

Preparation of Bis-Pyrylium Salts

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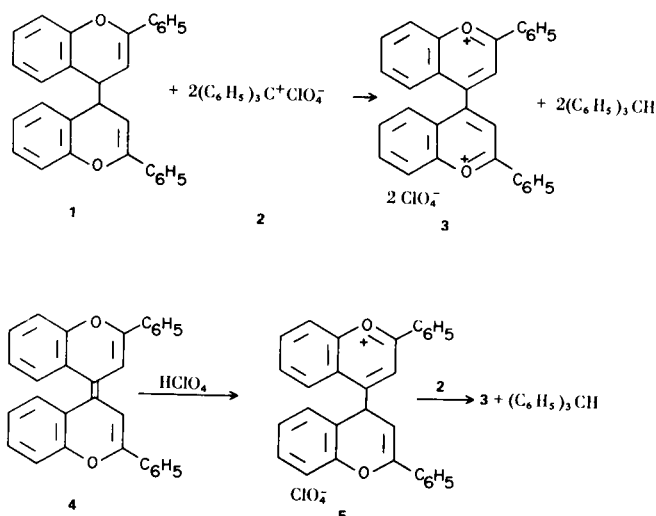
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Six methods are described for the preparation of bis-pyrylium salts: (1) treatment of 4,4'-bi-2-flavene or 4-(4*H*-flav-2-en-4-yl)flavylium perchlorate with triphenylmethyl perchlorate; (2) reaction of an aromatic *o*-hydroxyaldehyde and 1,4-diacetylbenzene under acidic conditions; (3) reaction of *o*-hydroxyacetophenone, 1,4-diacetylbenzene, perchloric acid and acetic acid; (4) reaction of a 2- or 4-methylpyrylium salt with 2- or 4-pyrone in the presence of phosphorus oxychloride; (5) oxidation of a 1,2-ethanediylidenebis-flavene or -thiaflavene, a bis-flavenylidene or -thiaflavenylidene, and a bis-pyranylidene or -thiapyranylidene by means of cupric perchlorate; and (6) reaction of 4-methylflavylium and -thiaflavylium perchlorate with bromine in acetic acid.

In connection with another program we required some bis-pyrylium salts, preferably of the flavylium type, in which the heterorings are conjugated through the 2- or 4-positions. Only a few examples of bis-pyrylium salts have been reported (1); the present paper describes several new methods for the synthesis of this type of compound. The first three methods are extensions of procedures which have been used to prepare monoprylium salts, but the last three methods are novel.

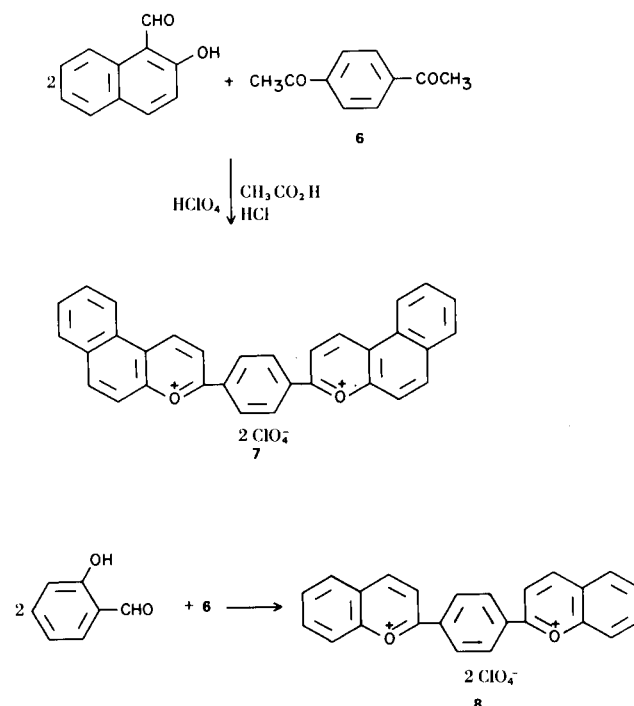
Method I.

The dimer (1), which is readily prepared from flavylium perchlorate (2), was converted to 4,4'-biflavylium bisperchlorate (3) by means of triphenylmethyl perchlorate (2). Compound 3 has also been prepared from the flavylium salt (5) in a similar manner. These reactions are new examples of the use of 2 as a hydride abstracting agent (3).



Method II.

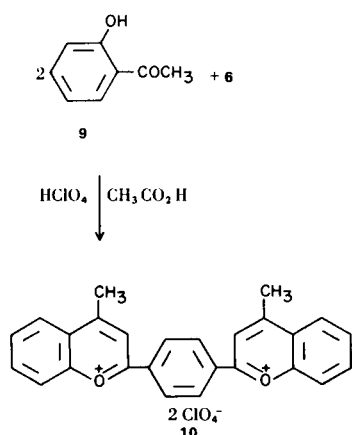
A procedure which is frequently used to prepare flavylium salts involves the condensation of an *o*-hydroxy aromatic aldehyde with acetophenone under acidic conditions (4). We have used this method to prepare the bis-pyrylium salts (7 and 8) by employing the diketone (6) instead of acetophenone.



Method III.

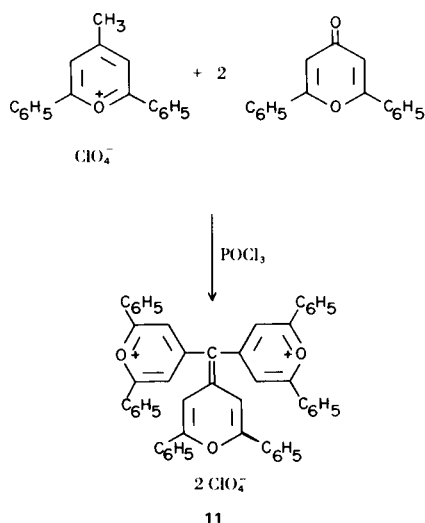
Probably the best method for the preparation of 4-methylflavylium perchlorate consists of the reaction of *o*-hydroxyacetophenone (9) with acetophenone in the

presence of acetic acid and perchloric acid (5). We have carried out a similar reaction with **9** and the diketone (**6**), and the bis-flavylium salt (**10**) was obtained in satisfactory yield.



Method IV.

The preparation of the complex cyanine-like dye (**11**) has been reported (6). Since this compound is a bis-pyrylium salt, this method is included in the present paper.

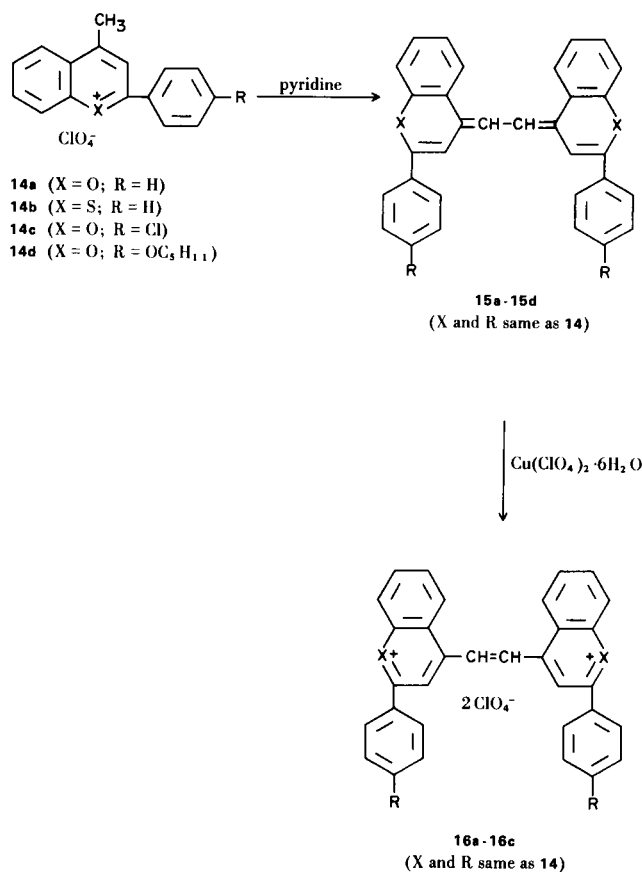


The reaction was also successful with 2-methyl-4,6-diphenylpyrylium perchlorate and 2,6-diphenyl-4-pyrone, yielding 4,4'-(2,4-diphenylpyran-6-ylidene)methylenebis(2,6-diphenylpyrylium perchlorate) (**12**), and with 4,6-diphenyl-2-pyrone and 2-methyl-4,6-diphenylpyrylium perchlorate to give 2,2'-(2,4-diphenylpyran-6-ylidene)methylenebis(4,6-diphenylpyrylium perchlorate) (**13**). When flavone or 4-methylflavylium perchlorate was used in this reaction, the simple pyrylium cyanine-like dyes

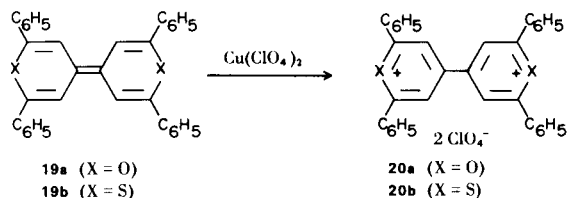
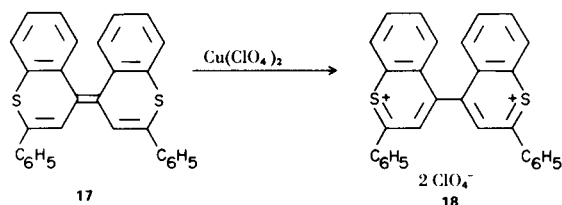
derived from one equivalent of each of the reactants were obtained.

Method V.

We have given a preliminary account of the preparation of bis-flavylium salts which were obtained from 4,4'-(1,2-ethanediyldene)bis(4*H*-flavene) (**15a**) (7). This reaction sequence has been extended to other similar compounds, and the compounds which were prepared in this manner are shown below. Difficulty was experienced when 4'-alkoxy flavylium salts were treated with pyridine: for example, **15d** was obtained in poor yield, and the corresponding methoxy derivative could not be purified. The oxidation of **15d** was not attempted because of insufficient starting material.



The cupric perchlorate oxidation procedure has also been used to prepare 4,4'-biflavylium bisperchlorate (**3**) from $\Delta^{4,4'}$ -bi-2-flavene (**4**), and other examples of this type are given below.



Method VI.

In an attempt to brominate 4-methylflavylium perchlorate (**14a**) with bromine in acetic acid, the major product was the bis-flavylium salt (**16a**). The same results were obtained with the thia-analog (**14b**). The mechanism of this reaction has not been established. When 4-methyl-2,6-diphenylpyrylium perchlorate or 2-methyl-4,6-diphenylpyrylium perchlorate was substituted for **14a** or **14b** in this reaction, the normal side-chain bromination products were obtained.

EXPERIMENTAL

Method I.

4,4'-Biflavylium bisperchlorate (**3**).

A mixture of 4.3 g. (0.01 mole) of 4,4'-bi-2-flavene (**1**), 6.8 g. of triphenylmethyl perchlorate and 100 ml. of acetic acid was heated on a steam bath for 3 hours, cooled, and the resulting solid was collected and stirred at room temperature with 75 ml. of acetone. Recrystallization of the insoluble material from acetonitrile afforded 1.1 g. of **3**, m.p. 288° (explodes).

Anal. Calcd. for $C_{30}H_{20}Cl_2O_{10}$: C, 58.9; H, 3.3; Cl, 11.6. Found: C, 58.8; H, 3.3; Cl, 11.4.

A similar procedure for the preparation of **3** consisted in heating a mixture of 1.03 g. of $\Delta^{4,4'}$ -bi-2-flavene (**4**), 0.8 g. of triphenylmethyl perchlorate, 0.5 ml. of 70% perchloric acid, and 10 ml. of acetic acid on a steam bath for 2 hours and working up the reaction mixture as described above to give 0.4 g. of **3**.

Method II.

1,4-Phenylenebis-2-naphtho[2,1-b]pyrylium perchlorate (**7**).

Hydrogen chloride was passed through a solution of 8.6 g. of 2-hydroxy-1-naphthaldehyde, 4 g. of 1,4-diacetylbenzene (**6**), and 8 ml. of 70% perchloric acid in 100 ml. of acetic acid for 2 hours, and after standing overnight the mixture was filtered and the solid was recrystallized from formic acid to yield 11 g. of **7**, m.p. 310° (explodes).

Anal. Calcd. for $C_{32}H_{20}Cl_2O_{10}$: C, 60.5; H, 3.2; Cl, 11.2. Found: C, 60.4; H, 3.3; Cl, 11.1.

1,4-Phenylenebis(2-benzo[b]pyrylium perchlorate) (**8**).

A mixture of 6.1 g. of salicylaldehyde, 4 g. of **6**, 8 ml. of 70% perchloric acid, and 100 ml. of acetic acid was allowed to react by the procedure described for the preparation of **7** to give 1.1 g. of **8**, m.p. 282° (explodes) after recrystallization from formic acid; λ max (acetonitrile) ($\epsilon \times 10^{-3}$) 255 (18.8), ~280 (8.0), 395 μ (20.0).

Anal. Calcd. for $C_{24}H_{16}Cl_2O_{10}$: C, 53.8; H, 3.0; Cl, 13.2. Found: C, 53.8; H, 3.3; Cl, 12.9.

Method III.

1,4-Phenylenebis(4-methyl-2-benzo[b]pyrylium perchlorate) (**10**).

A mixture of 8 g. of **6**, 14 g. of *o*-hydroxyacetophenone, 35 ml. of 70% perchloric acid and 200 ml. of acetic acid was refluxed for 6 hours, cooled, and the solid was collected and crystallized from formic acid to give 4 g. of **10**, m.p. 270° (explodes); λ max (acetonitrile) ($\epsilon \times 10^{-3}$) 248 (25.0), 292 (27.2), 325 (14.0), 365 μ (15.0).

Anal. Calcd. for $C_{26}H_{20}Cl_2O_{10}$: C, 55.4; H, 3.6; Cl, 12.6. Found: C, 55.3; H, 3.8; Cl, 12.3.

Method IV.

4,4'-(2,4-Diphenylpyran-6-ylidenemethylene)bis(2,6-diphenylpyrylium perchlorate) (**12**).

A mixture of 2.5 g. of 2,6-diphenyl-4-pyrone, 1.7 g. of 2-methyl-4,6-diphenylpyrylium perchlorate and 25 ml. of phosphorus oxychloride was heated on a steam bath for 2 hours, and the excess phosphorus oxychloride was removed *in vacuo*. To the residue was added 5 ml. of 70% perchloric acid and 100 ml. of methyl alcohol; the mixture was heated to boiling, chilled, and the solid was collected and recrystallized from acetonitrile to give 1.1 g. of **12**, m.p. 305° (explodes); λ max (acetonitrile) ($\epsilon \times 10^{-3}$) 239 (35.3), 268 (33.9), 361 (33.1) 585 μ (31.2).

Anal. Calcd. for $C_{52}H_{36}Cl_2O_{11}$: C, 68.8; H, 4.0; Cl, 7.8. Found: C, 69.1; H, 3.8; Cl, 7.5.

2,2'-(2,4-Diphenylpyran-6-ylidenemethylene)bis(4,6-diphenylpyrylium perchlorate) (**13**).

The procedure described for the preparation of **12** was repeated with 4,6-diphenyl-2-pyrone and 2-methyl-4,6-diphenylpyrylium perchlorate to give 1.3 g. of **13**, m.p. 330° (explodes); λ max (methylene chloride) ($\epsilon \times 10^{-3}$) 250 (26.6), 385 (27.0), 351 (66.0), 600 μ (41.5).

Anal. Calcd. for $C_{52}H_{36}Cl_2O_{11}$: C, 68.8; H, 4.0; Cl, 7.8. Found: C, 68.4; H, 4.0; Cl, 7.9.

Method V.

4,4'-(1,2-Ethanediyldene)bis(4H-flavene) (**15a**).

A mixture of 10 g. of 4-methylflavylium perchlorate and 25 ml. of pyridine was heated at reflux for 10 minutes, cooled, and the solid was collected by filtration and recrystallized from pyridine to give 3.3 g. (48%) of **15a**, m.p. 280-281°; the mass spectrum showed a parent peak at *m/e* 438 and a large peak at *m/e* 219.

Anal. Calcd. for $C_{32}H_{22}O_2$: C, 87.6; H, 5.1. Found: C, 87.4; H, 5.2.

To a solution of 1 g. of **15a** in 35 ml. of trifluoroacetic acid was added 1 ml. of 70% perchloric acid. The pale yellow 4,4'-(1,2-ethylene)bis(flavylium perchlorate) was collected and washed with ether; yield 1.4 g., m.p. 288° (explodes).

Anal. Calcd. for $C_{32}H_{24}Cl_2O_{10}$: C, 60.1; H, 3.8; Cl, 11.1. Found: C, 60.2; H, 3.9; Cl, 11.3.

The nmr spectrum of **15a** at 60 MHz in trifluoroacetic acid showed that **15a** had protonated to give 4,4'-(1,2-ethylene)bis-

(flavylium trifluoroacetate): absorption was at δ 2.63 (S) 4H, 6.13-7.16 ppm (M) 20H.

4,4'-(1,2-Ethanediyldene)bis(4*H*-thiaflavene) (**15b**).

This compound was prepared by the procedure described for the preparation of **15a** and was obtained in 49% yield, m.p. 278-279° (from dimethylformamide).

Anal. Calcd. for C₃₂H₂₂S₂: C, 81.7; H, 4.7; S, 13.6. Found: C, 82.0; H, 4.9; S, 13.5.

4,4'-(1,2-Ethanediyldene)bis(4'-chloro-4*H*-flavene) (**15c**).

This compound was obtained using the same procedure as for **15a** in 45% yield, m.p. 304-305° (from dimethylformamide).

Anal. Calcd. for C₃₂H₂₀Cl₂O₂: C, 75.7; H, 3.9; Cl, 14.0. Found: C, 75.5; H, 4.2; Cl, 13.8.

4,4'-(1,2-Ethanediyldene)bis(4'-amyloxy-4*H*-flavene) (**15d**).

This compound was obtained using the same procedure as above in 20% yield after three recrystallization from 1,2,3-trichloropropane, m.p. 235-237°.

Anal. Calcd. for C₄₂H₄₂O₄: C, 82.6; H, 6.9. Found: C, 82.8; H, 7.1.

4,4'-(1,2-Vinylene)bis(4-flavylium perchlorate) (**16a**).

A solution of 1.9 g. of cupric perchlorate hexahydrate in 10 ml. of acetonitrile was added to a stirred solution of 1.1 g. of **15a** in 100 ml. of benzonitrile. The reaction mixture immediately turned blue, but the color was rapidly discharged and a rouge solid separated. The solid was collected and washed thoroughly with acetonitrile followed by ether; yield 1.4 g., m.p. 275° (explodes).

Anal. Calcd. for C₃₂H₂₂Cl₂O₁₀: C, 60.3; H, 3.5; Cl, 11.1. Found: C, 60.2; H, 3.7; Cl, 10.9.

4,4'-(1,2-Vinylene)bis(4-thiaflavylium perchlorate) (**16b**).

This compound as prepared by the procedure described for **16a** and was obtained in 92% yield, m.p. 258° (explodes).

Anal. Calcd. for C₃₂H₂₂Cl₂O₈S₂: C, 57.4; H, 3.3; Cl, 10.6. Found: C, 57.4; H, 3.5; Cl, 10.4.

4,4'-(1,2-Vinylene)bis(4'-chloroflavylium perchlorate) (**16c**).

This compound was obtained in 96% yield using the same procedure as that for **16a**, m.p. 275° (explodes).

Anal. Calcd. for C₃₂H₂₀Cl₄O₁₀: C, 54.4; H, 2.9; Cl, 20.1. Found: C, 54.6; H, 3.1; Cl, 19.8.

4,4'-Biflavylium bisperchlorate (**3**).

A solution of 1.9 g. of cupric perchlorate hexahydrate in 50 ml. of acetonitrile was added to a stirred suspension of 1 g. of $\Delta^{4,4'}$ -bi-2-flavene (**4**) in 50 ml. of acetonitrile. The solid dissolved to give a deep red solution which rapidly faded to pale yellow. The solution was stirred for 0.5 hour, chilled, and the solid was collected and washed with water, alcohol, and ether to give 0.85 g. of **3** which was identical (m.p. and ir) with the material prepared by Method I.

Compounds **18**, **20a**, and **20b** were prepared by the procedure described for **3** above.

4,4'-Bithiaflavylium bisperchlorate (**18**).

This compound was obtained in 96% yield, m.p. 280° (explodes).

Anal. Calcd. for C₃₀H₂₀Cl₂O₈S₂: C, 56.1; H, 3.1; S, 10.0. Found: C, 56.4; H, 3.2; S, 9.9.

4,4'-Bi-2,6-diphenylpyrylium bisperchlorate (**20a**).

This compound was obtained in essentially quantitative yield, m.p. 290° (explodes).

Anal. Calcd. for C₃₄H₂₄Cl₂O₁₀: C, 61.6; H, 3.7; Cl, 10.7. Found: C, 61.3; H, 3.5; Cl, 10.5.

4,4'-Bi-2,6-diphenylthiapyrylium bisperchlorate (**20b**).

This compound was obtained in 91% yield, m.p. 310° (explodes).

Anal. Calcd. for C₃₄H₂₄Cl₂O₈S₂: C, 58.6; H, 3.5; S, 9.2. Found: C, 58.3; H, 3.8; S, 8.9.

Method VI.

4,4'-(1,2-Vinylene)bis(flavylium perchlorate) (**16a**).

A solution of 3.2 g. of 4-methylflavylium perchlorate, 1 ml. of bromine and 100 ml. of acetic acid was heated at reflux for 6 hours. An orange solid began to separate after about 0.5 hour, but a slow evolution of hydrogen bromide continued throughout the period of heating. The solid was collected, and the ir curve was shown to be identical with that of a sample prepared by Method V. The elemental analysis of the sample showed that bromine was present, but we believe that this is due to the presence of some of the bromide or perbromide salt of **16a**. The crude material was dissolved in 50 ml. of boiling formic acid, 0.5 ml. of 70% perchloric acid was added, the solution was chilled, and the solid (1.1 g.) was collected, m.p. 275° (explodes).

Anal. Calcd. for C₃₂H₂₂Cl₂O₁₀: C, 60.3; H, 3.5; Cl, 11.1. Found: C, 60.0; H, 3.4; Cl, 11.1.

4,4'-(1,2-Vinylene)bis(thiaflavylium perchlorate) (**16b**).

This compound was prepared as described above for **16a**. In this case the product was not contaminated by the bromide or perbromide salt. The yield was 1.5 g. and the elemental analysis and physical properties were identical with those of a sample prepared by Method V.

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