The Reactions of Pyranylidenemethylpyrylium Salts with Sodium Sulfide

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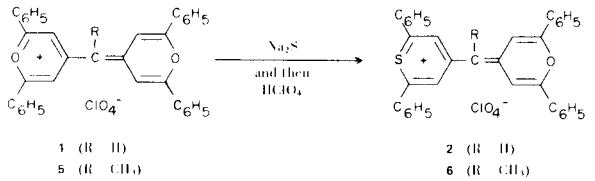
Symmetrical pyranylidenemethylpyrylium salts react with sodium sulfide to give, after acidification, pyranylidenemethylthiapyrylium salts. In the case of unsymmetrical salts in which the methylene group is joined at the 2-position of one ring and the 4-position of the other, the ortho oxygen atom is displaced by sulfur. An unsymmetrical dye which is substituted in the 2,6-positions of one ring with phenyl groups and with alkyl groups in the other ring gave a product which contained the sulfur atom in the aryl-substituted ring.

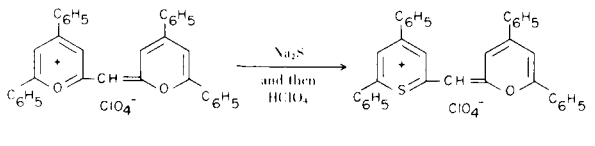
The most frequently used procedure for preparing thiapyrylium salts consists of the reaction between a pyrylium salt and sodium sulfide in aqueous acetone, followed by treatment with a mineral acid. Wizinger and Ulrich have reported that this procedure is satisfactory for the preparation of 2,4,6-triarylthiapyrylium salts and their vinyl homologs (1); that it is unreliable when a methyl group is present in the 2-position (2); and that it fails for the class of compounds that they referred to as symmetrical tetraarylpyrylocyanine salts (2), but which we will call symmetrical pyranylidenemethylpyrylium salts. We have found that treatment of pyranylidenemethylpyrylium salts with sodium sulfide resulted in replacement of one of the hetero-oxygen atoms with sulfur, and the present paper describes our results with symmetrical and unsymmetrical monomethine pyrylium compounds.

The reaction of the symmetrical pyrylium salt **1** with sodium sulfide by the standard procedure (1) gave compound **2**, which had been prepared previously by another method (2). The reaction was also successful with the symmetrical salts **3** and **5**, although the yields were lower than those obtained with **1**.



1 (R = H)
5 (R = CH3)

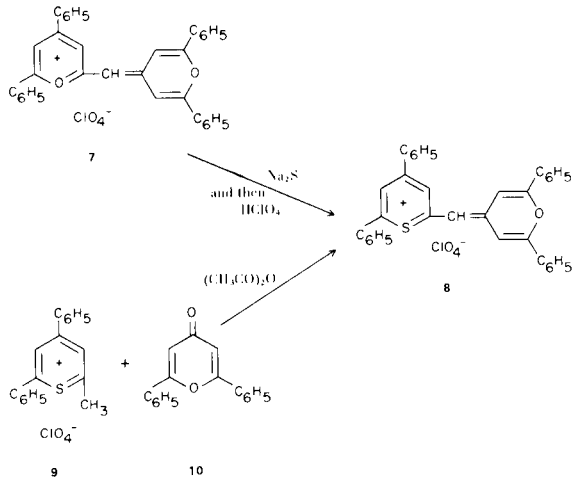
2 (R = H)
6 (R = CH3)



3 4

The reaction of unsymmetrical monomethine pyrylium salts with sodium sulfide presents an added complication, since two products can be formed resulting from the replacement of either of the oxygen atoms. In practice, we found that only one product was isolated, and the structures of some of the products were determined by alternative syntheses.

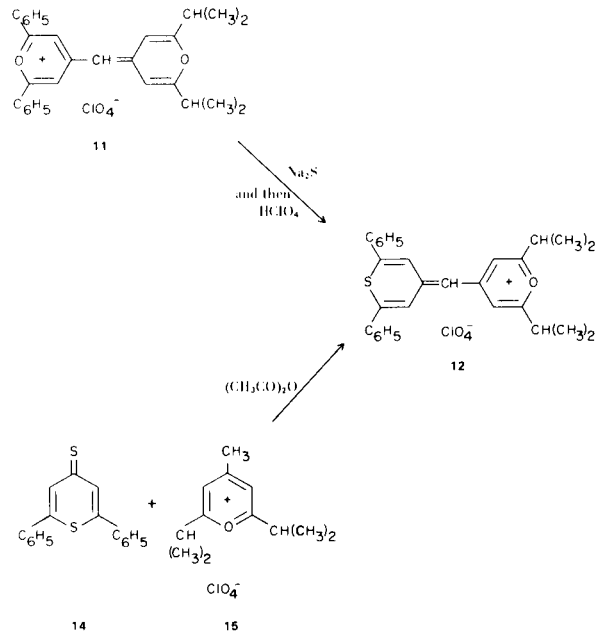
For the case in which the pyrylium oxygen atoms are *ortho* and *para* to the methine group, the *ortho* oxygen atom is displaced by sulfur as shown by the reaction of **7** to give **8**. The structure of **8** was demonstrated by its synthesis from **9** and **10**.



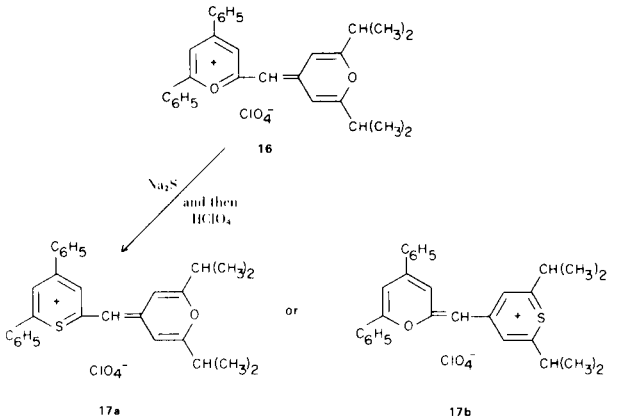
7 8

9 10

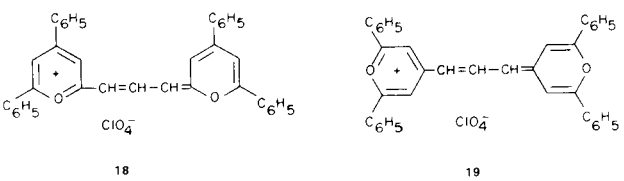
Another example of an unsymmetrical monomethine pyrylium salt is one in which one ring is substituted in the 2,6-positions with phenyl groups and the other ring, by alkyl groups. The reaction of a compound of this type, **11**, with sodium sulfide gave the product, **12**, resulting from the replacement of the oxygen atom of the aryl-substituted ring by sulfur. Compound **12** was also prepared by the reaction of **14** with **15**.



A final type of unsymmetrical pyrylium salt is the mixed 2,6-dialkyl and diarylpyrylium compound in which the methine group is joined to the 2-position of one ring and the 4-position of the other, as exemplified by **16**. The reaction of **16** with sodium sulfide also gave a single product, but we were unable to establish the structure of this compound because an alternate, unambiguous synthesis was not found.



The reaction of sodium sulfide with trimethine pyrylium salts was investigated briefly. The dyes **18** and **19** gave noncrystalline, brown products, melting over a large range, which could not be further purified or characterized.



An attempt was made to prepare a symmetrical monomethine thiapyrylium dye containing two sulfur atoms by treating **2** with sodium sulfide, but the reaction failed, and the brown amorphous solid which was obtained was not characterized.

The dyes described in this communication provide useful pyrylium salt sensitizers for organic photoconductive compositions as described previously (3).

EXPERIMENTAL

General Procedure for the Preparation of Pyranylidenemethylthiapyrylium Salts.

A solution of 2 g. of sodium sulfide in 10 ml. of water was added to 2 g. of the pyranomethylenepyrylium salt in 50 ml. of acetone. The mixture was stirred for 0.5 hour, then made strongly acidic with dilute perchloric acid, and stirred for an additional hour. The solid was collected, washed with water and crystallized.

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

Compound **2** was obtained in 75% yield and melted at 270-271° after recrystallization from acetonitrile.

The λ max (acetonitrile) (ϵ x 10^{-3}) were 238 (33.5), 257 (31.7), 390 (21.6), ~555, and 585 mμ (80.1).

Anal. Calcd. for $C_{35}H_{25}ClO_5S$: C, 70.9; H, 4.3; S, 5.4. Found: C, 70.9; H, 4.2; S, 5.4.

Compound **2** had been prepared previously (2) from 2,6-diphenylthiapyran-4-one and 4-methyl-2,6-diphenylpyrylium perchlorate, but the reported m.p. was 235-238°. We prepared a sample of **2** by a similar procedure using 2,6-diphenylpyran-4-one and 4-methyl-2,6-diphenylthiapyrylium perchlorate and obtained a product which melted at 271-272° and showed ir and λ max that were identical with those of the product we had obtained by the sodium sulfide procedure.

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

The dye **4** was obtained in 25% yield and melted at 283-284° (from acetic acid).

The λ max (methylene chloride) (ϵ x 10^{-3}) were 230 (26.5), 283 (27.3), 325 (44.5), 430 (5.5), 460 (3.8), 600 (40.0), and 650 mμ (63.0).

Anal. Calcd. for $C_{35}H_{25}ClO_5S$: C, 70.9; H, 4.3; S, 5.4. Found: C, 71.1; H, 4.4; S, 5.6.

A mixture of 0.72 g. of 2-methyl-4,6-diphenylthiapyrylium perchlorate and 0.5 g. of 4,6-diphenyl-2*H*-pyran-2-thione in 25 ml. of acetic anhydride was refluxed for 0.5 hour, diluted with ether, chilled, and the solid was collected and crystallized from acetic acid yielding 0.6 g. of **4**, m.p. 281-283°. The product showed ir absorption and λ max identical with those of the sample prepared by the sodium sulfide method.

2,6-Diphenyl-4-[1-(2,6-diphenyl-4*H*-pyran-4-ylidene)ethyl]thiapyrylium Perchlorate (**6**).

The dye **6** was obtained in 28% yield and melted at 249-250° (from a mixture of acetonitrile and alcohol).

The λ max (methylene chloride) (ϵ x 10^{-3}) were 247 (33.9); 264 (32.8); 397 (26.6), and 655 mμ (76.8).

Anal. Calcd. for $C_{36}H_{27}ClO_5S$: C, 71.2; H, 4.5; S, 5.3. Found: C, 71.4; H, 4.7; S, 5.6.

4,6-Diphenyl-2-[(2,6-diphenyl-4*H*-pyran-4-ylidene)methyl]thiapyrylium Perchlorate (**8**).

The salt **8** was obtained in 36% yield and melted at 302-303° after crystallization from acetonitrile.

Anal. Calcd. for $C_{35}H_{25}ClO_5S$: C, 70.9; H, 4.3; S, 5.4. Found: C, 70.8; H, 4.6; S, 5.4.

Compound **8** was also prepared in the sollowing manner. A mixture of 0.4 g. of 2-methyl-4,6-diphenylthiapyrylium perchlorate (**9**), 0.3 g. of 2,6-diphenyl-4*H*-pyran-4-one (**10**) and 20 ml. of acetic anhydride was refluxed for 0.5 hour, chilled, and the solid was collected and crystallized from acetonitrile yielding 0.3 g. of **8**, m.p. 304-305°.

The λ max (methylene chloride) (ϵ x 10^{-3}) of **8** prepared by both procedures were 230 (24.9), 280 (25.5), 370 (38.0), ~596 (50.0), and 630 mμ (73.4).

4-[(2,6-Diphenyl-4*H*-thiapyran-4-ylidene)methyl]-2,6-diisopropylpyrylium Perchlorate (**12**).

Compound **12** was obtained in 40% yield and melted at 176-177° after two recrystallizations from alcohol.

Anal. Calcd. for $C_{29}H_{29}ClO_5S$: C, 66.3; H, 5.6; S, 6.1. Found: C, 66.1; H, 5.5; S, 6.2.

Compound **12** was also prepared from 1.3 g. of 2,6-diisopropyl-4-methylpyrylium perchlorate (**15**) and 1.3 g. of 2,6-diphenyl-4*H*-thiapyran-4-thione (**14**) in 15 ml. of acetic anhydride by the procedure described for the preparation of **8**, yielding 1.2 g. of **12**, m.p. 175-176°. The ir absorption curves of the dyes prepared by both procedures were identical and both showed λ max (acetonitrile) (ϵ x 10^{-3}) at 250 (24.5), 315 (9.0), 380 (11.0), and 548 mμ (92.8).

2-[(2,6-Diisopropyl-4*H*-pyran-4-ylidene)methyl]-4,6-diphenylthiapyrylium Perchlorate (**17a**) or 4-[(4,6-Diphenyl-2*H*-pyran-2-ylidene)methyl]-4,6-diisopropylthiapyrylium Perchlorate (**17b**).

The structure of compound **17** (either **17a** or **17b**) is not known, but the following data were obtained. The dye was obtained in 42% yield by the general procedure and melted at 180-181° after two recrystallizations from acetic acid.

The λ max (methylene chloride) (ϵ x 10^{-3}) were 255 (14.5), 270 (14.9), 352 (25.6), ~395 (9.8), 568 (42.0), and 590 mμ (41.0).

Anal. Calcd. for $C_{29}H_{29}ClO_5S$: C, 66.2; H, 5.6; S, 6.1. Found: C, 66.5; H, 5.5; S, 5.8.

REFERENCES

(1) R. Wizinger and P. Ulrich, *Helv. Chim. Acta*, **39**, 207 (1956).

(2) R. Wizinger and P. Ulrich, *ibid.*, **39**, 217 (1956).

(3) J. A. Van Allan, C. C. Natale and F. J. Rauner, U.S. Patent 3,250,615, issued May 10, 1966.