tion, the solution was made to volume and the absorbance at 5100 Å was measured. The number of ferrous ions produced per unit time was then determined from a standard calibration graph prepared by the reported procedure.[24]

Luminescence Studies.—The luminescence spectra were prepared with apparatus similar to that which was previously described.[24] The degassed solutions [conventional freeze (−78°)-thaw (25°) technique] were contained in 1.00-cm quartz cells which were sealed under vacuum.

Registry No.—**1**, 5253-87-2; **2**, 4599-96-6; **3**, 5254-01-3; **4**, 35191-44-7; **8**, 35140-90-0; dimethyl 1,2-dideuterio-5,6-acenaphthenedicarboxylate, 35140-91-1; diisopropyl 5,6-acenaphthenedicarboxylate, 35140-92-2; 5,6-acenaphthenedicarboxylic acid di-*p*-methoxyanilide, 35140-93-3; diethyl 5,6-acenaphthenedicarboxylate, 35140-94-4.

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The Photochemistry of Aryl Alkyl Carbonates. II. The Methoxyphenyl Ethyl Carbonates

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The photochemical reaction of the three methoxyphenol ethyl carbonates has been examined. Each of the compounds undergoes a photo-Fries type of reaction to produce methoxyhydroxybenzoates. A free-radical mechanism is proposed based on the substitution patterns observed in the products and on the quantum yields of the reactions. A minor reaction observed was the apparent free-radical displacement of the methoxy group by the carboethoxy radical to produce the corresponding hydroxybenzoate.

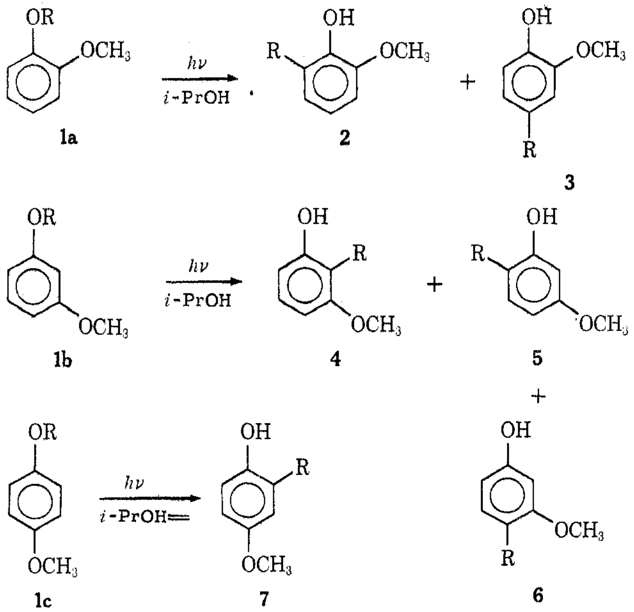
As part of our continuing study of the photochemistry of the aryl alkyl carbonates,[2] we would like to report our observations on the photolysis of the methoxyphenyl ethyl carbonates. Several investigators have shown that phenyl ethyl carbonate undergoes a photo-Fries type of reaction to give ethyl salicylate and ethyl *p*-hydroxybenzoate.[2,3] In contrast with this, we have shown that the chlorophenyl ethyl carbonates do not undergo the photo-Fries type of reaction, but instead undergo photodechlorination.[2] However, the methoxyphenyl ethyl carbonates do undergo a photo-Fries type of reaction and, in addition, an apparent free-radical displacement of the methoxyl group also occurs.

Results

o-, *m*-, and *p*-methoxyphenyl ethyl carbonate (**1a–c**) have been photolyzed in isopropyl alcohol, and the major reaction products are indicated as follows. In addition to the photo-Fries products obtained in this reaction, there is also obtained in each case a product that results from the substitution of the carboethoxy group ($-COOC_2H_5$) for the methoxyl group.

***o*-Methoxyphenyl Ethyl Carbonate (1a).**—Two photo-Fries-type products were isolated from the reaction mixture ethyl 2-hydroxy-3-methoxybenzoate (**2**), constituting about 10% of the reaction mixture, and ethyl 4-hydroxy-3-methoxybenzoate (**3**), constituting about 13% of the reaction mixture (see Table I). The remainder of the reaction mixture was mostly unreacted starting material.

Compound **2** was obtained by preparative gas-liquid partition chromatography (glpc) and its structure was ascertained through the use of nmr, ir, and mass spectroscopy (ms). The second photo-Fries-type product isolated was ethyl vanillate (**3**), a well-characterized compound. A sample isolated from the reaction mixture by preparative glpc was identical in all respects to an authentic sample of ethyl vanillate. The presence of ethyl salicylate in the reaction mixture was shown by the identity of its mass spectrum with that of an authentic sample of ethyl salicylate.



$R = -C(=O)OC_2H_5$

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[1] Abstracted from the Ph.D. Thesis of Ira Rosenberg, The George Washington University, 1969.

[2] Part I: E. Caress and I. Rosenberg, *J. Org. Chem.*, **36**, 769 (1971).

[3] C. Pac and S. Tsutsumi, *Bull. Chem. Soc. Jap.*, **37**, 1392 (1964); C. Pac, S. Tsutsumi, and H. Sakurai, *Kogyo Kagaku Zasshi*, **72** (1), 224 (1969).

TABLE I

PHOTOLYSIS OF *o*-METHOXYPHENYL ETHYL CARBONATE

Compound	Gc retention time, sec	Column temp, °C	%	Deviation, ±
Pinacol[a]	120	100	0.7	0.1
Phenol	52	150	0.3	0.1
o-Methoxyphenol	96	150	7.4	0.2
Ethyl salicylate	258	150	1.5	0.2
Unknown peak	288	150	0.5	0.1
o-Methoxyphenyl ethyl carbonate	520	150	66.2	0.7
Ethyl 2-hydroxy-3-methoxybenzoate	810	150	10.1	0.8
Ethyl 3-methoxy-4-hydroxybenzoate	1056	150	13.2	0.1

[a] Separate run.

***p*-Methoxyphenyl Ethyl Carbonate (1c) (see Table II).**—The photolysis of **1c** produced only one photo-Fries-type product; it was identified as ethyl 2-hydroxy-5-methoxybenzoate (**7**).

TABLE II

PHOTOLYSIS OF *p*-METHOXYPHENYL ETHYL CARBONATE

Compound	Gc retention time, sec	Column temp, °C	%	Deviation, ±
Pinacol	120	100	0.6	0.1
p-Methoxyphenol	210	150	12.9	0.5
p-Methoxyphenyl ethyl carbonate	684	150	49.1	0.6
Ethyl 2-hydroxy-5-methoxybenzoate	792	150	30.2	0.7
Ethyl *p*-hydroxybenzoate	960	160	7.2	0.5

One other compound was found in this reaction mixture and it was identified as ethyl *p*-hydroxybenzoate. The identification was made by comparing the reaction mixture compound's spectrum (obtained by glpc–ms) with that of a known sample of ethyl *p*-hydroxybenzoate.

***m*-Methoxyphenyl Ethyl Carbonate (1b).**—Three photo-Fries-type products were identified in the reaction mixture that resulted from the photolysis of **1b** (see Table III). Ethyl 4-hydroxy-2-methoxybenzoate (**6**) was identified on the basis of the following evidence. The nmr spectrum showed, in addition to the expected aromatic and aliphatic signals, a singlet at τ 2.2 (1 H), indicating that the compound is not a salicylate. That the compound is not a salicylate was also shown in the mass spectrum in that the base peak was found to be *m/e* 151 (M − C_2H_5O) rather than *m/e* 150 (M − C_2H_5OH). If the material is not a salicylate, it must be either ethyl 4-hydroxy-2-methoxybenzoate (**6**) or ethyl 3-hydroxy-5-methoxybenzoate. The pattern of the reactions described in this paper (a point which will be developed later) strongly suggests that the compound must be **6**.

TABLE III

PHOTOLYSIS OF *m*-METHOXYPHENYL ETHYL CARBONATE

Compound	Gc retention time, sec	Column temp, °C	%
Pinacol	120	120	2.3
m-Methoxyphenol	180	150	4.7
Ethyl *m*-hydroxybenzoate	208	150	4.7
m-Methoxyphenyl ethyl carbonate	624	150	76.6
Ethyl 2-hydroxy-4-methoxybenzoate	684	150	2.1
Ethyl 2-methoxy-6-hydroxybenzoate	804	150	5.7
Ethyl 2-methoxy-4-hydroxybenzoate[a]		194	3.8

[a] Peak was eluted by programming the column temperature at 4°/min to 194° after the ethyl 2-methoxy-6-hydroxybenzoate had been eluted.

Ethyl 2-hydroxy-4-methoxybenzoate (**5**) and ethyl 2-hydroxy-6-methoxybenzoate (**4**) were identified in the reaction mixture as follows. Both materials were shown to be salicylates on the basis that their mass spectra show base peaks at *m/e* 150. A sample of the material comprising the larger peak in the chromatograph was obtained by preparative glpc. The nmr of this material has a singlet (1 H) at τ −0.8 (confirming the salicylate assignment) and expansion of the aromatic region of the spectrum does not show the doublet, doublet, triplet pattern found for **2**, thus indicating the absence of the 1,2,3 substitution pattern on the benzene ring. The smaller peak, identified as compound **4**, could not be successfully collected because of its small size and its closeness to the large, unreacted starting material peak. The above evidence clearly indicates that the larger peak is quite reasonably identified as compound **5** and the smaller peak must, therefore, be compound **4**.

There was also found in this reaction mixture a compound with a molecular ion at *m/e* 166 whose mass spectrum does not correspond to that of phenyl ethyl carbonate, ethyl salicylate, or ethyl *p*-hydroxybenzoate. On the basis of this nonidentity and its fragmentation pattern, this compound is identified as ethyl *m*-hydroxybenzoate.

The quantum yields for the conversion of the aryl ethyl carbonates to the various products were determined and found to be 0.21 and 0.20 for the *o*- and *p*-methoxyphenyl compounds, respectively. The *m*-methoxy isomer, however, had a quantum yield of only 0.02.

Discussion

In our study of the photolysis of aryl alkyl carbonates we have been trying to examine the mechanism of the reaction by observing the effect of various ring substituents on the course of the reaction. Our hypothesis has been that, by changing from electron-donating to electron-attracting substituents, we could induce a change in mechanism. For example, Zimmerman[4] has shown that, in the case of meta-substituted benzyl acetates, a change from free-radical to ionic solvolysis occurs as you change from electron-attracting to electron-donating substituents. In his example, the electron-donating methoxyl substituent is able to stabilize in the excited state the developing carbonium ion. In our case, Zimmerman's approach would lead one to predict that an electron-withdraw-

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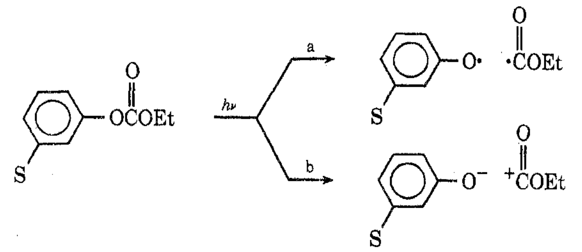
[4] H. Zimmerman, in "Advances in Photochemistry," Vol I, W. Noyes, Jr., G. Hammond, and J. Pitts, Jr., Ed., Interscience, New York, N. Y., 1963, p 200.

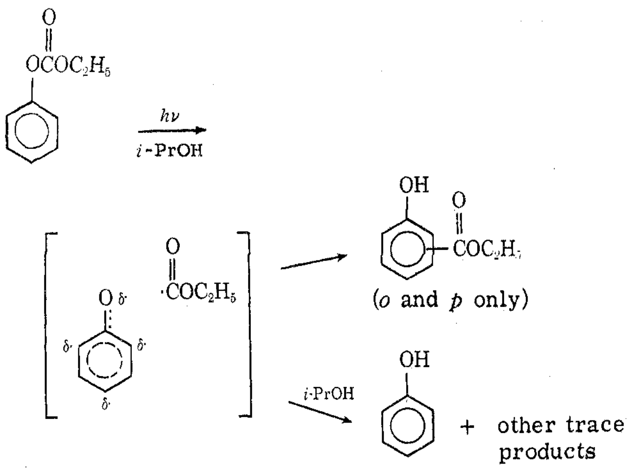
ing group will stabilize in the excited state a developing phenoxide anion. Therefore, pathway b would be



favored by electron withdrawal in the excited state by substituent S. Pathway a, which is analogous to the mechanism generally accepted for the related photo-Fries reaction, would then be the pathway expected for cases where S was electron-donating in the excited state. Thus, we would predict a change in mechanism from free radical to ionic as we move from electron-donating to electron-withdrawal substituents. The change in mechanism might be indicated in the trends of the quantum yields, shifts in the proportions of the various products, and/or in the nature of the products.

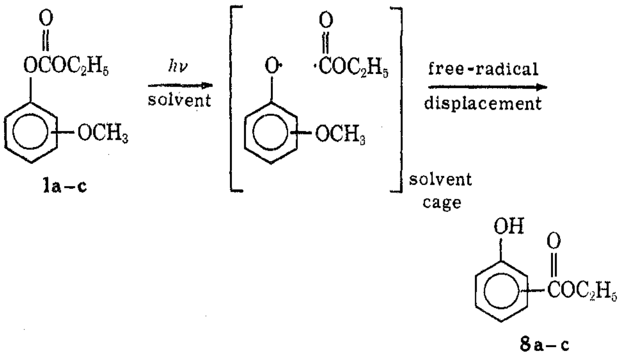
Recently, we reported our results on the chlorophenyl ethyl carbonate[2] series, which followed a non-photo-Fries reaction course, and now we are reporting our results on the methoxyphenyl ethyl carbonates. Our results for the methylphenyl ethyl carbonates will be reported in the near future.[5]

The three photoreactions in the present study each give products that result from carboethoxy substitution in all of the open ortho and para positions. These products are consistent with the mechanism proposed by Kobsa[6] for the photo-Fries reaction, which is outlined below for the phenyl ethyl carbonate case.



The observation that the quantum yield for the *m*-methoxyphenyl ethyl carbonate is an order of magnitude lower than for the ortho- and para-substituted compounds indicates that stabilization of an anionic excited state is not occurring. The greater quantum yield observed for the latter two compounds is attributed to the expected resonance stabilization of a phenoxy radical by *o*- and *p*-methoxy substitution, stabilization which cannot occur in meta-substituted phenoxy radicals.

The substitution of the carboethoxy group for the methoxy group can be explained as a radical displacement reaction, examples of which have been reported in the similar photo-Fries reaction.[6,7]



A molecular pathway for the photo-Fries reaction has been proposed[8] and could be written for the reactions presented in this paper. However, the recent report by Kalmus and Hercules[9] of their success in obtaining spectroscopic evidence for the presence of phenoxy radicals and substituted cyclohexadienones in the photo-Fries reaction seems to substantiate the mechanism proposed by Kobsa. On the basis of this spectroscopic evidence and our results, a molecular pathway does not appear to play an important part in these reactions.

The multiplicity of the photo-Fries reaction has been recently studied in the case of *p*-tolyl acetate[8] and phenyl benzoate.[10] Trecker and coworkers conclude from their results that for *p*-tolyl acetate the overall transformations occur from the singlet excited state or from a very short-lived triplet state. In the case of phenyl benzoate, Plank concludes that the triplet state is the reacting species. We are presently investigating the multiplicity of the reactive state in the photolysis of the aryl ethyl carbonates.

Experimental Section

The pmr spectra were obtained using a 60-MHz Hitachi Perkin-Elmer high-resolution nmr spectrometer, Model R-20. The spectra were obtained in carbon tetrachloride and perdeuterioacetone solution using tetramethylsilane as an internal reference. The chemical shift values are reported in ppm, using the τ scale. The mass spectra were obtained with an ionizing voltage of 70 eV, using a Perkin-Elmer Model 270 gc–ms, which is a medium-resolution, double-focusing mass spectrometer interfaced with a gas chromatograph. Gas chromatographic analyses and sample collections were carried out on a Hewlett-Packard Model 200 gas–liquid partition chromatograph equipped with a thermal conductivity detector, a Model 240 temperature programmer, and a Disc integrator equipped Honeywell recorder. The analytical work was performed using a 6 ft × $^1/_8$ in. column packed with 10% UC-W98 on Chromosorb A. Sample collections were made using a 3 ft × $^1/_4$ in. column packed with 20% SE-52 on Chromosorb A.

The methoxyphenyl ethyl carbonates, 1a–c, were prepared from ethyl chlorocarbonate and the appropriate phenol, using the method of Smith and Kosters.[11] It was found that, by allowing

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[5] I. Rosenberg, *Diss. Abstr. B*, **31**, 1839 (1970).

[6] H. Kobsa, *J. Org. Chem.*, **27**, 2293 (1962).

[7] R. Finnigan and D. Knudson, *Chem. Ind. (London)*, 1837 (1965).

[8] M. Sandner, E. Hedaya, and D. Trecker, *J. Amer. Chem. Soc.*, **90**, 7249 (1968).

[9] C. E. Kalmus and D. M. Hercules, Abstracts, 163rd National Meeting of the American Chemical Society, Boston, Mass., April 9–14, 1972, ORGN No. 28.

[10] D. Plank, *Tetrahedron Lett.*, **No. 50**, 4365 (1969); **No. 52**, 5423 (1968).

[11] G. Smith and B. Kosters, *Chem. Ber.*, **93**, 2403 (1960).

the reaction mixtures to stand for 24–48 hr longer than indicated, the yields could be increased over those reported. The boiling points, yields, and uv maxima (in isopropyl alcohol solution) are as follows: **1a** (ortho) {bp 99–100° (0.5 Torr) [lit.[11] 106–107° (1.6 Torr)]; 82%; 270 mμ (ϵ 6.63 × 10^3), 276 (ϵ 5.85 × 10^3)}; **1b** (meta) {bp 171–172° (39 Torr) [lit.[11] 111–113° (2.5 Torr)]; 79%; 270 mμ (ϵ 2.06 × 10^3), 276 (2.02 × 10^3)}; **1c** (para) {bp 84° (0.01 Torr) [lit.[11] 111–113° (2.2 Torr)]; 69%; 276 mμ (ϵ 2.26 × 10^3), 282 (ϵ 1.89 × 10^3)}.

The photolyses of the methoxyphenyl ethyl carbonates were carried out as follows. The carbonate (5 ml, 5.3 g, 0.027 mol) was dissolved in 250 ml of Spectrograde isopropyl alcohol and the solution was placed in a standard immersion-well-type photochemical apparatus. The solution was stirred with a magnetic stirrer and purged with nitrogen for 15 min. The solution was then irradiated with a 450-W Hanovia[12] medium-pressure mercury lamp through a Corex filter sleeve. The photolyses were carried out under a positive nitrogen pressure for the following lengths of time: **1a**, 24 hr; **1b**, 45 hr; **1c**, 15.5 hr. The composition of the reaction mixtures can be found in Tables I–III.

A control reaction was carried out for each of the methoxyphenyl ethyl carbonates, and gc analysis showed that no dark reaction had occurred. The photolyses were monitored by gc and were stopped when it appeared that no new products were being formed. During the course of the reactions there was a smooth conversion of starting material to products. The product peaks increased in size throughout the photolysis period and did not plateau or diminish in size. This observation strongly suggests that the observed products were not labile under the conditions of the reaction. At the conclusion of the photolysis, the solvent was evaporated under reduced pressure and the remaining solution was analyzed by gc and gc–mass chromatography and were analyzed further by nuclear magnetic resonance and by infrared spectroscopy.

Product Identification.—The pinacol and the phenols that were formed in the reactions were identified by their retention times.

Ethyl Salicylate.—The retention time, infrared spectrum, and mass spectrum were identical with those obtained from an authentic sample.

Ethyl 2-Hydroxy-3-methoxybenzoate (2).—The nmr spectrum, the ir spectrum, and the mass spectrum obtained from a sample collected from the gc support this identification. The ir spectrum (liquid film) shows absorption at 3100 (O–H stretch) and 1660 cm^{-1} (C=O stretch), both of which are common for intramolecularly-hydrogen-bonding compounds.[13] The nmr spectrum shows the following signals: τ −0.8 (s, 1 H), 2.6–3.4 (m, 3 H), 5.6 (q, 2 H), 6.3 (s, 3 H), and 8.6 (t, 3 H). The intramolecular nature of the hydrogen bonding is also revealed by the position of the singlet (1 H) at τ −0.8. Dyer[14] states that, at ordinary concentrations, phenols absorb in the region of τ 2.3 to 4.0. *o*-Hydroxybenzoates, however, show very strong intramolecular hydrogen bonding and absorb in the region of τ −2.5 to −0.5. For example, methyl salicylate absorbs at τ −0.58. The value of τ −0.8 measured for **2** clearly establishes the relative positions of the hydroxyl and benzoate groups. The position of the methoxyl group relative to the hydroxyl group is fixed in the starting compound.

Expansion of the aromatic region of the nmr spectrum of **2** shows that there are two sets of doublets at 2113 and 2105 Hz and 2088 and 2808 Hz. A triplet appears at 2074, 2066, and 2058 Hz. When the absorption system was spin-decoupled by irradiating the 2066-Hz signal of the triplet, both of the doublets collapsed into singlets. These results are in accordance with the behavior expected for three aromatic protons on adjacent carbons, thus confirming the 1,2,3 substitution pattern on the aromatic ring.

The mass spectrum is as follows and confirms the structural assignment (*m/e*, % of base peak): 197, 4.1; 196, 28.5; 151, 26.0; 150, 61.0; and 122, 100. It is possible to use ms to distinguish between salicylates and *p*-hydroxybenzoates because the major mode of fragmentation for salicylates is the loss of alcohol from the molecular ion, while the major mode of fragmentation for *p*-hydroxybenzoates is the loss of the alkoxy group.[15] In the mass spectrum of **2** there is a major peak at *m/e* 150 (M − C_2H_5OH), while the peak at *m/e* 151 is relatively small.

Ethyl 3-Methoxy-4-hydroxybenzoate (Ethyl Vanillate) (3).—The nmr spectrum and the ir spectrum of this compound, as isolated by preparative gc from the reaction mixture, were identical with those obtained from an authentic sample.

Ethyl 2-Hydroxy-4-methoxybenzoate (5).—A sample was isolated from the reaction mixture and the nmr and mass spectral data obtained are nmr τ −0.8, (s, 1 H), 2.4 (d, 1 H), 3.7 (m, 2 H), 5.6 (q, 2 H), 6.2 (s, 3 H), and 8.6 (t, 3 H); mass spectrum *m/e* (% of base peak) 197 (4.1), 196 (27.5), 151 (36.0), 150 (100), and 122 (35).

Ethyl 2-Methoxy-6-hydroxybenoate (4).—The identification was made on the basis of the mass spectrum obtained by gc–ms, which is mass spectrum *m/e* (% of base peak) 197 (3.2,) 196 (23.5), 151 (27.0), 150 (100), and 122 (26.0).

Ethyl 2-Methoxy-4-hydroxybenzoate (7).—A sample was obtained by preparative gc and the identification was made on the basis of the following nmr and mass spectral data: nmr τ 2.27, (s, 1 H), 2.7–3.5 (m, 3 H), 5.65 (q, 2 H), 6.2 (3 H), and 8.6 (t, 3 H); mass spectrum *m/e* (% of the base peak) 197 (4.5), 196 (25.0), 151 (100), 150 (13.0), and 122 (7.0).

Ethyl 2-Hydroxy-5-methoxybenzoate.—A sample was isolated by preparative gc and the identification was made on the basis of the following spectral information: nmr τ −0.2, (s, 1 H), 3.0 (m, 3 H), 5.6 (q, 2 H), 6.2 (s, 3 H), and 8.6 (t, 3 H); ir (liquid film) 3110 and 1669 cm^{-1}; mass spectrum *m/e* (% of base peak) 197 (2.1), 196 (20.0), 151 (20.0), 150 (100), and 122 (17.0). The nmr spectrum shows a τ −0.2 singlet (1 H) and the ir has bonds at 3110 (O–H) and 1669 cm^{-1} (C=O). These are all indicative of strong intramolecular hydrogen bonding as found in *o*-hydroxybenzoates. The mass spectrum has a *m/e* 176 molecular ion and a base peak at *m/e* 150 (M − C_2H_5OH); the latter peak is indicative of a salicylate.

Ethyl *p*-Hydroxybenzoate.—The identification was made on the basis of the identity of the mass spectrum of an authentic sample with that obtained from the gc peak using gc–ms.

Ethyl *m*-Hydroxybenzoate.—The identification was made on the basis of the relative retention time of this material compared to that of ethyl salicylate and ethyl *p*-hydroxybenzoate, and on the mass spectrum obtained by gc–ms. The material showed a molecular ion at *m/e* 166 and has a fragmentation pattern similar to but not identical with ethyl salicylate and ethyl *p*-hydroxybenzoate.

Quantum Yields.—The quantum yields[16] for the conversion of the methoxyphenyl ethyl carbonates to products are as follows: **1a**, 0.21; **1b**, 0.02; **1c**, 0.20. The actinometer used was the benzophenone–benzohydrol type described by Beckett and Porter.[17] The apparatus used to determine the quantum yields was a Rayonet photochemical reactor equipped with a Merry-go-round (The Southern New England Ultraviolet Co., Middletown, Conn.).

Registry No.—**1a**, 1847-84-3; **1b**, 35030-97-8; **1c**, 22719-84-2; **2**, 35030-98-9; **4**, 35030-99-0; **5**, 35031-00-6; **6**, 35031-01-7; **7**, 22775-40-2.

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[12] Engelhard-Hanovia, Inc., Newark, N. J.

[13] L. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1959, pp 103 and 184.

[14] J. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Englewood Cliffs, N. J., 1965, p 90.

[15] H. Budzikiewicz, C. Djerassi, and D. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, pp 200–201.

[16] The determinations were made by Patricia Ann Tatem as part of her M.S. thesis at The George Washington University.

[17] A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963).