reactions, the excited state involved in the present system is most likely a triplet, presumably n–π*.

Experimental Section

Each of the six esters used in this study was synthesized by the reaction of the appropriate acid chloride and alcohol. After being refluxed for 24 hr, the reaction mixture was distilled through a Vigreux column. After a number (usually three to four) of careful distillations in which only the middle half of the distillate was taken, no impurities were observed by gas chromatography using both diisodecyl phthalate and Hallcomid columns.

Mercury sensitized photolyses were conducted in a cylindrical quartz cell containing a drop of mercury. The light source was a Hanovia 87A-45 low-pressure mercury vapor lamp. Since the envelope of this lamp is Vycor, the radiation is pure 253.7 nm and contains none of the 184.9-nm mercury line. The reaction is entirely mercury sensitized since the long wavelength cutoff of absorption by aliphatic esters is 240 nm. The pressure of the esters was generally 2–5 Torr and nitric oxide was added to remove products of free-radical reactions. The data given in Table I were determined at conversions of 0.5% in the presence of 10% nitric oxide.

Hydrocarbon products were analyzed using a 30 ft long, 0.25 in. o.d. column packed with 20% squalane on 60–80 mesh Chromosorb P, operated at ambient temperature and a helium flow of 70 ml/min. Methyl acetate was analyzed using a 10 ft long 0.25 in. o.d. column packed with 10% diisodecyl phthalate on 60–80 mesh Chromosorb P, operated at 80° and a helium flow of 30 ml/min.

Registry No.—Isopropyl butyrate, 638-11-9; *n*-propyl butyrate, 105-66-8; isobutyl butyrate, 539-90-2; ethyl valerate, 539-82-2; *n*-butyl valerate, 591-68-4; isobutyl valerate, 10588-10-0.

Acknowledgment.—We would like to thank Professor S. J. Weininger for his interest in this work.

The Preparation and Certain Reactions of 3-Formyl-4*H*-flavene

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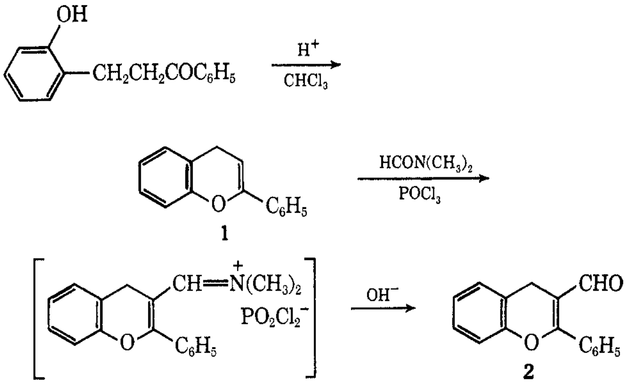
Recently we described[1] a convenient method for the preparation of 4*H*-flavene (2-phenyl-4*H*-1-benzopyran) (**1**). The present paper describes the formylation of **1** to give 3-formyl-4*H*-flavene (**2**) and the reaction of **2** with some active methyl compounds.

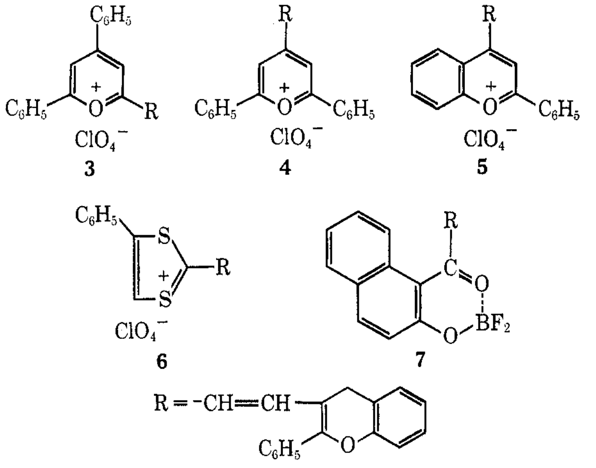
The Vilsmeier reagent reacts with **1** to give an intermediate iminium salt (not characterized) which was hydrolyzed to give **2**, as shown in Scheme I. It is interesting that the aldehyde **2** is stable, in contrast to **1**, which is quite unstable and decomposes to a tar in several hours. We have found that it is not necessary to isolate **1** but, instead, to treat the chloroform reaction mixture containing **1** directly with the Vilsmeier reagent.

The aldehyde **2** was allowed to react with some charged heterocyclic compounds which contained active methyl groups to give the compounds listed in Scheme II. Only compounds which contain very reactive methyl groups react with **2**. No reaction took place between **2** and 1-ethyl-2-methylquinolinium perchlorate or 1,2-dimethylnaphtho[1,2-*d*]thiazolium perchlorate under the conditions employed for the preparation of the compounds in Scheme II.

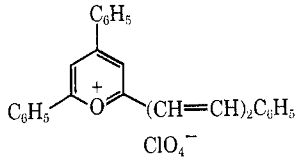
SCHEME I



SCHEME II



The dyes listed in Scheme II show absorption at longer wavelengths than the corresponding simple styryl dyes. For example, in acetonitrile solution, 2,4-diphenyl-6-(4-phenyl-1,3-butadienyl)pyrylium perchlorate[2] (**8**) shows absorption at λ_{max} 490 mμ (ϵ 30,200) while **3** shows λ_{max} 539 mμ (ϵ 28,900). It is evident that the oxygen atom of the flavene nucleus has affected the absorption of **3**, and therefore canonical forms such as A must be considered. However, comparison of the



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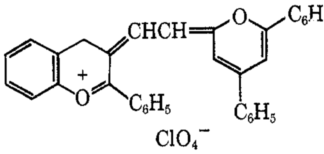

A

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[1] J. A. VanAllan, G. A. Reynolds, and T. H. Regan, *J. Org. Chem.*, **32**, 1897 (1967).

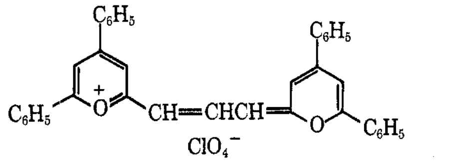
[2] R. Wizinger and K. Wagner, *Helv. Chim. Acta*, **34**, 2290 (1951).

TABLE I
PHYSICAL PROPERTIES AND ANALYTICAL DATA

Compd no.	Method of prepn	Mp, °C	Yield, %	Solvent of recrystn	Empirical formula	Calcd, % C	Calcd, % H	Calcd, % Cl	Found, % C	Found, % H	Found, % Cl	Absorption, λ_{max} ($\epsilon \times 10^{-3}$) in $CHCl_3$
2		65–66	56	Ligroin (bp 63–75°)	$C_{16}H_{12}O_2$	81.3	5.1		81.1	5.3		295 (11.8)
3	A	260–261	42	Acetic anhydride	$C_{34}H_{25}ClO_6$	72.1	4.5	6.3	71.9	4.7	6.4	274 (16.3), 352 (35.4), 539 (39.9)
4	A	264–265	53	Acetonitrile	$C_{34}H_{25}ClO_6$	72.1	4.5	6.3	71.9	4.6	6.6	269 (23.1), 406 (21.3), 313 (9.8), 523 (55.3)
5	A	253–254	67	Acetic anhydride	$C_{32}H_{23}ClO_6$	71.3	4.3	6.6	71.0	4.5	6.7	249 (21.1), 390 (19.7), 263 (17.0), 562 (45.5)
6	A	85–86	61	Acetic anhydride	$C_{26}H_{19}ClO_5S_2$	61.0	3.7	12.5	60.6	4.0	12.4	~240 (18.4), 525 (33.3), ~280 (7.2)
7	A	214–215	20	Alcohol	$C_{28}H_{19}BF_2O_3$	74.4	4.2	8.4	74.1	4.4	8.6	238 (29.0), ~380 (7.2), 340 (14.2), ~520 (34.0), 540 (46.4)
8	. . .[a]	207–209		Acetonitrile	$C_{27}H_{21}ClO_5$	70.2	4.6	7.7	70.0	4.3	7.5	264 (13.8), ~368 (22.0), 345 (28.0), 490 (30.2)
9		125–126		Acetic anhydride	$C_{37}H_{27}ClO_6$	73.0	4.5	5.8	72.9	4.7	6.0	267 (27.5), 452 (3.0), 308 (30.0), 482 (3.0), 249 (27.0), 527 (1.0), 388 (25.5), 720 (76.0), ~413 (11.0), 790 (99.0)
11	A	297	87	Acetic anhydride	$C_{28}H_{22}ClNO_5$	69.0	4.8	2.9	69.2	5.2	2.7	270 (19.2), 385 (21.6), 325 (11.6), 550 (90.5)
12	A	287	88	Acetonitrile	$C_{28}H_{22}ClNO_5$	69.0	4.8	2.9	68.7	4.8	2.7	268 (29.8), 570 (40.4), 353 (28.4)

[a] Reference 2.

spectrum of **3** with that of the symmetrical pyrylium cyanine dye **9** [λ_{max} 790 mμ (ϵ 99,000)] demonstrates that A is not an important resonance contributor in the dye **3**.



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In order to determine the effect of the basicity of the heteroatom on the absorption spectra, the dyes **11** and **12** were prepared by the reaction sequence shown in Scheme III.

The nitrogen containing dyes **11** and **12** showed absorption at approximately 30-mμ longer wavelength than the corresponding oxygen dyes **3** and **4** (see Table I).

Several attempts were made to prepare 3-formylflavylium perchlorate by treatment of **1** with triphenylmethyl perchlorate, but the only product that was identified in the reaction mixture was triphenylmethane.

Experimental Section

The physical properties of the compounds are collected in Table I.

3-Formyl-4*H*-flavene (2).—A mixture of 5 g (0.22 mol) of 2-hydroxydihydrochalcone, 0.5 g of *p*-toluenesulfonic acid, and 50 ml of chloroform was refluxed for 2 hr while the water which is formed in a Dean-Stark water separator was collected. The cooled solution was shaken with dilute aqueous sodium bicarbonate, and the organic phase was dried (magnesium sulfate) and filtered from the drying agent. The filtrate was added to a cooled mixture of 4.5 ml of dimethylformamide and 2.3 ml of phosphorus oxychloride, and the resulting mixture was stirred for 2 hr at room temperature. The reaction mixture was mixed with 50 ml of 5% aqueous sodium hydroxide, and the mixture was stirred for 1 hr. The organic phase was separated, washed with water, and dried (magnesium sulfate), and the chloroform was removed by means of a rotary evaporator. The oily residue solidified on standing. The nmr spectrum[3] of **2** in deuteriochloroform showed absorptions at δ 3.69, singlet (2 H) for the methylene protons, a multiplet at δ 7.19–7.52 (9 H) for the aromatic protons, and a singlet at δ 9.62 for the aldehyde proton. A sample of **2** was converted to the dinitrophenylhydrazone, mp 237–238°.

Anal. Calcd for $C_{22}H_{16}N_4O_5$: C, 63.6; H, 3.6; N, 13.5. Found: C, 64.0; H, 3.8; N, 13.5.

Method A.—The dyes listed in Table I were prepared by the following procedure. A mixture of 1 mmol of **2** and 1 mmol of the appropriate methyl-substituted heterocyclic compound in 25 ml of acetic anhydride was refluxed for 30 min. The colored reaction mixture was chilled and the solid was collected. In some cases it was necessary to dilute the reaction mixture with ether to obtain the product.

3-Formyl-1-methylindole (10).—A solution of 6 g of dimethylformamide, 7.2 ml of phosphorus oxychloride, 10 g of 1-methylindole, and 50 ml of chloroform was stirred at room temperature for 1 hr. The reaction mixture was washed with water, 50 ml of 5% aqueous sodium hydroxide was added to it, and the stirring was continued for an additional hour. The chloroform layer was separated, washed with water, and dried (magnesium sulfate). The solvent was removed to yield 11 g of the aldehyde, mp 62–64° (reported[4] mp 65°).

4,6-Diphenyl-2-[3-(4,6-diphenyl-2*H*-pyran-2-ylidene)propenyl]-pyrylium Perchlorate (9).—A mixture of 3.5 g of 2-methyl-4,6-diphenylpyrylium perchlorate, 6 ml of triethyl orthoformate, 50 ml of acetic acid, and 5 ml of pyridine was refluxed for 0.5 hr and then chilled. The solid was collected and recrystallized from acetic acid and then again from acetic anhydride to yield 1.2 g of **9**.

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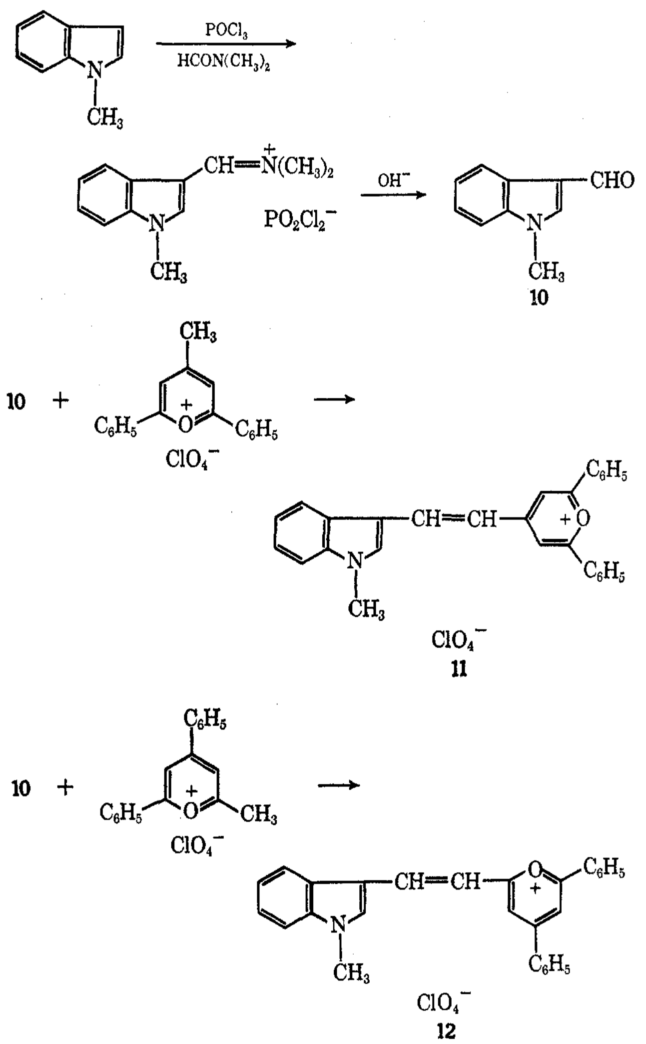
(3) The nmr spectrum was measured at 60 MHz on a Varian A-60 spectrometer with tetramethylsilane as an internal standard.

(4) H. Wieland, W. Kronz, and H. Mittasch, *Justus Liebigs Ann. Chem.*, **518**, 1 (1934).

Scheme III



Registry No.—**2**, 27179-40-4; **2** 2,4-DNP, 27179-41-5; **3**, 27179-42-6; **4**, 27179-43-7; **5**, 27179-44-8; **6**, 27179-45-9; **7**, 22181-72-2; **8**, 6802-23-9; **9**, 27179-48-2; **11**, 27179-49-3; **12**, 27179-50-6.

Acknowledgment.—We are indebted to Dr. T. H. Regan and Mr. R. L. Young for the determination and interpretation of the nmr spectrum.

Reaction of 2-Thiouracils with Formaldehyde under Acidic Conditions

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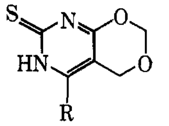
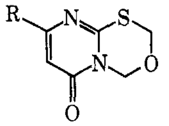
The reaction of 6-methyl- and 6-phenyl-2-thiouracil with formaldehyde under acidic conditions has previously been investigated. Structures **1b** and **1c** were assigned to the products.[1] The basis for this assignment was the observation that the same products were obtained also by reaction of the 5-hydroxymethyl derivatives of these thiouracils with formaldehyde under the same reaction conditions.[1] Thus it appeared that substitution at position 5 of the 2-thiouracil ring had been incontrovertibly demonstrated. Since these results were not in agreement with the available evidence, which indicated that the sulfur atom could be a very reactive center,[2-5] we reinvestigated these reactions and included 2-thiouracil because of its biological significance.

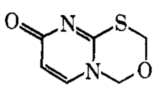
First we ascertained that 2-thiouracil itself reacts with formaldehyde under acidic conditions giving the pyrimidooxathiazine **2a**. Confirmation of the assigned structure seemed necessary not only in order to exclude possible isomeric formulas **1a** and **3**, but also because the reaction product crystallized from water giving two crystalline forms, aggregates of orthorhombic needles and monocline crystals. This was accomplished by X-ray analysis (see Experimental Section). The two crystalline forms were shown to represent a single substance having the assigned structure (**2a**).



1a, R = H
b, R = CH$_3$
c, R = C$_6$H$_5$



2a, R = H
b, R = CH$_3$
c, R = C$_3$H$_7$



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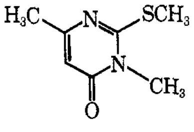
Nmr, ir, and uv data were fully compatible with this assignment. In particular the nmr spectra of the two crystalline forms were identical and fully compatible with structures **2a** and **3**, since position 5 of the original 2-thiouracil ring was shown to be unsubstituted.

The ir spectra in Nujol mull were different because of the different crystal-packing effects while spectra in chloroform solutions were identical; all these spectra showed the presence of the carbonyl bands.

Uv spectra of both crystalline forms of **2a** in water were identical and very similar to the uv spectra of the pyrimidothiazine **5** (methanol), 3,6-dimethyl-2-methylthiopyrimidin-4-one (**4**) (methanol),[6] and the thiazolopyrimidine **6** (water), displaying a maximum in the range 285–295 mμ and two very close maxima in the range 224–245 mμ. Because of this we concluded that all the above-mentioned substances had the same *o*-quinoid chromophore shown to be present in **2a**; structures **5** and **6** were previously supported only by ir analysis.[4]



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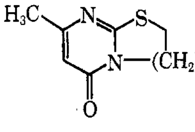
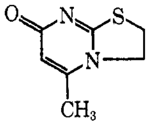


5, *n* = 2
6, *n* = 1



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The presence of two very close maxima in the uv spectrum of **4** in methanol at about 230 and 240 mμ

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[4] N. G. Pashkurov and V. S. Reznik, *Khim. Geterotsikl. Soedin.*, 1918 (1968).

[5] I. Wempen, and J. J. Fox, *J. Org. Chem.*, **34**, 1020 (1969).

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