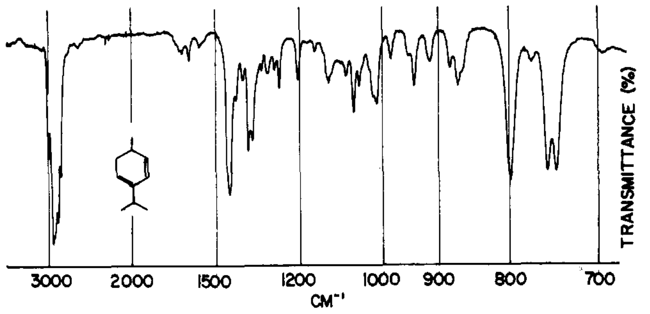

Fig. 1.—Infrared spectrum of 2,4-*p*-menthadiene.

p-menthane. Spectroscopic data indicated the presence of a triply substituted conjugated homoannular diene which was shown not to be 1,5-*p*-menthadiene (*p*-mentha-1,8-diene) by comparative infrared analysis. This previously uncharacterized terpene was identified as 2,4-*p*-menthadiene (*p*-mentha-2,4-diene).

The new terpene was synthetically obtained following dehydrohalogenation of 3,4-dibromo-*p*-menthane which resulted from the bromination of *p*-menth-3-ene. It was separated from both the orange oil and products of dehydrohalogenation by preparative gas chromatography.

Experimental

Isolation of 2,4-*p*-menthadiene.—Cold-pressed Valencia orange oil (300 ml.) was slowly added with stirring to 540 g. of silica gel in 500 ml. of hexane. The temperature was maintained at 5° throughout the addition. Upon complete addition the hexane solution was decanted and the silica gel washed three times with 300-ml. portions of hexane. The combined hexane solutions were distilled in a 5-ft. vacuum-jacketed packed column to give 30 ml. of material that boiled from 130–174°. Redistillation in a semimicro spinning-band column gave 10 ml. that boiled from 150–174°. The fourth peak of a gas chromatographic separation[1] of this fraction, having a retention time of 16 min. and following camphene, was collected to give the infrared spectrum shown in Fig. 1. Absorption at 795 cm.$^{-1}$ showed the presence of a triply substituted double bond and that at 750 cm.$^{-1}$ a *cis*-disubstituted double bond. The material was reduced with platinum black to yield *cis*- and *trans*-*p*-menthane. Its ultraviolet absorption at $\lambda_{\max}^{\text{ethanol}}$ 260 mμ shows it to be a homoannular diene having at least two alkyl constituents by Woodward's rule.[3] Comparative infrared spectroscopy ruled out 1,5-*p*-menthadiene, the only *p*-menthadiene whose structural characteristics are similar. The parent mass spectral peak occurred at 136. 2,4-*p*-Menthadiene appears in the oil in trace amounts.

3,4-Dibromo-*p*-menthane.—*p*-Menth-3-ene was dissolved in ether and treated with equimolar amounts of bromine with stirring. The temperature was maintained at 25° by controlling the rate of bromine addition. The solution was washed with sodium bisulfite, extracted with ether, and distilled; b.p. 85–90° (0.025 mm.), n^{23}_{D} 1.5276; lit.[4] n^{20}_{D} 1.5260.

2,4-*p*-Menthadiene.—3,4-Dibromo-*p*-menthane was added to absolute ethanol containing an excess of potassium hydroxide and heated on a steam bath for 30 min. The mixture was filtered, neutralized with dilute hydrochloric acid, and then gas chromatogrammed to give a major peak having a retention time of 16 min.; n^{23}_{D} 1.4660; ultraviolet, $\lambda_{\max}$ 260 mμ; the infrared spectra was identical with that shown in Fig. 1 (b.p. 56° at 25 mm. by the method of Garcia[5]). The compound gave *p*-menth-3-ene upon treatment with sodium and alcohol. Molecular weight by mass spectrometry was 136.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.24; H, 11.76. Found: C, 88.20; H, 11.80.

Acknowledgment.—The authors thank G. S. Fisher, Naval Stores Laboratory, Olustee, Florida, for the 3-*p*-menthene.

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[1] Column, 0.5 in. × 36 ft., containing 30% Carbowax 20M[2] on Chromosorb-W; flow rate, 200 ml./min.; temperature, 145°.

[2] Mention of brand names is for identification of type of material and does not constitute endorsement.

[3] L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Co., New York, N. Y., 1959, p. 17.

[4] N. L. McNiven and J. Read, *J. Chem. Soc.*, 153 (1952).

[5] C. R. Garcia, *Ind. Eng. Chem., Anal. Ed.*, **15**, 648 (1943).

Synthesis and Spectra of Derivatives of α-Bromo-*p*-phenylisobutyrophenone. A Comment upon the Mechanism of Quasi-Favorskiĭ Rearrangement

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Silver nitrate in acetonitrile has for several years been recognized as a useful reagent for conversion of alkyl halides into alkyl nitrates.[2] It has been found that this reagent is very selective towards a direct replacement of halogen. Tertiary α-bromo ketones, very sensitive to rearrangement or dehydrobromination, will react with this reagent to give an excellent yield of the corresponding α-nitrato ketone.

Although reaction of tetraethylammonium nitrate with α-bromo-*p*-phenylisobutyrophenone (I) leads to a complex mixture of products, reaction of silver nitrate with an acetonitrile solution of I has been found to give an excellent yield of the direct replacement product, α-nitrato-*p*-phenylisobutyrophenone (II), with no evidence for any significant amount of rearrangement or elimination product. For instance, from reaction at 92° was isolated a 77% yield of II and about 8% of a high melting point material[3] with an infrared spectrum indicating the absence of nitrate groups. The structure of II was confirmed by conversion to the known[4] 1,2-epoxy-2-methyl-1-methoxy-1-(4-biphenylyl)-propane (III) and α-hydroxy-*p*-phenylisobutyrophenone (IV). Spectral characteristics of III, of IV, and of α-acetoxy-*p*-phenylisobutyrophenone (V) are reported for the first time.

In acetonitrile solution, under identical conditions, silver nitrate was found to react with α-bromo ketone I at 130 times the rate of silver perchlorate and at 13 times the rate of tetraethylammonium nitrate. These results represent over-all initial rates, and the kinetics were not further investigated, but it is possible that in the rate-determining stage of the silver nitrate reaction, both electrophilic assistance by silver ion and nucleophilic assistance by nitrate ion are operative.

Reaction of α-bromo ketone I with silver nitrate in aqueous ethanol previously has been shown to give a 69% yield of 2-(4-biphenylyl)-2-methylpropanoic acid (VI)[5] formed by a Favorskiĭ rearrangement. α-Bromoisobutyrophenone similarly has been shown[6]

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[1] To whom communications concerning this paper should be addressed.

[2] L. F. Fieser and W. Von E. Doering, *J. Am. Chem. Soc.*, **68**, 2252 (1946).

[3] This product probably represents a small amount of reaction involving solvent participation; see, for example, J. Cast and T. S. Stevens, *J. Chem. Soc.*, 4180 (1953).

[4] C. L. Stevens and S. J. Dykstra, *J. Am. Chem. Soc.*, **75**, 5975 (1953).

[5] N. H. Cromwell and P. H. Hess, *ibid.*, **83**, 1237 (1961).

[6] A. C. Cope and E. S. Graham, *ibid.*, **73**, 4702 (1951).

to give a 40% yield of rearranged acid. These Favorskiĭ rearrangements are of interest, since, α-hydrogens being absent, they cannot proceed through the usual cyclopropanone intermediate.[7] Mechanisms proposed for these silver ion-catalyzed rearrangements have been a push–pull type, involving nucleophilic assistance from water molecules either directly[7] or after prior hydration of the carbonyl group.[6]

Nucleophilic assistance in the rate-determining step of these electrophilically assisted rearrangements in aqueous ethanol has, however, never been established. The absence of any aryl migration during reaction in acetonitrile suggests that reactions proceeding to rearranged products may involve a rate-determining electrophilic removal of the halide ion with accompanying aryl migration. The rearranged carbonium ion intermediate subsequently can react with a water molecule with formation of the acid.

Two alternative explanations are possible for the observation that I undergoes displacement with silver nitrate in acetonitrile but rearrangement in aqueous ethanol; it is possible that these two effects may act in unison, both being partially responsible for the observation. In acetonitrile the silver ion is complexed by the solvent with a reduction in its electrophilicity and, under these conditions, aryl migration may be unable to provide sufficient driving force towards the silver ion-assisted rupture of the carbon–bromine bond such that intervention by the nucleophilic nitrate ions is required. It also has been established[8] that protic solvents inhibit the reactivity of anions in displacement reactions by hydrogen bonding to the anions. In aprotic solvents, such as acetonitrile, anions are much less solvated, and hence less energy must be supplied to overcome solvation of the anion in going to the transition state for the displacement. In the present case I may undergo silver ion-assisted rearrangement with aryl migration in aqueous ethanol, because the competing silver ion-assisted displacement reaction has been greatly slowed by hydrogen-bonding solvation of the nitrate ion.

The proton magnetic resonance spectrum of the reaction product formed from an acetonitrile solution 0.16 *M* in α-bromo ketone I and 0.32 *M* in tetraethylammonium bromide maintained at 92° for 23 hr. showed that I has been completely destroyed with formation of a 25% yield of the α,β-unsaturated ketone, α-methyl-*p*-phenylacrylophenone (VI), and a 64% yield of the β-bromo ketone, β-bromo-*p*-phenylisobutyrophenone (VII), formed through an elimination–addition reaction.[5] The conversion of VI to VII was completed by dissolving the product in an ether solution of hydrogen bromide.

Hydrogen Bonding in α-Hydroxy-*p*-phenylisobutyrophenone (IV).—The infrared spectrum of the α-hydroxy ketone (IV) shows a weak hydroxyl stretching absorption at 3608 cm.$^{-1}$ and a relatively strong absorption at 3477 cm.$^{-1}$, ascribed to nonhydrogen-bonded and hydrogen-bonded species, respectively. Dilution studies show that the hydrogen bonding is intramolecular in nature.

Reeves, Allan, and Strømme[9] have attempted, for intramolecularly hydrogen-bonded phenols and naphthols, to correlate the shift in the hydroxyl stretching frequency on formation of the hydrogen bond, $\Delta\nu$OH, with the proton magnetic resonance chemical shift of the hydroxyl proton at infinite dilution relative to the shift for the parent phenol or naphthol at infinite dilution, $\Delta\tau$OH. A rough correlation was found to exist; the best graphical correlation for twenty-four *ortho*-substituted phenols and naphthols was $\Delta\nu$OH (cm.$^{-1}$) = 67 $\Delta\tau$OH (p.p.m.). Differing classes of compounds differed in value since the treatment neglects the additional chemical shift caused by the diamagnetic anisotropy of the group introduced *ortho* to the hydroxyl group. For example, values (in cm.$^{-1}$/p.p.m.) of 50 for *o*-chlorophenol, 51 for *o*-methoxyphenol, 68 for *o*-bromophenol, and 79 for *o*-iodophenol were obtained.

The value for $\Delta\nu$OH in α-hydroxy-*p*-phenylisobutyrophenone (IV) is 131 cm.$^{-1}$, conveniently obtained (with use of lithium fluoride optics), since the infrared spectrum shows the stretching frequencies of both hydrogen-bonded and nonhydrogen-bonded hydroxylic groups. *t*-Butyl alcohol was chosen as the standard to which to refer the chemical shift in the p.m.r. spectrum, the required value at infinite dilution in carbon tetrachloride (τ 9.41) has been accurately obtained by Saunders and Hyne.[10] Dilution studies showed the chemical shift of the hydroxyl proton in IV to be τ 6.30 at infinite dilution, giving a value for $\Delta\tau$OH of 3.11 p.p.m. and a relationship $\Delta\nu$OH (cm.$^{-1}$) = 42 $\Delta\tau$OH (p.p.m.). It will be of interest to see whether the fairly good agreement between the value for the aryl α-hydroxyalkyl ketone (IV) and the previously determined values for *ortho*-substituted phenols and naphthols is fortuitous, or whether this criterion for intramolecular hydrogen bonding is of more general application than has been indicated previously.

Experimental[11]

The preparation of α-bromo-*p*-phenylisobutyrophenone (I) previously has been described.[5] The acetonitrile was Eastman Organic Chemicals Spectro Grade. Anhydrous silver perchlorate (G. F. Smith Chemical Co.) was recrystallized from aqueous dioxane and dried under vacuum at 80°. Tetraethylammonium nitrate and tetraethylammonium bromide were prepared by neutralization of an aqueous solution of the hydroxide, evaporation to dryness and recrystallization from acetonitrile.

The α-bromo ketone (I) was converted *via* the epoxy ether (III) to the α-hydroxy ketone (IV) and, hence, to the α-acetoxy ketone (V) by the methods of Stevens and Dykstra.[4]

1,2-Epoxy-2-methyl-1-methoxy-1-(4-biphenylyl)propane (III).—The melting point was 79–80°; ν 1240 (51), 1138 (85), 1118 (89), 1061 (59), 1031 (39), 940 (49), and 906 (34), cm.$^{-1}$. The p.m.r. spectrum shows nine aromatic protons and three peaks, each corresponding to three protons, at τ 6.82 (the methoxy group) and at τ 8.50 and 8.98 (the two methyl groups).

α-Hydroxy-*p*-phenylisobutyrophenone (IV).—The melting point was 94–95°; ν 3598 (12, free OH), 3472 (41, hydrogen-bonded OH), 1679 (86, sh, free C=O), 1672 (94, hydrogen-

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[7] R. B. Loftfield, *J. Am. Chem. Soc.*, **73**, 4707 (1951).

[8] A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

[9] L. W. Reeves, E. A. Allan, and K. O. Strømme, *Can. J. Chem.*, **38**, 1249 (1960).

[10] M. Saunders and J. B. Hyne, *J. Chem. Phys.*, **29**, 1319 (1958).

[11] Melting points were read with a calibrated thermometer. Infrared spectra were measured with a Perkin-Elmer Model 21 double beam recording instrument employing, unless otherwise stated, sodium chloride optics and matched sodium chloride cells with 10 mg./ml. carbon tetrachloride solutions. The ultraviolet spectra were determined with a Cary Model 11-MS recording spectrophotometer using reagent grade methanol solutions. The proton magnetic resonance spectra were obtained with a Varian A-60 instrument using carbon tetrachloride solutions with a trace of tetramethylsilane (τ 10.00) as internal reference.

TABLE I

POTENTIOMETRIC TITRATIONS

α-Bromo ketone I, 0.0800 *M*; [$AgNO_3$], 0.0160 *M*
(titers are in milliliters of 0.0100 *M* KCl; initial velocity is 3.4 × 10^{-7} moles l.$^{-1}$ sec.$^{-1}$)

Time (min.)	0	155	340	1220	1300	1790	2880
Titer	7.86	6.59	5.30	2.65	2.50	1.96	1.01
Time (min.)	4560	7380					
Titer	0.55	0.29					

α-Bromo ketone I, 0.0800 *M*; [$AgClO_4$], 0.0160 *M*
(titers are in milliliters of 0.0100 *M* KCl; initial velocity is 2.6 × 10^{-9} moles l.$^{-1}$ sec.$^{-1}$)

Time (min.)	0	1220	1300	1790	2880	4560	7380
Titer	7.96	7.86	7.86	7.83	7.80	7.60	7.40

α-Bromo ketone I, 0.0800 *M*; [NEt_4NO_3], 0.0160 *M*
(titers are in milliliters of 0.0100 *M* $AgNO_3$; initial velocity is 2.6 × 10^{-8} moles l.$^{-1}$ sec.$^{-1}$)

Time (min.)	0	30	60	90	120	190	270
Titer	0.06	0.10	0.11	0.14	0.16	0.20	0.26
Time (min.)	370	2950					
Titer	0.35	2.33					

bonded C═O), 1370 (72), 1179 (99), 966 (84); λ_{max} 283 mμ (ϵ 22,800).

Dilution studies with lithium fluoride optics show superimposed infrared spectra for solutions 10 mg./ml. in 1-mm. cell and 3.3 mg./ml. in 3-mm. cell; ν 3608 (16), 3477 (38), 1678 (72, sh), 1671 (76) cm.$^{-1}$.

The p.m.r. spectrum of α-hydroxy-*p*-phenylisobutyrophenone shows in addition to peaks corresponding to nine aromatic protons, a peak corresponding to six methyl protons, and a peak due to the hydroxyl proton. Due to hydrogen bonding, the positions of hydroxyl protons in p.m.r. spectra are, in general, concentration dependent even at low concentrations; this dependence is minimized when intramolecular hydrogen bonding is operative.[12] Dilution studies with IV (mg./ml.) showed little concentration dependence, consistent with the evidence for extensive intramolecular hydrogen bonding from infrared spectroscopy.

IV	67	43	25	17	10	6
τOH	6.22	6.25	6.28	6.30	6.30	6.30
τCH_3	8.43	8.42	8.42	8.40	8.40	8.40

α-Acetoxy-*p*-phenylisobutyrophenone (V).—The melting point was 125–127°; $\nu_{C=O}$ 1745 (93) and 1691 (93); λ_{max} 283 mμ (ϵ 23,000).

Preparation of α-Nitrato-*p*-phenylisobutyrophenone (II).—In a sealed tube, 20 ml. of acetonitrile, 0.95 g. of α-bromo ketone I, and 1.00 g. of silver nitrate were heated at 92° for 17 hr. The solvent was removed by evaporation, and the residue was ether extracted; evaporation yielded 0.76 g. of residue which gave a negative Beilstein test. The infrared spectrum was identical with that of pure II except for a slight shoulder around 1680 cm.$^{-1}$; in particular, no disturbance was observed at 1663 cm.$^{-1}$ where the α,β-unsaturated ketone shows carbonyl absorption.[5] A small amount (0.08 g.) of product was found to be insoluble in boiling benzene–petroleum ether (b.p. 60–70°), m.p. 224–227°, $\nu^{KBr}_{C=O}$ 1681 cm.$^{-1}$.

Reaction of an identical mixture for 9 days at room temperature led to 69% reaction as measured by silver bromide precipitation; recrystallization from petroleum ether–benzene gave pure II, m.p. 127–128°; λ_{max} 288 mμ (ϵ 23,800); $\nu_{C=O}$ 1692 (93), ν_{NO_2} 1647 (95) and 1306 (94).

Anal. Calcd. for $C_{16}H_{15}NO_4$: C, 67.35; H, 5.30; N, 4.91. Found: C, 67.32; H, 5.32; N, 4.70.

Reaction of α-Nitrato-*p*-phenylisobutyrophenone (II).—Using a method identical with that which Stevens and Dykestra[4] employed for α-bromo ketone I, derivatives III and IV were prepared from II and were identified by melting points and infrared spectra.

Reaction of α-Bromo Ketone I with Silver Perchlorate.—A solution of 1.00 g. of I and 1.00 g. of silver perchlorate in 20 ml. of acetonitrile was maintained, in a sealed tube, at 91.9° for 48 hr. Silver bromide was removed by filtration, and the solution evaporated to dryness and extracted with ether and water. An insoluble, dark green fraction (0.52 g.), after recrystallization from acetone, charred on heating but did not melt below 250°. Evaporation of the ether solution yielded 0.35 g. of material, m.p. 73–95°. The infrared spectrum of the ether soluble portion included ν 1739 (30), 1691 (72, sh), 1680 (90), and 1666 (42, sh) cm.$^{-1}$. The shoulder at 1666 cm.$^{-1}$ may represent a small quantity of VI. It is possible that VI is initially formed in reasonable yield only for it to undergo further reactions.[13]

Reaction Velocities for Attack upon α-Bromo Ketone I.—Sealed ampoules, each containing 5.00 ml. of reaction mixture, were maintained at 74.0°. Ampoules were removed from time to time, and reaction was quenched by immersion in Dry Ice–alcohol slush until the extent of reaction was determined by potentiometric titration in a titration medium of 30 ml. of acetone containing 1 ml. of 1 *N* nitric acid using a silver wire electrode and a potassium nitrate–agar bridge to a calomel reference electrode. (See Table I.)

Preparation of β-Bromo-*p*-phenylisobutyrophenone (VII).—A sealed tube containing 20 ml. of an acetonitrile solution 0.165 *M* in α-bromo ketone I and 0.333 *M* in tetraethylammonium bromide was maintained at 92° for 23 hr. A 1.00-ml. aliquot was removed and titration in acetone, using Lacmoid as indicator, required 3.90 ml. of 0.0114 *M* methanolic morpholine for neutralization. This titer corresponds to 27% acid formation from the α-bromo ketone (I). The remaining solution was evaporated to dryness, extracted with ether, washed with water, and the ether solution was evaporated to dryness to give 0.80 g. of an orange oil (from 0.95 g. of I).

A portion of the oil was retained for p.m.r. investigation, and the remainder was dissolved in an ether solution of hydrogen bromide; evaporation to dryness gave a white solid whose p.m.r. spectrum indicated the absence of α-methyl-*p*-phenylacrylophenone (VI). Recrystallization from petroleum ether gave pure β-bromo-*p*-phenylisobutyrophenone (VII), m.p. 72.5–73.5°, λ_{max} 285 mμ (ϵ 23,600), $\nu_{C=O}$ 1683 (89). The p.m.r. spectrum shows two equivalent β′ aromatic protons at τ 2.07 and two equivalent γ′ protons at τ 2.41 ($J_{\beta'\gamma'}$ = 8 c.p.s.), other peaks to give a total of nine aromatic protons, several peaks corresponding in total to three protons in the region τ 6–7 and three methyl protons, as a doublet (J = 7 c.p.s.), at τ 8.71.

Anal. Calcd. for $C_{16}H_{15}OBr$: C, 63.38; H, 4.99; Br, 26.36. Found: C, 63.37; H, 4.88; Br, 26.19.

The p.m.r. spectrum of the 0.80 g. of oil formed by reaction in acetonitrile showed no disturbance around τ 1.82 where the signals from the β′ aromatic hydrogens of the α-bromo ketone (I) occur, consistent with I having been completely destroyed. The α-bromo ketone (I) also shows two γ′ hydrogens at τ 2.43 ($J_{\beta'\gamma'}$ = 8 c.p.s.) and six methyl hydrogens at τ 7.97.

The α,β-unsaturated ketone (VI), previously prepared in these laboratories,[5] was found to have doublets ($J_{\beta'\gamma'}$ = 8 c.p.s.) due to β′ and γ′ protons at τ 2.26 and 2.42 and to have two broad peaks, with fine srructure, each corresponding to one ethylenic proton at τ 4.20 and 4.43. The peak corresponding to the three methyl protons, at τ 7.95 has a characteristic structure, identical

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(12) T. M. Connor and C. Reid, *J. Mol. Spectry.*, **7**, 32 (1961).

(13) Olefins in the presence of acids are known to be somewhat reactive towards acetonitrile; see, for example, H. Plaut and J. J. Ritter, *J. Am. Chem. Soc.*, **73**, 4076 (1951).

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.

Acknowledgment.—The investigation was supported in part by Grants No. G-14469 and G-20149, from the National Science Foundation.

[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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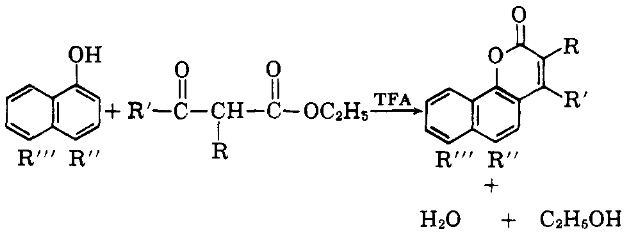
Received August 5, 1963

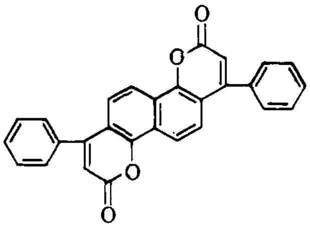
We recently reported a one-step method for preparing coumarins,[2] esters of coumarin acetic acids,[3] and coumarin carboxylic acids obtained from phenolic acids.[4] This contribution deals with the condensation of 1-naphthol and 1,4- and 1,5-naphthalenediols with β-keto esters in the presence of trifluoroacetic 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.

[2] L. L. Woods and J. Sapp, *J. Org. Chem.*, **27**, 3703 (1962).

[3] L. L. Woods and J. Sapp, *J. Chem. Eng. Data*, **8**, 235 (1963).

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

[5] H. Von Pechmann and C. Duisberg, *Ber.*, **16**, 2122 (1883).

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

[7] R. A. Kloss and C. Wiener, *J. Org. Chem.*, **28**, 1671 (1963).

[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.