

Synthesis and Absorption Spectra of Some 2,6-Disubstituted-4-(4-Dimethylaminophenyl)pyrylium Perchlorates

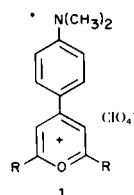
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The effects of substituents on the absorption spectra of pyrylium salts have interested us for years. Wizinger published many papers on this subject (1), and several theoretical papers dealing with the spectra of pyrylium salts have appeared (2).

The present report describes the shifts in the absorption spectrum of **1** that result from changing the R groups at the 2- and 6-positions of the pyrylium nucleus. We had previously investigated spectral changes in **1** when the R groups were substituted aryl groups and found that in most cases the long-wavelength band stayed relatively constant and the second-longest band was dependent on the substituent in the aryl group (3).



(a) R = C₆H₅; (b) R = p-CH₃OC₆H₄;
(c) R = CH₃; (d) R = H

An example of this effect is illustrated by **1a** and **1b**. We thought it would be of interest to extend the study of this class of compounds to include members which did not contain the aryl groups at positions two and six, and **1c** and **1d** were prepared. A comparison of the spectra of these compounds (Table I) shows that electron-donating groups at the 2- and 6-positions cause a shift in the long-wavelength absorption to shorter wavelengths, but the large shift in going from methyl to hydrogen was not anticipated. These spectra also clearly demonstrate that the intermediate absorption bands shown by **1a** and **1b** are the result of the aryl groups.

TABLE I

Absorption Spectra λ max nm ($\epsilon \times 10^{-3}$) in Acetonitrile

1a	550 (98.0)	382 (26.3)	295 (14.5)	270 (15.8)	
1b	525 (77.6)	431 (28.8)	333 (8.0)	296 (19.6)	265 (22.4)
1c	485 (63.0)			282 (12.3)	
1d	430 (31.4)			252 (16.0)	

Wizinger had reported the preparation of **1a** by the reaction of 2,6-diphenyl-4*H*-pyran-4-one with dimethylaniline and phosphorous oxychloride (4), and this method was used to prepare **1b** from the appropriate pyrone. This procedure did not work for the preparation of **1c** and **1d** so the latter compounds were prepared from *p*-dimethylaminophenylmagnesium bromide and 2,6-dimethyl-4*H*-pyran-4-one or 4*H*-pyran-4-one.

EXPERIMENTAL

4-(4-Dimethylaminophenyl)-2,6-(4-methoxyphenyl)pyrylium Perchlorate (**1b**).

A mixture of 2 g. of 2,6-(4-methoxyphenyl)-4*H*-pyran-4-one, 2 ml. of *N,N*-dimethylaniline and 10 ml. of phosphorus oxychloride was heated on a steam bath for 2 hours, cooled, and diluted with ether. The solid was collected and added to 100 ml. of ethyl alcohol containing 2 ml. of 70% perchloric acid. The mixture was heated at reflux for 15 minutes, cooled, and the solid was collected. The product was purified by extraction into acetonitrile in a Soxhlet extractor, yield 2.8 g., m.p. 325-326°.

Anal. Calcd. for C₂₇H₂₆ClNO₇: C, 63.3; H, 5.1; N, 2.7. Found: C, 63.4; H, 5.4; N, 2.4.

2,6-Dimethyl-4-(4-dimethylaminophenyl)pyrylium Perchlorate (**1c**).

A mixture of 15 g. of *p*-bromodimethylaniline, 2.5 g. of magnesium, and 100 ml. of dry tetrahydrofuran was refluxed until the magnesium had dissolved (about 2 hours) and the solution was cooled in an ice bath. A solution of 6 g. of 2,6-dimethyl-4*H*-pyran-4-one in 100 ml. of dry tetrahydrofuran was chilled and the cold Grignard reagent was added with stirring and cooling. The bright red mixture was stirred in an ice bath for 0.5 hour and then made strongly acidic by the addition of 5% aqueous perchloric acid. The solid was collected and crystallized from alcohol, yield 8 g., m.p. 236-237°.

Anal. Calcd. for C₁₅H₁₈ClNO₅: C, 55.0; H, 5.5; N, 4.3. Found: C, 55.3; H, 5.6; N, 4.6.

4-(4-Dimethylaminophenyl)pyrylium Perchlorate (**1d**).

The Grignard reagent was prepared as described above for the preparation of **1c**, 7 g. of 4*H*-pyran-4-one in 50 ml. of dry tetrahydrofuran was added, and the mixture was worked up as described for **1c** giving 5 g. of **1d** after crystallization from alcohol, m.p. 195-196°.

Anal. Calcd. for C₁₃H₁₄ClNO₅: C, 52.1; H, 4.7; N, 4.7. Found: C, 52.0; H, 4.6; N, 4.8.

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