Trimethine Pyrylium Dyes

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The synthesis and electronic absorption spectra of some pyranylidene trimethine pyrylium salts are described.

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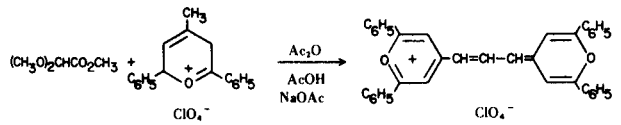
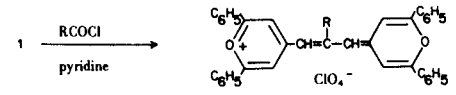
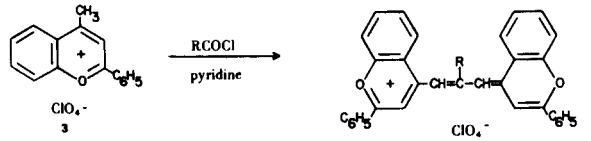
Simple aryl-substituted pyrylium salts are sensitizers for photoconductive systems. Their effectiveness varies greatly with the nature of the substituent (1). In the course of studying substituent effects, we have prepared a number of pyranylidene trimethine pyrylium salts, and the present paper describes their synthesis and absorption spectra. Several examples of trimethine pyrylium salts have been described previously (2-6), but there has been no systematic comparison of the spectra of this class. Many of the examples to be described have substituents on the methine carbon atoms, and some flavylium trimethine dyes have been included for comparison with corresponding pyrylium dyes.

The parent member of the series, **2**, was prepared from methyl dimethoxyacetate and 4-methyl-2,6-diphenylpyrylium perchlorate (**1**) in refluxing acetic anhydride, acetic acid and sodium acetate. The symmetrical pyranylidene salts are conveniently prepared from either **1** or 4-methylflavylium perchlorate (**3**) and either acetic anhydride or an acid chloride in the presence of pyridine.



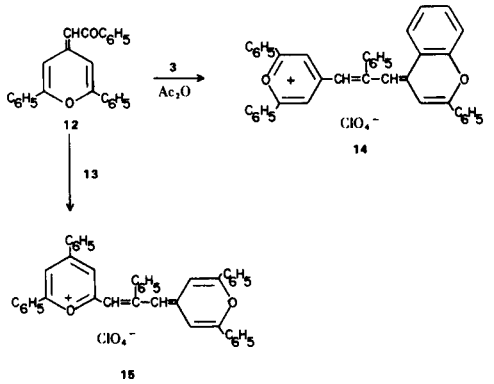


4 (R = C_6H_5)
5 (R = 4-$CH_3OC_6H_4$)
6 (R = 4-$NO_2C_6H_4$)
7 (R = CH_3)
8 (R = C_2H_5)

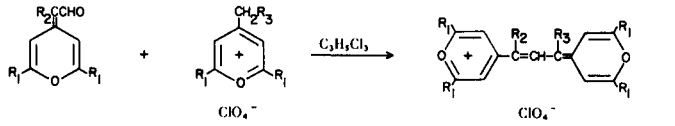


9 (R = CH_3)
10 (R = C_2H_5)
11 (R = C_6H_5)

The unsymmetrical salts **14** and **15** were obtained by the condensation of 4-phenacylidene-2,6-diphenyl-4*H*-pyran (**12**) with **3** or from 2-methyl-4,6-diphenylpyrylium perchlorate (**13**) and **12**.



The trimethine dyes having substituents on the α- or γ- position were prepared from a formylmethylenepyran derivative and a 4-alkylpyrylium salt in refluxing 1,2,3-trichloropropane.



16 (R_1 = Ph; R_2 = H)
17 (R_1 = Ph; R_2 = CH_3)
18 (R_1 = *t*-Bu; R_2 = H)
19 (R_1 = Ph; R_3 = CH_3)
20 (R_1 = *t*-Bu; R_3 = H)
21 (R_1 = Ph; R_2 = CH_3; R_3 = H)
22 (R_1 = Ph; R_2 = CH_3; R_3 = CH_3)
23 (R_1 = *t*-Bu; R_2 = H; R_3 = H)

The electronic spectra of the dyes are collected in Table I. These dyes exhibit weak negative solvatochromism in respect to the long-wavelength region of the spectrum.

For example, **2** gives a spectral shift of -5 nm when methylene chloride (ϵ = 5.2) is replaced by nitromethane (ϵ = 39.5). Substituents in the meso position produce a small bathochromic shift of about 5-20 nm in both the λa and λb bands in the pyrylium and flavylium dyes. The oscillator strengths are consistently higher for the pyrylium dyes than for the flavylium dyes, but the flavylium dyes absorb at longer wavelength. α-Methyl substituents are similar to the mesomethyl substituents in that they produce a bathochromic shift of about 10 nm with a decrease in the extinction coefficient, but the addition of a second methyl group at the γ-position results in a 25 nm bathochromic shift with a very large decrease in ϵ. Replacement of the 2,6-phenyl groups in the pyranylidene and pyrylium rings by *t*-butyl groups has a profound influence on the spectrum. The long-wavelength absorption (λb) is shifted hypsochromically by about 80 nm and the λa band by 100 nm.

Table I

Absorption Spectra

Compound Number	Solvent	λ max (ε x 10^{-3}) a	b	O.S.
2	Dichloromethane	628 (60.0)	685 (270)	0.80
	Nitromethane	625 (65.0)	680 (240)	0.79
4	Dichloromethane	635 (61.7)	690 (310)	0.91
5	Dichloromethane	635 (56.0)	693 (300)	0.77
6	Dichloromethane	638 (50.0)	695 (244)	0.79
7	Dichloromethane	650 (51.0)	696 (189)	0.72
8	Acetonitrile	640 (35.0)	688 (125)	0.54
9	Dichloromethane	665 (36.0)	728 (101)	0.63
10	Dichloromethane		727 (59.9)	0.41
11	Dichloromethane	660 (45.0)	728 (129)	0.66
14	Dichloromethane	645 (56.6)	704 (195)	0.925
15	Dichloromethane		736 (111)	
21	Acetonitrile	640 (57.0)	698 (210)	0.76
22	Acetonitrile	~675 (57.5)	723 (129)	0.73
23	Acetonitrile	562 (43.0)	603 (267)	0.73

Table II

Compound Number	M.p., °C	Method of Preparation	% Yield	Empirical Formula	*Anal.* Calcd./Found C	H	Cl
2	332-333		64	$C_{37}H_{27}ClO_6$	73.7	4.5	5.9
					73.6	4.2	5.9
4	303-304 dec.	B	86	$C_{43}H_{31}ClO_6$	76.1	4.6	5.2
					75.8	4.7	5.3
5	312-313 dec.	B	57	$C_{44}H_{33}ClO_7$	74.5	4.7	5.0
					74.3	4.7	4.9
6	328-329 dec.	B	61	$C_{43}H_{30}ClNO_8$	71.3	4.2	4.9
					71.3	4.4	4.9
7	255-256 dec.	B	68	$C_{38}H_{29}ClO_6$	74.0	4.7	5.7
					74.4	4.7	6.0
8	237-238 dec.	B	52	$C_{39}H_{31}ClO_6$	74.2	5.0	5.6
					74.4	5.2	5.3
9	239-240	B	55	$C_{34}H_{25}ClO_6$	72.5	4.5	6.3
					72.5	4.8	6.0
10	195-196 dec.	B	34	$C_{35}H_{27}ClO_6$	72.6	4.7	6.1
					72.6	4.4	6.4
11	298-299 dec.	B	53	$C_{39}H_{27}ClO_6$	74.7	4.4	5.7
					74.6	4.6	5.3
14	299-300 dec.	C	86	$C_{41}H_{29}ClO_6$	75.4	4.5	5.4
					75.7	4.8	5.3
15	262-264 dec.	C	67	$C_{43}H_{31}ClNO_6$	76.0	4.6	5.2
					75.8	4.8	5.3
21	292-293 dec.	D	60	$C_{38}H_{29}ClO_6$	74.0	4.7	5.7
					73.8	4.9	5.9
22	281-283	D	32	$C_{39}H_{31}ClO_6$	74.2	5.0	5.6
					73.9	5.1	5.5
23	163-165	D	36	$C_{29}H_{43}ClO_6$	66.6	8.3	6.8
					66.7	8.5	6.8

EXPERIMENTAL

The melting points were determined by means of a Meltemp apparatus and are uncorrected. The spectra were measured on a Cary 14 spectrometer.

4-[3-(2,6-Diphenyl-4*H*-pyran-4-ylidene)propen-1]-2,6-diphenylpyrylium Perchlorate (**2**).

A mixture of 3.5 g. of **1**, 0.8 g. of methyl dimethoxyacetate, 25 ml. of acetic anhydride and 25 ml. of acetic acid was refluxed for 10 minutes, 0.4 g. of sodium acetate was added and reflux was continued for 15 minutes. After cooling, the solid was collected and boiled with 100 ml. of acetonitrile and filtered hot. The insoluble material was extracted in a Soxhlet with acetonitrile giving lustrous metallic needles.

4-[3-(2,6-Diphenyl-4*H*-pyran-4-ylidene)-2-methylpropen-1]-2,6-diphenylpyrylium Perchlorate (**7**).

Method A.

A mixture of 10 g. of **1**, 30 ml. of acetic anhydride and 5 ml. of pyridine was refluxed for 15 minutes and cooled; the solid was collected and purified by extraction with acetonitrile in a Soxhlet.

4-[3-(2,6-Diphenyl-4*H*-pyran-4-ylidene)-*p*-methoxyphenylpropen-1]-2,6-diphenylpyrylium Perchlorate (**5**).

Method B.

A mixture of 5 g. of **1**, 10 ml. of acetonitrile, 10 ml. of *p*-anisoyl chloride and 5 ml. of pyridine was refluxed for 5 minutes and cooled; the solid was collected and extracted in a Soxhlet with acetonitrile.

Other dyes prepared by this procedure using either **1** or **3** and the appropriate acid chlorides are collected in Table II and indicated by method B.

4-[3-(2,6-Diphenyl-4*H*-pyran-4-ylidene)-2-phenylpropen-1]flavylium Perchlorate (**14**).

Method C.

A mixture of 1 g. of 2,6-diphenyl-4-phenacylidene-4*H*-pyran (**12**), 1.3 g. of **3** and 20 ml. of acetic anhydride was refluxed for 15 minutes and chilled; the solid was collected and purified by extraction.

Other dyes prepared in this manner are listed in Table II under method C.

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

Method D.

A mixture of 1 g. of 2,6-diphenyl-4-formylmethylene-4*H*-pyran (**16**) (7), 1.5 g. of 2,6-diphenyl-4-ethylpyrylium perchlorate (**19**) and 25 ml. of 1,2,3-trichloropropane was refluxed for 30 minutes, cooled and diluted with ether. The solid was collected and purified by extraction.

Other examples prepared by method D are found in Table II.

REFERENCES AND NOTES

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