2.08 (s, 3, $OCOCH_3$), 3.58 (s, 3, $COOCH_3$), 5.40 ppm (q, 2, J_{AB} = 6.3 Hz, $\delta\nu_{AB}$ = 3.9 Hz).

Anal. Calcd for $C_{20}H_{28}O_4$: C, 72.26; H, 8.49. Found: C, 72.23; H, 8.44.

Methyl 12-Acetoxypodocarp-11,13-dien-19-oate (2).—The procedure of Dauben, *et al.*, was used.[9] To a solution of 1.00 g (3.58 mmol) of unsaturated keton 1 (mp 126–130°) in 30 ml of isopropenyl acetate was added 0.300 g of *p*-toluenesulfonic acid monohydrate, and the mixture was heated at reflux under nitrogen, using the same apparatus and technique as above, for 4.5 hr. At the end of this period, 20 ml of distillate was obtained and, after cooling, the organic product was isolated *via* hexane extraction. Evaporation of the solvents gave 1.13 g (95%) of a light yellow oil, the pmr spectrum of which showed it to consist of 90% of acetoxy diene **2** and 10% of ketone **1**. There were no discernible absorptions of the acetoxy diene **3** present. Crystallization from dry hexane at 0° gave 0.80 g (70%) of **2** as colorless needles: mp 78–80°; ir 1760 (acetate C=O), 1730 (ester C=O), 1650, 1600 cm^{-1} (diene); uv λ_{max} 262 mμ (ϵ 3400); ORD (concn 0.1 mg/ml CH_3OH), 22°, $[\Phi]_{650}$ +1000°, $[\Phi]_{589}$ +1500°, $[\Phi]_{400}$ +1500°, $[\Phi]_{250}$ +7000°, $[\Phi]_{220}$ +12,600°; pmr δ 0.69 (s, 3, C-20 CH_3), 1.22 (s, 3, C-18 CH_3), 2.18 (s, 3, $OCOCH_3$), 3.77 (s, 3, $COOCH_3$), 5.70 (s, 2, $W_{1/2}$ = 4 Hz, C-13 and C-14 vinylic H), 5.87 ppm (d, 1, J = 1.0 Hz, C-11 H).

Anal. Calcd for $C_{20}H_{28}O_4$: C, 72.26; H, 8.49. Found: C, 72.40; H, 8.38.

When the pure acetoxy diene **2** was heated at reflux under nitrogen in acetic anhydride for 2 hr in the presenec of a crystal of *p*-toluenesulfonic acid and worked up *via* hexane, the thermodynamic mixture of 59% **3**, 36% **2**, and 5% **9** was obtained.

Methyl 12-Acetoxypodocarp-8(14),11-dien-19-oate (9).—To a solution of 100 mg (3.6 mmol) of methyl 12-oxopodocarp-8(14)-en-19-oate (**7**) in 5.0 ml of isopropenyl acetate was added 25 mg of *p*-toluenesulfonic acid monohydrate, and the mixture was heated at reflux under nitrogen in the same apparatus as above for 3 hr. At the end of this period 3.0 ml of distillate was obtained and, after cooling, the organic product was isolated *via* hexane. Evaporation of the solvents afforded 108 mg (94%) of oily crystals. The pmr spectrum of this showed the product to consist of 60% **9**, 25% **3**, and 15% methyl podocarpate **10**. Chromatographhy on Florisil removed the methyl podocarpate but did not achieve separation of **9** and **3**. Tlc on silica gel in a number of solvents was similarly unsuccessful. An enriched sample of **9** (containing 17% of **3** by integration of the C-20 CH_3 absorptions) was obtained by repeated crystallization from hexane and it showed ir 1760 (acetate C=O), 1730 (ester C=O), 1670 cm^{-1} (olefinic); uv (featureless except for absorption due to 17% of **3**); pmr δ 0.60 (s, 3, C-20 CH_3), 1.15 (s, 3, C-18 CH_3), 2.05 (s, 3, $OCOCH_3$), 2.5–2.85 (m, 2, C-14 allylic H), 3.58 (s, 3, $COOCH_3$), 5.35 ppm (m, 2, $W_{1/2}$ = 10 Hz, C-11 and C-14 H).

Anal. Calcd for $C_{20}H_{28}O_4$: C, 72.26; H, 8.49. Found: C, 72.12; H, 8.67.

Registry No.—**1**, 24402-16-2; **2**, 33608-33-2; **3**, 33495-78-2; **7**, 24412-03-1; **9**, 33537-22-3.

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19-Hydroxy Steroids. III. Reactions with Lead Tetraacetate[1]

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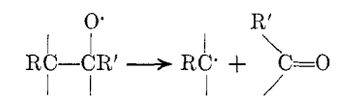
Since it was first reported[2] that treatment of secondary alcohols with lead tetraacetate could lead to cyclic ethers, this reaction has been used extensively to functionalize or to remove the methyl group at C-10 of certain steroids[3] in attempts to enhance the biological activity of such compounds and as a means of preparing estrogens[4] from androgens.

In addition to these important applications, the reaction *per se* has been extensively investigated and a number of generalizations[5] have been found to apply. One of these correlations relates to the limits of favorable internuclear distance (2.5–2.7 Å) between the oxyradical and the carbon atom from which hydrogen atoms can be abstracted intramolecularly. If more than one alkyl group is appropriately situated for hydrogen atom abstraction, it has been found that the reactivity of hydrogen atoms decreases in the order tertiary > secondary > primary. Hydrogen atoms attached to an oxygen-bearing carbon atom are more reactive than those attached to a carbon atom having another carbon atom as neighbor. More recently,[6] the effects of a methoxy group adjacent to the reacting hydroxy group have been evaluated.

Once an oxygen radical has been produced by oxidation with lead tetraacetate, fragmentation can also take place, as shown below. The amount of cleavage which occurs increases with the stability of the alkyl radical formed[5] but a number of other factors can also influence the course of this reaction.



While investigating approaches to the synthesis of cardiac-active steroids some model compounds containing a hydroxy group at C-19 were prepared. Following is a report of the course of the lead tetraacetate oxidation of one of these compounds in which it is shown that the reaction proceeds by intramolecular hydrogen abstraction.

Steroids with a double bond at C-5,C-6 are normally unaffected[7] in reactions with lead tetraacetate. However, Moriarty and Kapadia[8] have reported that the lead tetraacetate oxidation of 3β-acetoxycholest-5-en-19-ol (**1**) results in oxidative fragmentation, with loss of the hydroxymethyl group at C-10, yielding a product tentatively identified as 3β,6β-diacetoxy-19-norcholest-5(10)-ene (**2b**). The authors postulated a mechanism involving the concerted intramolecular transfer of an acetoxy group from the C-19 lead ester to C-6 which implies stereospecificity in the resulting C-6 acetoxy group. An analogous fragmentation reaction has also been observed[9] in the lead tetraacetate oxidation of the diethylene ketal of 19-hydroxyandrost-5-ene-3,17-dione.

The preparation of the 5α,6α- and 5β,6β-oxides (**3** and **4**) (Scheme I) from 3β-acetoxycholest-5-en-19-ol

(1) For part II, see P. Morand and M. Kaufman, *Can. J. Chem.*, **49**, 3185 (1971).

(2) G. Cainelli, M. Lj. Mihailović, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **42**, 1124 (1959).

(3) See, for example, A. Bowers and E. Denot, *J. Amer. Chem. Soc.*, **82**, 4956 (1960); H. Immer, M. Lj. Mihailović, K. Schaffner, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **45**, 753 (1962); J. F. Bagli, P. Morand, and R. Gaudry, *J. Org. Chem.*, **28**, 1207 (1963); M. E. Wolff, W. Ho, and R. Kwok, *Steroids*, **5**, 1 (1965).

(4) *Cf.* A. Bowers, R. Villotti, J. A. Edwards, E. Denot, and O. Halpern, *J. Amer. Chem. Soc.*, **84**, 3204 (1962); J. F. Bagli, P. Morand, K. Wiesner, and R. Gaudry, *Tetrahedron Lett.*, 387 (1964).

(5) K. Heusler and J. Kalvoda, *Angew. Chem.*, **76**, 518 (1964).

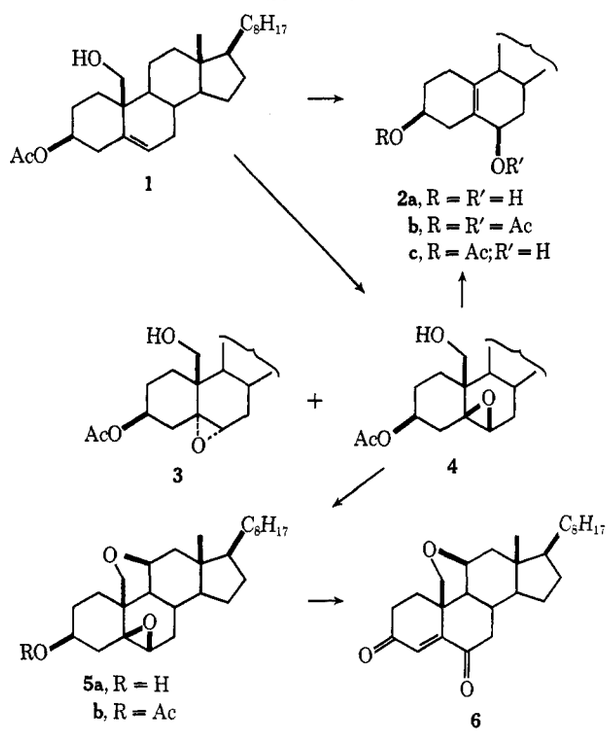
(6) P. Morand and M. Kaufman, *J. Org. Chem.*, **34**, 2175 (1969).

(7) *Cf.* G. Cainelli, B. Kamber, J. Keller, M. Lj. Mihailović, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **44**, 518 (1961).

(8) R. M. Moriarty and K. Kapadia, *Tetrahedron Lett.*, 1165 (1964).

(9) M. Amorosa, L. Caglioti, G. Cainelli, H. Immer, J. Keller, H. Wehrli, M. Lj. Mihailović, K. Schaffner, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **45**, 2682 (1962).

SCHEME I



(1) by treatment with perphthalic acid has been reported and the structures of these compounds have been established on the basis of physical[10] and chemical[1] evidence. It was subsequently observed that, when neutral alumina instead of Florisil was used as adsorbant to remove excess phthalic acid, the yield of the 5β,6β-oxide **4** decreased sharply and a third product could be isolated in 23% yield. That this substance was produced from the 5β,6β-oxide **4** was confirmed by treating the latter in a similar manner. The 5α,6α-oxide **3** was found to be stable under these conditions. The structure of this compound[11] is formulated as **2c** on the basis of the analytical and spectral data reported in the Experimental Section. On repeating the reaction reported by Moriarty and Kapadia[8] and hydrolyzing the product isolated, we obtained the diol **2a**, which was found to be identical in all respects with the diol obtained by hydrolysis of 3β-acetoxy-19-norcholest-5-(10)-en-6β-ol (**2c**) which was prepared in the manner described above. This therefore confirms the structure **2b** formulated by these authors and also provides support for their proposed mechanism.

We then proceeded to investigate the course of the reaction with lead tetraacetate in a C-19 steroidal alcohol in which the C-5,C-6 double bond was absent. Treatment of 3β-acetoxy-5,6β-oxido-5β-cholestan-19-ol (**4**) with this reagent led to the isolation (43%) of a substance identified as 3β-acetoxy-5,6β:11β,19-dioxido-5β-cholestane (**5b**). The empirical formula, $C_{29}H_{46}O_4$, for this compound was confirmed by elemental and mass spectral analyses. Examination of the nmr spectrum indicated that the 5β,6β-oxide group was intact. Signals for three protons attributable to the formation of an oxide ring were also observed. Since fragmentation apparently had not occurred in this reaction, the question remained as to which proton (C-2, C-4, C-8, or C-11) had been abstracted, as it is the alkyl group δ to the reacting alcohol that is normally involved[5] in the formation of such oxides. At C-2 and C-4, it is clearly the axial proton which would be abstracted, resulting in the formation of the β oxide in each case. Although the situation is not so clear-cut at C-11, it is most likely[12] that the β oxide would be formed since the isomeric α oxide would introduce considerably more strain into the molecule.

That the tertiary hydrogen atom at C-8 was not abstracted was established by examination of the nmr spectrum of **5b**. The integrated spectrum indicated five downfield protons whereas four would have been observed if the C-19 oxyradical had abstracted the δ hydrogen atom at C-8. Measurement of internuclear distances (Dreiding models) between the oxy radical and the relevant δ carbon atoms, C-2, C-4, and C-11, indicated a separation of 2.9 Å for the C-2 and C-4 positions and of 2.3 Å for the C-11 position. It is apparent, therefore, that the most likely hydrogen atom to be abstracted is one attached to C-11 since, by rotation of the oxy radical away from the C-11 atom, the critical distance[5] of 2.5–2.7 Å can be approached.

Confirmation that the ether linkage was not at C-4 (and therefore not at C-2 since both these carbon atoms are equidistant from the oxy radical) was obtained by hydrolysis of **5b** to the corresponding alcohol **5a** and subsequent oxidation to a compound identified as 11β,19-oxidocholest-4-ene-3,6-dione (**6**). The empirical formula, $C_{27}H_{40}O_3$, for this substance was confirmed by elemental and mass spectral analyses and the uv spectrum showed the characteristic absorption[13] for an enedione. As expected, the nmr spectrum exhibited a singlet at δ 6.48 (olefinic proton at C-4) as well as the appropriate signals for the five-membered oxide ring indicating that the latter was intact.

Experimental Section[14]

3β,6β-Dihydroxy-19-norcholest-5(10)-ene (2a). A. From 3β-Acetoxy-5,6β-oxido-5β-cholestan-19-ol (4).—The preparation of **4** by treatment of 3β-acetoxycholest-5-en-19-ol (**1**) with perphthalic acid has been described[10] elsewhere. It was subsequently found, however, that, when an ethereal solution of the crude product was eluted on a column of neutral alumina instead of Florisil to remove excess phthalic acid and the products were separated by chromatography over silica gel (600 g), a third product (in addition to the isomeric 5,6-oxides) could be isolated in 23% yield. It was also observed that the yield of the 5β,6β-oxide **4** decreased significantly from that previously obtained. The substance isolated was purified by crystallization from petroleum ether (bp 30–60°) and was identified as 3β-acetoxy-19-norcholest-5(10)-en-6β-ol (**2c**): mp 108–109°; ir

(10) R. R. Fraser, M. Kaufman, P. Morand, and G. Govil, *Can. J. Chem.*, **47**, 403 (1969).

(11) Treatment of 5,6β-oxido-19-oxo-5β-cholestan-3β-ol with KOH in CH_3OH has been reported [M. Akhtar and D. H. R. Barton, *J. Amer. Chem. Soc.*, **86**, 1528 (1964)] to give the diol **2a**, which was characterized by its elemental analysis, optical rotation, and melting point.

(12) For example the 11β-oxy radical leads to formation of the 11β,19-oxide whereas the 11α-oxy radical leads to formation of the 1β,11α-oxide [K. Heusler, *Tetrahedron Lett.*, 3975 (1964)].

(13) L. F. Fieser and M. Fieser, "Steroids," Reinhold, New York, N. Y., 1959, p 44.

(14) Melting points were determined on a Hoover Uni-Melt apparatus and are uncorrected. Ir, nmr, uv, and mass spectra were recorded on a Beckman IR-8 infrared spectrophotometer, a Varian V-4302 60-Mc spectrometer, a Perkin-Elmer 202 recording spectrophotometer, and a Hitachi Perkin-Elmer R. M. U. 6D spectrometer. Microanalyses were determined in the laboratory of Dr. A. Bernhardt, Elbach uber Engelskirchen, West Germany. SilicaR (200–300 mesh) and neutral alumina (Woelm, activity I) were used as adsorbants in column chromatography. In working up the products of reactions, the organic extracts were washed with dilute HCl solution and/or $NaHCO_3$ solution, dried over anhydrous $MgSO_4$, and evaporated to dryness under reduced pressure.

($CHCl_3$) 1670 cm^{-1} (C=C); nmr ($CDCl_3$) δ 5.1 (m, 1, $W_{1/2}$ = 15 Hz, CHOAc), 3.84 (m, 1, $W_{1/2}$ = 8 Hz, CHOH), 2.06 (s, 3, $OCOCH_3$); mass spectrum (70 eV) *m/e* 412, 370, 352.

Anal. Calcd for $C_{28}H_{46}O_3$: C, 78.09; H, 10.77. Found: C, 77.63; H, 10.61.

Hydrolysis of **2c** (51 mg) with a 10% solution (10 ml) of KOH in methanol–water (9:1) at room temperature for 12 hr gave, after working up in the usual way and crystallizing the product from CH_3OH, an analytical sample of 3β,6β-dihydroxy-19-norcholest-5(10)-ene (**2a**): mp 164–166° (lit.[8,11] mp 174–175°, 165–168°); mass spectrum (70 eV) *m/e* 388 (M^+), 370, 352.

B. From 3β-Acetoxycholest-5-en-19-ol (1).—The product obtained by treatment of **1** with lead tetraacetate in the manner reported by Moriarty and Kapadia[8] was hydrolyzed as described above. Isolation of the product and crystallization from CH_3OH gave a substance identical in all respects with the 3β,6β-dihydroxy-19-norcholest-5(10)-ene (**2a**) obtained from **4**.

Lead Tetraacetate Oxidation of 3β-Acetoxy-5,6β-oxido-5β-cholestan-19-ol (4).—Lead tetraacetate (6.5 g, 14.6 mmol, previously dried over P_2O_5) and dry calcium carbonate (7.0 g) were added to cyclohexane (200 ml) and the solution was refluxed for 40 min by means of a 500-W lamp. Iodine and 3β-acetoxy-5,6β-oxido-5β-cholestan-19-ol (**4**) (0.53 g, 1.15 mmol) were then added and the mixture was refluxed for 5 hr. The insoluble white residue was removed by filtration and the filtrate was washed with a 30% aqueous solution of $Na_2S_2O_3$ (200 ml) and water. Removal of the solvent gave an oil (0.50 g) which was chromatographed over silica gel. Elution with benzene afforded a solid (216 mg) which, upon crystallization from aqueous CH_3OH, gave an analytical sample of a substance identified as **3β-acetoxy-5,6β:11β,19-dioxido-5-cholestane (5b)**: mp 109–111°; nmr ($CDCl_3$) δ 4.85 (m, 1, $W_{1/2}$ = 25 Hz, CHOAc), 4.02 (m, 2, CH_2OC), 3.75, 3.65, (m, 1, CHOC), 3.2 (m, 1, CHOC), 2.05 (s, 3, $OCOCH_3$); mass spectrum (70 eV) *m/e* 458 (M^+), 440, 398, 382, 380, 351.

Anal. Calcd for $C_{29}H_{46}O_4$: C, 75.94; H, 10.11. Found: C, 75.73; H, 9.74.

Hydrolysis and Oxidation of 3β-Acetoxy-5,6β:11,19-dioxido-5β-cholestane (5b).—Treatment of **5b** (70 mg) with a solution of $NaHCO_3$ (10 mg) in methanol–water (9:1, 5.0 ml) at 60° for 4 hr gave, after working up in the usual way, the crude alcohol **5a** (65 mg) which was subsequently oxidized with Sarett reagent[15] without further purification. Isolation of the product (52 mg) in the usual way gave, after crystallization from ether, a substance identified as **11β,19-oxidocholest-4-ene-3,6-dione (6)**: mp 156–158°; uv max ($CHCl_3$) 260 mμ (ϵ 11,600); ir ($CHCl_3$) ($CHCl_3$) 1690 cm^{-1} (C=C—C=O); nmr ($CDCl_3$) δ 6.49 (s, 1, CH=C), 4.29 (m, 1, CHOC), 4.20, 4.01, 3.85, 3.65 (m, 2, J = 10 Hz, CH_2OC); mass spectrum (70 eV) *m/e* 382, 370 (the mass spectrum of cholest-4-ene-3,6-dione prepared in our laboratory also exhibits a peak at $M^+ - 42$).

Anal. Calcd for $C_{27}H_{40}O_3$: C, 78.59; H, 9.77. Found: C, 78.69; H, 9.73.

Registry No.—**2c**, 33487-93-3; **5b**, 33537-29-0; **6**, 33487-94-4; lead tetraacetate, 546-67-8.

Acknowledgments.—The financial support of the National Research Council of Canada is gratefully acknowledged.

(15) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Amer. Chem. Soc.*, **75**, 422 (1953).

Esters and Flavenes from 2-Hydroxychalcones and Flavylium Salts

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Esters prepared from hydroxychalcones are well known except for those of the 2-hydroxychalcones. 2-Acetoxy-2′,3,4′-trimethoxy- and 2-acetoxy-2′,4′,6-trimethoxychalcones[1] in addition to the tetra-*p*-chlorobenzoate of 2,5,2′,5′-tetrahydroxychalcone[2] are reported. Such references are few in number probably because acetylation of 2-hydroxychalcone could yield either the ester of the chalcone itself or the esters of the 2-phenylbenzopyranols, **2** and **3**. The latter flavene esters would be 2-acetoxy-2-phenyl-2*H*-1-benzopyran or 4-acetoxy-2-phenyl-4*H*-1-benzopyran. In addition these esters have not been readily distinguishable and, therefore, the structure of 2-hydroxychalcone esters and a flavene are determined here.

Experimental Section

Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Clark Microanalytical Laboratory, Urbana, Ill., performed the C,H analyses and the University of Illinois provided the nmr spectra with a Varian HA 100 spectrometer using TMS internal standard. Ir spectra were obtained with a Beckman IR-8 spectrometer utilizing KBr pellets or neat liquid.

2-Hydroxychalcone, mp 154–155° dec (lit.[3] mp 154–156° dec), and 4-hydroxychalcone, mp 183–184° (lit.[4] mp 182.5°), were synthesized by condensation of acetophenone and salicylaldehyde or 4-hydroxybenzaldehyde. Flavylium perchlorate, mp 190–191° (lit.[5] mp 190–191°), and flavylium tetrachloroferrate(III), mp 137–138° (lit.[6] mp 137–138°), were prepared from 2-hydroxychalcone. Acetylation of 4-hydroxychalcone yielded 4-acetoxychalcone, mp 128–129° (lit.[4] mp 129°).

2-Acetoxychalcone.—Acetylation of 2-hydroxychalcone with acetic anhydride and acid,[7] or sodium acetate[8] catalysts, at 50–60° for 15 min, and recrystallization of the crude product with hexane yielded 2-acetoxychalcone, 60%, mp 65–66°.

Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.29. Found: C, 76.90; H, 5.28.

Flavylium Tetrachloroferrate(III) from 2-Acetoxychalcone.—A stream of dry hydrogen chloride was bubbled into 13 g of 2-acetoxychalcone stirred in 200 ml of glacial acetic acid for 2 hr. Addition of 10g of anhydrous ferric chloride to the solution produced a precipitate which was recrystallized with glacial acetic acid. The yield of flavylium tetrachloroferrate(III) was 17 g (72%), mp and mmp 137–138°.

Hydrolysis of 2-Acetoxychalcone.—2-Acetoxychalcone, 8.0 g, in 250 ml of water containing 4.3 g of dissolved sodium hydroxide was refluxed for 3 hr. The reaction mixture was extracted with ether which was washed, dried with Drierite, and allowed to evaporate. An oil remained, 3 g (48.5%), ir 2.95 (OH) and 6.08 μ (C=C), which was converted to flavylium tetrachloroferrate(III) (52%) as for 2-acetoxychalcone. Acidification of the basic hydrolysis solution, filtration, and recrystallization with ethanol yielded 2-hydroxychalcone, 2.8 g (45%).

2-Benzoyloxychalcone.—To 25 g of 2-hydroxychalcone in 200 ml of 1 *M* aqueous sodium hydroxide was added 20 g of benzoyl chloride in 200 ml of chloroform dropwise with cooling and stirring for 3 hr. The chloroform layer was separated, washed, dried, and allowed to evaporate. The solid residue was recrystallized from cyclohexane, yielding 24 g (63%) of yellow crystals, mp 101–102°.

Anal. Calcd for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91. Found: C, 80.78; H, 4.68.

Piperidinoflavene.[9]—To a suspension of 15.3 g (0.05 mol) of

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(9) Procedure after R. E. Schaeffer, "Studies of the Structure of Compounds Resulting from Reactions of Flavylium Salts and *sec*-Amines," M.S. Thesis, University of Iowa, Iowa City, Iowa, 1953.