with that for the similarly situated ethylenic methyl group in methacrylates.[14]

The p.m.r. spectrum of the reaction product showed protons from both α,β-unsaturated ketone VI and from β-bromo ketone VII, and the intensities of the signals indicated that the product contained 64% of β-bromo ketone VII and 25% of α,β-unsaturated ketone VI. After treatment with hydrogen bromide in ether, all signals due to VI disappeared, and the p.m.r. spectrum was essentially identical with that for pure β-bromo ketone VII.

Reaction of α-Bromo Ketone I with Tetraethylammonium Nitrate.—Reaction, in a sealed tube, at 89.4° for 21 hr. of 1.00 g. of I and 2.60 g. of tetraethylammonium nitrate in 20 ml. of acetonitrile followed by evaporation to dryness, ether extraction, water washing, and ether evaporation gave 0.74 g. of solid product. A portion (10%) of the product was insoluble in carbon tetrachloride. The melting point of this portion, 222–228°, indicated identity with the small amount of material, m.p. 224–227°, obtained in reaction of an acetonitrile solution of I with silver nitrate. P.m.r. signals at τ 4.20 and 4.43 (olefinic protons) and at 7.95 (three methyl protons) all corresponded in intensity to a 0.26 mole fraction of α,β-unsaturated ketone VI. Other intense peaks occurred at τ 8.15 and 8.29, and less intense peaks occurred at τ 8.22 and 8.45. Infrared peaks at 1647 and 1300 cm.$^{-1}$ indicated some incorporation of nitrate groups. Further characterization of the apparently complex mixture of products was not attempted.

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[14] See, for example, the spectrum of methyl methacrylate [N. S. Bhacca, L. F. Johnson, and J. L. Shoolery, "N.M.R. Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, spectrum 113].

A New Synthesis of Naphtho[1,2-*b*]pyran-2-ones

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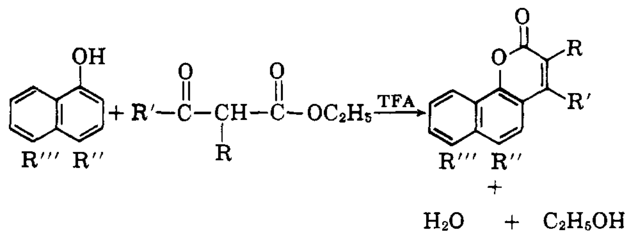
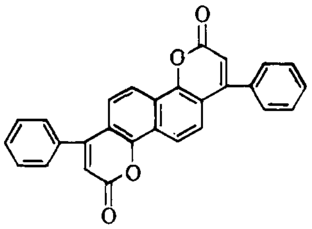
We recently reported a one-step method for preparing coumarins,[2] esters of coumarin acetic acids,[3] and coumarin carboxylic acids obtained from phenolic acids.[4] This contribution deals with the condensation of 1-naphthol and 1,4- and 1,5-naphthalenediols with β-keto esters in the presence of trifluoroacetic acid as shown in Chart I. The compounds synthesized are listed in Table I. 2-Naphthols fail to undergo the reaction.

The reaction of 1,5-naphthalenediol and ethyl acetoacetate using the Von Pechmann conditions[5] has been reported[6] to give the naphthopyrone Ie, dec. pt. 299–302°. With trifluoroacetic acid, we obtained a product with dec. pt. 225°; under the previous conditions,[6] a product with dec. pt. above 360° was obtained. The *p*-nitrobenzoyl derivative was probably the 3-[4-nitrobenzoyl]5-hydroxynaphtho[1,2-*b*]pyran-2-one from the recent observations of Kloss and Wiener[7] who prepared an acetyl coumarin in a similar manner. With trifluoroacetic acid as the catalyst and solvent we were unable to condense 1-naphthol with ethyl benzoylacetate; however, with 1,5-naphthalenediol two equivalents condensed smoothly and in high yield to form the interesting compound If whose proposed structure is shown.

CHART I



	R	R′	R″	R‴
Ia	H	CH_3	H	H
b	$CH_2C_6H_5$	CH_3	H	H
c	CH_3	CH_3	H	H
d	H	C_3H_7	H	H
e	H	CH_3	H	OH
g	H	CH_3	OH	H



If

Table II describes the ultraviolet, infrared, and fluorescence spectral characteristics of the series.

Efforts have been made to prepare suitable derivatives of the series; however, none of the usual derivatives of coumarins could be prepared from all the compounds. Therefore, we have adapted a C-acylation method developed previously[8] for the preparation of a uniform series of benzoylated compounds (see Table III).

The benzoyl group presumably enters the 3-position of these naphthopyran-2-ones except in compounds Ib and Ic in which substitution of the naphthalene 6-position would be expected.

Experimental[9]

Preparation of the Members of the Ia–g Series.—A mixture consisting of 0.1 mole of the naphthol, 0.1 mole of the β-keto ester, and 25 ml. of trifluoroacetic acid was refluxed for the period of time indicated in Table I. In the case of the compound If, 0.1 mole of the naphthol was used along with 0.2 mole of the β-keto ester and 50 ml. of trifluoroacetic acid. At the termination of the reflux period the solutions were diluted with 250 ml. of water (500 ml. in the case of If), chilled, filtered with suction, and dried in air. Purification of the crude naphtho[1,2-*b*]pyran-2-ones was effected by taking the dry compounds up in the smallest amount of ethyl acetate possible and then filtering the ethyl acetate solution into about ten volumes of heptane. Chilling the heptane–ethyl acetate mixtures produced a precipitate which was taken through this same procedure for a second and a third purification.

Determination of the Fluorescence of the Members of the Ia–g Series.—A small amount of the compound (about a milli-

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[1] Submitted in partial fulfillment of the requirements for the Master of Science degree.

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[4] L. L. Woods and J. Sterling, *Texas J. Sci.*, **15**, 200 (1963).

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[6] R. Robinson and F. Weygand, *J. Chem. Soc.*, **387** (1941).

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[8] L. L. Woods and P. A. Dix, *ibid.*, **24**, 1126 (1959); L. L. Woods, *ibid.*, **24**, 1804 (1959).

[9] Analyses were performed by Dr. Carl Tiedcke, Teaneck, N. J., and Galbraith Laboratories, Knoxville, Tenn. All melting points were determined on a Fisher-Johns melting point block.

TABLE I

COMPOUNDS OF Ia–g SERIES

No.	Phenol used	β-Keto ester used	Yield, %	M.p., °C.	Reaction time, hr.	Empirical formula	Analysis, % Calcd. (found) Carbon	Hydrogen
Ia[b]	1-Naphthol[a]	Ethyl acetoacetate	90	175	5	$C_{14}H_{10}O_2$	79.98 (79.74)	4.79 (4.71)
Ib[c]	1-Naphthol	Ethyl α-benzylacetoacetate	93	199–200	24	$C_{21}H_{16}O_2$	83.97 84.03	5.36 (5.32)
Ic[d]	1-Naphthol	Ethyl α-methylacetoacetate	91	208.5–209.5	24	$C_{15}H_{12}O_2$	80.33 (80.46)	5.39 (5.26)
Id[e]	1-Naphthol	Ethyl butyroylacetate	37	104–104.5	24	$C_{16}H_{14}O_2$	80.64 (80.87)	5.92 (5.91)
Ie[f]	1,5-Naphthalenediol	Ethyl acetoacetate	95	225–dec.	3	$C_{14}H_{10}O_3$	74.32 (74.23)	4.45 (4.67)
If[g]	1,5-Naphthalenediol	Ethyl benzoylacetate	100	239–240	16	$C_{28}H_{16}O_4$	80.75 (80.49)	3.87 (4.11)
Ig[h]	1,4-Naphthalenediol	Ethyl acetoacetate	98	Above 254 dec.	2.5	$C_{14}H_{10}O_3$	74.32 (74.56)	4.45 (4.47)

[a] Prepared previously by Kurt Bartsch, *Ber.*, **36**, 167 (1903); m.p. 167°. [b] Ia, 4-methylnaphtho[1,2-*b*]pyran-2-one. [c] Ib, 3-benzyl-4-methylnaphtho[1,2-*b*]pyran-2-one. [d] Ic, 3,4-dimethylnaphtho[1,2-*b*]pyran-2-one. [e] Id, 4-propyl-naphtho[1,2-*b*]pyran-2-one. [f] Ie, 4-methyl-7-hydroxynaphtho[1,2-*b*]pyran-2-one. [g] If, 1,10-diphenyl[1]benzopyrano[8,7-*h*][1]benzopyran-3,8-dione. [h] Ig, 4-methyl-6-hydroxynaphtho[1,2-*b*]pyran-2-one.

TABLE II

SPECTRAL CHARACTERISTICS OF THE MEMBERS OF THE Ia–g SERIES

No.	Infrared absorptions in cm.$^{-1}$[a]	Ultraviolet absorption bands range of 200–350 mμ (log ε)[b]	Fluorescence measured in q.r.u.[c]
Ia	1717, 1582, 1374, 1083, 942, 810, 756	220.7 (4.40), 265.7 (4.51), 274 (4.40)	3.40
Ib	1695, 1597, 1488, 1093, 1019, 815, 759, 749, 699	225 (4.13), 268 (sh, 4.36), 277 (3.61)	1.90
Ic	1701, 1605, 1093, 804, 767	221 (4.45), 267 (4.42), 275.5 (4.49)	0.77
Id	1712, 1678, 1626 w, 1377, 841, 813, 796, 777, 760	221 (4.36), 265 (4.26), 274.5 (4.35)	0.04
Ie	3300, 1595, 1372, 1290, 1263, 925, 772	230 (4.15), 300 (3.71), 330 (3.15)	0.15
If	3300, 1658, 1595, 1372, 1261, 1203, 925, 772	230 (4.55), 292 (4.19), 330 (3.55)	0.01
Ig	3322, 1686, 1592, 1558, 1418, 1342, 1269, 1244, 1078	217 (4.23), 287 (4.24)	0.10

[a] Spectra run on Beckman IR-5 using potassium bromide pellets; w, weak. [b] Spectra run on Bausch and Lomb 505 spectrophotometer in Spectro Grade methanol; sh, shoulder. [c] See Experimental.

TABLE III

BENZOYL DERIVATIVES OF THE MEMBERS OF Ia–g SERIES

Compound used	Emperical formula of compound produced	M.p. °C.	Analysis, % Calcd. (found) Carbon	Hydrogen
Ia	$C_{21}H_{14}O_3$	177–178	80.24 (80.20)	4.48 (4.68)
Ib	$C_{28}H_{20}O_3$	196–197	83.14 (83.29)	4.98 (4.84)
Ic	$C_{22}H_{16}O_3$	203	80.47 (80.60)	4.91 (5.01)
Id	$C_{23}H_{18}O_3$	121.5–122.5	80.68 (80.84)	5.29 (5.14)
Ie	$C_{28}H_{18}O_4$	122.5–123	80.36 (80.49)	4.33 (4.50)
If	$C_{42}H_{24}O_6$	120–124.5	80.75 (80.97)	3.87 (3.99)
Ig	$C_{28}H_{18}O_4$	218	80.36 (80.05)	4.33 (4.60)

gram) was weighed accurately, dissolved in 10 ml. of methanol, and then diluted to 50 ml. in distilled water. If the fluorescence of this solution was too concentrated, then subsequent dilutions were made on aliquots from this stock solution.

The fluorescence of the compound as measured on a Turner fluorophotometer Model 110 using a 365-mμ filter was compared with that of a quinine sulfate solution prepared the same way and the results given in Table IV as q.r.s. (quinine reference units). The formula for the calculation of the units is q.r.u. = concn. of quinine sulfate (g./ml.) × dial reading for substance/concn. of substance (g./ml.) × dial reading for quinine.

Preparation of the Benzoates of the Compounds of the Ia–g Series.—To 0.01 mole of the naphtho[1,2-*b*]pyran-2-one was added 10 ml. of trifluoroacetic acid and 0.01 mole of benzoyl chloride, except in the cases of Ie–g in which 0.02 mole of benzyl chloride was used. The mixtures were gently heated at reflux in the hood until hydrogen chloride vapors were no longer evolved—about 0.5 hr. The solutions were diluted with 100 ml. of water, chilled, and the precipitates filtered. The air-dried samples were recrystallized three times from boiling heptane to give the analyses and melting points indicated in Table III.

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Preparation of (S)-(−)-2,4-Dimethyl-4-isopropylcyclopent-2-enone

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2,3-Dimethyl-4-isopropylcyclopent-2-enone was required and, in repeating the work of Short and Read,[2]

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[2] A. G. Short and J. Read, *J. Chem. Soc.*, 1040 (1939).