Photorearrangement of *o*-Phenoxybenzoic Acid to Phenyl Salicylate and Related Reactions

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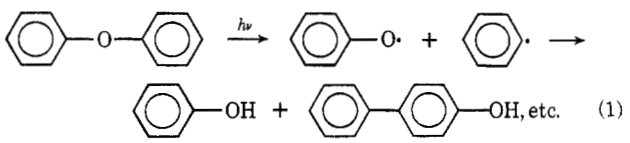
Irradiation of *o*-phenoxybenzoic acid and its derivatives with ultraviolet light yields phenyl salicylate in moderate to high yield. The reaction involves the migration of the phenyl group from the phenoxy oxygen to the acyl oxygen.

Kharasch, Stampa, and Nudenberg reported that diphenyl ether under the influence of ultraviolet light underwent cleavage and rearrangement to give phenol and hydroxybiphenyl in low efficiency and poor yields.[2] The photochemistry of diaryl ethers had been subsequently investigated in some detail, and it was suggested that the reaction proceeded *via* radical intermediates (reaction 1).[3,4] In connection with our study



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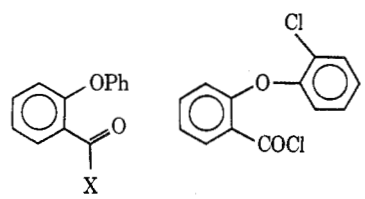
on the intramolecular photoacylation,[5] we investigated the photochemistry of *o*-phenoxybenzoic acid (**1a**, X = OH) and its derivatives. It was found that *o*-phenoxybenzoic acid undergoes a novel photorearrangement to give phenyl salicylate in excellent yield (>80%). The study was extended to the corresponding acid chloride (**1b**, X = Cl), the methyl ester (**1c**, X = OCH_3), and an *o*-chloro substituted chloride (**2**). The results obtained were compared with that obtained from the irradiation of methyl *p*-phenoxybenzoate (**3**).



1a, X = OH
b, X = Cl
c, X = OCH_3

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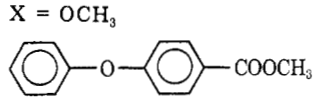

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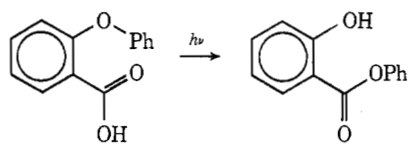
Results and Discussion

When a solution of *o*-phenoxybenzoic acid (**1a**) in benzene was irradiated through a Corex D filter (λ >280 nm), phenyl salicylate was the only product isolated (80%) together with a small amount of high molecular weight material in the acid fraction (reaction 2). However, the conversion was low (33%),



(2)

which may be attributed to the high absorbance of the product in the spectral excitation region [λ_{max} (MeOH) 308 nm (ε 4970)][6] as compared to the starting material [λ_{max} EtOH) 260 nm (ε 4500)].[7]

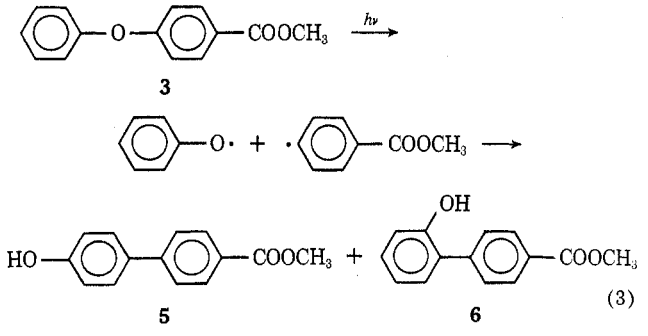
The quantum yield of this photorearrangement was determined to be 0.0014 ± 0.0002 at 313 nm with the aid of a 2-hexanone secondary actinometer.[8] Since **1a** does not exhibit appreciable emission (ϕ <0.001), there are very effective nonradiative decay processes involving the excited states of **1a**. In view of this low quantum efficiency, detailed mechanistic investigation on this process will be difficult and only qualitative measurements were made. We found that the rearrangement was retarded by *cis*-1,3-pentadiene and **1a** sensitized the geometrical isomerization of the diene, indicating that the triplet state of **1a** may participate in the photorearrangement.

Since it is well known that the esters and acyl chloride absorb at longer wavelengths than the corresponding benzoic acid,[9] the photochemistry of *o*-phenoxybenzoyl chloride (**1b**) and methyl *o*-phenoxybenzoate (**1c**) was investigated. When **1b** was prepared from **1a** and thionyl chloride, it was contaminated with small but variable amounts of xanthone and unreacted **1a**. Irradiation of the acid chloride **1b** thus prepared in benzene did lead to a higher conversion of the starting material, and phenyl salicylate was again isolated as the major product. However, the irradiation of the methyl ester **1c** yielded methyl salicylate and phenol as the major products together with a small amount of dibenzpyrone (**4**). In order to determine whether there is any solvent participation (benzene) during the irradiations or any positional rearrangement in the migrating phenyl group, the photochemistry of *o*-(*o*-chlorophenoxy)benzoyl chloride (**2**) was studied. We found that *o*-chlorophenyl salicylate was a major product, indicating that there was no solvent participation nor positional rearrangement in the migrating group during the reaction.

The photochemistry of methyl *p*-phenoxybenzoate (**3**) was then investigated in order to determine whether the photorearrangement was positional specific to the ortho-isomers. We found that the irradiation of **3** in benzene yielded methyl 4′-hydroxybiphenyl-4-carboxylate (**5**) and methyl 2′-hydroxybiphenyl-4-carboxylate

(1) National Institutes of Health Postdoctoral Fellow, 1969–1970.
(2) M. S. Kharasch, G. Stampa, and W. Nudenberg, *Science*, **116**, 309 (1952).
(3) H. J. Hageman, H. L. Louwerse, and W. J. Mijs, *Tetrahedron*, **26**, 2045 (1970).
(4) Y. Ogata, K. Takagi, and I. Ishino, *ibid.*, **26**, 2703 (1970).
(5) N. C. Yang, L. C. Lin, A. Shani, and S. S. Yang, *J. Org. Chem.*, **34**, 1845 (1969).
(6) The Sadtler Standard Ultraviolet Spectra, No. 841.
(7) O. H. Wheeler, *Can. J. Chem.*, **39**, 2603 (1961).
(8) D. R. Coulson and N. C. Yang, *J. Amer. Chem. Soc.*, **88**, 4511 (1966).
(9) The Sadtler Standard Ultraviolet Spectra, No. 252, 2, and 319.

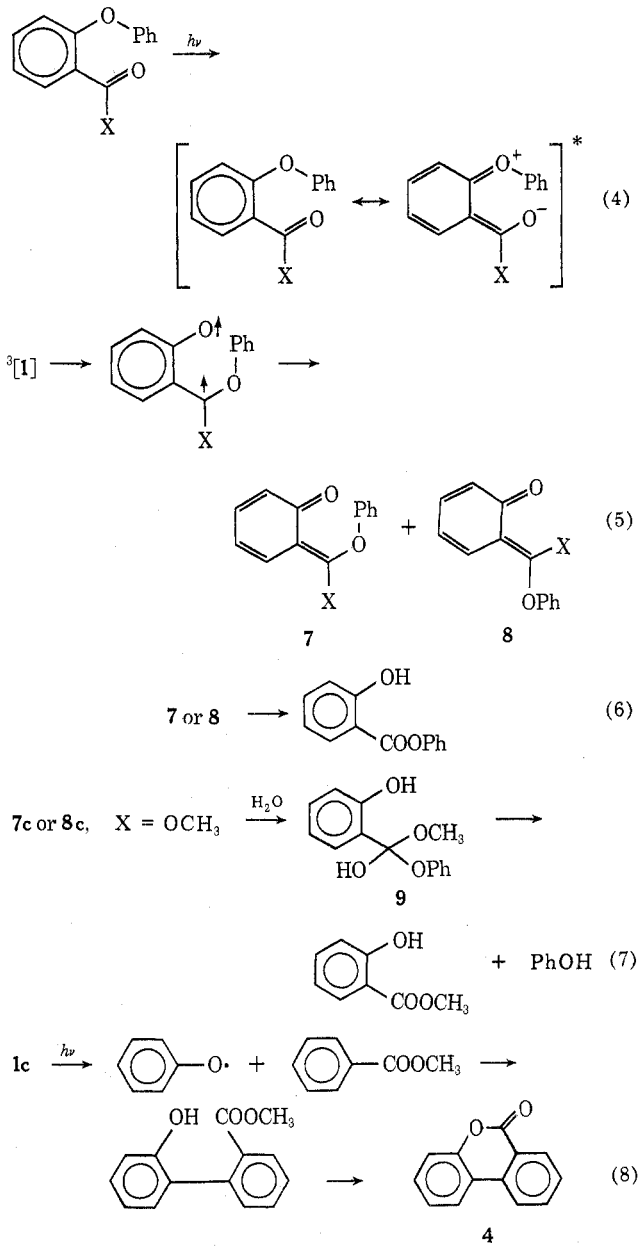
(6) among the isolated products. The photochemistry of **3** resembles that of diphenyl ether. The reaction may be rationalized to proceed *via* the cleavage of **3** to give a phenoxy radical and a substituted phenyl radical followed by the recombination of these radicals to give the products in addition to unidentified polymeric material (reaction 3). Qualitative investigation



(3)

on the effect of *cis*-1,3-pentadiene on this reaction indicated that **3** sensitized the geometrical isomerization of the diene and the diene retarded the formation of products.

The photochemistry of *o*-phenoxybenzoic acid derivatives differs from that of diphenyl ether. The derivatives rearrange or cleave in high yields to give derivatives of salicylic acid. The results imply that the *o*-acyl group may have participated in the reaction. *o*-Phenoxybenzoic acid derivatives contain an electron-donating group and an electron-withdrawing group ortho to each other. Their excited states may exhibit substantial charge transfer character which may be indicated by reaction 4.[10,11] Therefore, the migration of a phenyl group in these compounds to the acyl group is facilitated in the excited state, which may lead to an *o*-quinonemethide intermediate. If the migration takes place from the triplet state of **1**, the triplet of the *o*-quinonemethide intermediate formed may relax to either isomeric forms **7** or **8** (reaction 5). The migration of a phenyl group to an acyl oxygen had been noted previously in photochemistry,[12-14] and such a migration would not be possible in the para isomer. It is interesting to note that no xanthone was formed from **1b** under the influence of light, although its formation is rapid under the influence of heat. Since the charge transfer at excited states occurs between the functional groups, there is little delocalization into the phenoxy phenyl group and the cyclization of **1b** to xanthone is not favored at the excited state. The intermediate **7** or **8** may then be readily converted to phenyl salicylate (reaction 6). Since phenyl esters are known to be more readily hydrolyzable than methyl esters, the selective cleavage of the intermediate **9** to give methyl salicylate is expected (reaction 7).[15] The formation of dibenzpyrone (**4**) as a minor product from the irradiation of **1c** may be visualized to proceed in the manner of a conventional diaryl ether photorearrangement (reaction 1) to give methyl 2′-hydroxybiphenyl-2-carboxylate (**8**) which subsequently cyclizes to give the minor product (reaction 8).



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Although several attempts were made to trap the postulated quinonemethide intermediate (**7c** and/or **8c**) derived from methyl *o*-phenoxybenzoate (**1c**) with various olefins *in situ*, they were not successful. Olefins used included dimethyl acetylenedicarboxylate, maleic anhydride, *N*-phenylmaleimide, styrene, *cis*-1,3-pentadiene, and 1,1-diethoxyethylene. Moisture was rigorously excluded from these reactions. In the cases of maleic anhydride and *N*-phenylmaleimide, sensitized dimerization of these compounds was observed. It is probable that the quinonemethide intermediate, which contains an aryloxy and other functional groups at the methide carbon, is highly reactive toward nucleophilic agents and is rapidly consumed before they may react with olefins.

When the irradiation of *o*-phenoxybenzoyl chloride (**1b**) was carried out in the presence of an equimolar amount of *o*-phenoxybenzoic acid (**1a**), a second photoproduct, phenyl *o*-phenoxybenzoylsalicylate (**9**), was

(10) P. E. Stevenson, *J. Mol. Spectrosc.*, **15**, 220 (1965).
(11) A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Pergamon Press, New York, N. Y., 1964, p 115.
(12) H. E. Zimmermann, H. G. Dürr, R. S. Givens, and R. G. Lewis, *J. Amer. Chem. Soc.*, **89**, 1863 (1967); H. E. Zimmermann, H. G. Dürr, R. G. Lewis, and S. Bram, *ibid.*, **84**, 4149 (1962).
(13) G. W. Griffin and E. J. O'Connell, *ibid.*, **84**, 4148 (1962).
(14) H. Schmid, M. Hochweber, and H. von Halben, *Helv. Chim. Acta*, **30**, 1135 (1947).
(15) J. F. Kirsch and W. P. Jencks, *J. Amer. Chem. Soc.*, **86**, 837 (1964).

formed in addition to phenyl salicylate. A similar product was formed from the *o*-(*o*-chlorophenoxy)-benzoyl chloride and *o*-chlorophenoxybenzoic acid. Although **10** may be prepared by the acylation of phenyl salicylate and *o*-phenoxybenzoyl chloride in the presence of pyridine, no acylation takes place in the absence of light or pyridine. Nor is the product formed from phenyl salicylate and **1a** under the influence of light. Therefore, the product must be formed from some reactive intermediate generated from **1a** and **1b** in the presence of light.

Finally, irradiation of *o*-anisyl chloride yields no detectable change in this compound, indicating that the alkyl group does not rearrange under similar conditions.

Experimental Section

General Procedure.—The light source used was a Hanovia 450-W medium pressure mercury arc. Irradiations were carried out in an apparatus consisting of a quartz water-cooled Hanovia 5-l. flask immersion well and a Pyrex outer jacket fitted with a fritted nitrogen inlet at the bottom and septum covered inlet in the midsection for withdrawing aliquots during irradiation. Different jackets varying in capacity from 100 to 250 ml were used. The solution level was always kept above the top of the mercury arc to prevent pyrolysis. The solution was deaerated with nitrogen for 0.5 hr prior to and during the irradiation. Melting points and boiling points were uncorrected. Mass spectra were recorded with an AEI MS-9 high-resolution mass spectrometer, uv spectra with a Cary 14 spectrometer, and ir spectra with a Perkin-Elmer Infracord or a Beckman IR-7 spectrometer. Nmr spectra were obtained on a Varian A-60 or A-60A spectrometer in CCl_4 or $CDCl_3$ with TMS as an internal standard. Microanalyses were carried out by Micro-Tech, Inc., Skokie, Ill., or by Dr. A. Bernhardt, Mulheim, Germany.

***o*-Phenoxybenzoic Acid (1a).**—*o*-Phenoxybenzoic acid was prepared by a modification of the Ullmann method.[16] To a methanolic solution of sodium phenoxide, prepared by dissolving phenol (48 g) in a solution of sodium methanolate–methanol (3.6 g of sodium in 78 ml of methanol) which was concentrated under diminished pressure to a paste, the potassium salt of *o*-chlorobenzoic acid (20 g) and copper powder (0.6 g) were mixed thoroughly by shaking. The mixture was then heated on an oil bath at 180–190° for 10 min. After cooling, the reaction mixture was diluted with water (50 ml) and neutralized with 10% hydrochloric acid and then extracted with ether (50 ml × 4). The combined ethereal extract was then washed with 5% aqueous sodium bicarbonate solution (50 ml × 4). Upon acidification of the bicarbonate extract the crude acid was obtained (91% yield) and recrystallized twice (aqueous MeOH) to give 18 g of the pure acid (73%, mp 113°): ir (KBr) 3075–2880, 1685, 1240, and 1070 cm^{-1}; nmr (Me_2CO) δ 6.95–7.85 (m, 8, general aromatic H's), 8.09 (2 d, 1, J = 7.5 and 2.0 Hz, aromatic H ortho to COOH), 9.45 ppm (s, 1, COOH).

Irradiation of 1a.—A solution of *o*-phenoxybenzoic acid (1.50 g) in benzene (80 ml) was irradiated with the Hanovia 450-W arc with a Corex D filter for 16 hr. The reaction was monitored by tlc every 4 hr. The formation of phenyl salicylate was essentially constant after 12 hr. The solution was extracted with 2 × 50 ml of 5% aqueous $NaHCO_3$, washed with water, and dried. After the removal of benzene under reduced pressure a yellow oil (500 mg) was obtained which solidified upon standing and exhibited an ir spectrum virtually identical with that of phenyl salicylate.[17] Tlc analysis indicated that the compound was about 95% pure. The crude product was subjected to a short-path distillation to give phenyl salicylate (450 mg, mp 40–42°) identical in all respects with an authentic sample. Crude *o*-phenoxybenzoic acid (1.0 g) was recovered from the bicarbonate extract after acidification. The crude acid was purified by filtering a CH_2Cl_2–$CHCl_3$ solution through silica gel (40 g). From the effluent 935 mg of the acid was obtained, mp 109–111°. The yield of phenyl salicylate based on the acid reacted was over 80%.

(16) F. Ullmann and M. Zlokasoff, *Ber.*, **38**, 2112 (1905).

(17) Sadtler Standard Infrared Spectra, No. 2931.

Irradiation of *o*-Phenoxybenzoyl Chloride (1b).—*o*-Phenoxybenzoyl chloride was prepared by a modification of the known method.[18] *o*-Phenoxybenzoic acid (1.08 g) was treated with freshly distilled thionyl chloride (3.0 g) and heated at 58–60° for 10 min on a water bath. The excess thionyl chloride was removed under reduced pressure at 40–50°. The reaction mixture was diluted with benzene (1 ml), warmed at 50° for 2 min, and concentrated under reduced pressure at 50° to constant weight. The same process was repeated three times to remove any thionyl chloride left in the reaction mixture. The acid chloride thus prepared was dissolved in freshly distilled benzene (85 ml), and the solution was flushed with pure nitrogen for 30 min prior to the irradiation. The purity of the acid chloride was estimated by tlc of the corresponding ethyl ester. An aliquot of the acid chloride solution in benzene (1 ml) was taken and added to absolute alcohol (0.5 ml). The reaction mixture was heated at 60° for 10 min, spotted on a Kodak fluorescent silica gel strip, and developed with benzene. In comparison to authentic samples of ethyl *o*-phenoxybenzoate, xanthone, and *o*-phenoxybenzoic acid (the R_f values were 0.40, 0.23, and 0.04, respectively), the acid chloride was shown to be about 90% pure, contaminated with 5% of xanthone and 3% of the unreacted *o*-phenoxybenzoic acid.[19]

The benzene solution of the acid chloride was then irradiated with a 450-W medium-pressure mercury lamp with a Pyrex filter. Aliquots of the irradiated solution were taken from time to time, treated with absolute ethanol, and checked with tlc for new spots with a uv lamp. At the second hour, a new spot having a R_f value of 0.53 appeared. The intensity of the new spot increased while that of the ethyl *o*-phenoxybenzoate spot decreased on further irradiation. The intensity of xanthone remained essentially unchanged during the whole process of irradiation. The irradiation was stopped after 17 hr, because at this stage the intensity of the new spot was the most predominant one and the original ethyl ester spot had almost completely disappeared.

The irradiated solution was concentrated under reduced pressure at 40°, and treated with water (0.5 g) at 40–50° for 5 hr. Benzene was added to the mixture, which was then dried over sodium sulfate. The dried mixture was concentrated under reduced pressure to yield a liquid (0.95 g). A portion of *o*-phenoxybenzoic acid (160 mg) was recovered by sodium bicarbonate extraction. The liquid was chromatographed on a silica gel column (7 g) eluting first with carbon tetrachloride and then with benzene. Molecular distillation of the material isolated from the CCl_4 eluate gave phenyl salicylate (0.45 g, 57% based on acid chloride reacted), mp 40–42°, identical in all respects with an authentic sample. Xanthone (0.10 g) was isolated in 12% yield.

Methyl *o*-Phenoxybenzoate (1c).—Methyl *o*-phenoxybenzoate was prepared according to the method of Tomita and Ikawa:[20] bp 91–93° (0.04 mm); λ_{max} (EtOH) 286 nm (ϵ 3900) and 272 (shoulder, 2970); ir (neat) 1720 (C=O), 1240, and 1080 cm^{-1} (ArO); nmr (CCl_4) δ 3.68 (s, 3, CH_3), 6.80–7.60 (m, 8, ArH) and 7.81 ppm (2 d, 1, J = 7.5 and 2.0 Hz, ArH ortho to COOMe).

Irradiation of 1c.—A 2.307-g sample of the ester was dissolved in 250 ml of benzene, and the solution was irradiated through a Corex D insert for 18 hr. After the irradiation the solvent was removed under reduced pressure and the residue was divided into two equal fractions. One fraction was separated by preparative layer chromatography (plc) using a 20 × 100 cm plate of silica gel of *ca.* 2-mm thickness. The plate was developed five times using benzene–petroleum ether (bp 30–60°) (1:1) as the eluent. Five major zones were observed and they are listed in the order of increasing polarity. Zone 1 was identified as methyl salicylate by comparison with an authentic sample, 142 mg (59% based on reacted **1c**); zone 2 was identified as unreacted **1c**, 0.746 g (65%); zone 3 was identified as phenol, its yield could not be estimated owing to its volatility; zone 4 was identified as dibenzopyrone by comparison with an authentic sample,[21] mp 92–93°, 57 mg (15%); zone 5 was polymeric material, 160 mg.

(18) G. Lock and F. H. Kempter, *Monatsh.*, **67**, 25 (1936).

(19) The method of analysis cannot differentiate the possibilities between a mixture of acid chloride and free acid and a mixture of acid chloride and acid anhydride; the acid chloride may be about 89% pure, contaminated with 5% of xanthone and 6% of the anhydride.

(20) M. Tomita and K. Ikawa, *J. Pharm. Soc. Jap.*, **74**, 1060 (1954).

(21) N. C. Yang, A. Shani, and G. R. Lenz, *J. Amer. Chem. Soc.*, **88**, 5369 (1966).

The yield of phenol was estimated by vpc using a SF-96 column at 220° to be 89 mg (56%).

Irradiation of Methyl *p*-Phenoxybenzoate (3).—Methyl *p*-phenoxybenzoate (2.158 g, mp 58–60°)[22] was dissolved in 250 ml of benzene and the solution was irradiated through a Corex D filter for 20 hr. After the irradiation the solution was evaporated and triturated with ether. An amorphous tan solid (172 mg) was removed by filtration and was found to be a polymeric material and was not further characterized. The filtrate was evaporated and the residue was separated by plc using two 20 × 100 cm plates of silica gel of *ca.* 2-mm thickness. The plates were developed five times using CH_2Cl_2–benzene (2:1) as the eluent. Three minor components (<50 mg) were not characterized further. Four major fractions were isolated and they are listed according to the order of increasing polarity. Fraction 1 was identified as the starting material, 1.248 g. Fraction 2 was identified as methyl 2′-hydroxy-4-biphenylcarboxylate: 193 mg; mp 127–129° which was raised to 129–131° after one recrystallization from cyclohexane (lit.[23] mp 133–133.5°); λ_{max} 270 nm (log ϵ 4.17) and 302 (4.04); nmr ($CDCl_3$) δ 3.93 (s, 3, CH_3), 5.70 (s, broad, 1, OH), 6.80–7.45 (m, 4, ArH), and 7.85 ppm (A_2B_2 q, 4, ArH, J = 31 and 8.5 Hz); mass spectrum parent peak at m/e 228. Fraction 3 was identified as methyl 4′-hydroxy-4-biphenylcarboxylate: 143 mg; mp 221–223° which was raised to 224–225° after one recrystallization from benzene (lit.[24] mp 224–225°); λ_{max} 298 nm (log ϵ 4.35); nmr ($CDCl_3$–CF_3COOH) δ 4.02 (s, 3, CH_3), 7.15 (A_2B_2 q, 4, ArH, J = 25 and 9 Hz), and 7.88 ppm (A_2B_2 q, 4, ArH, J = 29 and 8 Hz); mass spectrum parent peak at m/e 228. Fraction 4 appeared to be the same polymeric material removed by ether trituration, 165 mg.

o-(o′-Chlorophenoxy)benzoic Acid.—o-(o′-Chlorophenoxy)benzoic acid was prepared by a modification of the Goldberg method.[25] In a 500-ml round-bottomed flask equipped with a mechanical stirrer, a mixture of *o*-chlorobenzoic acid (31.3 g), *o*-chlorophenol (28 g), K_2CO_3 (35 g), and cuprous chloride (0.2 g) was stirred with nitrobenzene (200 ml) at 160–165° for 13 hr. Having been cooled to 5°, the reaction mixture was filtered to collect the solid. The filtrate was washed with water (5 × 30 ml) and the nitrobenzene layer was discarded. The combined aqueous solution was used to dissolve the collected solid. After the removal of insoluble impurities by filtration, the filtrate was neutralized gradually with 10% HCl. At the beginning, a tar was precipitated. As the acidification continued, the precipitate deposited gradually changed from dark brown to light brown in color. At pH 5, the solution was filtered to remove the mixture of tar and precipitate. Upon further acidification of the filtrate, a white solid was collected. The solid was purified by dissolving it in 5% $NaHCO_3$ (250 ml) and washed with ether (3 × 100 ml). After aeration, the aqueous solution was neutralized with 10% HCl. The crude acid (15 g, 30%, mp 100–110°) was collected and recrystallized three times from 79% ethanol to yield 3.5 g of the product: mp 124–125°; ir (KBr) 3075–2850, 1685, 1240, and 1060 cm^{-1}; nmr (acetone) δ 6.86–7.81 (m, 7, ArH), 8.10 (2, d, 1, ArH ortho to COOH, J = 7.5 and 2 Hz), and 8.93 ppm (s, 1, COOH).

Irradiation of o-(o′-Chlorophenoxy)benzoyl Chloride.—o-(o′-Chlorophenoxy)benzoyl chloride was prepared from the acid (1.70 g) with thionyl chloride in the same way as described in the preparation of **1b**. The acid chloride prepared was analyzed by tlc to show that it contained 67% of the chloride, 31% of the acid, and only a trace of the xanthone (less than 1%).

The acid chloride thus prepared was dissolved in benzene (85 ml) and irradiated. The irradiation was continued for 20 hr, and the reaction was monitored by tlc. The mixture was worked up as in the case of *o*-phenoxybenzoyl chloride to yield a liquid crude product (1.50 g). The crude product was chromatographed on a silica gel column (20 g).

A new product was isolated from the carbon tetrachloride eluate: mp 46.5–48.5° (ethanol); R_f (silica gel–benzene) 0.53; ir (film) 3190 and 1685 cm^{-1}; nmr (CCl_4) δ 6.65–7.75 (m, 7, ArH), 8.11 (2 d, 1, J = 7.5 and 2.0 Hz, ArH ortho to COOPh), 10.32 ppm (s, 1, intramolecular H-bonded ArOH); identical with an authentic sample of *o*-chlorophenyl salicylate.[26]

The second photoproduct (0.69 g), R_f (silica gel–benzene) 0.43, was contaminated with a small amount of the xanthone. Attempted molecular distillation resulted in the sublimation of the xanthone at 140° (0.05 mm). The residue was purified through another silica gel column and a very viscous mass was thus obtained. It exhibited ir (film) 1750 cm^{-1}; nmr (CCl_4) 6.7–7.8 (m, 14, ArH), 8.16 (2 d, 1, J = 7.5 and 2.0 Hz), and 8.26 ppm (2 d, 1, J = 7.5 and 2.0 Hz). The spectroscopic properties of this product suggested that it might be *o-chlorophenyl [o-(o′-chlorophenoxy)benzoyl]salicylate*. An authentic sample was prepared in the following manner. *o*-Chlorophenoxybenzoic acid (190 mg) was treated with freshly distilled thionyl chloride at 60° for 10–20 min. The excess thionyl chloride was removed under reduced pressure at 50°. The acid chloride thus prepared was treated with *o*-chlorophenyl salicylate (190 mg) and a drop of pyridine. The mixture was heated at 60° for 10 min, cooled to room temperature, and filtered. The filtrate was evaporated and chromatographed over a column of silica gel (5 g). A small amount of *o*-chlorophenyl salicylate was recovered from the CCl_4 effluent and the desired diester (140 mg) was obtained from the benzene effluent, identical in all respects with the photoproduct.

Anal. Calcd for $C_{26}H_{16}O_5Cl_2$: C, 65.16; H, 3.36; Cl, 14.80. Found: C, 65.77; H, 3.66; Cl, 14.85.

Unreacted *o*-chlorophenoxybenzoic acid (0.5 g) was also recovered from the chromatography of the irradiation mixture from the ethyl acetate eluate.

Irradiation of a Mixture of 1a and 1b.—*o*-Phenoxybenzoyl chloride (0.46 g) was prepared from the acid (0.45 g) as before which was analyzed by tlc to be about 85% pure and contaminated with xanthone (15%). *o*-Phenoxybenzoic acid (0.46 g) was added to the acid chloride and the mixture was dissolved in 85 ml of benzene and irradiated for 7 hr. After the usual work-up, the mixture (0.85 g) was chromatographed over silica gel (10 g). Phenyl salicylate (240 mg) and xanthone (80 mg) were isolated from the CCl_4 effluent. By further elution of the column with benzene, a second photoproduct (250 mg) was isolated. The product was subjected to molecular distillation to give a viscous mass: ir (film) 1745 cm^{-1}; nmr (acetone) δ 6.85–7.90 (m, 16, ArH) and 8.29 ppm (2 d, 2, J = 7.5 and 2.0 Hz, ArH ortho to C=O); mass spectrum parent ion m/e 410.

Anal. Calcd for $C_{26}H_{18}O_5$: C, 76.08; H, 4.42. Found: C, 75.79; H, 4.42.

Attempted synthesis of the diester from *o*-phenoxybenzoic acid (0.38 g), thionyl chloride (1.30 g), and phenyl salicylate (0.38 g) using the method described for the *o*-chloro derivative resulted in the formation of the diester in about 20% yield. The mixture exhibited four spots on silica gel tlc developed with benzene. R_f values were 0.53, 0.36, 0.23, and 0.04, corresponding to phenyl salicylate, the diester, xanthone, and *o*-phenoxybenzoic acid. The same four spots were detected from the irradiation mixture. Authentic phenyl *o*-(*o*-phenoxybenzoyl)-salicylate was isolated by silica gel chromatography and was identical in all respects with the photoproduct.

Irradiation of a Mixture of 1a and Phenyl Salicylate.—*o*-Phenoxybenzoic acid (106 mg, 0.5 mmol) and phenyl salicylate (106 mg, 0.5 mmol) and phenyl salicylate (106 mg, 0.5 mmol) were dissolved in benzene (80 ml) and irradiated for 3 hr. The reaction was monitored by tlc, and no new product was detected.

Irradiation of o-Anisyl Chloride.—*o*-Anisyl chloride was prepared from *o*-anisic acid by the method of Billon.[27] A solution of the chloride (1.54 g) in benzene (85 ml) was irradiated through a Corex D filter for 21 hr, and no visible change was detected spectroscopically.

Quantum Yield Determination and Other Mechanistic Studies.—The quantum yield of formation of phenyl salicylate during irradiation of *o*-phenoxybenzoic acid (0.010 M in benzene) at 313 nm was determined with the aid of the 2-hexanone secondary actinometer and an apparatus previously described.[8] The formation of phenyl salicylate was followed by vpc using a 5 × 0.25 in. column packed with 20% SF-96 on firebrick at 200°. The rate of formation was linear with the time and the quantum yield was found to be 0.0014 ± 0.002.

The possibility of formation of a photoadduct between methyl *o*-phenoxybenzoate with olefins was investigated. The olefinic systems used included dimethyl acetylenedicarboxylate in benzene up to 3 M, maleic anhydride in dioxane, *N*-phenylmaleimide

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in ether, *cis*-1,3-pentadiene in benzene, styrene in benzene, and 1,1-diethoxyethylene in ether. No adduct was detected in all these systems.

The quenchings of photorearrangements of *o*-phenoxybenzoic acid (**1a**) and methyl *p*-phenoxybenzoate (**13**) in benzene by *cis*-1,3-pentadiene were also investigated. Because of their low quantum efficiencies, only qualitative investigations were carried out. Parallel irradiations through a Corex D filter were performed with solutions containing 0.015 *M* of the substrate in benzene with or without 0.5 *M* of the diene. In the case of **1a**, we found that the formation of phenyl salicylate was reduced approximately 43% and about 20% of the diene had been isomerized to the trans isomer as indicated by vpc analysis. In the case of **3**, we found that the formation of products was reduced by approximately 85% but the consumption of the substrate was increased by about threefold as indicated by both tlc and vpc analyses. In the meantime, about 15% of the diene had isomerized.

Registry No.—**1a**, 2243-42-7; phenyl salicylate, 118-55-8; *o*-(*o'*-chlorophenoxy)benzoic acid, 36809-08-2; *o*-chlorophenyl [*o*-(*o'*-chlorophenoxy)benzoyl]salicylate, 36809-09-3; phenyl *o*-phenoxybenzoylsalicylate, 36809-10-6.

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Photochemical Reductions of Unsymmetrical Benzils[1]

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Eight 4-substituted benzils have been subjected to photoreduction by 2-propanol, where one of two carbonyl groups is selectively reduced; *i.e.*, on irradiation, the corresponding benzoins and/or benzilpinacols together with 4-substituted benzoic acid derivatives were obtained. The benzoyl group substituted by a more electron-withdrawing group is preferentially reduced in the order 4-CN > 4-Cl > H > 4-Me > 4-MeO ~ 4-NMe_2. The configuration of unsymmetrical benzils in the lowest excited triplet state was also discussed by comparing their absorption and emission spectra with their photochemical reactivities.

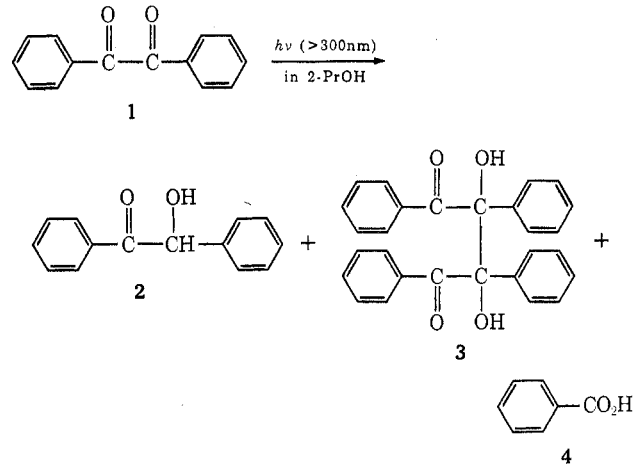
The photochemical reduction of α-dicarbonyl compounds has been an intriguing subject to a number of photochemists.[2] Some knowledge of the excited state is required to understand the photoreduction of α diketones. Reactivity might be influenced by their excited state geometries, which have been suggested to be coplanar based on absorption and emission spectra.[3] Although biacetyl is photoreduced to acetylpinacol,[4] aliphatic α diketones capable of intramolecular hydrogen abstraction through a six-membered transition state are transformed to 2-hydroxybutanones on irradiation.[5] An unsymmetrical α diketone, bornanedione, in which the carbonyl groups are essentially held in the s-cis configuration, equally yields two isomeric reduction products through a common transition state.[6]

An aromatic α diketone, benzil, is known to be twisted *ca.* 90° around its central bond at the ground state; the conjugation between two carbonyls is reduced by cross conjugation between a CO group and a phenyl group attached to the CO.[7] However, the phenyl–carbon interaction is again decreased with increasing steric hindrance at the ortho carbon of benzil. As reported by Bunbury,[8] the photoreduction of benzil by 2-propanol gives benzoin and benzilpinacol together with a small amount of decomposition products, *i.e.*, benzoic acid and benzaldehyde. Maruyama, *et al.*,[9] reported in their study on the photolyses of polymethylbenzils that ortho-substituted benzils are very photounreactive and afford low quantum yield for intersystem crossing.

The authors wish to report the photoreduction of unsymmetrical 4-substituted benzils and to correlate excited $n\pi^*$ triplet-state geometries with reductive behaviors and emission and absorption spectra.

Results and Discussion

Irradiation of benzil (**1**) in 2-propanol (~10^{-2} *M*) through a Pyrex filter under nitrogen for 12 hr results in the disappearance of benzil and the formation of a precipitate of benzilpinacol (**3**, 22.5%). The product was identified by melting point, molecular weight (420), and ir spectrum (COH). The mother liquior gave benzoin (**2**, 13.5%) and benzoic acid (**4**, 9.4%).



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