Synthesis of 2[(4,6-Diphenyl-2*H*-pyran-2-ylidene)methyl]-4,6-diphenylpyrylium Perchlorate

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The title compound was prepared by the condensation of 4,6-diphenyl-2*H*-pyran-2-one and acetophenone in phosphorus oxychloride. The absorption spectrum of this 2,2-methine dye is compared with those of the corresponding 2,4- and 4,4-methine dyes.

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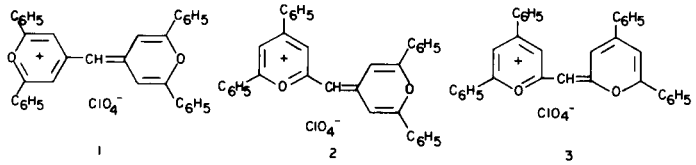
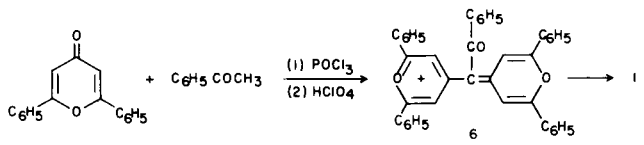
Pyrylium monomethine dyes **1** and **2** are prepared by the condensation of 2,6-diphenyl-4*H*-pyran-4-one with 4-methyl-2,6-diphenylpyrylium perchlorate or the corresponding 2-methyl homolog in acetic anhydride (1). The corresponding 2,2-dye (**3**) cannot be prepared by this

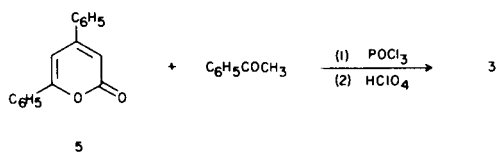


procedure. The following methods also have been investigated for the synthesis of **3**. Method A: 2-methyl-4,6-diphenylpyrylium perchlorate (**4**) and 4,6-diphenyl-2*H*-pyran-2-one (**5**) in phosphorus oxychloride were heated, giving on work-up an unidentified material. Method B: **4**, 2-methylmercapto-4,6-diphenylpyrylium perchlorate, sodium acetate, acetic acid, and acetic anhydride were refluxed giving a blue coloration, but no crystalline material was isolated. Method C: **4** and 4,6-diphenyl-2*H*-pyran-2-thione in refluxing acetic anhydride gave **3** in 10% yield.

Several years after these discouraging attempts to synthesize **3**, we were investigating the synthesis of the methine dye **6** by the following route. The isolated product, however, was the debenzoylated dye **1** presumably due to hydrolysis of the benzoyl group of **6**



during work-up. This result suggested a synthesis for **3** which in practice was very effective. Thus the readily available **5** (2) and acetophenone on heating in phosphorus oxychloride gave **3** in 85% yield.



It is interesting to compare the spectrum of the 4,4-dye (**1**) with that of the 2,2-dye (**3**). It is usual for a pyrylium compound with an electron-donating group in the 2-position to absorb at longer wavelength but with a lower extinction coefficient than the corresponding 4-substituted derivative, and these two examples constitute an extreme case. The absorption of the unsymmetrical 2,4-dye (**2**) does not occur at the arithmetic mean of the two symmetrical dyes, but is closer to that of the 2,2-dye (**3**) and the ϵ is approximately one-half that of **1**.

Table

Spectra of Dyes in Acetonitrile

1		**2**		**3**	
λ_{nm}	$\epsilon \times 10^{-3}$	λ_{nm}	$\epsilon \times 10^{-3}$	λ_{nm}	$\epsilon \times 10^{-3}$
543	120.0	596	62.8	628	37.8
379	27.2	560	47.6	585	34.5
268	26.4	347	38.0	335	45.5
230	21.6	268	26.0	285	33.0
		228	26.5		

EXPERIMENTAL

Melting points are not corrected. The absorption spectra were determined on a Cary 17 spectrometer.

2[(4,6-Diphenyl-2*H*-pyran-2-ylidene)methyl]4,6-diphenylpyrylium Perchlorate (**3**).

A.

A mixture of 5 g. (0.02 mole) of 4,6-diphenyl-2*H*-pyran-2-one (**5**), 5 ml. of acetophenone, and 10 ml. of phosphorus oxychloride was heated on a steam bath for two hours and then 50 ml. of methanol was added in portions to the hot reaction mixture. When the decomposition of the excess phosphorus oxychloride was completed, 3 ml. of 70% perchloric acid was added to the solution which was then chilled and the solid collected. The product was extracted in a Soxhlet extractor with acetonitrile to give 4.9 g. (85%) of bronze-colored needles, m.p. 254-255°.

When the reaction was repeated using 1.2 g. (0.01 mole) of acetophenone, the yield of **3** was only 26%.

Anal. Calcd. for $C_{35}H_{25}ClO_6$: C, 72.8; H, 4.4; Cl, 6.2. Found: C, 72.9; H, 4.6; Cl, 5.9.

B.

A mixture of 2.6 g. (0.01 mole) of 4,6-diphenyl-2*H*-pyran-2-thione, 3.5 g. (0.01 mole) of **4**, and 75 ml. of acetic anhydride was refluxed for 0.5 hour. The deep blue solution was diluted with ether and chilled, and the sticky solid was collected. The solid was boiled with acetic acid, and the insoluble material was collected and recrystallized twice from acetic anhydride yielding

0.6 g. (10% yield) of **3**, m.p. 249-250°. The ir and electronic absorption spectra of this sample were identical with those of the material described above.

4[(2,6-Diphenyl-4*H*-pyran-2-ylidene)methyl]4,6-diphenylpyrylium Perchlorate (**1**).

Procedure A for the preparation of **3** was carried out using 2,6-diphenyl-4*H*-pyran-4-one in place of **5**, giving 5 g. (85%) of **1** plus an additional 0.8 g. of dye from the filtrate, m.p. 311-312°. The ir and absorption spectra were identical with those of previously prepared samples of **1**.

Anal. Calcd. for $C_{35}H_{25}ClO_6$: C, 72.8; H, 4.4; Cl, 6.2. Found: C, 72.5; H, 4.2; Cl, 5.9.

REFERENCES AND NOTES

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(2) F. Arndt and B. Eistert, *Chem. Ber.*, **58**, 2318 (1925).