δ 1.97 (s, 6, CH_3CO—), 5.03 (s, 4, $ArCH_2O$—), and 7.25 ppm (m, 4, aromatic).

Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.9; H, 6.4. Found: C, 65.1; H, 6.5.

Oxidation of Mesitylene in Acetic Acid.—The procedure described under IV was followed using 60.0 g (0.50 mol) of mesitylene instead of *o*-xylene and half of the amounts of the other reactants. After the usual work-up, distillation gave 25.0 g (41.6% recovery) of mesitylene and 4.5 g (5.0% based on mesitylene charged) of 3,5-dimethylbenzyl acetate, bp 154° (35 mm) [lit.[20] bp 99–105° (4 mm)], identified by its ir spectrum. The pot residue (2.7 g) contained 20 unknown peaks by glpc.

V. Oxidation of Toluene in Propionic Acid.—A charge of 250.0 g (3.34 mol) of propionic acid, 36.8 g (0.46 mol) of lithium propionate, 36.8 g (0.40 mol) of toluene, 7.1 g (0.03 mol) of stannous acetate, and 17.2 g (0.008 mol) of 5% palladium on charcoal was stirred at 100° for 6 hr. The usual work-up gave (by glpc) [compound, wt (g), % yield] toluene, 4.8, 13.0; benzaldehyde, 0.1, 0.2; benzyl acetate, 0.3, 0.5; benzyl propionate, 13.7, 20.8; and benzylidene dipropionate, 0.8, 0.8.

Distillation gave 11.3 g (17.3%) of pure benzyl propionate, bp 87–88° (1 mm) [lit.[21] bp 222° (760 mm)], identified by its ir spectrum. The other products were identified by their glpc retention times.

VI. Oxidation of Hexamethylbenzene in Propionic Acid.—A charge of 592.0 g (8.00 mol) of propionic acid, 88.0 g (1.10 mol) of lithium propionate, 36.6 g (0.226 mol) of hexamethylbenzene, 28.4 g (0.12 mol) of stannous acetate, and 34.4 g (0.016 mol) of 5% palladium on charcoal was stirred at 145° for 4 days. After the usual work-up, 17.8 g (48.6% recovery) of hexamethylbenzene was obtained by sublimation. Distillation of the sublimation residue gave 14.1 g (26.5%) of 2,3,4,5,6-pentamethylbenzyl propionate, bp 170° (5 mm). The distillate solidified on standing and after crystallization from petroleum ether (bp 60–70°) had mp 78–79°; ir (KBr) 5.80 (ester C=O) and 8.40 μ (propionate); nmr ($CDCl_3$) δ 1.14 (t, 3, J = 7.5 Hz, $CH_3CH_2CO_2$—), 2.24 (m, 17, $CH_3CH_2CO_2$— and $ArCH_3$), and 5.29 ppm (s, 2, $ArCH_2O$—).

Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.9; H, 9.5. Found: C, 77.2; H, 9.8.

Registry No.—Toluene, 108-88-3; *p*-xylene, 106-42-3; *o*-xylene, 95-47-6; *m*-xylene, 108-38-3; mesitylene, 108-67-8; durene, 95-93-2; hexamethylbenzene, 87-85-4; ethylbenzene, 100-41-4; $Pd(OAc)_2$, 3375-31-3; $Sn(OAc)_2$, 638-39-1; $(C_6H_5)_3P$, 603-35-0; $(C_2H_5O)_3P$, 122-52-1; $C_6H_5CH_2OAc$, 140-11-4; *m*-xylylene diacetate, 17604-82-9; 2,3,4,5,6-pentamethylbenzyl propionate, 17604-83-0.

Acknowledgment.—We wish to thank Mr. John R. Morrison for his excellent technical assistance in the development of these procedures.

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[20] S. D. Ross, M. Finkelstein, and R. C. Peterson, *J. Amer. Chem. Soc.* **86**, 4139 (1964).

[21] I. M. Heilbron, Ed., "Dictionary of Organic Compounds," Vol. 5, Oxford University Press, New York, N. Y., 1965, p 2786.

The Photorearrangements of 2,4-Disubstituted Phenyl Esters[1–3]

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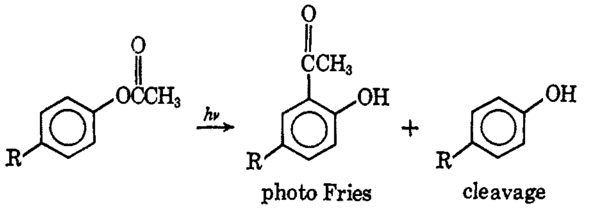
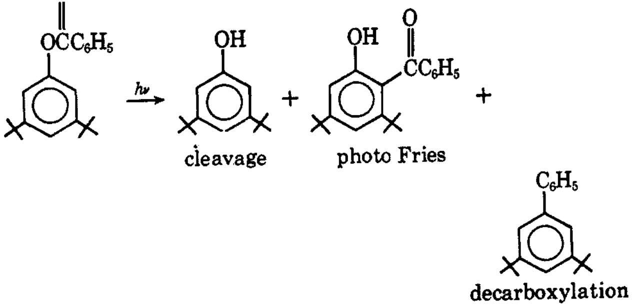
Various 2- and 2,4-disubstituted phenyl esters have been irradiated by ultraviolet light, and the products have been isolated and characterized. The relative large numbers of products obtained (up to six) showed that at least five different reactions were taking place: (1) photo Fries rearrangements resulting in *o*-hydroxyacetophenones, (2) photo Fries rearrangements in which methoxy groups were displaced resulting in *o*- and *p*-hydroxyacetophenones, (3) cleavage reactions resulting in phenols and in one case benzaldehyde, (4) decarboxylation reactions resulting in methylbenzene and biphenyl compounds, and (5) phototransposition of the ring carbon atoms resulting in rearranged methylbenzene and biphenyl compounds. Mechanisms for the various reactions are discussed.

The photochemical reactions of aryl esters have drawn considerable interest in recent years.[4–8] The photo Fries rearrangement of these esters to yield hydroxyaceto- and hydroxybenzophenone was first reported by Anderson and Reese[4] and Kobsa.[5] Along with the photo Fries, these workers also observed a considerable amount of cleavage products. More recently some attention has been given to the mechanisms of this reaction.[6,7]



With sterically hindered aryl esters, the normal photo Fries and cleavage reactions are accompanied by decarboxylation[8] and, in some cases, decarbonylation[8d] reactions. For example, the photolysis of 3,5-di-*t*-butylphenyl benzoate gave 3,5-di-*t*-butylbiphenyl



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[1] Supported by the Research Division, Brigham Young University, and the United Fund of Utah County.

[2] Nuclear magnetic resonance spectra were obtained on a Varian A-60A spectrometer purchased under the National Science Foundation Grant GP-6837.

[3] Presented in part by E. L. Loveridge at the student section of the Pacific Northwest Regional American Chemical Society Meeting, Richland, Wash., June 1967.

[4] (a) J. C. Anderson and C. B. Reese, *Proc. Chem. Soc.*, 217 (1960); (b) J. C. Anderson and D. B. Reese, *J. Chem. Soc.*, 1781 (1963).

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

[6] G. M. Coppinger and E. R. Bell, *J. Phys. Chem.*, **70**, 3479 (1966).

[7] M. R. Sandner and D. J. Trecker, *J. Amer. Chem. Soc.*, **89**, 5725 (1967).

[8] (a) R. A. Finnegan and A. W. Hagen, *Tetrahedron Lett.*, 365 (1963); (b) R. A. Finnegan and J. J. Mattice, *Tetrahedron*, **21**, 1015 (1965); (c) R. A. Finnegan and D. Knutson, *Chem. Ind.* (London), 1837 (1965); (d) R. A. Finnegan and D. Knutson, *J. Amer. Chem. Soc.*, **89**, 1970 (1967).

TABLE I

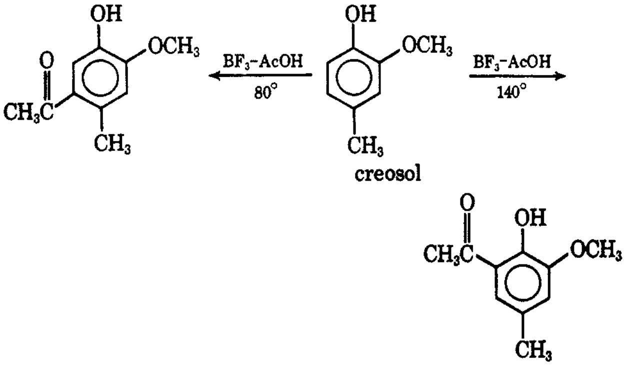
THE PHOTOREARRANGEMENTS OF VARIOUS SUBSTITUTED PHENYL ACETATES

Run	Substituent[a]	Solvent[b]	Time, hr	Recovered ester, %	Yields of products, %[c] II	III	IV	V	VI	VII
1	Ia	B	4	52	7	0	17	48	14	14
2[d]	Ib	B	4	2	10	0	8	55	13	8
3[e]	Ib	E	4	10	Trace[f]	0	20	61	11	4
4	Ic	B	4	3	15	4	19	56	6	0
5	Ic	E	8	0	Trace[f]	0	24	68	8	0
6[g]	Ic	H	4	90	16	5	18	55	6	0
7	Id	B	4	3	34	3[h]	8	54	0	0

[a] Two grams of substrate in 150 ml of solvent. [b] B = benzene; E = ethanol; H = hexane. [c] Products were analyzed and isolated by vpc and characterized by spectroscopy. [d] A 6% yield of another product was observed. This material could not be isolated since the peak was too close to Ib. [e] A 4% yield of another product was observed. This material could not be isolated since the peak was too close to Ib. [f] Vapor phase chromatogram shows a trace amount of material believed to be this product. [g] Same vpc as run 4. [h] Not isolated, but believed to be this product.

in addition to 3,5-di-*t*-butylphenol and 2-hydroxy-4,6-di-*t*-butylbenzophenone.[8c] It was this competition of reactions as well as the unusual thermal Fries rearrangements of the 2,3-disubstituted phenyl esters that prompted us to undertake this study.

The thermal Fries reaction of the 2,4-disubstituted phenyl esters has been reported to give rearrangements of both the *ortho* and the *meta* positions.[9,10] Indeed, the acylation of 2-methoxy-4-methylphenol (creosol) with carboxylic acids in the presence of boron trifluoride, which involves a Fries rearrangement,[11] gave both *ortho* and *meta* isomers.[10] At ordinary temperatures (80° and below) only the *meta* isomer was formed, while at elevated temperatures (140° and above) only the *ortho* isomer was obtained.[10] Presumably the intermediate creosyl acetate cleaves heterolytically at ordinary temperatures to give the acyl carbonium ion which substitutes to the most active *meta* position (*meta* to the original ester group, but *ortho,para* to methyl and methoxy groups). At elevated temperatures, a homolytic cleavage occurs yielding an acyl radical which adds to the *ortho* position.



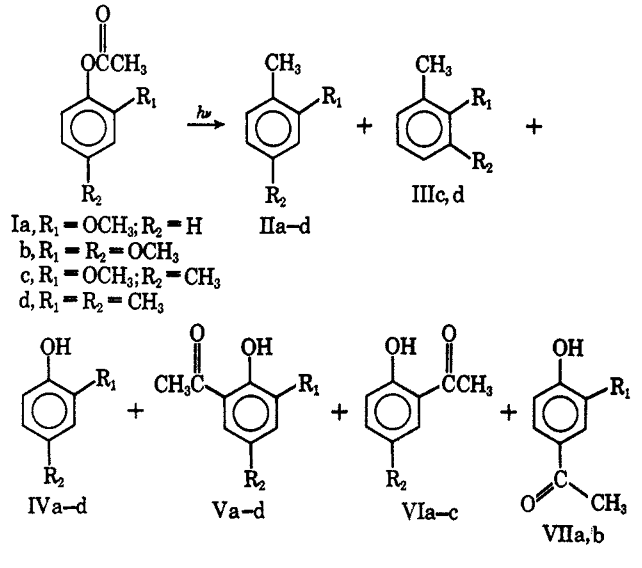
At the outset of this study, we expected to find only *ortho* rearrangement, cleavage, and decarboxylation-type reactions taking place. Not only products from these reactions were formed, but also products from the phototransposition of carbon atoms on the benzene ring[12] and *ortho* and *para* Fries rearrangements in which a methoxy group was displaced. At no time was a *meta*-rearranged product isolated.[13]

Results and Discussion

All the esters used in this study were purchased or prepared from the corresponding phenols. After the esters were dissolved in the appropriate solvent, the solutions were saturated with nitrogen and irradiated through quartz. The reaction products were analyzed and isolated by means of vapor phase chromatography (vpc). The products were characterized by infrared (ir) and nuclear magnetic resonance (nmr) spectroscopy and by elemental or mass spectrometric analysis (see Experimental Section).

In many cases the ir spectrum of the product compound was found to be the same as that found in the Sadtler series of spectra. In some of these cases, further analysis was not carried out. A general reaction scheme for the acetates can be written as shown in Scheme I. As shown in Table I, not all of these products are formed in every reaction. Products VI and VII were not formed in those cases where methyl groups occupied the *ortho* and/or *para* positions (runs 4-7). Also, little of product II and none of product III were observed when the substrates were irradiated in ethanol. No *meta*-rearranged product was isolated in any of these reactions even at low temperatures (−25 to 30°).[13]

SCHEME I



2-Methoxy-4-methylphenyl benzoate gave similar results (Scheme II, Table II).

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(9) A. Ballio and L. Almuante, *Ric. Sci.*, **21**, 85 (1951).

(10) P. Da Re and L. Cimatoribus, *J. Org. Chem.*, **26**, 3650 (1961).

(11) K. Kindler, H. Oelschlager, and P. Henrich, *Arch. Pharm.*, **287**, 210 (1954).

(12) See L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, *J. Amer. Chem. Soc.*, **87**, 675 (1965), and other papers of this series.

(13) This result was not surprising as others had also reported that the *meta*-rearranged product was not formed.[4,5]

SCHEME II

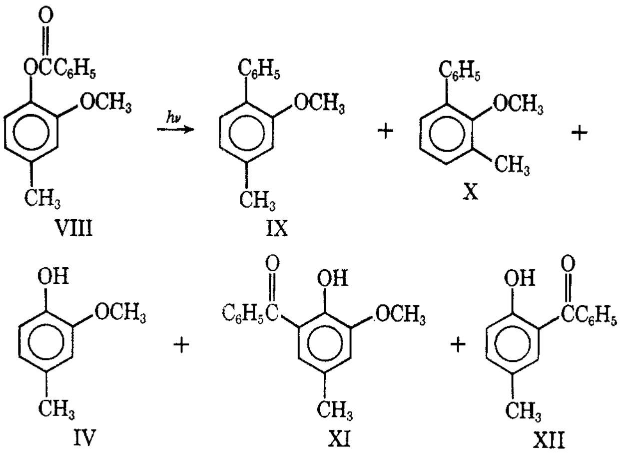


TABLE II

PHOTOREARRANGEMENT OF 2-METHOXY-4-METHYL BENZOATE[a]

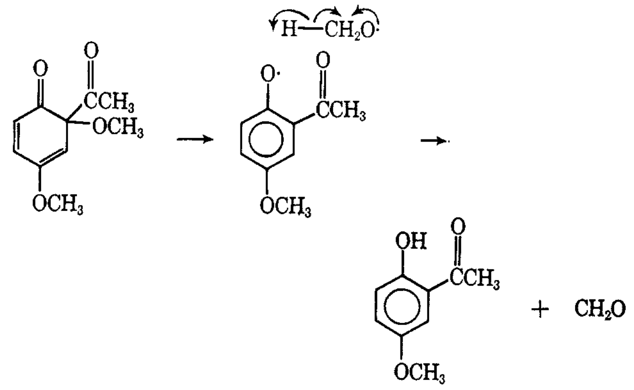
Run	Solvent[b]	Time, hr	Recovered ester, %	Yields of products, %[c] IX	X	IVc	XI	XII
8[d]	B	4	14	27	8	16	40	6
9[e]	E	4	22	2	0	25	63	7

[a] Two grams of substrate in 150 ml of solvent. [b] B = benzene; E = ethanol. [c] Products were analyzed and isolated by vpc and characterized by spectroscopy. [d] Benzaldehyde (3%) was also isolated. [e] Another unidentified product (3%) was present.

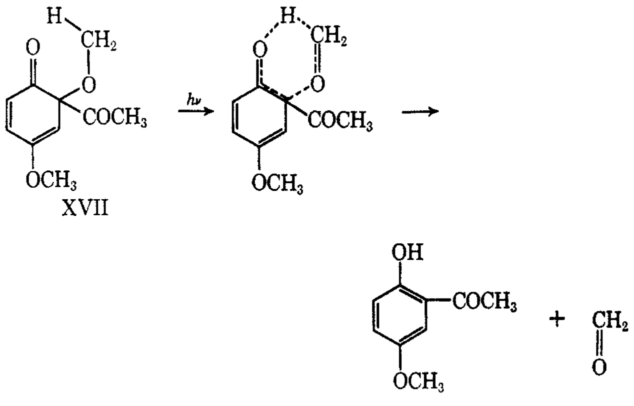
The displacement of a methoxy group during the photo Fries rearrangement has not previously been reported. To our knowledge, this reaction does not take place in the thermal Fries rearrangement.[14] Indeed, the thermal reaction with the 2,4-dimethoxy- and 2-methoxy-4-methylphenyl acetates did not result in a loss of a methoxy group but gave *ortho* and *meta* rearrangements as reported above.[9,10,15]

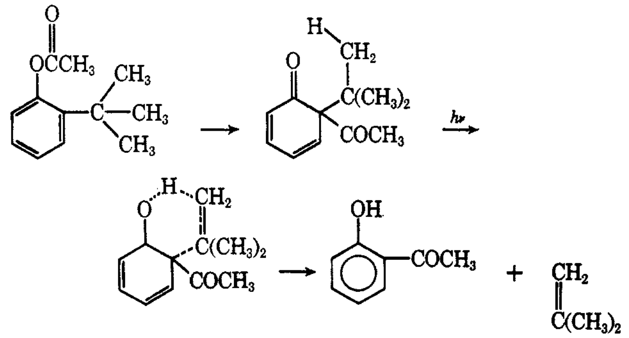
The displacement of a methoxy group probably takes place much like that reported by Kobsa for the rearrangement of 4-*t*-butyl-2,6-dichlorophenyl acetate. In that case a loss of chlorine was observed.[5] An over-all mechanism for the photo Fries reaction in these systems is proposed in Scheme III. There is some evidence to support this mechanism. The fact that no *meta*-rearranged product forms suggest that no heterolytic cleavage of the C–O bond occurs. Furthermore, the quantum yield of the photo Fries rearrangement is not affected by wide variations of solvent viscosity, and the presence of oxygen does not alter the product yield.[7] The intermediate XIII, XIV, or XV must, therefore, be a tightly bound neutral species. This may be a photoactivated charge-transfer complex,[6,7] a bridged diradical with neutral charge,[4b,7] or very tightly held radical fragments as suggested by Sandner and Trecker.[7] As seen in Tables I and II, most of the reaction proceeds along path 1 to the unoccupied *ortho* position. This is probably due to steric hindrance. The occupied *ortho* position is more susceptable to rearrangement than the occupied *para* position (runs 2 and 3), probably because the *ortho* is closer to the attacking acyl group.

The fate of the departing methoxy group is not known. It is quite likely that the group would leave as a radical and could be the source of hydrogen necessary to complete the reaction. Thus, a small amount of formaldehyde would be produced. This possibility is under further study. It is likely that the formaldehyde contributes to the polymer that is always observed in these reactions.



The *o*-methoxy group could possibly be cleaved by a secondary photochemical reaction of the dienone intermediate XVII.[16] This would follow the well-known Norrish type-II cleavage.[17] This possibility was examined by preparing and irradiating *o*-*t*-butylphenyl acetate. If a Norrish type-II cleavage of a dienone intermediate (similar to XVI, XVII, or XVIII) is operative, then some 2-hydroxyacetophenone should be present. None of this latter product was observed.





Only normal *ortho*- and *para*-rearrangement products were isolated. Thus intermediates like XVII are probably not undergoing secondary photochemical reactions.

Intermediates XIII, XIV, and XV could be involved in the formation of phenolic materials. In this case

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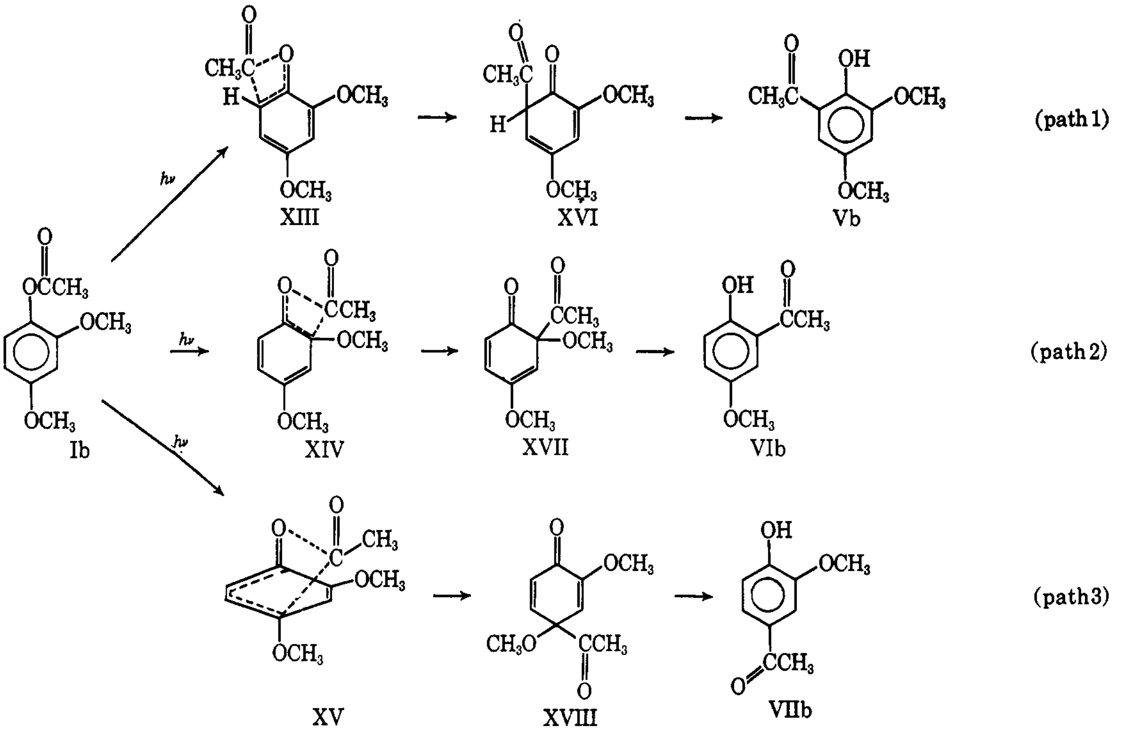
(14) For a review, see A. Gerecs in "Friedel–Crafts and Related Reactions," Vol. III, part I, G. A. Olah, Ed., John Wiley & Sons, Inc., New York, N. Y., 1964, p 499.

(15) A. Ballio, *Gazz. Chim. Ital.*, **79**, 924 (1949).

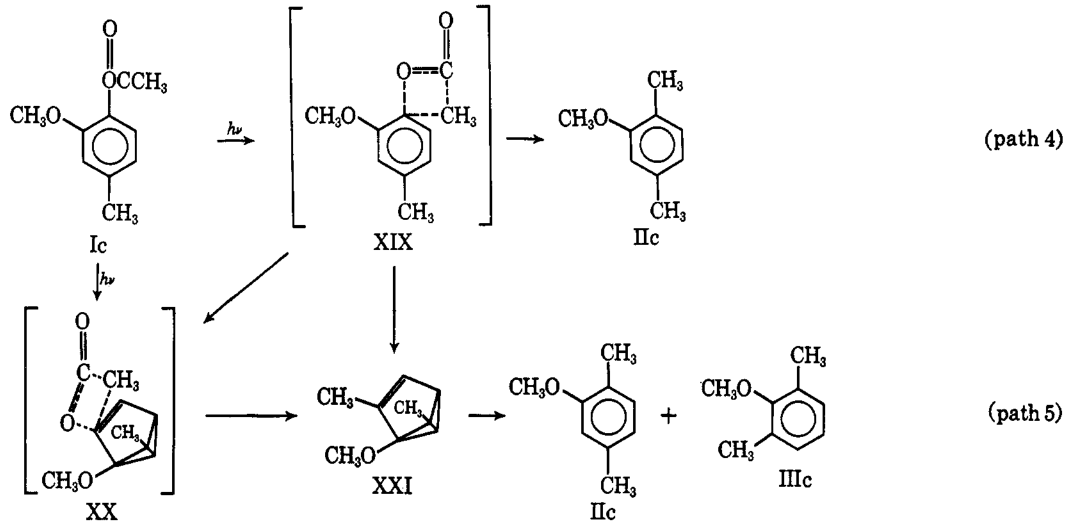
(16) This possibility was suggested by one of the referees.

(17) See J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 382.

Scheme III



Scheme IV



the tightly bound species could separate into an aryloxy and an acyl radical. The fate of the acyl radical has been the subject of numerous conjectures. These radicals are no doubt responsible in part for the polymer produced in these reactions. They can also lead to aldehydes[5] as shown by the isolation of 3% benzaldehyde in run 8 (Table III). The small amounts of acetaldehyde that would be formed in the acetate reaction would be lost either during the reaction or upon work-up.

The decarboxylation reactions show a marked dependence on the solvent. Essentially no product (II) was formed in alcohol. The reasons for this solvent dependence are not fully understood.[18] Since radical reactions generally show little or no dependence on the polarity of the solvent, this may mean that there is more polar character to these reactions than previously thought. At any rate a meaningful explanation must await a more detailed study of this reaction.[8d] We were somewhat surprised to find no decarbonylation products (1,2,4-trimethoxybenzene in the case of substrate Ib) present in the reaction mixtures. It has been proposed that the decarbonylation reaction occurs because carbon monoxide separates prior to the diffusion of the aryloxy and acyl radicals from the solvent cage.[8d] In our system the steric requirements of the *o*-methoxy (or methyl) group may force the forming radicals to separate more rapidly. Thus the radicals would be out of the cage before carbon monoxide could separate.

Phototransposition of carbon atoms on the benzene ring[12] was observed by the isolation of 2,6-dimethylanisole (IIIc in run 4) and 2-methoxy-3-methylbiphenyl (X in run 8). 1,2,3-Trimethylbenzene (IIId in run 7) may also have been formed; however, not enough was present to isolate and characterize. No

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[18] Finnegan and Knutson[8d] have also observed a solvent dependence in the decarboxylation reaction.

TABLE III

A LIST OF REACTION PRODUCTS

Run	Fraction	Compound	Yield, $\%^a$	Remarks
1	1	IIa	7	Ir same as Sadtler 28945; nmr δ m 7.1 (4), s 4.02 (3), s 2.35 (3)
	2	IVa	17	Ir and nmr same as an authentic sample
	3	VIa	14	Ir and nmr same as an authentic sample
	4	Ia	52	Ir and nmr same as an authentic sample
	5	Va^b	48	Ir band at 1640 cm^{-1}; nmr δ s 12.2 (1), m 7.0 (3), s 3.85 (3), s 2.57 (3)
	6	VIIa	14	Ir same as Sadtler 19571; nmr δ s 7.45 (1), m 6.9 (2), s 5.93 (1), s 3.95 (3), s 2.44 (3)
2	1	IIb	10	Ir same as Sadtler 24448; nmr δ m 6.9 (1), m 6.25 (2), s 3.78 (3), s 3.72 (3), s 2.10 (3)
	2	IVb	8	Ir and nmr same as authentic sample
	3	VIb^b	13	Ir same as Sadtler 32461; nmr δ s 11.6 (1), m 7.0 (3), s 3.78 (3), s 2.59 (3)
	4	VIIb^b	8	Ir same as Sadtler 19571; nmr δ s 7.54 (1), m 6.9 (2), s 5.93 (1), s 3.95 (3), s 2.44 (3)
	5	Ib	2	Ir and nmr same as authentic sample
	6	Vb^b	55	Ir band at 1635 cm^{-1}; nmr δ s 11.7 (1), s 6.61 (2), s 3.83 (3), s 3.73 (3), s 2.56 (3)
	7		6	Could not be separated from fraction 6
4	1	IIIc	4	Ir same as Sadtler 18712
	2	IIc	15	Ir same as Sadtler 19397; nmr δ m 6.7 (3), s 3.72 (3), s 2.29 (3), s 2.13 (3)
	3	IVc	19	Ir and nmr same as authentic sample
	4	VIc^b	6	Ir same as Sadtler 20306; nmr δ s 11.8 (1), m 7.0 (3), s 2.54 (3), s 2.28 (3)
4	5	Ic	3	Ir and nmr same as authentic sample
	6	Vc^b	56	Ir has band at 1640 cm^{-1}; nmr δ s 12.0 (1), s 7.02 (1), s 6.78 (1), s 3.78 (3), s 2.50 (3), s 2.23 (3)
7	1	IId	34	Ir same as Sadtler 1038
	2	Unknown	3	Possibly 1,2,3-trimethylbenzene
	3	IVd	8	Ir and nmr same as authentic sample
	4	Id	4	Ir and nmr same as authentic sample
	5	Vd^b	54	Ir has band at 1626 cm^{-1}; nmr δ s 12.2 (1), s 7.14 (1), 2 6.97 (1), s 2.41 (3), s 2.18 (3), s 2.11 (3)
8	1		3	Vpc retention time same as benzaldehyde; ir and mp, after oxidation, same as benzoic acid; ir and nmr same as authentic sample
	2	IVc	16	Ir and nmr same as authentic sample
	3	X	8	Ir bands at 1590, 1465, 1410, 1260, 1215, 1100, 1070 d, 1010, 805, 787, 760, 748, 695 cm^{-1}; mass spectrum showed parent peak at mass 198.
	4	IX	27	Ir bands at 1600, 1580, 1500, 1478, 1455, 1395, 1285, 1250, 1188, 1160, 1130, 1070, 1035, 1005, 920, 845, 810, 765, 725, 695 cm^{-1}; nmr δ m 8.4 (6), m 7.86 (2), s 4.26 (3), s 2.70 (3); mass spectrum showed a parent peak at mass 198
	5	XII^b	6	Ir same as Sadtler 29391
	6	VIII	14	Ir and nmr same as authentic sample
	7	XI^b	40	Ir has band at 1610 cm^{-1}; nmr δ s 13.1 (1), m 8.77 (5), m 8.05 (2), s 4.51 (3), s 2.63 (3)
	8	Unknown	3	Not isolated

[a] Esters of Ia, Ib, Ic, Id, and VIII are recovered starting materials. All others are percentage of total products. [b] Acceptable analytical data (±0.3) were obtained on these compounds.

phototransposition products were observed in the 2,4-dimethoxyphenyl acetate reaction (run 2). In previous studies of these types of reactions, only the rearrangement of alkyl groups was reported.[12]

The phototransposition reaction is believed to occur during the course of the decarboxylation reaction. This suposition is based on two facts. First, no Fries-rearranged products were observed in which the ring substituents had "migrated." This indicates that the transposition did not take place on the starting materials before they reacted. Second, the prolonged irradiation of 2-methoxy-4-methyl acetate (run 4 for 24 hr) failed to change the ratio of 2,5-dimethylanisole (IIc) to 2,6-dimethylanisole (IIIc). This indicates that the transposition did not take place after the formation of IIc. The phototransposition reaction has been reported to involve a benzvalene intermediate.[12,19] This intermediate then could be involved in our methyl "migration" reaction. There is good evidence for decarboxylation intermediate XIX since a concerted decarboxylation process has been demonstrated using optically active esters.[8d] Whether this intermediate XIX rearranges to the benzvalene compound XXI or a benzvalene is formed directly from the starting esters is not readily apparent from our results. If it can be assumed that the benzvalene XXI aromatizes to compounds IIc and IIIc with equal probability, then about 25% of the decarboxylation product IIc is obtained through path 5 (see Scheme IV).

Experimental Section

Materials and Apparatus.—Many of the chemicals used in this study were purchased and used as received: 2-methoxyphenylacetate (Ia), 2,4-dimethylphenol (IVd), 2-methoxy-4-methyl-

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[19] Benzvalene was recently isolated in the photolysis of benzene: K. E. Wilzback, J. S. Ritscher, and L. Kaplan, *J. Amer. Chem. Soc.*, **89**, 1031 (1967).

phenol (creosol) (IVc), *m*-dimethoxybenzene, and N-methylformanilide from Eastman Kodak and acetyl chloride, benzoyl chloride, and pyridine from J. T. Baker. 2,4-Dimethylphenyl acetate (Id) was generously supplied to us by Professor W. J. Horton. An Aerograph 202 B temperature-programmed vapor phase chromatograph was used to analyze and separate all photochemical products. All ir spectra were obtained on Beckman IR-8 or IR-7 spectrophotometers. The nmr spectra were taken on a Varian A-60A spectrometer.[2] Ultraviolet irradiations were carried out using a Hanovia quartz immersion reactor inserted into the reaction solution. A Hanovia 450-W medium-pressure lamp was used in all experiments.

Preparation of Starting Materials. Acetate Esters.—2,4-Dimethoxyphenol (IVb) was prepared by the peracetic acid oxidation of 2,4-dimethoxybenzaldehyde.[20] The latter compound was prepared by the procedure of Sommers, Michaels, and Weston from *m*-dimethoxybenzene.[21] The oxidation was carried out using 5.17 g of 90% hydrogen peroxide in 100 ml of glacial acetic acid added to 22.0 g (0.16 mol) of 2,4-dimethoxybenzaldehyde in 200 ml of glacial acetic acid to give phenol IVb (60% yield), bp 110–112° (1 mm).[20] The ir spectrum of a purified (vpc) sample contained a strong hydroxy band at 3220 cm^{-1}; the nmr spectrum exhibited the following peaks, δ m 6.5 (3), s 4.75 (1), s 3.8 (3), and s 3.6 (3).

Anal. Calcd for $C_8H_{10}O_3$: C, 62.33; H, 6.50. Found: C, 61.99; H, 6.79.

2,4-Dimethoxyphenyl acetate (Ib) was prepared by mixing equal molar amounts of crude 2,4-dimethoxyphenol and acetyl chloride in pyridine. After standing for 1 hr, the reaction mixture was added to water, and the aqueous mixture was extracted with ether. The ether extracts were washed with dilute aqueous acid and then dilute sodium bicarbonate solution and dried over anhydrous calcium chloride. After distillation, the product acetate [yield 75%, bp 97–98° (1 mm)] was found to contain a small amount of 2,4-dimethoxybenzaldehyde. The aldehyde was effectively removed by stirring an ether solution of acetate Ib overnight with aqueous sodium bisulfite. An analytical sample was isolated by vpc. The ir spectrum contained a band at 1755 cm^{-1}; the nmr spectrum exhibited the following peaks, δ m 6.6 (3), s 3.66 (3), s 3.61 (3), and s 2.14 (3).

Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17. Found: C, 61.18; H, 6.13.

2-Methoxy-4-methylphenyl acetate (Ic) was prepared by the above procedure to give an 80% yield: bp 77–79° (1 mm); $n^{25}\mathrm{D}$ 1.5070. A band at 1755 cm^{-1} was observed in the ir spectrum, and the nmr spectrum had the following peaks, δ m 6.7 (3), s 3.06 (3), s 2.22 (3), and s 2.12 (3).

Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.59; H, 6.71. Found: C, 66.63; H, 6.67.

Benzoate Esters.—2-Methoxy-4-methylphenyl benzoate (VIII) was prepared by mixing equal molar amounts of 2-methoxy-4-methylphenol and benzoyl chloride in pyridine. The resulting reaction mixture was treated as reported above for the acetates yielding a solid product, mp 74–75°. The ir spectrum exhibited a band at 1725 cm^{-1}, and the nmr spectrum had the following peaks, δ m 6.5–8.3 (8), s 3.65 (3), and s 2.28 (3).

Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.40; H, 5.82. Found: C, 74.45; H, 5.99.

2-Methyl-4-methoxy-5-hydroxyacetophenone (Nonphotochemical *meta*-Rearranged Product).—The procedure of Da Re and Cimatoribus[10] was used to prepare this compound using creosol, acetic acid, and boron trifluoride, mp 124–126° (lit. mp 129–130°).[10] The ir spectrum contained bands at 3100 and 1650 cm^{-1}, and the nmr spectrum had peaks at δ s 8.45 (1), m 7.80 (1), s 6.59 (1), s 4.58 (3), and d 2.83 (6).

Irradiation Reactions.—The substrate (about 2 g) was dissolved in 150 ml of the appropriate solvent. The solution was placed in a reactor into which the quartz immersion well was fitted. A small stream of nitrogen was sparged into the bottom of the reactor 30 min before the reaction was started and continued throughout the duration of the reaction. Upon completion of the irradiation, the solvent was removed under vacuum (30–40 mm), and the remaining oil was subjected to vpc analysis using SE-30 on Chromosorb W and programming the temperature from 100 to 250° or 285°. Yields were calculated from the relative peak areas. Pure samples of the products were collected for analysis. The results are shown in Tables I and II. Table III contains a detailed list of products in runs 1, 2, 4, 7, and 8. Run 3 gave the same results as run 2 except only a trace amount of fraction 1 and different relative amounts of fractions 2, 3, 4, 5, and 7 were obtained (see Table I). Runs 5 and 6 gave the same compounds as run 4 but in different yields. Run 9 gave the same products as run 8 except in different yields.

Registry No.—Ib, 7203-46-5; Ic, 879-67-4; IVb, 13330-65-9; Va, 703-98-0; Vb, 17605-00-4; Vc, 7452-85-9; Vd, 1198-66-9; VIII, 17605-03-7; IX, 17603-90-6; X, 17603-91-7; XI, 17603-92-8.

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