2 g. of flavylium perchlorate, 1 g. of malonic acid, 1.5 g. of sodium acetate and 100 ml. of acetic acid was refluxed for 15 minutes, cooled, and crystallized from acetic acid yielding 2.9 g. of **24**, m.p. 257-258°. The λ max ($\epsilon \times 10^{-3}$) are 241 (29.4), ~261 (21.9), 352 (20.4), 388 (27.4), and 600 m μ (67.8).

Anal. Calcd. for C₃₁H₂₁ClO₆: C, 70.9; H, 4.0; Cl, 6.8. Found: C, 70.7; H, 4.1; Cl, 6.7.

Acknowledgment.

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- (4) The electronic absorption spectra were measured in acetonitrile except for one sample, which has been indicated. The mass spectra for all compounds that are not perchlorates have been determined, and they gave parent ions and fragmentations consistent with the assigned structures.
- (5) R. Wizinger and A. Luthiger, *Helv. Chim. Acta.* **36**, 526 (1953).