Synthesis of Some Phenothiazinyl and Carbazolyl Pyrylium Salts

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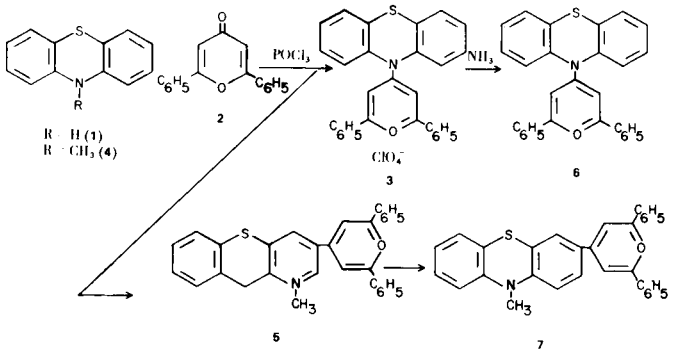
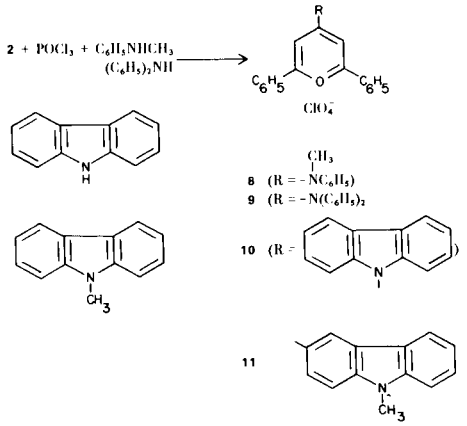
2,6-Diphenyl-4*H*-pyran-4-one in the presence of phosphorus oxychloride reacted with phenothiazine to give a pyrylium salt which was bonded in the 4-position to the nitrogen atom of phenothiazine. Carbazole gave a similar type of product. When the *N*-methyl derivatives of phenothiazine and carbazole were allowed to react under the same conditions, the coupling took place on the phenyl ring *para* to the nitrogen atom. In contrast to phenothiazine, benzo[*a*]-phenothiazine gave a product arising by coupling into the phenyl ring.

Our study of the preparation of pyrylium salts containing amino functions (1) has been extended to include the phenothiazinyl, benzo[*a*]phenothiazinyl, and carbazolyl groups.

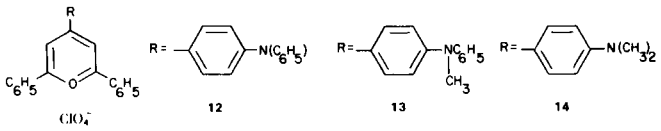
One of the methods for preparing aminopyryliums involves the displacement of a methoxy group by an amine. For example, 4-methoxy-2,6-dimethylpyrylium perchlorate reacts with morpholine and piperidine to give the corresponding morpholino and piperidinopyrylium salts (2). When this procedure was tried with 4-methoxy-2,6-diphenylpyrylium perchlorate and phenothiazine (**1**), no reaction took place. However **1** reacted with 2,6-diphenyl-4*H*-pyran-4-one (**2**) in the presence of phosphorus oxychloride to give **3**. Under the same conditions, *N*-methylphenothiazine (**4**) gave **5**. The *N*-substituted derivative (**3**) can be distinguished from the C-substituted derivative **5** by their mass spectral cracking patterns (see discussion of mass spectra). The pyrylium salts **3** and **5** were converted to pyridine derivatives **6** and **7**, respectively, by treatment with ammonia (3).



Other weakly basic amines, such as *N*-methylaniline, diphenylamine, and carbazole, reacted with **2** and phosphorus oxychloride to give the *N*-alkylation products **8**, **9**, and **10**. However, the electronic spectrum of **10** showed absorption at 100 nm longer wavelength than the other *N*-alkylated pyrylium salts (**3**, **8**, and **9**). The mass spectral cracking pattern supports structure **10**, and we therefore attribute the bathochromic shift to ortho fusion of the phenyl groups. For comparison of the mass spectra, **11** was prepared from **2** and *N*-methylcarbazole under the same conditions. Chemical evidence for structure **10**, rather than a structure analogous to **11**, was obtained by converting **10** to the pyridine derivative, which, in turn, could not be acetylated (see conversion of **18** to **19**).



In order to determine the effects of the amino groups on the electronic absorption spectra of the pyrylium dyes, **2** and phosphorus oxychloride were treated with the tertiary amines triphenylamine, methyldiphenylamine, and dimethylaniline (4), giving **12**, **13**, and **14**, respectively.



Is is apparent from examination of the absorption data in Table I that fusion of the phenyl groups attached to the nitrogen atom by a sulfur atom, as in **5**, produces a significant bathochromic shift of about 50 nm relative to **12**, **13**, and **14**. On the other hand, the carbazole derivative **11**, in which the phenyl groups are joined, shows a hypsochromic shift of approximately 30 nm relative to **12**, **13**, and **14**. The hypsochromic shift of the carbazole derivative **11** is in marked contrast to the bathochromic effect of the carbazole group on the absorption of **10**.

In contrast to phenothiazine (**1**), benzo[*a*]phenothiazine (**15**) reacted with **2** in phosphorus oxychloride to give the dye 16. The same dye (**16**) was obtained with an unusual concomitant demethylation when *N*-methylbenzo[*a*]phenothiazine (**17**) was used in the place of **15**. The structure **16** is preferred to its isomer in which the pyrylium residue is coupled to the 9-position of **15** in analogy to other coupling reactions which occur at the 5-position of **15** (5). The dealkylation that occurred when **17** reacted with **2** is unusual, but there are known examples (6) even though the reaction conditions are not analogous to ours. The pyrylium nucleus in **16** reacted normally to give the derivative **18**, which was acetylated to give **19**. We were unable to detect the NH absorption of **16** either by the ir or the nmr spectra. The dye **16** showed strong positive solvatochromism in that the long-wavelength band shifted to shorter wavelengths in solvents of increasing dielectric

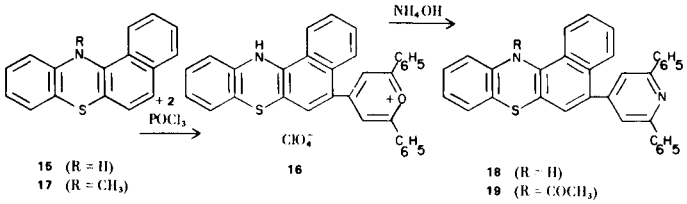


Table I

Physical Properties

Compound Number	Molecular Formula	M.p., °C	Yield, %	Solvent for recrystn.	Analysis % Calcd./Found C	H	N	Electronic absorption spectra (CH_3CN) λ nm (ε x 10^{-3})
3	$C_{29}H_{20}ClNO_5S$	219-220	83	Ac_2O	65.7 65.6	3.8 3.6	3.6 2.7	262 (27.2); 338 (34.8)
5	$C_{30}H_{22}ClNO_5S$	319-320	87	Ethanenitrile	66.2 66.4	4.1 4.1	2.6 2.6	273 (26.0); 392 (34.0); 585 (24.0)
6	$C_{29}H_{20}N_2S$	223-224	91	pyridine + methanol	81.3 81.6	4.7 4.6	6.5 6.5	
7	$C_{30}H_{22}N_2S$	170-171	76	Ethanenitrile	81.4 81.3	5.0 5.0	6.3 6.1	
8	$C_{24}H_{20}ClNO_5$	220-221	91	Ethanenitrile	65.8 65.7	4.6 4.4	3.2 3.2	260 (20.5); 323 (17.4)
9	$C_{29}H_{22}ClNO_5$	244-245	67	Ethanenitrile	69.7 69.7	4.4 4.6	2.8 2.6	335 (43.0)
10	$C_{29}H_{20}ClNO_5$	299-300	96	Ethanenitrile	69.9 69.6	4.1 4.4	2.8 2.6	272 (28.0); 380 (28.0); 445 (21.2)
11	$C_{30}H_{22}ClNO_5$	237-238	84	Nitromethane	70.4 70.4	4.3 4.4	2.7 2.6	270 (25.0); 338 (15.5); 390 (21.0); 498 (39.0)
12	$C_{35}H_{26}ClNO_5$	257-258	89	Ethanenitrile	73.0 72.7	4.6 4.6	2.4 2.4	272 (17.6); 390 (17.6); 535 (42.0)
13	$C_{30}H_{23}ClNO_5$	219-220	91	Ethanenitrile	70.2 70.3	4.5 4.7	2.7 2.7	265 (26.0); 290 (26.0); 378 (27.0); 530 (64.0)
14	$C_{25}H_{22}ClNO_5$	324-325	82	Ethanenitrile	66.4 66.7	4.9 4.7		233 (12.2); 263 (15.2); 287 (13.1); 375 (20.3); 537 (63.8)
16	$C_{33}H_{22}ClNO_5S$	300-301	69	Ethanenitrile	68.3 68.3	3.8 3.8	2.4 2.5	~255 (23.8); 275 (30.4) 398 (20.5); 655 (12.5)
18	$C_{33}H_{22}N_2S$	202-203	64	Pyridine	82.8 82.9	4.6 4.8	5.9 5.9	
19	$C_{35}H_{24}N_2OS$	261-262	74	Pyridine + methanol	80.7 80.7	4.6 4.5	5.4 5.3	

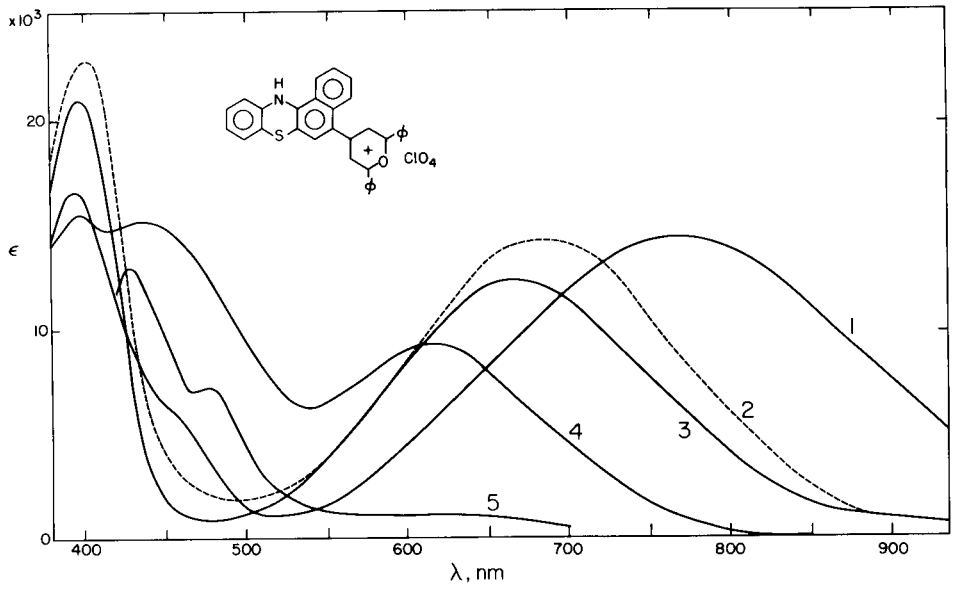


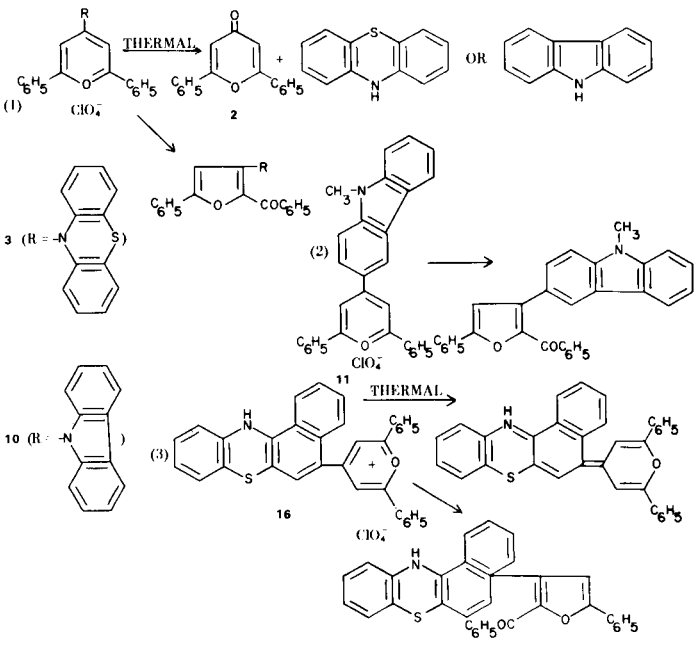
Figure 1. Spectra of **16**.

Solvents: (1) Chloroform; (2) methanol; (3) acetonitrile; (4) dimethylsulfoxide; (5) formamide.

constants. This band is broad and of relatively low extinction coefficient (see Figure 1), which suggests that the planarity of the chromophore is disturbed by the fused benzo group. There is no evidence for the presence of radicals in solutions of **16** as determined by esr and nmr analysis.

It has been mentioned above that mass spectral analysis has proved useful in distinguishing the pyrylium salts that have coupled at a nitrogen atom (**3** and **10**) from those coupled by a carbon atom (**11**). The salt **10** thermally decomposed in the spectrometer into diphenylpyrone **2**, carbazole (identified by comparison with known spectra), and 2-benzoyl-3-(9-carbazolyl)-5-phenylfuran, which further fragments as follows: 413 M^+ (100%), 396 M-OH (5.8%), 280 M-C-CC_6H_5 (15%), and 105 COC_6H_5 (33%). The analogous phenothiazine derivative **3** gave **2**, phenothiazine, and 2-benzoyl-3-phenothiazinyl-5-phenylfuran, which, in turn, fragmented in a manner similar to the corresponding carbazolylpyran derivative. In contrast, **11** fragments to give only 2-benzoyl-3-(9-methyl-3-carbazolyl)-5-phenylfuran, which, in turn, fragments in the usual manner. The conversion of aryl-substituted pyrylium perchlorates into aroylfuran derivatives during mass spectral analysis is characteristic of these salts, and we first observed it during the analysis of 2,4,6-triphenylpyrylium perchlorate about fifteen years ago. The source of the oxygen atom in the furan and pyrone derivatives is thought to be the perchlorate anion, since other salts fragment in a different way. The benzo[*a*]phenothiazine derivative (**16**) undergoes still another type of fragmentation which is characteristic of pyrylium salts with NH groups in the 2- or 4-positions, namely, the loss of $HClO_4$ to give a parent ion of mass 479 and in addition the ubiquitous furan derivative. The mass spectral cracking patterns of the

Three Types of Mass Spectral Cracking (a)



(a) For convenience the cation radical nature of the products has not been indicated.

three classes of compounds are summarized in the following diagram.

EXPERIMENTAL

The methods of preparation are described as general procedures, and the pertinent data are collected in Table I. The melting points are uncorrected.

Preparation of Pyrylium Salts.

A mixture of 0.02 mole each of the amine and pyrone **2** in 25 ml. of phosphorus oxychloride was heated on a steam bath for 2 hours. After cooling, the reaction mixture was carefully diluted with alcohol and 5 ml. of 70 percent perchloric acid was added. The solid was collected, washed with alcohol, and recrystallized.

Preparation of Pyridine Derivatives.

A mixture of 5 mmoles of pyrylium salt, 5 ml. of 28 percent ammonium hydroxide, and 20 ml. of pyridine was refluxed for 2 hours. In some cases the product separated on cooling, and in others methanol had to be added to precipitate the product.

4-(*N*-Acetylbenzo[*a*]phenothiazin-4-yl)-2,6-diphenylpyridine (19).

A mixture of 0.5 g. of **18**, 3 ml. of acetic anhydride, and a drop of concentrated sulfuric acid was refluxed for one-half hour and poured into water. The solid was collected and recrystallized.

Acknowledgment.

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