

## Some Reactions of 5*H*-Indeno[2,1-*b*]pyrylium, Thiopyrylium and Pyridinium Derivatives

*J. A. Van Allan and G. A. Reynolds*

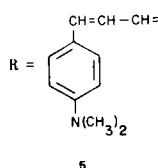
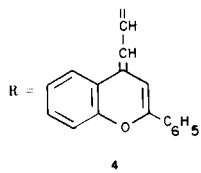
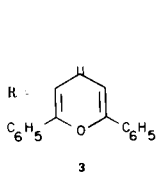
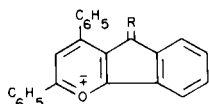
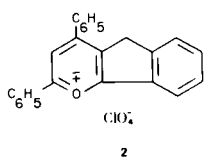
Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

October 15, 1976

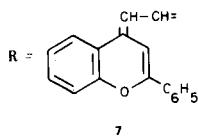
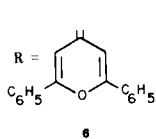
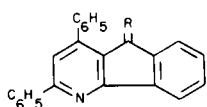
The reactions of 5*H*-indeno[2,1-*b*]pyrylium, thiopyrylium and pyridinium derivatives with aldehydes and 2,6-diphenyl-4*H*-pyran-4-one are described. The products obtained from the pyrylium salt and piperidine as well as the Vilsmeier reagent are reported.

*J. Heterocyclic Chem.*, 14, 119 (1977).

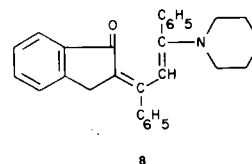
Pyrylium salts having a methyl or methylene group in the 2- or 4-position react readily in acetic anhydride with aldehydes or 2,4-diphenyl-4*H*-pyran-4-one (**1**) (**1**). Similar reactions fail with 3-methyl-2,4,6-triphenylpyrylium perchlorate. We have found that 2,4-diphenyl-5*H*-indeno[2,1-*b*]pyrylium perchlorate (**2**) (**2**), which may be considered to be related to **1**, is an exception to this behavior, since it will undergo reactions in acetic anhydride with **1**, 4-formylmethylene-4*H*-flavene and *p*-dimethylaminocinnamaldehyde to give **3**, **4** and **5**, respectively.



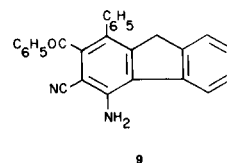
The salts **3** and **4** were converted to the pyridine derivatives **6** and **7**, respectively. The mass spectra of these materials are reported in Table I and are in agreement with the assigned structures.



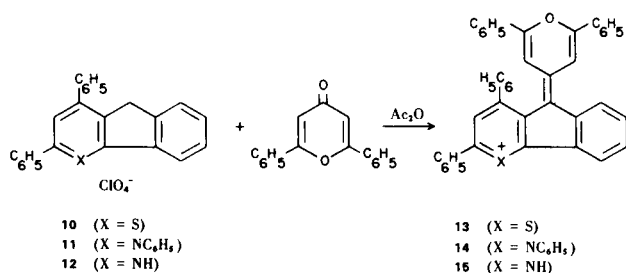
An attempt to prepare **3** by the condensation of **2** with 4-methoxy-2,6-diphenylpyrylium perchlorate in acetonitrile and an equivalent amount of piperidine resulted in the formation of **8**. Compound **8** was also prepared from **2** and piperidine in ether. This is an example of the reaction described by Lombard and Kress for pyrylium salts and secondary amines (**3**). The mass spectral data indicate that the piperidine has added to the 2-position of **2**.



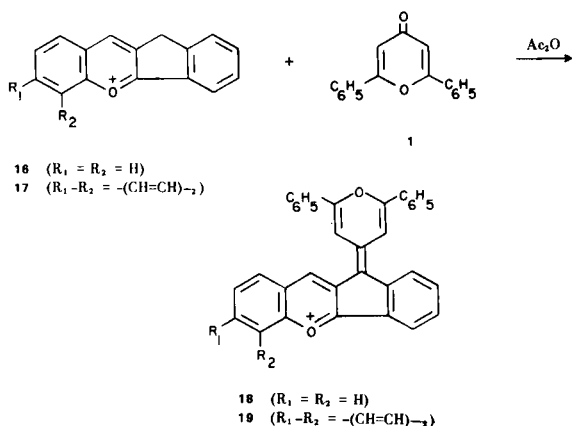
Compound **2** reacted with malononitrile in the presence of piperidine to give **9**. Dimroth has described similar reactions between malononitrile and 2,4,6-triarylperrylium salts using potassium *t*-butoxide as the base (**4**).



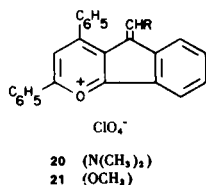
The thiopyrylium and pyridinium salts **10**, **11** and **12** (**2**) also reacted with 2,6-diphenyl-4*H*-pyran-4-one to yield **13**, **14** and **15**, respectively. The free base **6** obtained from **15** is identical to the product obtained by treatment of **3** with ammonia indicating that the hetero oxygen of the indenopyrylium ring reacted with the ammonia.



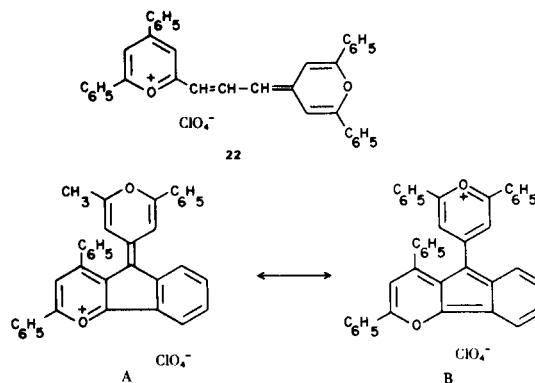
The pyrylium salts **16** and **17** also reacted with **1** to give **18** and **19**.



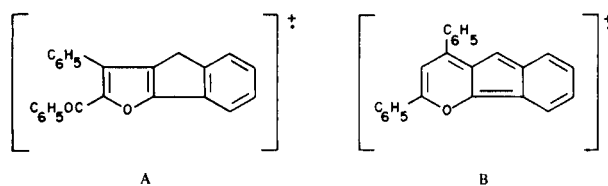
We had hoped to obtain some other derivatives of **2** by the introduction of an aldehyde group in the 5-position of **2** and subsequently condensing the aldehyde with an active methylene group but were unsuccessful. The indenopyrylium salt **2** reacted with dimethylformamide in acetic anhydride to give **20**, but attempts to hydrolyze **20** to the aldehyde were unsuccessful. Treatment of **2** with the Vilsmeier reagent and subsequent work up in methanol gave the methoxy derivative **21** which also could not be converted to the aldehyde. Compound **21** was also obtained from **2** and trimethylorthoformate. Neither **20** nor **21** reacted with active methylene compounds.



The electronic absorptions of the pyrylium salts (see Table II) are of interest. For example, the  $\lambda$  max of **3** is at 525 nm ( $\epsilon = 27 \times 10^3$ ) and that of the similar compound **22** is 685 nm ( $\epsilon = 178 \times 10^3$ ). This suggests that the resonance form B is of much higher energy than A.



The mass spectrum of **2** shows fragments typical of a pyrylium perchlorate. The significant fragments correspond to a benzoylfuran derivative A ( $m/e$  330) and a pseudoazulene B ( $m/e$  320). High resolution mass spectrometric analysis of **8** showed the loss of C<sub>6</sub>H<sub>10</sub>N and C<sub>6</sub>H<sub>11</sub>N, and the occurrence of a fragment



$\text{C}_6\text{H}_5\text{C}\equiv\text{C}-\text{C}=\text{NC}_5\text{H}_{10}$  ( $m/e$  274) indicating that the piperidine had added to the 2-position of **2**. The spectra of **6** and **7** have in common a doubly charged parent ion at 374.5 mass units. The cleavage of the styryl flavylium ion from **7** is interesting. The mass spectral data are collected in Table I.

## EXPERIMENTAL

Where possible, the preparative methods will be described as general procedures. The physical properties of the compounds are collected in Table II. The melting points were determined in a Mel-Temp apparatus and are uncorrected. The absorption spectra were recorded by a Cary model 17 spectrometer and the mass spectrum by a Hitachi RMS-4 spectrometer.

### 2,4-Diphenyl-5*H*-indeno[2,1-*b*]pyrylium perchlorate (**2**).

A mixture of 10.7 g. of chalcone, 7 g. of 1-indanone and 20 ml. of boron trifluoride etherate was heated on a steam bath for 4 hours, cooled and the solid was collected and recrystallized from acetic acid which contained perchloric acid.

Compounds **3**, **4**, and **5** were prepared by the following general procedure (A).

A mixture of 0.01 mole of **2** and 0.01 mole of **1** (4-formylmethylene-4*H*-flavone or *p*-dimethylaminocinnamaldehyde) in 40 ml. of acetic anhydride was refluxed for 15 minutes. After cooling the product was collected and recrystallized.

Table I

## Mass Spectral Data

Compound Number	M/e (%)				
2	336 (7.0)	320 (100)	289 (20)	245 (24)	
6	549 (100)	444 (1.5)	274.5 (29)		
7	549 (100)	274.5 (27)	233 (33)	207 (4.9)	
8	405 (46)	321 (100)	320 (16)	274 (96)	
9	386 (100)	385 (69)	269 (8.2)	309 (17)	281 (17)

Table II

## Physical Properties

Compound Number	M.p. °C	% Yield	Recrystallization Solvent	Empirical Formula	Anal. Calcd./Found			λ max nm (ε × 10 <sup>-3</sup> ) in acetonitrile	
					C	H	Other Atom		
2	303-305	60	acetic acid	C <sub>24</sub> H <sub>17</sub> ClO <sub>5</sub>	68.5 68.3	4.1 4.2	8.4 (Cl) 8.6	419 (32.5) 350 (22.8)	278 (14.0) 232 (19.0)
3	309-310	87	formic acid	C <sub>41</sub> H <sub>27</sub> ClO <sub>6</sub>	75.6 75.6	4.1 4.3	5.5 (Cl) 5.6	525 (27.0) 430 (25.0)	345 (32.0)
4	321 (explodes)	86	acetonitrile	C <sub>41</sub> H <sub>27</sub> ClO <sub>6</sub>	75.6 75.4	4.1 4.4	5.5 (Cl) 5.3	555 (46.8) 422 (26.5)	332 (26.8)
5	283-284	94	acetonitrile	C <sub>35</sub> H <sub>24</sub> ClNO <sub>5</sub>	73.3 73.4	4.2	6.2 (Cl) 6.5	550 (37.0) 425 (19.1)	338 (15.0) 270 (14.0)
6	267-268	60	pyridine + methanol	C <sub>41</sub> H <sub>27</sub> NO	89.7 89.4	4.9 4.9	2.6 (N) 2.4		
7	242-243		pyridine + methanol	C <sub>11</sub> H <sub>27</sub> NO	89.7 89.9	4.9 4.9	2.6 (N) 2.6		
8	134-135	85		C <sub>29</sub> H <sub>27</sub> NO	85.9 85.6	6.7 6.6	3.5 (N) 3.4	450 (25.6) 255 (18.2)	
9	229-230	89	pyridine + methanol	C <sub>27</sub> H <sub>17</sub> N <sub>2</sub> O	84.1 84.4	4.4 4.7	7.3 (N) 7.4		
12 (free base)	144-145	67	acetonitrile	C <sub>24</sub> H <sub>17</sub> N	90.4 90.6	5.3 5.1	4.4 (N) 4.5		
13	356-357	60	formic acid	C <sub>41</sub> H <sub>27</sub> ClO <sub>5</sub> S	73.9 73.6	4.1 4.0	4.8 (S) 4.6	561 (33.0) 437 (45.0)	342 (38.0)
14	359-360	70	formic acid	C <sub>47</sub> H <sub>30</sub> ClNO <sub>5</sub>	78.0 77.8	4.1 4.4	1.9 (N) 1.9	585 (29.4) 462 (19.0)	345 (27.9) 262 (31.6)
15	319-320	84		C <sub>41</sub> H <sub>23</sub> NClO <sub>5</sub>	76.0 76.2	4.3 4.5	5.5 (Cl) 5.6		
17	> 300	82	acetic acid + acetonitrile	C <sub>20</sub> H <sub>13</sub> ClO <sub>5</sub>	65.2 65.0	3.5 3.7	9.6 (Cl) 9.8		
18	325-326	84	acetic anhydride	C <sub>33</sub> H <sub>21</sub> ClO <sub>6</sub>	72.2 72.2	3.8 3.5	6.5 (N) 6.6	486 (38.5) 409 (43.0)	317 (25.2) 253 (27.0)
19	322-323	83	acetonitrile	C <sub>37</sub> H <sub>23</sub> ClO <sub>6</sub>	74.1 73.8	3.8 3.7	5.8 (N) 5.6	474 425	300 228 (not complete solution)
20	303-304	76		C <sub>27</sub> H <sub>22</sub> ClNO <sub>5</sub>	68.3 68.5	4.6 4.5	3.0 (N) 2.8	420 (52.0)	
21	384-385	73	nitromethane	C <sub>26</sub> H <sub>19</sub> ClO <sub>6</sub>	67.6 67.7	4.1 4.3	7.7 (Cl) 7.6	418 (35.0)	

Compounds **6** and **7** were prepared by procedure (B).

A suspension of 5 mmoles of **3** or **4** in 8 ml. of pyridine and 5 ml. of concentrated ammonium hydroxide was refluxed for 30 minutes. After chilling the solid was collected and crystallized.

2-(1,3-Diphenyl-1-piperidino-1,3-propenylidene)-1-indanone (**8**).

A suspension of 0.01 mole of **2** in 100 ml. of ether was treated with 3 ml. of piperidine, stirred 1 hour and filtered. The filtrate was evaporated to give dark red crystals.

1-Phenyl-2-benzoyl-3-cyano-4-aminofluorene (**9**).

A mixture of 2.1 g. (0.005 mole) of **2**, 1 g. (0.015 mole) of malononitrile and 2 ml. of piperidine in 10 ml. of acetonitrile was refluxed 2 hours, cooled and the solid was collected and recrystallized.

2,4-Diphenyl-5*H*-indeno[1,2-*b*]pyridinium perchlorate (**12**).

The free base of **12** was prepared from **2** by procedure B and converted to the perchlorate with perchloric acid in acetic acid.

Preparation of Compounds **13**, **14** and **15**.

Procedure A was employed using **10** (2), **11** (2) and **12**. 12*H*-Indeno[1,2-*b*]naphtho[1,2-*c*]pyrylium Perchlorate (**17**).

A solution of 8.6 g. of 2-hydroxy-1-naphthaldehyde and 6.6 g. of 1-indanone in 40 ml. of acetic acid and 10 ml. of 70% perchloric acid was heated on a steam bath while passing hydrogen chloride through the solution. The mixture was cooled and the solid collected.

Preparation of Compounds **18** and **19**.

Procedure A was used with **16** (2) and **17**.

5-Dimethylaminomethylene-2,4-diphenyl-5*H*-indeno[1,2-*b*]pyrylium Perchlorate (**20**).

A solution of 2 g. of **2** in 50 ml. of acetic anhydride containing 6 ml. of dimethylformamide was refluxed for 2 hours, cooled and the solid collected.

5-Methoxymethylene-2,4-diphenyl-5*H*-indeno[1,2-*b*]pyrylium Perchlorate (**21**).

(a) A solution of 2 g. of **2**, 4 ml. of dimethylformamide and 6 ml. of phosphorylchloride was heated on a steam bath for 1 hour and then poured into methyl alcohol. Perchloric acid (2 ml.) was added to the solution, and after cooling the solid was collected.

(b) The same product was obtained in 78% yield from **2** and excess methyl ethyl orthoformate in refluxing acetic anhydride.

Acknowledgment.

We are indebted to Mr. D. P. Maier for the mass spectral data.

#### REFERENCES AND NOTES

- (1) J. S. Buck and T. M. Heilbron, *J. Chem. Soc.*, **123**, 2521 (1924); W. Schneider, *Ann. Chem.*, **432**, 297 (1923); W. Dilthey and J. Fischer, *Chem. Ber.*, **57**, 1653 (1924); R. Wizinger and K. Wagner, *Helv. Chim. Acta*, **34**, 2290 (1951).
- (2) G. V. Boyd, *J. Chem. Soc.*, 55 (1959).
- (3) R. Lombard and A. Kress, *Bull. Soc. Chem. France*, 1528 (1960).
- (4) K. Dimroth and G. Neubauer, *Angew. Chem.*, **69**, 720 (1957).