($CHCl_3$) 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

RUSSELL SUTTON

Department of Chemistry, Knox College, Galesburg, Illinois 61401

Received August 19, 1971

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

---

[1] D. N. Dhar, *J. Indian. Chem. Soc.*, **38**, No. 10 (1961).

[2] V. G. Manecke and D. Zerpner, *Makromol. Chem.*, **108**, 198 (1967).

[3] R. C. Elderfield and T. P. King, *J. Amer. Chem. Soc.*, **76**, 5439 (1954).

[4] P. Klinke and H. Gilian, *Chem. Ber.*, **94**, 26 (1961).

[5] R. L. Shriner and R. Sutton, *J. Amer. Chem. Soc.*, **85**, 3989 (1963).

[6] A. N. Nesmeyanov, N. K. Kochetkov, and M. I. Rybinskaya, *Dokl. Akad. Nauk SSSR*, **93**, 71 (1953); *Chem. Abstr.*, **49**, 3953*d* (1955).

[7] A. J. Vogel, "Elementary Practical Organic Chemistry, Small Scale Preparations, Part I," Longmans, Green and Co., New York, N. Y., 1957, p 324.

[8] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, Wiley, New York, N. Y., 1964, p 247.

[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.

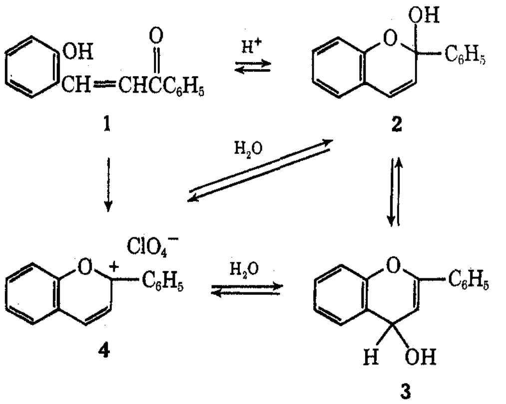
flavylium perchlorate stirred in 600 ml of petroleum ether (bp 60–70°) cooled to 0–5° was added 9 g (0.105 mol) of piperidine dissolved in 150 ml of petroleum ether. The addition required 1.25 hr and the mixture was stirred for an additional 3.5 hr. White piperidinium hydroperchlorate, 9.2 g (0.05 mol), was filtered from the yellow petroleum ether solution which then deposited 13 g of yellow, oily crystals upon evaporation. The product was recrystallized with petroleum ether, yielding 9.1 g (62%) of product, mp 83–85°.

Anal. Calcd for $C_{20}H_{21}NO$: C, 82.44; H, 7.62; N, 4.81. Found: C, 82.43; H, 7.42; N, 5.00.

A stream of dry hydrogen chloride was directed into 5 g of piperidinoflavene in 200 ml of glacial acetic acid for 2 hr followed by addition of 5 ml of 70% perchloric acid. The precipitate was collected and recrystallized from glacial acetic acid. The yield of flavylium perchlorate was 3.5 g (67%), mp and mmp 190–191°.

Discussion

The reactions of 2-hydroxychalcone (**1**) and flavylium salts are complicated by the ease of their interconversion through the probable 2-phenyl-2*H*-1-benzopyran-2-ol intermediate (**2**).



The cyclization occurs in syntheses of flavylium salts from 2-hydroxychalcones. Hydrolysis of flavylium perchlorate (**4**) yields an oil which is a mixture[5] because the intermediate **2** isomerizes to **1** and 2-phenyl-4*H*-1-benzopyran-4-ol (**3**). Thus Hill and Melhuish[10] isolated the unstable 4-*O*-ethyl derivative of **3** and other products characteristic of this mixture, while Jurd[11] has identified chalcones in the hydrolysis products of flavylium salts.

Hydrolysis of the acetate of 2-hydroxychalcone, prepared with sodium acetate or acid catalysts, yielded 2-hydroxychalcone and an oil which was converted to flavylium tetrachloroferrate(III). In addition, the chalcone acetate formed flavylium tetrachloroferrate(III) when allowed to react directly with hydrogen chloride and ferric chloride. These reactions are characteristic of either 2-acetoxychalcone or esters of the benzopyranols, **2** and **3**. Similarly, it was not possible for Freudenberg, *et al.*,[12] to give the structure of the ester from acetylation of 7-hydroxy-4-methoxyflavylium chloride. Some chalcone or flavene esters from flavylium salts have been characterized by hydrogenation but others gave indistinguishable amorphous polymers.[13]

For comparison, a flavene was synthesized by treating piperidine with flavylium perchlorate. Flavylium perchlorate is reactive in the 2 and 4 positions[5,10] while the 2° melting point range and nmr spectrum prove that the product is a mixture of flavenes **5** and **6**.

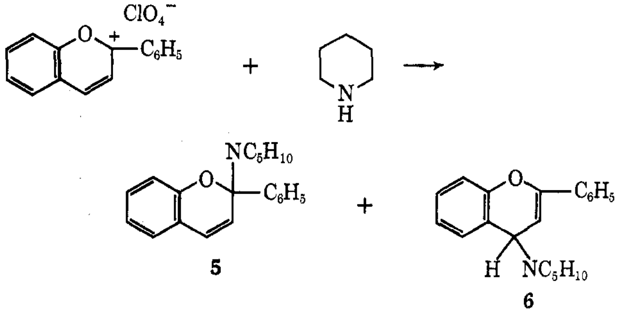


Table I lists the positions, splitting, and assignments of the two typically distorted AB quartets in the nmr spectrum of the flavene mixture. The splitting (J = 10 Hz) and chemical shift of the A′B′ quartet are typical of cis olefinic hydrogens, as in 2-piperidino-2-phenyl-2*H*-1-benzopyran (**5**). The hydrogens in 4-piperidino-2-phenyl-4*H*-1-benzopyran (**6**) are responsible for the AB quartet being at the lower chemical shift.

TABLE I

100-MHz NMR SPECTRUM OF PIPERIDINOFLAVENE ($CDCl_3$)

	A′ B′ quartet	AB quartet	$C_5H_{10}N$- multiplets	C_6H_4, C_6H_5 multiplet
J, Hz	10, 10	4, 4		
δ, ppm	6.44, 5.68	5.80, 4.59	2.42, 1.42	7.8–6.8
Area	8	12	100	87

Flavylium perchlorate was regenerated from the piperidino flavene mixture as additional evidence for the structure assignment. The double bond, 6.00 μ, in the ir spectrum of the piperidinoflavene is found where the carbonyl group of 2-hydroxychalcone absorbs, 6.03–6.09 μ. This is in agreement with the observation of Freudenberg and Weingas[13] that flavene and chalcone double bond absorptions are not distinctive in ir spectra.

The AB or A′B′ quartets of the flavenes are absent from the nmr spectra of 2-acetoxychalcone and 2-benzoyloxychalcone. The nmr peaks from the olefinic hydrogens in these two esters, and for 4-acetoxychalcone, are buried in the aromatic multiplets. Therefore, esterification of 2-hydroxychalcone yielded chalcone esters.

Registry No.—**5**, 33777-35-4; **6**, 33777-36-5; 2-acetoxychalcone, 33777-37-6; flavylium tetrachloroferrate(III), 33775-42-7; 2-benzoyloxychalcone, 33777-38-7.

Acknowledgment.—Students who participated in this work are David Noyes, Robert Rothstein, Kaye Pinkerton, and Gretchen Schulp.

---

[10] D. W. Hill and R. R. Melhuish, *J. Chem. Soc.*, 1161 (1935).

[11] L. Jurd, *Tetrahedron*, **25**, 2367 (1969).

[12] K. Freudenberg, J. H. Stocker, and J. Porter, *Chem. Ber.*, **90**, 960 (1957).

[13] K. Freudenberg and K. Weingas, *Justus Liebigs Ann. Chem.*, **613**, 61 (1958).