Heterocyclic Polynitrobenzylidene Dyes

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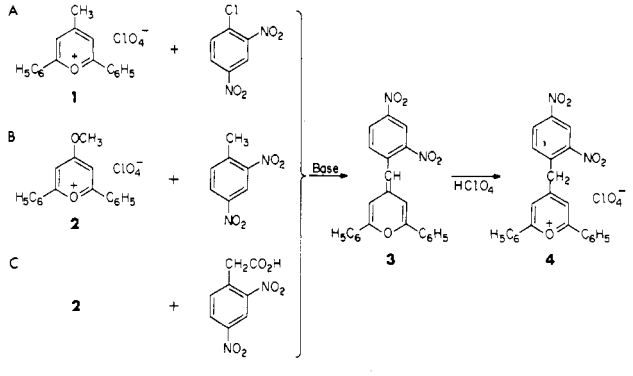
Three methods for the preparation of polynitrobenzylidene dyes are described. The protonated form of the dyes containing the pyran residue react with aldehydes and pyrones to give pyrylium dyes. Conversion of the pyran derivatives to pyridines and reduction of the nitro group are also described. The mass spectra and electronic spectra are discussed.

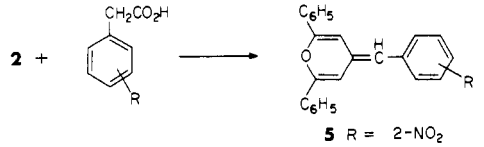
The use of quaternary salts in photoconductive systems has been described (*1*), and 1-methyl-2-(2,4-dinitrobenzyl) pyridinium salts (**24**) were particularly useful. The reported synthesis of **24** involved the preparation of 2-benzylpyridine and a subsequent nitration (*2*). This procedure was inconvenient for the preparation of related compounds.

We have developed three methods which make this class and related materials readily accessible. Scheme I illustrates these methods, using as an example the preparation of 4-(2,4-dinitrobenzylidene)-2,6-diphenyl-4H-pyran (**3**), which is the precursor to the salt **4**. Subsequently, **3** was converted to the pyridine derivative **15**.

Scheme I

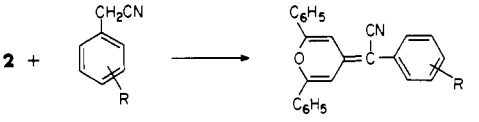


The mononitro derivatives **5** and **6** were prepared from *o*-nitrophenylacetic acid and *p*-nitrophenylacetic acid, respectively, by method C. The yield of **6** was 87%, but that of **5** was only about 40%. Since the yield of **5** was low, an alternative synthesis was attempted in which **2** was allowed to react with *o*-nitrobenzonitrile to give **7**, which was hydrolyzed with acid. The hydrolysis product was of unknown constitution and is being investigated (*4*). The same reaction applied to *p*-nitrobenzonitrile gave **8**, which on acid hydrolysis gave **6** in good yield.



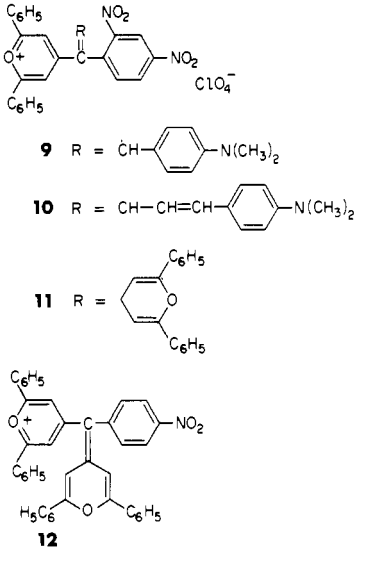
5 R = 2-NO_2
6 R = 4-NO_2

[1] To whom correspondence should be addressed.



7 R = 2-NO_2
8 R = 4-NO_2

The pyranylidene derivatives can be converted to other dyes or can serve as intermediates for the synthesis of pyridine derivatives. For example, the perchlorate salt **4** was condensed with 4-dimethylaminobenzaldehyde and 4-dimethylaminocinnamaldehyde in acetic anhydride, giving the dyes **9** and **10**, respectively. The condensation of **4** with 2,6-diphenyl-4-pyrone in the presence of phosphoryl chloride resulted in the formation of the pyranylidene dye **11**. The perchlorate salt from **6** with 2,6-diphenyl-4-pyrone gave 4-(2,6-diphenylpyranylidene-*p*-nitrophenyl)-methyl-2,6-diphenylpyrylium perchlorate **12**.

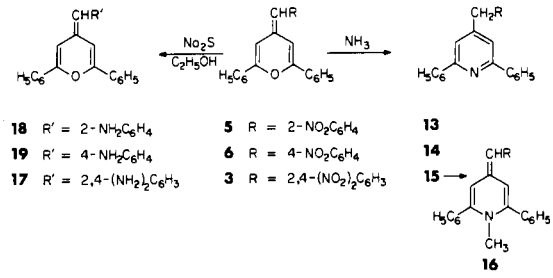


The principal peaks in the electronic spectra of these dyes are collected in Table I (λ nm, $\epsilon \times 10^{-3}$).

The compounds containing the 4H-pyran moiety (**3**, **5**, and **6**) reacted with ammonia to give the corresponding pyridine derivatives (**15**, **13**, and **14**), respectively. Methylation of **15** with methyl fluorosulfonate gave the dihydropyridine derivative **16**, which was also prepared from 1,4-dimethyl-2,6-diphenylpyridinium perchlorate and 2,4-dinitrochlorobenzene. The nitro compounds **3**, **5**, and **6** were reduced with sodium sulfide in alcohol to the amines **17**, **18**, and **19**, respectively. We could not selectively reduce **3** by this method.

Table I. Absorption Spectra in Acetonitrile

9	...	390 (20.0)	632 (77.0)
10	...	390 (12.7)	725 (63.0)
11	270 (39.0)	394 (28.0)	578 (76.0)
12	255 (43.0)	385 (28.0)	580 (37.0)



18 R′ = 2-$NH_2C_6H_4$ **19** R′ = 4-$NH_2C_6H_4$ **17** R′ = 2,4-$(NH_2)_2C_6H_3$

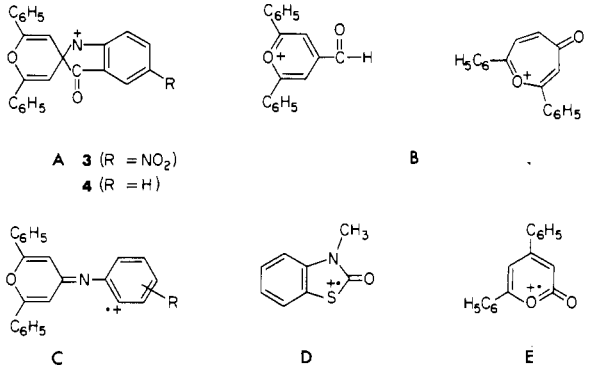
5 R = 2-$NO_2C_6H_4$ **6** R = 4-$NO_2C_6H_4$ **3** R = 2,4-$(NO_2)_2C_6H_3$

13 **14** **15** **16**

The derivatives that contain at least one nitro group in the ortho position of the benzylidene moiety undergo rearrangement on exposure to light, and the structures of the photolysis products of **3, 5,** and **40** are described in a separate paper (*3*). The pyridine derivative **15** is photochromic, turning yellow on exposure to light, in contrast to 2-(2,4-dinitrobenzyl)pyridine which turns blue on irradiation.

The data obtained from the mass spectral analysis of the nitrobenzylidene derivatives are collected in Table II. All compounds gave an abundant molecular ion. The compounds **3** and **5,** which have an *o*-nitrobenzylidene group in the para position of the pyran ring, showed an ion A corresponding to the loss of —OH and an ion corresponding to the loss of RC_6H_4NO which can be formulated as either of the structures shown for B. The ion A underwent further cleavage by the loss of CO to give ion C. Replacement of the methylene hydrogen with CN, as in **7,** prevented the formation of ion A.

The compounds **25** and **28,** in which the nitrobenzylidene group is ortho-fused, again gave ions corresponding to M—OH, but these ions did not subsequently lose CO; instead, the very prominent ions D and E were produced. This fact suggested that the molecular ion and/or A for **25** and **28** had an oxygen atom connected to the ring carbon rather than the exomethylene carbon. The pyridine derivative **16** showed no fragments corresponding to C or D. The *p*-nitrobenzylidene derivatives **6** and **8** exhibited intense molecular ions followed by the normal nitro group cleavage M—NO and M—NO_2. No ions corresponding to A, B, or C were present in their spectra.



A **3** (R = NO_2) **4** (R = H) B C D E

The electronic spectral data for representative members of these methine dyes are collected in Table III. With the exception of **7,** the dinitro and trinitro derivatives absorb well into the visible region; the extinction coefficients for the long wavelength absorption vary from 10,000 to 49,000. These extinction coefficients are approximate because some fading was noted during the determination of the electronic spectra. The spectra of these compounds are solvent dependent, a property characteristic of merocyanine dyes.

The physical data for the derivatives obtained by the arylation of 2-methyl-4,6-diphenylpyrylium perchlorate, 4-methylflavylium perchlorate, 1,2-dimethylpyridinium perchlorate, 1,2-dimethylquinolinium-*p*-toluenesulfonate, 2-methyl-1,4,6-triphenylpyridinium perchlorate, 2,3-dimethylbenzothiazolium perchlorate, and 2,3-dimethylnaphtho(2,1-*b*)thiazolium perchlorate are summarized in Table IV, and the preparation of these derivatives is described in the Experimental section.

Experimental

The methods for the preparation of the compounds are described as general procedures, and the data for the compounds are collected in Table IV.

Method A. A mixture of 0.1 mole of **1** or the appropriate 2- or 4-methyl quaternary salt and 0.1 mole of 1-chloro-2,4-dinitrobenzene was brought to reflux temperature, and 30 ml of diisopropylethylamine was added slowly (5 min). On completion of the addition, reflux was continued for 1 hr. After cooling, the product was collected and recrystallized from the appropriate solvent.

Method B. A mixture of 0.01 mole of **2** and 0.01 mole of 2,4-dinitrotoluene in 15 ml of methanol and 4 ml of diisopropylethylamine was heated to reflux for 1 hr. The solid was collected and recrystallized.

Method C. A mixture of 0.1 mole of **2** and 0.1 mole of 2,4-dinitrophenylacetic acid in 150 ml of methanol (or acetonitrile) was heated to reflux, and 50 ml of diisopropylethylamine was added. A vigorous reaction ensued, and the reaction mixture solidified in about 5 min. Reflux was continued for about 1 hr, the mixture was cooled, and the product was collected and recrystallized.

Table II. Mass Spectral Data[a]

Compound no.	M+	A	B	C	Other ions
3	412 (33)	395 (36)	261 (100) M—$C_6H_3N_2O_3$	367 (12)	105 (95) $C_6H_5C{\equiv}O^+$
8	392 (100)				362 (40) M—NO 240 (13)
6	367 (100)				337 (31) M—NO 321 (8) M—NO_2
7	392 (44)		286 (100) M—C_6H_4NO		105 (12) $C_6H_5C{\equiv}O^+$
5	367 (45)	350 (36)	261 (100) M—C_6H_4NO	322 (29)	105 (66) $C_6H_5C{\equiv}O^+$
16	425 (20)	408 (43)	274 (100) M—$C_6H_3N_2O_3$		118 (40) $\phi C{\equiv}NCH_3$
25	329 (100)	312 (100)	178 (100) M—$C_6H_3N_2O_3$		165 (16) (E)
28	457 (100)	440 (62)	261 (73) M—$C_6H_2N_3O_5$		248 (D)

[a] Figures in parentheses are relative percentage.

Table III. Electronic Spectral Uv Spectra[a]

3	250 (20.2)		315 (10.0)	490 (11.6)
5	245 (26.0)	275 (16.5)	340 (17.8)	Tails into vis
16	280 (11.0)			595 (49.0)
20	246 (30.0)		310 (12.0)	515 (10.8)
21	260 (8.4)		300 (17.4)	585 (11.4)
22	260 (26.8)			617 (31.7)
23	250 (10.5)		330 (2.7)	565 (41.0)
25	293 (7.3)		330 (3.6)	510 (26.0)
27	290 (11.6)			548 (26.7)

[a] Electronic spectra were determined in acetonitrile as solvent. The units are λ nm ($\epsilon \times 10^{-3}$).

Table IV. Methods of Preparation[a]

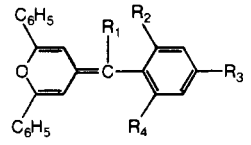
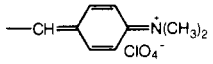
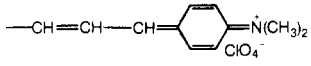
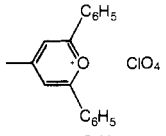
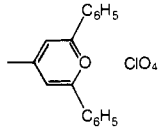
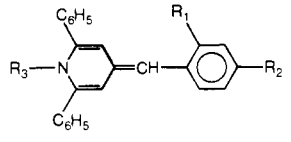
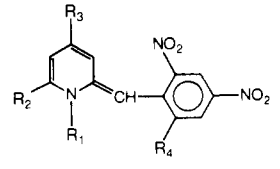
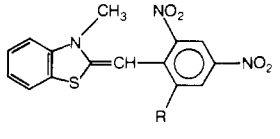
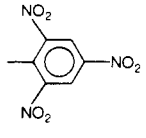
Compound no.	R_1	R_2	R_3	R_4	Mp	Method of prep	Yield, %	Solvent for recrystall[b]
								
3	H	NO_2	NO_2	H	210	A	68	3
4					222	D	50	6
5	H	NO_2	H	H	110	A	40	2
6	H	H	NO_2	H	207	C	57	4
7	CN	NO_2	H	H	204	B	88	1
8	CN	H	NO_2	H	236	B	63	4
9		NO_2	NO_2	H	287	G	80	3
10		NO_2	NO_2	H	231	G	38	3
11		NO_2	NO_2	H	210	H	80	3
12		H	NO_2	H	316	H	58	3
17	H	NH_2	NH_2	H	153	E	63	4
18	H	NH_2	H	H	108	E	85	1
19	H	H	NH_2	H	170	E	60	1
20	H	NO_2	NO_2	NO_2	110	B, C	75	3
								
13	NO_2	H	H		65	F	90	5
14	H	NO_2	H		135	F	90	5
15	NO_2	NO_2	H		135	F	50	1
16	NO_2	NO_2	CH_3		170	A	80	1
								
21	C_6H_5	C_6H_5	C_6H_5	NO_2	220	A	46	1
22	C_6H_5	C_6H_5	C_6H_5	H	236	A	93	1
23	CH_3	H	H	H	206	A	95	3
24[c]					125	D	80	6
25				R=H	218	A	50	1
26[d]				R=H	166	D	95	6
27				$R=NO_2$	198	A	89	3
28						A	48	1

Table IV. Continued

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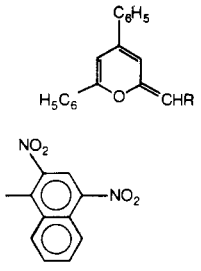
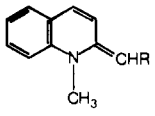
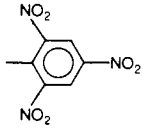
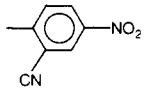
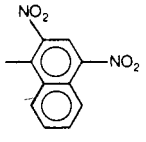
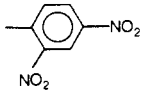
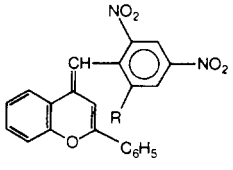
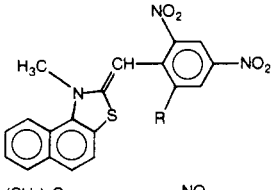
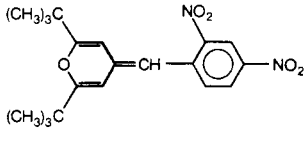
29						A	48	2

Compound no.		Mp	Method of prep	Yield, %	Solvent for recrystall
	30 	200	B, C	75	1
	31 	250	A	74	1
	32[e]	204	D	80	6
	33 	205	A	90	1
	34 	202	A	56	2
	35 R=H	181	A	33	2
	36 $R=NO_2$	184	A	35	1
	37[f]	186	D	80	6
	38 R=H	210	A	53	1
	39 $R=NO_2$	205	A	83	1
	40	125	A	43	1

[a] Elemental analyses (C, H, N, Cl) in agreement with theoretical values were obtained and submitted for review. [b] Solvent: 1, pyridine–methanol; 2, nitromethane; 3, acetonitrile; 4, toluene; 5, ethanol; 6, acetic acid. [c] Chloride of **23**. [d] Perchlorate of **25**. [e] Perchlorate of **31**. [f] Perchlorate of **36**.

Method D. The perchloric salts were made by adding 70% perchloric acid to solutions of the appropriate methylene heterocycles in acetic acid or in alcohol. Upon cooling, the salt precipitates. In some cases, ether is added to facilitate the isolation of the salts.

Reduction of Nitro Compounds to Amines

Method E. A mixture of 0.01 mole of the nitro compounds and 2 grams of sodium sulfide in 50 ml of alcohol was heated at reflux for 8 hr. A little insoluble material was filtered off, and the filtrate was reheated and diluted with H_2O until turbid and then chilled. The solid was collected and crystallized.

Preparation of Pyridine Derivatives

Method F. A solution of 0.01 mole of the methylenepyran (**13, 14, 15**) in 125 ml of acetic acid and 10 grams of ammonium carbonate was heated until the reaction mixture became light red (2–3 hr). After cooling, the solid was collected and recrystallized.

Condensation to Methine Dyes

Method G. A mixture of 0.01 mole of the perchlorate salt **4** and 0.01 mole of the *p*-dimethylaminobenzaldehyde or *p*-dimethylaminocinnamaldehyde in 25 ml of acetic anhydride was refluxed for 1 hr, cooled, and the dye was collected and recrystallized.

Method H. A mixture of 0.01 mole of the perchlorate salt **4** and 0.01 mole of the pyrone in 10 ml of phosphoryl chloride was heated on the steam bath for 1 hr. The reaction mixture was poured slowly into 100 ml of MeOH, and 5 ml of 70% $HClO_4$ was added. After cooling, the dye was collected and recrystallized.

Literature Cited

(1) Sagura, J. J., Van Allan, J. A., U.S. Patent 3,178,362 (1965).
(2) Schofield, K., *J. Chem. Soc.*, **1949**, p 2408.
(3) Van Allan, J. A., Farid, S., Reynolds, G. A., Chang, S. Chie, *ibid.*, **38**, 2834 (1973).
(4) Van Allan, J. A., Reynolds, G. A., *J. Heterocycl. Chem.*, **11**, 395 (1974).

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Halogenation of Arylsulfonylacetamides

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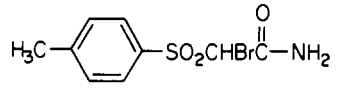
The bromination of 2-(*p*-toluenesulfonyl)acetamide (I) at 25–30° results in the formation of 2-bromo-2-(*p*-toluenesulfonyl)acetamide (VI); at 90–100° the product is 2,2-dibromo-2-(*p*-toluenesulfonyl)acetamide (VII). The structures assigned by Tröger and Hille are incorrect.

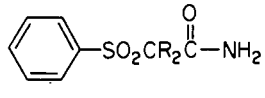
Tröger and Hille reported that halogenation of arylsulfonylacetamides gives *N*-halogenated products. The bromination of 2-(*p*-toluenesulfonyl)acetamide (I) was examined in detail. Tröger and Hille (*1*) reported that bromination of I at 25–30° gives *N*-bromo-2-(*p*-toluenesulfonyl)acetamide (II); at 90–100° the product is *N*-bromo-2-bromo-2-(*p*-toluenesulfonyl)acetamide (III). Chlorination of 2-(phenylsulfonyl)acetamide (IV) was reported to give *N*-chloro-2,2-dichloro-2-(phenylsulfonyl)-acetamide (V).

These structural assignments are incorrect. Bromination of I in acetic acid at 25–30° results in the formation of 2-bromo-2-(*p*-toluenesulfonyl)acetamide (VI); at 90–100° the product is 2,2-dibromo-2-(*p*-toluenesulfonyl)-acetamide (VII), and bromination of IV at 90–100° gives 2,2-dibromo-2-(phenylsulfonyl)acetamide (VIII). Monobromination of IV was not described by Tröger and Hille. Chlorination of IV in acetic acid does not give V as they reported. The product is 2,2-dichloro-2-(phenylsulfonyl)acetamide (IX) from chlorination of IV with either sulfuryl chloride or chlorine gas in acetic acid. No trichloro derivative was obtained even by chlorination of IV for 5 hr in acetic acid at 95–100°.

[1] To whom correspondence should be addressed.



VI



VIII R = Br
IX R = Cl

The pmr spectrum of VI has absorption in DMSO-d_6 of δ 2.46 (S, 3H, $ArCH_3$), 5.86 (S, 1H, $-\overset{|}{C}HBr$), 7.4–8.0 ($AA'BB'$, 4H, ArH), and in CD_3CN of δ 2.46 (S, 3H, $ArCH_3$), 5.40 (S, 1H, $-\overset{|}{C}HBr$), 6.5 (vbs, 2H, NH_2), 7.4–8.0 ($AA'BB'$, 4H, ArH) and is consistent with the assigned structure.

The pmr spectrum of VIII was observed in DMSO-d_6, CD_3CN, and dioxane. In all three cases, the only signals observed were the 5H aromatic multiplet and a broad signal for the NH_2 protons. No signal was observed in the region expected for $-SO_2CHBrCO$. The pmr spectrum of VII is similar to that of VIII. No signal for a proton in the 2-position was observed, indicating that geminal bromine substitution has taken place.

The ^{13}C spectrum in DMSO-d_6 of VIII showed the expected absorption at 162.5 (C=O), 136.4 (C—SO_2 and para aromatic carbons), 133.0, 129.9 (ortho and meta aromatic carbons), and 72.9 ($-SO_2-\overset{*}{C}-CO$) ppm vs. tetramethylsilane. The signal at 72.9 ppm remained a singlet during off resonance ^1H decoupling, verifying that there is no hydrogen on that carbon.

The pmr spectrum in DMSO-d_6 of IX shows typical phenyl absorption as a multiplet in the 7.4–8.1 ppm re-