The Photoinduced Alcoholysis of 3,4-Dihydrocoumarin and Related Compounds[1]

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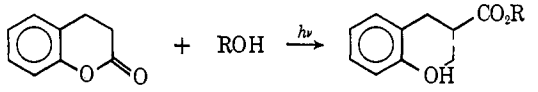
Abstract: The reaction of alcohols with 3,4-dihydrocoumarin and related compounds has been studied under ordinary conditions ("dark solvolysis") and under photolysis conditions ("photoinduced solvolysis"). The investigation has revealed the following: (a) the photoinduced alcoholysis of 3,4-dihydrocoumarin to an alkyl β-(2-hydroxyphenyl)propionate can be effected with methanol, ethanol, and isopropyl alcohol; *t*-butyl alcohol, however, fails to react and can be employed as a solvent for the photoinduced reaction with other more reactive alcohols; (b) both the higher and lower homologs of 3,4-dihydrocoumarin undergo photoinduced alcoholysis; the higher homolog, 2-keto-2,3,4,5-tetrahydrobenzoxepin, reacts in a fashion comparable to 3,4-dihydrocoumarin and yields an alkyl γ-(2-hydroxyphenyl)butyrate, while the lower homolog, 2-keto-2,3-dihydrobenzofuran, reacts in a different fashion and yields the alkyl ether of 2-hydrobenzyl alcohol; (c) the rates of the "dark solvolyses" of various 6- and 7-substituted 3,4-dihydrocoumarins are, in accordance with expectations, accelerated by electron-withdrawing groups and decelerated by electron-releasing groups; (d) the photoinduced solvolyses of various 6- and 7-substituted 3,4-dihydrocoumarins show quantum yields which, with one exception, correlate with the pK_a^* values for the phenol corresponding to the 3,4-dihydrocoumarin. On the basis of these data, it is postulated that the alcoholyses of 3,4-dihydrocoumarins and 2-keto-2,3,4,5-tetrahydrobenzoxepin may be examples of photoinduced Fries rearrangements in which an initially produced spirodiketone reacts with the alcohol to form the phenolic ester.

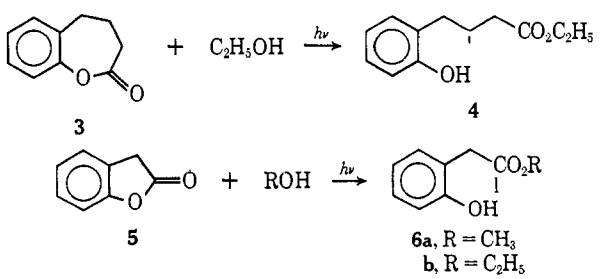
The work described in this paper had its inception in a study which attempted to demonstrate a chemical application of the Förster–Weller effect.[2] Manifestations of this effect, which imputes to photoexcited phenols an acidity vastly enhanced over that of the ground state, were sought in photoaccelerated rates of hydrolysis of methyl β-(2-hydroxyphenyl)propionate and esterification of β-(2-hydroxyphenyl)propionic acid. Neither result was realized, but it was observed in the course of these experiments that a photoinduced alcoholysis of 3,4-dihydrocoumarin to an alkyl β-(2-hydroxyphenyl)propionate could be effected. Anderson and Reese[3] reported one example of this reaction several years ago but did not pursue the subject beyond the initial experiment. Because of the interesting synthesis possibilities inherent in this reaction and because of its mechanistic appeal, we have extended the investigation of this process by studying (a) the reactivity of various alcohols, (b) the effect of the ring size, (c) the effect of substituents in the 6 and 7 positions of the 3,4-dihydrocoumarin on the rates of the "dark solvolysis" reaction, and (d) the product quantum yields for the ethanolysis of 3,4-dihydrocoumarin, its 6- and 7-substituted analogs, and its higher and lower homologs.

Reactivity of Alcohols. Photoinduced alcoholysis of 3,4-dihydrocoumarin (**1**) occurs with methanol, ethanol, and isopropyl alcohol to give the corresponding alkyl β-(2-hydroxyphenyl)propionates (**2a**, **2b**, **2c**) in yields of 86, 74, and 52%, respectively. *t*-Butyl alcohol, however, fails to yield any alcoholysis product whatsoever and can, in fact, be employed as a nonreactive solvent. Although the synthesis possibilities of the alcoholysis reaction were not probed in detail, they are adumbrated by one exploratory experiment in which farnesol, an alcohol sensitive to acid-catalyzed rearrangement,[4] was photochemically transformed to farnesyl β-(2-hydroxyphenyl)propionate (**2d**) from which farnesol could then be regenerated by thermolysis.



1 **2a**, R = CH_3; **b**, R = C_2H_5; **c**, R = $CH(CH_3)_2$; **d**, R = $C_{15}H_{28}$

Effect of Ring Size. The seven-membered lactone, 2-keto-2,3,4,5-tetrahydrobenzoxepin (**3**), undergoes ethanolysis in a fashion entirely comparable to that of its six-membered counterpart, 3,4-dihydrocoumarin (**1**), and yields ethyl γ-(2-hydroxyphenyl)butyrate (**4**). The five-membered lactone, 2-keto-2,3-dihydrobenzofuran (**5**), also undergoes a facile alcoholysis but yields the alkyl ether of 2-hydroxybenzyl alcohol (**6**) instead of the alkyl ester of α-(2-hydroxyphenyl)acetate. Further details of this reaction will be published in a separate communication.



3 **4** **5** **6a**, R = CH_3; **b**, R = C_2H_5

Effect of Substituents in the 6 and 7 Positions of 3,4-Dihydrocoumarin on the Rates of "Dark Solvolysis"

(1) This work was supported, in part, by Grant No. GP-4951 from the National Science Foundation and Grant No. 5 RO1 AM02398 from the National Institutes of Health, to whom the authors express their gratitude.

(2) T. Förster, *Z. Elektrochem.*, **54**, 42 (1950); A. Weller, *Progr. Reaction Kinetics*, **1**, 187 (1961).

(3) J. C. Anderson and C. B. Reese, *J. Chem. Soc.*, 1781 (1963).

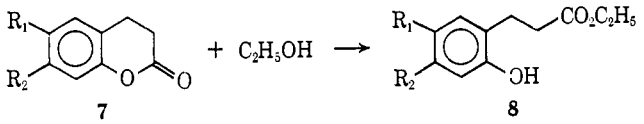
(4) L. Ruzicka and E. Capato, *Helv. Chim. Acta*, **8**, 259 (1925); C. D. Gutsche and J. R. Maycock, *Tetrahedron*, **24**, 859 (1968).

Reaction. 3,4-Dihydrocoumarin can undergo alcoholysis in a ground-state chemical reaction ("dark solvolysis"). Therefore, to assess the effect of substituents in the 6 and 7 positions of 3,4-dihydrocoumarin on the photoinduced ethanolysis, data were first acquired for the corresponding "dark ethanolysis." Inspection of the data in Table I reveals that, in accordance with expectations,[5] electron-withdrawing groups

Table I. Reaction Rates for the "Dark Ethanolysis" of 6- and 7-Substituted 3,4-Dihydrocoumarins

Substituted 3,4-dihydrocoumarin	k at 30°, min^{-1}, 10^{-4}	Rel rate
6-OCH_3 (**7b**)	0.001	0.002
6-CH_3 (**7a**)	0.0104	0.173
H (**1**)	0.602	1.000
7-CH_3 (**7e**)	1.452	2.407
7-OCH_3 (**7f**)	1.743	2.895
6-Br (**7d**)	3.110	5.162
7-NO_2 (**7g**)	74.3	123.5
6-NO_2 (**7c**)	164.2	272.5

in the 6 position (*e.g.*, nitro and bromo) accelerate the reaction, while electron-releasing groups in the 6 position (*i.e.*, methoxy and methyl) reduce the rate of reaction. Similarly, inductively electron-withdrawing groups in the 7 position (*e.g.*, nitro and methoxy) accelerate the reaction. Using the standard Hammett σ constants for the 6 and 7 substituents,[5a] a Hammett ρ value of 3.0597 was calculated from these data, all of the points except that for the 7-methyl compound falling on the straight line. The reasons for the unexpectedly rapid ethanolysis of the 7-methyl compound are not understood.



7 **8**

a, $R_1 = CH_3$; $R_2 = H$
b, $R_1 = CH_3O$; $R_2 = H$
c, $R_1 = NO_2$; $R_2 = H$
d, $R_1 = Br$; $R_2 = H$
e, $R_2 = H$; $R_2 = CH_3$
f, $R_1 = H$; $R_2 = CH_3O$
g, $R_1 = H$; $R_2 = NO_2$

Quantum Yield Measurements. Actinometer solutions (uranyl oxalate) and ethanolysis solutions contained in cuvettes were placed, in alternation, on the periphery of a "Hammond turntable"[6] equipped with a 400-W medium-pressure mercury lamp and a filter system transparent only to 248–264-mμ light. After photolysis for the appropriate length of time, the extent of decomposition of the actinometer solution was determined titrametrically, and the extent of alcoholysis of the lactones was determined spectrophotometrically. The quantum yields, calculated by the substitution of these data into an expression developed by Cornelisse,[7] are given in Table II.

Table II. Quantum Yields for the Ethanolysis of Lactones **1**, **3**, **5**, **7a**, **7b**, **7d**, **7e**, and **7f**

Lactone	Φ, 10^{-2}	Rel Φ
7-Methoxy-3,4-dihydrocoumarin (**7f**)	0.6 ± 0.2	0.081
6-Methyl-3,4-dihydrocoumarin (**7a**)	4.7 ± 0.3	0.635
7-Methyl-3,4-dihydrocoumarin (**7e**)	6.2 ± 0.5	0.839
6-Bromo-3,4-dihydrocoumarin (**7d**)	6.6 ± 0.2	0.893
3,4-Dihydrocoumarin (**1**)	7.4 ± 0.5	1.000
6-Methoxy-3,4-dihydrocoumarin (**7b**)	8.5 ± 0.5	1.149
2-Keto-2,3-dihydrobenzofuran (**5**)	10.0 ± 0.4	1.351
2-Keto-2,3,4,5-tetrahydrobenzoxepin (**3**)	10.3 ± 0.5	1.420

Mechanism of the Photoinduced Alcoholysis of 3,4-Dihydrocoumarin and Related Lactones. Photoinduced reactions involving cleavage of the X–Y bond in ArX–Y compounds are known in a variety of systems[8] including those in which X is oxygen and Y is carbon,[3,9–14] X is oxygen and Y is sulfur,[15] and X is nitrogen and Y is carbon.[16] The well-studied process known as the photoinduced Fries reaction occurs in systems in which X is oxygen and Y is a carbonyl function. One of the mechanisms that has been proposed for this reaction postulates homolysis of the O–CO bond to a phenoxy radical and an acyl radical which then recombine to produce *ortho*- and *para*-substituted acyl phenols.[13] If this mechanism were operative in the photolysis of 3,4-dihydrocoumarin (**1**), the initially formed biradical **10** might react directly with alcohol (pathway 2 in Scheme I) to yield the hydroxy ester **14**. Arguing against this, however, is the necessity for a homolytic cleavage of the strong O–H bond of the alcohol and the probability that competing intramolecular events would take place more rapidly. Another mechanism[8] postulates the formation of a ketene (*e.g.*, **13** *via* pathway 3 of Scheme I in the present system) followed by alcoholysis (*e.g.*, to **14**). Arguing against this is the failure to find any carbon-bound deuterium in the product **14** when the photolysis is carried out in CH_3OD. A third alternative postulates that the excited singlet from **1** undergoes rapid rebonding and internal conversion to the spirodiketone **12**, alcoholysis of which yields **14** (pathway 1 in Scheme I). Although attempts to isolate **12** (or its higher homolog from **3**) have been unsuccessful, this hypothesis is entertained because it allows an explanation of the quantum yields, the substituent effects, and the ring size effects that have been observed in the systems studied in the present research.

The strikingly different quantum yields for the 6-methoxy- and the 7-methoxy-3,4-dihydrocoumarins can be accommodated to the rebonding pathway 1 scheme by the assumption that the ease of rebonding is directly related to the charge density at the bridgehead carbon atom of the excited-state species. Calculations[17] as

(5) For discussions of substituent effects in ester hydrolysis, see (a) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); (b) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 556; (c) M. L. Bender, *Chem. Rev.*, **60**, 53 (1960).

(6) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, S. Bradshaw, D. O. Cowan, R. C. Cousell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

(7) J. Cornelisse, Ph.D. Thesis, University of Leiden, 1965. We are indebted to Dr. Cornelisse not only for developing the expression for calculating the quantum yields but also for carrying out the calculations.

(8) For a review of the photo-Fries reaction and related rearrangements, see V. I. Stenberg in "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 127.

(9) J. C. Anderson and C. B. Reese, *Proc. Chem. Soc.*, 217 (1960).

(10) C. H. Kuo, R. D. Hoffsommer, H. L. Slates, D. Taub, and N. L. Wendler, *Chem. Ind.* (London), 1627 (1960).

(11) H. Kobsa, *J. Org. Chem.*, 27, 2293 (1962).

(12) D. P. Kelly and J. T. Pinhey, *Tetrahedron Lett.*, 3427 (1964).

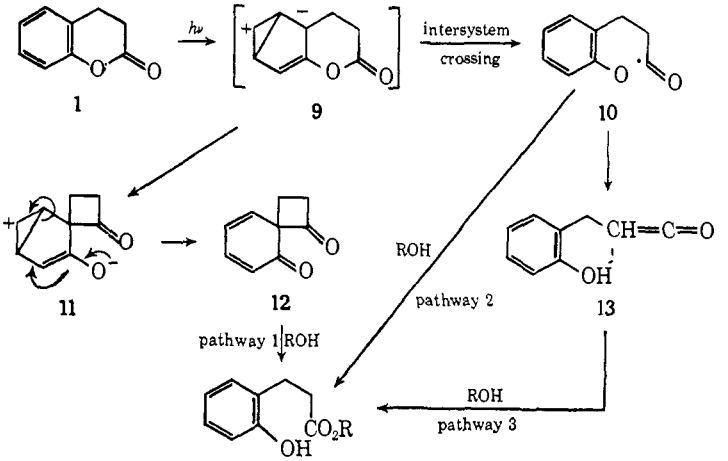
(13) R. A. Finnegan and J. J. Mattice, *Tetrahedron*, **21**, 1015 (1965).

(14) F. L. Bach, Abstracts of the 152nd National Meeting of the American Chemical Society, New York, N. Y., 1966, p S34.

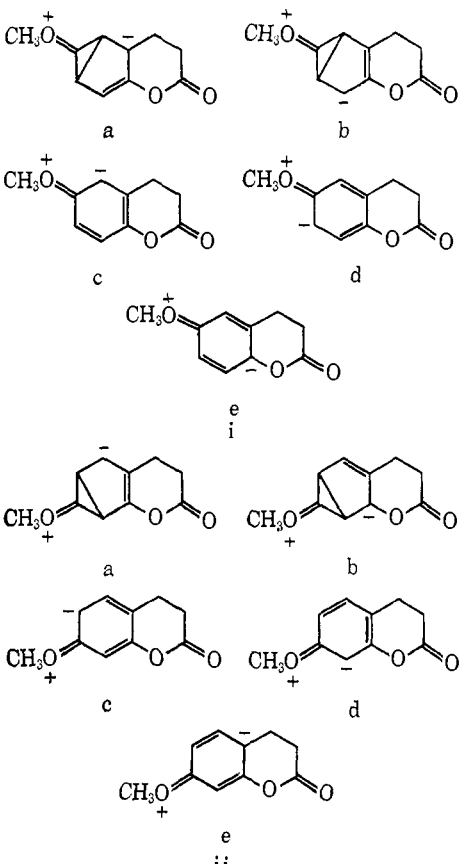
(15) J. L. Stratenus and E. Havinga, *Rec. Trav. Chim. Pays-Bas*, **85**, 434 (1966).

(16) D. Elad, *Tetrahedron Lett.*, 873 (1963).

Scheme I. Reaction Pathways for the Photoinduced Alcoholysis of 3,4-Dihydrocoumarins



well as experimental observations[18] support the contention that the electron distribution of variously substituted aromatic rings is different in the ground state and excited state, and it can be argued that the excited state obtained from 6-methoxy-3,4-dihydrocoumarin has a greater electron density at the bridgehead carbon than does the excited state obtained from 7-methoxy-3,4-dihydrocoumarin.[19] Accordingly, the



14-fold greater quantum yield for the 6-methoxy compound can be rationalized. It seems probable, however, that not only must rebonding propensities be taken into account but also the ease of cleavage of the O–CO bond. A correlation might be expected between the quantum yield and the pK^* of the corresponding phenols; an approximately linear relationship (with the exception of the 6-methoxy compound) is, in fact, observed, as shown in Figure 1. The failure of the 6-

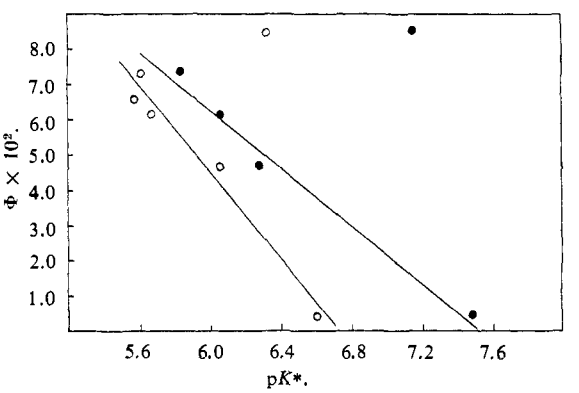
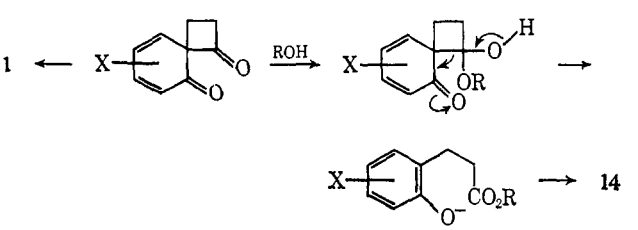


Figure 1. Product quantum yield of ethanolysis of 6- and 7-substituted dihydrocoumarins *vs.* pK^* of related phenols: ○, pK^* of parent phenols; ●, pK^* of methyl hydroxyphenylpropionates.

methoxy compound to fall on the line is ascribed to its particular effectiveness in providing electrons at the bridgehead position in the excited species,[19] this factor more than offsetting the inherently stronger O–CO bond in this compound.

In addition to the rebonding and O–CO cleavage factors, the quantum yield will also be dependent on the extent to which the spirodiketone **12** rearranges to 3,4-dihydrocoumarin. Partitioning between (a) rearrangement of **12** to **1** and (b) alcoholysis of **12** to **14**



(17) H. E. Zimmerman, *Tetrahedron Suppl.*, **19**, 396 (1963); H. E. Zimmerman and V. R. Sandel, *J. Amer. Chem. Soc.*, **85**, 915 (1963).

(18) E. Havinga, R. O. de Jongh, and W. Dorst, *Rec. Trav. Chim. Pays-Bas*, **75**, 378 (1956).

(19) The initially formed excited state from 6-methoxy-3,4-dihydrocoumarin can be represented, *inter alia*, by the resonance structures i-a to i-e with the structures i-a to i-d being major contributors and i-e (the most highly charge-separated structure) being a minor contributor. The initially formed excited state from 7-methoxy-3,4-dihydrocoumarin can be represented, *inter alia*, by the resonance structures ii-a to ii-e with structures ii-a to ii-d being major contributors and ii-e (the most highly charge-separated structure) being a minor contributor. Thus the electron density at the bridge head position (*e.g.*, i-a and ii-e) is predicted to be greater in i than in ii.

should be essentially independent of the substituents at the 6 and 7 positions, and changes in the product quantum yield should reflect the efficiency of the initial rebonding process. Conversely, the efficiency of the rebonding process for **1** and its higher homolog **3** should be approximately equal, and differences in the product quantum yield should reflect differences in the partitioning between rearrangement to starting material and alcoholysis to phenolic ester. Thus, the spiro[5.4]diketone from **3** (more resistant to rearrangement than the spiro[5.3]diketone from **1**) shows a higher product quantum yield.

If the alcoholysis of 3,4-dihydrocoumarin is, in fact, a special case of the photoinduced Fries reaction, the rebonding pathway 1 mechanism might also obtain for other reactions of this class. In a recent study of the role of steric and electronic factors in the photoinduced Fries reaction, Coppinger and Bell[20a] have suggested that the free-radical mechanism is a less satisfactory interpretation than a "molecular rearrangement" mechanism in which a certain amount of ionic character is developed along the reaction pathway. It is their contention that the initially formed excited state is rapidly transformed by internal conversion to a high vibrational level of the ground state, this premise based on the lack of fluorescence or phosphorescence in the systems with which they worked. Sandner and Trecker[20b] have also provided evidence for "a very tightly bound intermediate which proceeds to product unaffected by its reaction environment." Although each group of workers has developed and expressed its ideas in somewhat different fashions, it appears that the interpretations of Coppinger and Bell, of Sandner and Trecker, and of the present authors hold several points in common.

Experimental Section[21]

Synthesis of Substituted 3,4-Dihydrocoumarins. 6-Methyl-3,4-dihydrocoumarin (7a) was obtained in 84% yield by the method of Sato, *et al.*,[22] as a pale yellow solid which, after recrystallization from 50% ethanol, yielded shiny, colorless plates: mp 79–80° (lit.[22] mp 79–79.5°); $\bar{\nu}^{KBr}$ 1760 cm^{-1} (carbonyl); λ_{max}^{EtOH} (ϵ) 280 mμ (1025), 271 (1095).

6-Methoxy-3,4-dihydrocoumarin (7b) was prepared in 14.5% yield by the method of Sato, *et al.*,[22] and obtained as a colorless solid: mp 52–54° (lit.[22] mp 46–47°); $\bar{\nu}^{liq}$ 1777 cm^{-1} (carbonyl); λ_{max}^{EtOH} (ϵ) 283 mμ (2410); nmr ($CDCl_3$) (ppm), 3-proton multiplet at 6.50–7.15 (aromatic –H), 3-proton singlet at 3.80 (OCH_3), 4-proton multiplet at 2.50–3.17 (CH_2).

6-Nitro-3,4-dihydrocoumarin (7c). Following a literature procedure[23] a 9-g sample of 3,4-dihydrocoumarin in 60 ml of acetic anhydride was cooled to 0°, treated with a mixture of 6.2 g of nitric acid in 8.4 g of glacial acetic acid, and allowed to stand for 1 hr at 0° and an additional 2 hr at room temperature. The product, after recrystallization from 95% ethanol, consisted of 7.5 g (63%) of shining, silvery plates: mp 129.5–130° (lit.[23] mp 130°); $\bar{\nu}^{KBr}$ 1795 cm^{-1} (carbonyl); λ_{max}^{EtOH} (ϵ) 284 mμ (9680).

6-Bromo-3,4-dihydrocoumarin (7d) was prepared by the method of Fittig[24] and obtained in 92% yield as thin, shiny plates after recrystallization from petroleum ether (bp 63–68°): mp 107.5–108° (lit.[24] mp 106°); $\bar{\nu}^{KBr}$ 1775 cm^{-1} (carbonyl); λ_{max}^{EtOH} (ϵ) 283 mμ (640), 275 (730).

7-Methyl-3,4-dihydrocoumarin (7e). 7-Methylcoumarin[25] was reduced with 2.5% sodium amalgam[26] to give, in 90% yield, 7-methyl-3,4-dihydrocoumarin, mp 40–43°. Redistillation through a 12-cm Vigreux column provided a fraction with bp 98–100° (0.2 mm) and mp 44.5° (lit.[27] mp 44.5°); $\bar{\nu}^{KBr}$ 1775 cm^{-1} (carbonyl); λ_{max}^{EtOH} (ϵ) 277 mμ (745), 269 (729).

7-Methoxy-3,4-dihydrocoumarin (7f). β-(2-Hydroxy-4-methoxyphenyl)propionic acid[28] was lactonized by heating for 1 hr at 142°. The product was distilled through a 22-cm Vigreux column to give a 49% over-all yield of **7f** as a colorless oil: bp 132.5° (0.6 mm); $\bar{\nu}^{liq}$ 1780 cm^{-1} (carbonyl); λ_{max}^{EtOH} (ϵ) 284 mμ (1886), 278 (2027).

Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. Found: C, 67.62; H, 6.00.

7-Nitro-3,4-dihydrocoumarin (7g). A mixture of 11.5 g of 6-nitro-1-hydrindone[29] and 42 g of anhydrous disodium hydrogen phosphate in 48 ml of methylene chloride was treated dropwise over a period of 0.5 hr with a solution of 16 ml of trifluoroacetic anhydride and 2.7 ml of 90% hydrogen peroxide in 25 ml of methylene chloride.[30] After the addition was complete, the mixture was refluxed 1 hr and then worked up to give 9.5 g (76%) of crude material which, after recrystallization from methylene chloride followed by petroleum ether (bp 88–98°), provided 7.7 g (61%) of **7g** as pale yellow, shiny crystals: mp 122–123°; $\bar{\nu}^{KBr}$ 1780 cm^{-1} (carbonyl); λ_{max}^{EtOH} (ϵ) 270 mμ (8000).

Anal. Calcd for $C_9H_7NO_4$: C, 55.96; H, 3.65. Found: C, 56.09; H, 3.76.

Preparative-Scale Photolysis Experiments. Ethanolysis of 3,4-Dihydrocoumarin (1). A 4.03-g sample of 3,4-dihydrocoumarin in 270 ml of absolute ethanol was placed in a water-cooled, concentric quartz well apparatus, the air in the system was replaced with nitrogen, and the mixture was photolyzed for 147 min with a 400-W medium-pressure mercury lamp. The course of the reaction was followed by periodically withdrawing samples which were spectrophotometrically analyzed by noting the increase in absorption at 274 mμ. Evaporation of the solvent left 4.80 g (90%) of a pale yellow oil which was dissolved in ether and the ether solution extracted with two 30-ml portions of 4% aqueous sodium hydroxide. From the ether solution only traces of starting material could be recovered, while the base extract yielded 3.90 g (73%) of a crude solid which, after recrystallization from petroleum ether (bp 40–50°), yielded ethyl β-(2-hydroxyphenyl)propionate (**2b**) as colorless, fine needles: mp 34–35° (lit.[31] mp 36–36.5°); $\bar{\nu}^{KBr}$ 3500 (hydroxyl), 1705 cm^{-1} (carbonyl); λ_{max}^{EtOH} (ϵ) 274.5 mμ (2480).

Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.30; H, 7.52.

Methanolysis of 3,4-Dihydrocoumarin. A 4.05-g sample of 3,4-dihydrocoumarin in 260 ml of methanol was photolyzed as described above for 152 min. The crude product, consisting of 4.63 g (94%) of a solid, was recrystallized from petroleum ether (bp 32–37°) to yield 4.1 g (83%) of methyl β-(2-hydroxyphenyl)propionate (**2a**) as colorless needles: mp 45.8–46°; $\bar{\nu}^{KBr}$ 3550 (hydroxyl), 1690 cm^{-1} (carbonyl); λ_{max}^{EtOH} (ϵ) 274.5 mμ (2570).

Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.55; H, 6.70.

Methanolysis of 3,4-Dihydrocoumarin with CH_3OD. Following the procedure described above, a 3.0-g sample of 3,4-dihydrocoumarin was photolyzed in 50 ml of CH_3OD. The crude product was treated with water (to exchange oxygen-bound deuterium) and recrystallized from petroleum ether (bp 32–37°) to give colorless needles; nmr ($CDCl_3$) (ppm), 1-proton singlet at 2.47 (OH), 4-proton multiplet at 2.60–3.50 ($ArCH_2CH_2CO$–), 3-proton singlet at 6.38 (OCH_3), 4-proton multiplet at 6.83–7.67 (Ar–H).

(20) (a) G. M. Coppinger and E. R. Bell, *J. Phys. Chem.*, 70, 3479 (1966); (b) M. R. Sandner and D. J. Trecker, *J. Amer. Chem. Soc.*, **89**, 5725 (1967).

(21) Melting points are corrected; boiling points are uncorrected. The infrared spectra were recorded on a Perkin-Elmer Infracord spectrometer; the ultraviolet spectra were recorded on Cary Model 11 and Model 14 spectrometers; the nuclear magnetic spectra were recorded on a Varian HA 60 instrument, and the resonances are stated in parts per million downfield from tetramethylsilane used as an internal reference. Microanalyses were performed by Mikroanalytisches Laboratorium, Vienna, Austria.

(22) K. Sato, T. Amakasu, and S. Abe, *J. Org. Chem.*, **29**, 2971 (1964).

(23) T. R. Ingle and B. V. Bhide, *J. Univ. Bombay, Sect. A, 23, Sci. No.*, 33 (1954); *Chem. Abstr.*, 50, 322*e* (1956).

(24) R. Fittig and H. Hochstetter, *Ann.*, **226**, 355 (1884).

(25) K. Fries and W. Klosetermann, *Ber.*, **39**, 871 (1906).

(26) W. R. Bransen and C. R. Hauser, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 508.

(27) T. Nakabayashi, *J. Pharm. Soc. Jap.*, **74**, 23 (1954); *Chem. Abstr.*, **49**, 1717*d* (1955).

(28) W. D. Langley and R. Adams, *J. Amer. Chem. Soc.*, **44**, 2320 (1922).

(29) C. K. Ingold and H. A. Piggott, *J. Chem. Soc.*, **123**, 1469 (1923).

(30) W. D. Emmons and G. B. Lucas, *J. Amer. Chem. Soc.*, 77, 2287 (1955).

(31) L. Claisen, *Ber.*, **54**, 200 (1921).

Isopropanolysis of 3,4-Dihydrocoumarin. A 4.20-g sample of 3,4-dihydrocoumarin in 260 ml of isopropyl alcohol was irradiated, as described above, for 266 min and worked up to yield 25% of recovered starting material and 52% of isopropyl β-(2-hydroxyphenyl)propionate (**2c**): bp 119–122° (0.5 mm); $\bar{\nu}^{liq}$ 3450 (hydroxyl), 1700 cm^{-1} (carbonyl); λ_{max}^{EtOH} (ε) 274 mμ (2145); nmr ($CDCl_3$) (ppm) 4-proton multiplet at 6.70–7.28 (aromatic H), 1-proton quintet at 5.05 ($CH(CH_3)_2$), 4-proton multiplet at 2.50–3.15 (CH_2), 6-proton doublet at 1.23 ($CH(CH_3)_2$).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.43; H, 7.82.

***t*-Butyl Alcoholysis of 3,4-Dihydrocoumarin.** Irradiation for 1115 min of a sample of 4.32 g of 3,4-dihydrocoumarin in 270 ml of *t*-butyl alcohol yielded 95% of recovered starting material.

Pyrrolidinolysis of 3,4-Dihydrocoumarin. A 4.00-g sample of 3,4-dihydrocoumarin in 250 ml of pyrrolidine was irradiated for 34 min and worked up as described above to yield 5.72 g (97%) of a red solid, mp 126–138°, which was recrystallized three times from water to yield **N-[β-(2-hydroxyphenyl)propionyl]pyrrolidine** as white needles: mp 145–145.5°; $\bar{\nu}^{KBr}$ 3300 (hydroxyl), 1617 cm^{-1} (amide carbonyl); λ_{max}^{EtOH} (ε) 274 mμ (2445).

Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81. Found: C, 71.27; H, 7.83.

Alcoholysis of 6- and 7-Substituted 3,4-Dihydrocoumarins. A. Ethanolysis of 6-methyl-3,4-dihydrocoumarin (**7a**) yielded 63% of **ethyl β-(2-hydroxy-5-methylphenyl)propionate** (8a) as a colorless oil: bp 108–111° (0.24 mm); $\bar{\nu}^{liq}$ 3450 (hydroxyl), 1705 cm^{-1} (carbonyl); λ_{max}^{EtOH} (ε) 282 mμ (3675).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 68.92; H, 7.93.

B. Ethanolysis of 6-methoxy-3,4-dihydrocoumarin (**7b**) yielded 81% of **ethyl β-(2-hydroxy-5-methoxyphenyl)propionate** (8b) as a colorless oil: $\bar{\nu}^{liq}$ 3450 (hydroxyl), 1710 cm^{-1} (carbonyl); λ_{max}^{EtOH} (ε) 292 mμ (3370).

Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.26; H, 7.16.

C. Methanolysis of 6-nitro-3,4-dihydrocoumarin (**7c**) yielded (almost exclusively a "dark solvolysis" reaction) **methyl β-(2-hydroxy-5-nitrophenyl)propionate** as colorless, small needles mp 110°.

Anal. Calcd for $C_{10}H_{11}NO_5$: C, 53.33; H, 4.92. Found: C, 53.45; H, 4.91.

D. Ethanolysis of **7c** yielded (almost exclusively a "dark solvolysis" reaction) **ethyl β-(2-hydroxy-5-nitrophenyl)propionate** (8c) as colorless, small needles, mp 89.5–90°.

Anal. Calcd for $C_{11}H_{13}NO_5$: C, 55.23; H, 5.48. Found: C, 55.44; H, 5.53.

E. Ethanolysis of 6-bromo-3,4-dihydrocoumarin (**7d**) yielded 91% of **ethyl β-(2-hydroxy-5-bromophenyl)propionate** (8d) as a colorless oil: $\bar{\nu}^{liq}$ 3500 (hydroxyl), 1710 cm^{-1} (carbonyl); λ_{max}^{EtOH} (ε) 283 mμ (2530).

Anal. Calcd for $C_{11}H_{13}BrO_3$: C, 48.37; H, 4.76. Found: C, 47.73; H, 4.76.

F. Ethanolysis of 7-methyl-3,4-dihydrocoumarin (**7e**) yielded 82% of **ethyl β-(2-hydroxy-4-methylphenyl)propionate** (8e) as a colorless oil: $\bar{\nu}^{liq}$ 3450 (hydroxyl), 1700 cm^{-1} (carbonyl); λ_{max}^{EtOH} (ε) 276 mμ (2520).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.30; H, 7.69.

G. Ethanolysis of 7-methoxy-3,4-dihydrocoumarin (**7f**) yielded 77% of **ethyl β-(2-hydroxy-4-methoxyphenyl)propionate** (8f) as a colorless oil: $\bar{\nu}^{liq}$ 3450 (hydroxyl), 1700 cm^{-1} (carbonyl); λ_{max}^{EtOH} (ε) 279.5 mμ (2900).

Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.63; H, 7.16.

H. Methanolysis of 7-nitro-3,4-dihydrocoumarin (**7g**) yielded (almost exclusively a "dark solvolysis" reaction) **methyl β-(2-hydroxy-4-nitrophenyl)propionate** as colorless, small needles, mp 130–131°.

Anal. Calcd for $C_{10}H_{11}NO_5$: C, 53.33; H, 4.92. Found: C, 53.17; H, 4.80.

I. Ethanolysis of 7-nitro-3,4-dihydrocoumarin (**7g**) yielded (almost exclusively a "dark solvolysis" reaction) **ethyl β-(2-hydroxy-4-nitrophenyl)propionate** (8g) as colorless, small needles, mp 79–80°.

Anal. Calcd for $C_{11}H_{13}NO_5$: C, 55.23; H, 5.48. Found: C, 54.91; H, 5.49.

Ethanolysis of 2-keto-2,3,4,5-tetrahydrobenzoxepin (**3**) was carried out as described above to yield 37% of starting material and 40% of ethyl γ-(2-hydroxyphenyl)butyrate (**4**) as a colorless oil: $\bar{\nu}^{liq}$ 3500 (hydroxyl), 1705 cm^{-1} (carbonyl); λ_{max}^{EtOH} (ε) 274 mμ (2750).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.50; H, 7.91.

Alcoholysis of 2-Keto-2,3-dihydrobenzofuran (5). The starting material **5** was obtained by treatment of *o*-methoxymandelonitrile with hydriodic acid and red phosphorus according to literature directions[32] and was obtained as a colorless oil: bp 247–249° (760 mm) (lit.[28] bp 246° (726 mm)); $\bar{\nu}^{liq}$ 1800 and 1775 cm^{-1} (carbonyl); λ_{max}^{EtOH} (ε) 277 mμ (1210), 271 (1225). A 2.91-g sample of **5** was dissolved in 280 ml of methanol and irradiated, as described above, for 225 min. The resulting mixture was worked up in the usual fashion to yield 1.98 g (81%) of a base-soluble fraction which was shown by vpc to consist almost entirely of a single component identified as methyl 2-hydroxybenzyl ether (**6a**): bp 63–67° (2.5 mm) (lit.[33] bp 65–66° (2.5 mm)); $\bar{\nu}^{liq}$ 3450 cm^{-1} (hydroxyl); λ_{max}^{EtOH} (ε) 275 mμ (2750); nmr ($CDCl_3$) (ppm), 1-proton singlet at 7.54 (OH), 4-proton multiplet at 6.60–7.38 (aromatic H), 2-proton singlet at 4.65 ($ArCH_2O$), 3-proton singlet at 3.42 (OCH_3).

In similar fashion, a sample of **5** was photolyzed in ethanol solution to yield 64% of ethyl 2-hydroxybenzyl ether (**6b**) as a colorless oil: bp 84–85° (2.5 mm) (lit.[33] bp 79–82° (2 mm)); $\bar{\nu}^{liq}$ 3450 cm^{-1} (hydroxyl); λ_{max}^{EtOH} (ε) 275 mμ (2680); nmr ($CDCl_3$) (ppm), 1-proton singlet at 7.75 (OH), 4-proton multiplet at 6.75–7.50 (aromatic H), 2-proton singlet at 4.78 ($ArCH_2O$), 2-proton quartet at 3.75 (OCH_2CH_3), 3-proton triplet at 1.38 (OCH_2CH_3). Following the directions of de Jonge[33] an authentic sample of **5** was prepared and found to be identical in all of its spectral characteristics with the material obtained by photoinduced ethanolysis of **5**.

Methanolysis of 4-valerolactone, carried on for a period of 18 hr under the conditions described above, yielded 97% of recovered starting material.

"Dark Solvolysis" Experiments. General Method. Ethanol solutions 10^{-3} to 10^{-4} *M* with respect to the 3,4-dihydrocoumarin compound were prepared in volumetric flasks protected from the light, and the flasks were placed in a constant-temperature bath held at 30.00 ± 0.02°. The course of the reaction was followed by withdrawing samples of the reaction mixture at various intervals and recording the ultraviolet absorption changes. Knowing the individual extinction coefficients of the 3,4-dihydrocoumarin compound and its corresponding phenol ester at a specified wavelength and assuming the alcoholysis to be a pseudo-first-order process, the change in concentration of the 3,4-dihydrocoumarin compound can be measured as a function of the change in extinction coefficient at the specified wavelength. Thus, the first-order expression $c/c_0 = e^{-kt}$ can be expressed in terms of the extinction coefficient of the mixture (ε), the extinction coefficient of the dihydrocoumarin compound (ϵ_1), and the extinction coefficient of the phenolic ester (ϵ_2), in terms of the total concentration of the dihydrocoumarin compound and the phenolic ester (which remains invariant and equal to the initial concentration of the dihydrocoumarin compound), and in terms of the length of the absorption cell (l) in centimeters, *viz.*, $c/c_0 = e^{-kt} = [(\epsilon - \epsilon_2)/(\epsilon_1 - \epsilon_2)]cl$. From a plot of the value of ln $\{[(\epsilon_1 - \epsilon_2)/(\epsilon - \epsilon_2)]cl\}$ *vs.* time a value for the specific reaction rate constant was obtained, using the method of least squares[5a] to determine the best straight line through the observed points.

Solvolysis Results. Employing the procedure described above, the "dark ethanolysis" rates shown in Table III were obtained.

Product Quantum Yield Determinations. Actinometer Solutions. The actinometer solution was prepared from 30 ml of an aqueous solution containing 0.0998 mol/kg of oxalic acid and 30 ml of an aqueous solution containing 0.01997 mol/kg of uranyl sulfate. Careful studies by Leighton and Forbes[34] have shown that the quantum yield for this actinometer solution varies from 0.60 at 254 mμ to 0.58 at 435 mμ in stirred solutions, these values falling slightly in unstirred solutions.

Photolysis Apparatus. Employing the general features of a design attributed to Hammond[6] a turntable was constructed which allowed 16 absorption cells (1 × 1 cm) to be located equidistant from the light source (centered in the turntable) and to be rotated around the stationary light source at a rate of 0.5 rpm. The light source consisted of a double-walled quartz well (Hanovia design) containing a 400-W medium-pressure mercury lamp. The lamp

(32) S. Czaplicki, St. v. Kostanecki, and V. Lampe, *Ber.*, **42**, 827 (1909).

(33) J. de Jonge and B. M. Dibo, *Rec. Trav. Chim. Pays-Bas*, **74**, 1448 (1955).

(34) W. G. Leighton and G. S. Forbes, *J. Amer. Chem. Soc.*, **52**, 3139 (1930).

Table III. "Dark Ethanolysis" Experiments with 6- and 7-Substituted 3,4-Dihydrocoumarins

Compound	Initial concn, mol/l., 10^{-3}	λ of measurement, mμ	ϵ_1	ϵ_2	k, min^{-1}, 10^{-4}
3,4-Dihydrocoumarin (**1**)	1.073	280	79	2214	0.602
6-Methyl-3,4-dihydrocoumarin (**7a**)	0.926	286	207	3120	0.0104
6-Methoxy-3,4-dihydrocoumarin (**7b**)	0.424	300	404	2800	0.001
6-Nitro-3,4-dihydrocoumarin (**7c**)	0.184	320	3310	9920	164.2
6-Bromo-3,4-dihydrocoumarin (**7d**)	0.677	290	244	2180	3.110
7-Methyl-3,4-dihydrocoumarin (**7e**)	0.997	283	78	2411	1.452
7-Methoxy-3,4-dihydrocoumarin (**7f**)	0.493	284	1886	3080	1.743
7-Nitro-3,4-dihydrocoumarin (**7g**)	0.303	335	904	3500	74.3

Table IV. Quantum Yield Measurements for the Photoinduced Ethanolysis of 3,4-Dihydrocoumarin

Cell positions	Identity[a]	Soln, g	Optical density units at 280 mμ: $t = \infty$	$t = 0$	t	Moles of ester formed, 10^{-7}	Actinometer titrations $(KMnO_4)_{t=0}$	$(KMnO_4)_t$	Mole of oxalic acid decomposed, 10^{-4}	Φ, 10^{-2}
1	Soln B	2.4899					1.26101	1.21800	0.04356	
2	Soln A	1.9400[b]	18.553	0.575	1.088	5.8829				7.4
3	Soln B	2.4766					1.256274	1.21271	0.03653	
4	Soln C	1.9486[b]	18.553	0.565	0.570	0.0556				
7	Soln B	2.4749					1.25341	1.21688	0.04043	
8	Soln A	1.9435[b]	18.553	0.565	1.089	6.0058				7.6
9	Soln B	2.4848					1.25843	1.21800	0.03842	
11	Soln C	1.9508[b]	18.553	0.565	0.572	0.0786				
12	Soln B	2.4802					1.25610	1.21768	0.03945	
13	Soln A	1.9521[b]	18.553	0.568	1.085	5.9544				7.6
14	Soln B	2.4835					1.25777	1.21832		

[a] Soln A contains 3,4-dihydrocoumarin exposed to light source; soln B contains actinometer solution; soln C contains 3,4-dihydrocoumarin protected from light source. [b] Concentration of 3,4-dihydrocoumarin = 1.0608×10^{-5} mol/g = 8.380×10^{-3} mol/l.

Table V. Concentration Dependence of Apparent Quantum Yield in the Photoinduced Ethanolysis of 3,4-Dihydrocoumarin

Concn of 3,4-dihydrocoumarin, mol/l. $\times 10^{-3}$	Optical density units at 280 mμ: $t = \infty$	$t = 0$	t	Moles of ester formed, 10^{-8}	Moles of oxalic acid decomposed, 10^{-5}	Φ, 10^{-2}
10.628	23.530	0.860	1.420	64.362	4.4035	7.4
10.628	23.530	0.844	1.403	64.310	4.4035	7.4
10.438	23.110	0.752	1.228	54.767	3.6013	7.9
10.438	23.110	0.752	1.230	54.604	3.6013	7.8
8.380	18.553	0.575	1.088	58.829	4.0298	7.4
7.587	16.798	0.550	1.050	57.473	4.1168	7.3
5.091	11.272	0.370	0.850	56.228	4.1168	7.9
4.198	9.294	0.254	0.912	56.561	4.3490	7.4
2.950	6.531	0.245	0.697	52.285	5.9220	6.6
2.545	5.634	0.190	0.570	43.837	4.1168	6.1
2.347	5.307	0.170	0.760	67.668	7.3521	7.3
2.162	4.787	0.165	0.545	43.999	5.9220	5.8
1.195	2.646	0.080	0.320	27.534	4.1168	4.7
0.975	2.159	0.075	0.375	35.052	5.9220	6.7

source was surrounded by a pair of concentric quartz cylinders, providing annular spaces of 0.80 and 0.65 cm and accommodating two filter solutions: (a) an aqueous solution containing 330 g/l. of cobalt sulfate heptahydrate and 300 g/l. of nickel sulfate hexahydrate capable of filtering out light in the region 370–545 mμ; (b) an aqueous solution of 0.17 g/l. of iodine and 0.24 g/l. of potassium iodide which transmits light in the region above 380 mμ and between 248 and 264 mμ with a maximum transmission of 256 mμ. While the cobalt sulfate–nickel sulfate filter solution is completely light stable, the iodine–potassium iodide solution undergoes slight decomposition upon prolonged irradiation. As a precaution, therefore, this solution was always freshly prepared before each experiment, and the photolysis was never allowed to proceed beyond the point at which the filter capacity of this solution had resulted in a change in transmittance beyond 247–265 mμ (*i.e.*, a 2-mμ increase over the original).

Illustrative Experiment. A solution containing 1.0608×10^{-2} mol/kg of 3,4-dihydrocoumarin in ethanol was prepared, the exact concentration being ascertained by a measurement of the intensity of the ultraviolet absorption at 274 mμ. A carefully weighed portion of this solution (*ca.* 2.5 ml) was placed in a 1.00-cm path length absorption cell, the cell was tightly stoppered with a Teflon plug, and the cell was secured in the turntable apparatus. Five such cells were prepared in this fashion and were placed at various positions around the turntable. Two of these, however, were provided with hoods to protect them from the light source and to thereby provide a value for any "dark solvolysis" correction. Accurately weighed portions (*ca.* 2.5 ml) of the actinometer solution were placed in six other 1.00-cm path length absorption cells, care being taken during this process not to expose the actinometer solution to light. These cells were then placed on the turntable in positions such that each of the three dihydrocoumarin solutions which were exposed to the light source were flanked on either side by a cell containing the actinometer solution. When all of the cells were in place, the entire photolysis apparatus was covered with a box, the turntable was started in rotation, and the light source was turned on.

Analysis of Photolysis Solutions. The titer of the actinometer solutions before and after photolysis was determined with 0.20033 *N* potassium permanganate solution, employing a calibrated microburet for the titration. Before photolysis 0.50644 ± 0.00077

Table VI. Quantum Yield Measurements for the Photoinduced Ethanolysis of 6- and 7-Substituted 3,4-Dihydrocoumarins, 2-Keto-2,3,4,5-tetrahydrobenzoxepin, and 2-Keto-2,3-dihydrobenzofuran

Compound	Concn, mol/l. × 10^{-3}	λ for assay, mμ	Optical density units, $t = \infty$	Optical density units, $t = 0$	Optical density units, t	Moles of ester formed, 10^{-7}	Moles of oxalic acid decomposed, 10^{-6}	Φ, 10^{-2}
6-Methyl-3,4-dihydro-	8.53	290	22.103	0.414	0.793	3.665	3.924	4.8
coumarin (**7a**)	8.53	290	22.103	0.410	0.800	3.778	3.924	4.9
	4.27	290	11.051	0.190	0.555	3.528	3.924	4.6
	1.83	290	4.748	0.110	0.435	3.153	4.349	4.4
6-Methoxy-3,4-dihydro-	4.65	305	8.138	0.575	1.093	7.840	4.4035	9.0
coumarin (**7b**)	1.00	305	1.745	0.108	0.540	6.473	4.4035	8.7
	0.52	300	1.452	0.204	0.573	2.769	4.0298	8.6
	0.24	300	0.660	0.085	0.335	2.516	4.0298	8.3
6-Bromo-3,4-dihydro-	12.34	290	26.901	1.990	2.135	1.759	1.392	6.4
coumarin (**7d**)	9.77	290	20.290	1.362	1.693	4.167	2.674	6.6
	9.77	290	20.290	1.373	1.716	4.349	2.674	6.8
7-Methyl-3,4-dihydro-	10.23	283	24.654	0.781	1.280	5.242	4.010	6.6
coumarin (**7e**)	5.62	283	13.549	0.380	0.944	4.929	3.924	6.4
	5.62	283	13.549	0.365	0.918	4.784	3.924	6.4
	1.93	283	4.661	0.114	0.497	2.531	4.010	5.8
7-Methoxy-3,4-dihydro-	0.72	245	0.187	1.175	1.163	0.215	2.181	0.6
coumarin (**7f**)	0.72	245	0.187	0.178	1.168	0.180	2.181	0.6
	0.47	245	0.122	0.752	0.730	0.415	2.181	0.9
	0.47	245	0.122	0.748	0.734	0.262	2.181	0.5
2-Keto-2,3,4,5-tetrahydro-	9.85	280	20.473	0.320	0.918	7.1575	3.6013	10.3
benzoxepin (**3**)	7.90	280	17.222	0.270	0.902	7.4062	3.6013	10.2
	3.37	280	7.347	0.245	0.697	5.3110	3.8610	10.6
	2.21	280	4.818	0.165	0.545	4.4818	3.8610	9.7
2-Keto-2,3-dihydro-	9.51	285	14.258	0.440	0.860	7.112	3.601	10.1
benzofuran (**5**)	7.77	285	11.654	0.432	1.005	9.778	5.288	9.7
	5.02	285	7.532	0.265	0.660	6.693	4.219	9.9
	1.29	285	1.940	0.080	0.492	7.130	5.288	10.3

ml of potassium permanganate solution/g of actinometer solution was required, this value providing the entries in column 8 of Table IV. After photolysis, the contents of each cell containing the actinometer solution were pipetted into a test tube (the sides of which were painted black), the cell was rinsed with water and 1 ml of 18 *N* sulfuric acid (which were added to the contents of the test tube), the test tubes were heated for 15 min in a beaker of water at 80°, and the solutions were then titrated with potassium permanganate. The values from these titrations are recorded in column 9 of Table IV, and from the difference between the values of columns 8 and 9 the amount of decomposition of the actinometer solution was calculated (column 10 of Table IV). The extent of solvolysis of the dihydrocoumarin was determined spectrophotometrically from comparisons of the extinction coefficients before photolysis ($\epsilon_{t=0}$), after photolysis for the specified time (ϵ_t), and at 100% conversion to product ($\epsilon_{t=\infty}$). In the illustrative example detailed above, the wavelength employed was 280 mμ, and the results are recorded in columns 4, 5, and 6 in Table IV.

Calculation of Quantum Yields. Employing the method of Cornelisse[7] the product quantum yields were calculated. The quantum yields shown in Table IV are representative of the reproducibility of values at a given concentration; the quantum yields shown in Table V are representative of the spread in values as the concentration of the lactone is changed. Carrying out 8–15 separate determinations in each case, the quantum yields for the 6- and 7-substituted 3,4-dihydrocoumarins (**7**), 2-keto-2,3,4,5-tetrahydrobenzoxepin (**3**), and 2-keto-2,3-dihydrobenzofuran (**5**) were determined in the manner outlined above. A representative selection of these data is given in Table VI.

Table VII. p*K** Values for Phenols and Methyl *o*-Hydroxyphenylpropionates in 33% Aqueous Methanol

Substituent	p*K** values, Phenol	p*K** values, Methyl *o*-hydroxyphenylpropionate
p-Methoxyl	6.34	7.15
m-Methoxyl	6.59	7.46
p-Methyl	6.06	6.27
m-Methyl	5.67	6.05
p-Bromo	5.57	
H	5.63	5.84

Calculation of p*K Values.** Employing a method developed by Förster,[35] the p*K** values for the several phenols and methyl *o*-hydroxyphenylpropionates listed in Table VII were measured.

(35) For references to, explanations of, and applications of this method, see H. H. Jaffé and H. L. Jones, *J. Org. Chem.*, 30, 964 (1965).