Tetrahedron, 1965, Vol. 21, pp. 1015 to 1026. Pergamon Press Ltd. Printed in Northern Ireland

PHOTOCHEMICAL STUDIES—II[1]

THE PHOTO-REARRANGEMENT OF ARYL ESTERS[2,3]

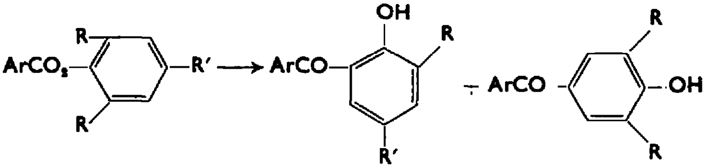
R. A. Finnegan[4] and J. J. Mattice[5,6]
Department of Medicinal Chemistry, School of Pharmacy,
State University of New York at Buffalo, Buffalo 14, New York
Wright Field Graduate Extension Center of the Ohio State University Dayton, Ohio,
Department of Chemistry, Ohio State University, Columbus 10, Ohio

(*Received* 28 *October* 1964; *in revised form* 10 *December* 1964)

Abstract—The photo-rearrangement of aryl esters (the Photo-Fries reaction) has been extended to a number of substituted phenyl benzoate and ferrocenoate derivatives. When the phenol moiety was unsubstituted, a mixture of *ortho-* and *para*-hydroxy ketones was obtained. An exception to this behaviour was observed in the case of phenyl ferrocenoate which provided the *para*-isomer only. *Para*-rearrangement products were obtained in good yield from two di-*ortho*-substituted phenyl esters. The results of additional experiments, including those obtained from a mixture irradiation, are presented and discussed with reference to the reaction mechanism. Finally, the possible generality of the reaction is pointed out.

INTRODUCTION

The classical Fries rearrangement[7] was recently reported to have a photochemical analogue. Anderson and Reese[8] found that UV irradiation of ethanol solutions of phenyl and catechol acetates produced the corresponding mono- and dihydroxy acetophenones. As subsequently pointed out by these authors,[9] this reaction was foreshadowed by some earlier results of Klinger and Standke.[10] This reaction was of interest as a potentially mild route to substituted benzophenones as well as a vehicle for a kinetic and mechanistic study. Although the latter objective was not realized, the scope of this new photochemical process was extended to include phenyl benzoate (Eq. 1, Ar = C_6H_5-, R = R′ = H) and a number of its ring substituted derivatives.



Equation 1.

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[1] Paper I, R. A. Finnegan and A. W. Hagen, *Tetrahedron Letters* 365 (1963).

[2] Presented before the *Organic Division at the* 145*th meeting of the American Chemical Society* New York September (1963), New York, *Abstracts* p. 3Q.

[3] The work done at the Buffalo and Columbus addresses was supported by a grant from the Petroleum Research Fund of the American Chemical Society.

[4] Author to whom inquiries may be sent at the Buffalo Address.

[5] This paper is based mainly on a thesis presented by J. J. M. to the Department of Chemistry, Ohio State University, Spring, 1963, in partial fulfillment of the requirements for the Master of Science degree.

[6] Present address: Air Force Materials Laboratory, Wright-Patterson AFB, Ohio.

[7] A. H. Blatt, *Organic Reactions* **1**, 342 (1942).

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

[9] J. C. Anderson and C. B. Reese, *J. Chem. Soc.* 1781 (1963).

[10] H. Klinger and O. Standke, *Ber. Dtsch. Chem. Ges.* **24**, 1340 (1891).

In addition, the reaction is applicable in the ferrocene series. After the bulk of this work was completed, Kobsa[11] published in detail his studies on the photo-rearrangement of the 4-t-butylphenyl esters of a number of aromatic acids to the corresponding 2-hydroxy-5-t-butylbenzophenones (Eq. 1, R = H, R′ = t-butyl). Furthermore, Taub *et al.*[12] were able to apply this reaction successfully to a poly-substituted aryl ester as a step in a total synthesis of griseofulvin. Finally, Anderson and Reese[9] extended their original studies[8] to include phenyl benzoate and Barton *et al.*[13] reported, by implication, the rearrangement of β-naphthyl acetate and benzoate. The present article contains the details of our experiments in this area.[2]

RESULTS AND DISCUSSION

Phenyl benzoate derivatives. The results obtained when dilute solutions of aryl esters in various solvents were irradiated with UV light are collected in Table 1. The products were isolated either by an extraction and steam distillation procedure or by chromatographic methods. In nearly all cases the yield figures refer to the amount of purified product obtained having the m.ps specified in the experimental section. It will be noted that those esters having an unsubstituted phenol moiety give rise in general to a mixture containing both the *ortho-* and *para*-hydroxyketone products. The *para* isomer predominates, in agreement with the findings of Anderson and Reese,[9] excepting in the case of phenyl *p*-chlorobenzoate where the isomer distribution is markedly different from that usually obtained. This apparent substituent effect is worthy of further study.

Under our conditions, the reaction is characterized by low conversions, possibly due to the known absorbing properties of the hydroxy-ketone products which may serve as internal filters, especially the *ortho*-isomers. This possibility is consistent with the observation of increased yields and conversions in cases (2,6-dialkylphenyl benzoates) where the *ortho*-isomer can not be formed for structural reasons. In two experiments with phenyl benzoate, the formation of the *ortho*-product was followed by noting the increase, in suitably diluted aliquots, of the characteristic absorption at 335 mμ of *o*-hydroxybenzophenone. In isopropanol solution the absorbance increased linearly for the first 5 hr whereupon the rate of increase steadily diminished. Similar behaviour was noted in dioxane solution, where, after 70 hr irradiation, the absorbance at 335 mμ reached a maximum value and began to decrease. This phenomenon is illustrated by the graph in Fig. 1. We hope to investigate the possibility that the *ortho*-product itself undergoes a slow photo-decomposition. Starting ester recovery was usually quite high, even after long irradiation times. A noticeable exception is the case of phenyl mesitoate. In our initial experiment with this ester a dilute solution in isopropanol was irradiated with a 450 watt lamp for 26 hr at 36°. No products from this reaction could be characterized and furthermore, no starting material was recovered. This result led us to suppose that the unique steric environment of the carbonyl group in this ester had exercised, in some way, a detrimental influence on the course of the rearrangement and was the basis for our original assertions regarding this compound.[2] Repetition of this photolysis in hexane or in

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

[12] D. Taub, C. H. Kuo, H. L. Slates and N. L. Wendler, *Tetrahedron* **19**, 1 (1963); C. H. Kuo, R. D. Hoffsommer, H. L. Slates, D. Taub and N. L. Wendler, *Chem. & Ind.* 1627 (1960).

[13] D. H. R. Barton, Y. L. Chow, A. Cox and G. W. Kirby, *Tetrahedron Letters* 1055 (1962).

TABLE 1. THE PHOTO REARRANGEMENT OF ARYL ESTERS TO *ortho*- AND *para*-HYDROXY KETONES[a]

Solvent	Conc. *M*	Time, hr	Temp °C	Conversion %	Recovered ester, %	Yield %[b]	
						ortho	*para*
Phenyl benzoate:							
cyclohexane	0·22	24	55	4	90	11	29
dioxane	0·21	24	61	4	88	13	23
benzene	0·13	8	52	4	90	13	20
p-*Tolyl benzoate:*							
cyclohexane	0·063	23	52	3	88	25	—
dioxane	0·25	24	63	3	84	20	—
isopropanol	0·057	20	57	7	80	34	—
benzene	0·059	19	55	17	67	53	—
p-*Chlorophenyl benzoate:*							
cyclohexane	0·051	19	54	5	87	37	—
isopropanol	0·052	19	54	10	67	29	—
benzene	0·055	19	53	7	86	51	—
2,6-*Dimethylphenyl benzoate :*							
isopropanol	0·012	24	26	20	38	—	33
2,6-*Diisopropylphenyl benzoate:*							
isopropanol	0·05	24	26	13	77	—	56
Phenyl p-*chlorobenzoate:*							
cyclohexane	0·054	19	46	9	83	49	6
benzene	0·052	19	52	5	91	42	14
Phenyl mesitoate:							
hexane	0·003	109	40	15	8	6	11[d]
benzene	0·008	332	40	12	41	9	12[d]
p-*Nitrophenyl* p-*nitrobenzoate:*							
benzene[c]	0·009	35	50	4	65	11	—
Mesityl benzoate:							
isopropanol[c]	0·027	24	37	—	17	—	—[e]
Phenyl ferrocenoate:							
cyclohexane	0·0034	26	25	3	71	0·0	9
cyclohexane[c]	0·0036	2	37	15	66	0·0	44
p-*Tolyl ferrocenoate:*							
cyclohexane[c]	0·011	24	35	—	49	0·0	—[f]
3,4-*Benzocoumarin:*							
benzene	0·098	119	68	—	90	—	—[g]
benzene[c]	0·011	45	80	0·08	92	—	—[h]

[a] Except where noted, a 100 watt source was used. [b] Yield is based on unrecovered starting material. [c] A 450 watt lamp was used in this experiment. [d] Mesitoic acid was also obtained. [e] A 12% yield of mesitol was obtained. [f] *p*-Tolylferrocene (5%) and ferrocenoic acid (2%) were obtained. [g] No products were identified. [h] 4-Hydroxyfluorenone (10%) was obtained.

benzene solution coupled with extensive chromatographical separations has, however allowed the isolation of the normal Fries rearrangement products, although in low yield as indicated in Table 1. In addition to the hydroxyketones, these experiments produced small quantities of mesitoic acid, biphenyl (when benzene was solvent), and a trace of a crystalline compound, m.p. 320°, whose IR spectrum showed bands for hydroxyl, carbonyl (1751 cm^{-1}) and carbon-carbon unsaturation (1613 cm^{-1}). This material was obtained when either hexane or benzene was used as solvent, although in yields too low for structural elucidation. At one stage in the examination of the phenyl mesitoate photolysis mixture, a sample of 2,4,6-trimethylbenzyl mesitoate was prepared for comparison purposes; however, this material was not encountered among the photolysis products.

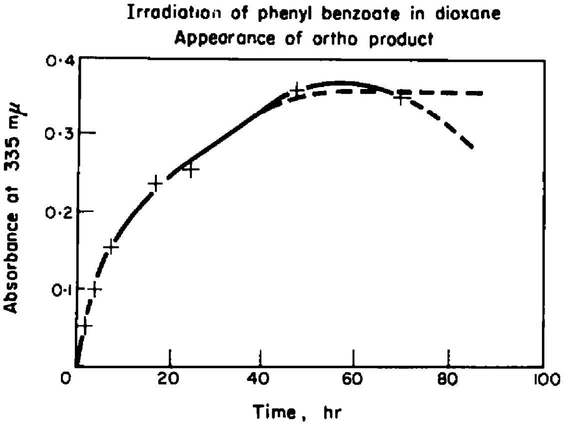
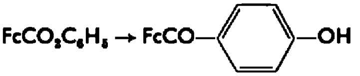


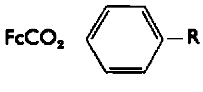
Fig. 1

Ferrocene derivatives. Phenyl ferrocenoate rearranged in fair yield to produce *p*-hydroxybenzoylferrocene (Table 1) (Eq. 2, Fc = ferrocenyl). The structure of

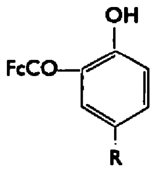


Equation 2

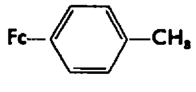
this product was verified by preparation of an identical substance by acylation of ferrocene with *p*-anisoyl chloride, followed by cleavage of the ether group in the resulting *p*-anisoylferrocene. Surprisingly, chromatographic work-up of the photoreaction mixtures failed to provide the *ortho*-isomer II (R = H), a sample of which was shown separately to be stable under the reaction conditions. This result prompted examination of the ester I (R = CH_3) which retains the unsubstituted *ortho*-sites but which carries a blocking group in the *para*-position. When *p*-tolyl ferrocenoate (I, R = CH_3) was irradiated under conditions which allowed an 88% recovery of



I



II



III

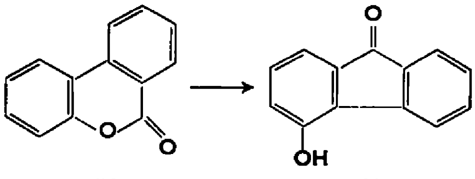
compound II (R = H), *no Fries rearrangement product was formed.* Specifically, compound II (R = CH_3) could not be recognized among the products although only 49% of the starting material was recovered. Two products were, however, identified. One of these, ferrocenoic acid, was isolated in 2% yield while the other was isolated in 5% yield and identified subsequently as *p*-tolyferrocene (III) by comparison with an authentic specimen. Compound III is formed by a process which does not seem to have been previously described: a photo-decarboxylation of an ester as generalized in Eq. 3.

$$RCO_2R \rightarrow R\text{—}R + CO_2 \qquad \text{Equation 3}$$

The formation of biaryls in our previous photolyses was not noted; however, these products might easily have escaped detection during work-up. In the present case, III was readily located in non-polar chromatographic fractions because of its orange colour. Analogous reactions have long been known to occur during pyrolysis of aromatic esters[14] and this reaction may be also formally related to the recently reported photo-expulsion of carbon disulphide from a carboxylic dithiocarbamic anhydride.[15] The scope of the decarboxylation reaction as well as the manner in which it competes with the rearrangement process is currently receiving attention.[16]

Observations on the mechanism. The intramolecular nature of the rearrangement appears to be reasonably well established. An experiment was carried out in which an equimolar mixture of phenyl *p*-chlorobenzoate and *p*-chlorophenyl benzoate were irradiated in isopropanol solution. Only those monochlorohydroxybenzophenones expected to result from intramolecular reactions were isolated after chromatography of the product mixture. Neither unchlorinated nor dichlorinated "cross-over" products were detected, thus adding weight to the original suggestions of Anderson and Reese.[8]

We[2,17] and others[8,9,11] have already made note of the conspicuous absence of *meta*-oriented hydroxyketones in the product mixtures. In this connection we have studied the photochemistry of 3,4-benzocoumarin (IV) in which structural considerations sensibly limit the migration of the aroyl group to the position *meta* to the



IV V

Equation 4

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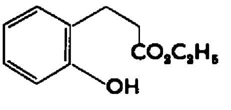
[14] P. E. Reininger, P. D. Ritchie and (in part) D. Ferguson, *J. Chem. Soc.* 2688 (1963) and Refs. contained therein.

[15] D. S. Tarbell and E. H. Hoffmeister, *Science* **144**, 568 (1964).

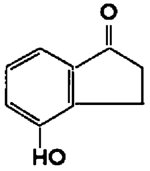
[16] D. Knutson, in a study of the application of the photo-Fries reaction to the preparation of highly hindered aryl ketones, has found that the irradiation of 3,5-di-t-butylphenyl esters of benzoic, *p*-methoxybenzoic and acetic acids provides not only the interesting hydroxyketones, but also in comparable yields the corresponding decarboxylation products tentatively identified as 3,5-di-t-butylbiphenyl, 3,5-di-t-butyl-4'methoxybiphenyl and 3,5-di-t-butyltoluene. These experiments will be published in due course.

[17] Footnote 8 in Ref. 1.

phenol oxygen atom.[18] Although our first experiments provided negative results,[17] the employment of a more efficient apparatus and a more intense light source did, however, allow the detection of the *meta*-rearrangement product, 4-hydroxyfluorenone (V), as illustrated in Eq. 4. Compound V was isolated in 10% yield (0·8% conversion) and identified by a direct comparison of its properties with those of an authentic sample. The exceptionally low conversion of IV to V confirms the general reluctance to form *meta*-substituted products.[19] Anderson and Reese[9] attempted to observe a similar rearrangement during the irradiation of 3,4-dihydrocoumarin in ethanol solution. This experiment resulted solely in the formation of the solvolysis product (VI), no hydroxyindanone (VII) being found.

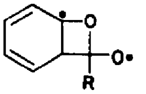


VI

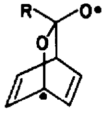


VII

It has been suggested[9] that the photo-rearrangement of phenyl esters proceeds by way of the bicyclic diradical intermediates (VIII and IX). These are then envisaged to collapse to a pair of dienones which, upon enolization, are converted to the aromatic *o*- and *p*-hydroxyketones respectively. Although an intermediate exactly analogous to VIII (except for being a dipole instead of a diradical) has been proposed earlier[20] to account for the pyrolytic rearrangement of vinyl benzoate to benzoylacetaldehyde, we believe that these (VIII and IX) represent an unnecessary complication. Although they can not at the present time be rigorously ruled out, the simpler but nonetheless adequate proposal advanced by Kobsa is preferred. In Kobsa's view,[11] the rearrangement is preceded by a photo-dissociation of the ester into a pair of radicals (acyl-oxygen fission) which are retained in a solvent cage for a time sufficient to allow recombination with the formation of dienones. Subsequent enolization leads to the products. The known reactivity of the aryloxy radical readily accommodates the predominate formation of *ortho*- and *para*-oriented products without, however, foreclosing on the possibility of *meta*-isomer production. Furthermore, migration from the cage, i.e., the production of free radicals, accounts in a general way for the formation of intractable polymeric materials usually observed as well as, in a specific way, the production of the corresponding phenol[11] by hydrogen abstraction. Also, the obtention of compounds derived from the solvent easily accords with this view of the reaction.



VIII



IX

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[18] The formation of other types of products, however, which stem from interaction of the aroyl group with other positions on the phenolic portion of the molecule can not, *a priori*, be ruled out.

[19] Biphenylene, the decarboxylation product of IV, was not detected.

[20] R. J. P. Allan, R. L. Forman and P. D. Ritchie, *J. Chem. Soc.* 2717 (1955).

A feature which this scheme has in common with that of Anderson and Reese[9] is the intermediacy of dienones. We had hoped to obtain direct evidence on this aspect by the irradiation of mesityl benzoate in which the dienones, if formed would be prevented from enolization by the methyl substituents. The only products identified in this reaction were mesitol (12%) and starting material (17%) which were obtained along with a relatively large quantity of uncharacterizable oils. Speculation concerning the possible nature and genesis of these products is best deferred until their re-examination, presently under way, is completed.

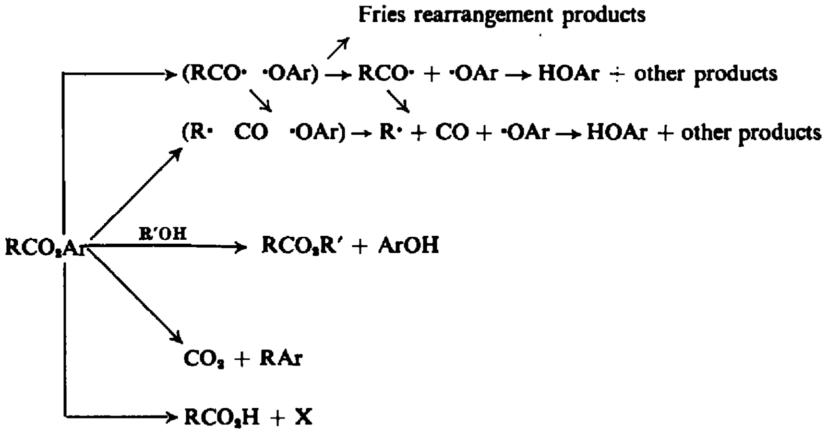

Fig. 2

Turning to another aspect of the reaction, it should be emphasized that no direct evidence bearing on the mode of photo-excitation of these aryl esters is yet available. The lack of information regarding the wavelength requirements, not to mention the multiplicity of the excited state(s), is especially critical in view of the fact that at least five different reactions have been observed to occur when aryl esters are irradiated. These reactions are outlined in Fig. 2. In the first case, the ester is promoted to a state, possibly by excitation of the aryloxy moiety as suggested by others,[13] which is considered to result in bond homolysis with the production of a caged radical pair whose fate has already been discussed. If the R group represents an exceptionally stable radical (e.g., 9-fluorenyl), decarbonylation is known to occur with the ultimate production of fairly good yields of the corresponding phenol.[13] Whether this decarbonylation ensues directly in a concerted process involving two bonds, or in subsequent steps, is not known and this ambiguity is indicated by the arrows interconnecting the two reaction pathways. A third reaction is the light-induced[9] solvolysis resulting in release of the phenol and formation of an ester. This reaction has been observed only when ethanol has been used as solvent (R′ = ethyl in Fig. 2). In the present work, isopropanol was chosen as solvent with a view to suppressing this side reaction. Yet another reaction, of a distinctly different type, is the photo-decarboxylation which was observed when *p*-tolyl ferrocenoate (see above) and other esters[16] are irradiated.

Finally, a fifth reaction has been observed which we believe to be a light-induced process and is exemplified by the production of the carboxylic acid corresponding to the starting ester. This has been described above in the cases of *p*-tolyl ferrocenoate and phenyl mesitoate. It was encountered previously as a result of vinyl benzoate photolysis[1] and was also observed by Taub *et al.*[12] In this latter example, the acid precipitated directly from the photolyzing reaction mixture *in* 90% *yield.* Although alternative explanations may be advanced, we wish to point out the possibility that the carboxylic acid may be derived from a concerted elimination reaction, a process which is well known to occur during pyrolysis[21] as well as photolysis[22] of *alkyl* esters producing carboxylic acids and olefins. Vinyl esters undergo a similar pyrolytic decomposition to form acids and acetylene,[23] and extension of the idea to aryl ester photolysis leads to the proposal that the production of an aryne intermediate (X in Fig. 2) is associated with the formation of the acid. Arynes have been produced photochemically in other systems[24–26] and we suggest that it represents one of the modes, albeit a minor one, of aryl ester photo-decomposition.

Concluding remarks. The photo-Fries rearrangement has been shown to be applicable to a considerable variety of aryl esters although its chief advantage in preparative work would seem to be its use in those cases where the usual acid catalyzed procedure would result either in undesirable side reactions[11,12,16] or in an unfavourable product distribution.[8]

Arguments based upon structural analogies have already been advanced[1] in support of the view that this rearrangement need not be limited to aryl esters. The rearrangement of vinyl benzoate to benzoylacetaldehyde[1] along with the independent and much more extensive studies of other enol benzoates by Feldkimel-Gorodetsky and Mazur[27] bear this out. In addition, the reaction has been applied to acyl anilides[28,29] as well as to benzanilide[30,31] and it is likely that other applications will be forthcoming.

EXPERIMENTAL PART

All starting materials were prepared by reaction of the acid chloride with the phenol either in aqueous alkali or in pyridine solution. The resulting esters were then purified by recrystallization until their m.ps remained constant. Except where noted otherwise, all m.ps were determined on a modified Hershberg apparatus[32] using a calibrated thermometer. The IR spectra were measured on a Perkin–Elmer Model 137B "Infracord" and, in a few cases, a Model 237. The UV spectra were recorded with a Bausch and Lomb "Spectronic" 505 or with a Perkin–Elmer Model 202, and the NMR spectra were determined on the Varian Associates A60 spectrometer. Microanalyses were performed by the Analytical Branch of The Air Force Materials Laboratory, Wright-Patterson AFB, Ohio, and Dr. A. Bernhardt, Mulheim, Germany.

General procedures. Three types of apparatus were used for the irradiation experiments and are designated A, B and C. The type A set-up consisted of a quartz vessel which was irradiated externally with a 100 watt Hanovia Model 30600 utility lamp. By means of standard tapered openings, the flask could be fitted with a water cooled condenser, a thermometer, and a N_2 inlet tube. A

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[21] C. H. DePuy and R. W. King, *Chem. Rev.* **60,** 431 (1960).

[22] R. Borkowski and P. Ausloos, *J. Amer. Chem. Soc.* **83,** 1053 (1961).

[23] W. I. Bengough, P. D. Ritchie and W. Stedman, *J. Chem. Soc.* 2697 (1963), and preceding papers.

[24] R. S. Berry, G. N. Spokes and M. Stiles, *J. Amer. Chem. Soc.* **84,** 3570 (1962).

[25] J. A. Kampmeier and E. Hoffmeister, *J. Amer. Chem. Soc.* **84,** 3787 (1962).

[26] E. LeGoff, J. Am. Chem. Soc., *J. Amer. Chem. Soc.* **84,** 3786 (1962).

[27] M. Feldkimel-Gorodetsky and Y. Mazur, *Tetrahedron Letters* 369 (1963).

[28] D. Elad, *Tetrahedron Letters* 873 (1963).

[29] V. I. Stenberg and D. V. Rao, *Abstracts of Papers, 145th meeting of The American Chemical Society* p. 90Q. New York, N.Y., September (1963).

[30] V. I. Stenberg, personal communication.

[31] R. A. Finnegan, A. M. Bachmann and A. W. Hagen, unpublished experiments.

[32] H. E. Drechsel, *Analyt. Chem.* **29,** 859 (1957).

fourth opening was available for the purpose of withdrawing aliquot samples as needed. The contents of the flask were stirred magnetically. In the type B set-up, a flask was employed which allowed the insertion of a water cooled, fused quartz double-walled immersion well. The well housed a 100 watt Hanovia type 608A high press. Hg arc lamp. The type C set-up was identical with type B, except that a 450 watt Hanovia 679A lamp was used as the light source. The output characteristics of these lamps are described in technical literature available from the Hanovia Lamp Division, Engelhard Industries, Newark, New Jersey. The water used for cooling the immersion well was replaced every 4 hr with fresh distilled water in order to prevent the possibility of reducing the transmission of light through the cooling system by contamination. In addition to the immersion well, the flask was fitted with a thermometer, a condenser, a N_2 inlet tube, and a magnetic stirring bar. For at least ½ hr before starting the lamp, N_2 (General Electric Co., Lamp Grade) was bubbled through the solution to be irradiated and the N_2 stream was continued throughout the reaction time. A few of the experiments were carried out using an apparatus (termed as modified type B or C set-up) in which the quartz immersion well was not water cooled. The temp of the reaction mixture was controlled by placing the entire reaction flask in a bucket which contained a cooling coil. In these cases, the flask and its condensers were evacuated and refilled with N_2 (Matheson Co., Prepurified Grade) 5 times prior to starting the lamp and a slight positive pressure of N_2 was maintained all during the time of irradiation.

Two methods were, in general, used in order to isolate the products of the reaction. In one of these, the residue remaining after evaporation of the solvent (rotatory evaporator, red. press.) was dissolved in ether and extracted successively with 10% $NaHCO_3$aq and 5% NaOHaq. After acidification, the NaOH extract was steam distilled in order to effect a separation of the steam volatile *o*-hydroxyketones from the non-volatile *para*-isomers. The bicarbonate extract was examined for the pressure of carboxylic acids by acidification and ether extraction. Usually, no acid was obtained. The starting material was then recovered from the original ether solution by evaporation of the solvent. Samples of esters which had not been irradiated were shown to be unchanged by this work-up procedure. The second method for the work-up some of the reactions made use of column chromatographic techniques. Thus, the residue obtained after evaporation of the solvent from the irradiated reaction mixture was placed in pet. ether on a column made either with reagent silica (G. Frederick Smith Chemical Co., Columbus, Ohio) or alumina (Merck, acid washed) and eluted with solvent mixtures of increasing polarity.

The irradiation times, solvents, concentrations, yields, and conversions have been indicated in Table 1. Table 2 summarizes the m.ps and other experimental details for most of the reactions. The remaining experiments are presented individually.

Irradiation of a mixture of p-*chlorophenyl benzoate and phenyl* p-*chlorobenzoate.* A solution containing 5 g each of *p*-chlorophenyl benzoate and phenyl *p*-chlorobenzoate in 750 ml isopropanol was irradiated for 17 hr at 26° in the type B apparatus. The resultant mixture was chromatographed on silica. Elution with pet. ether–ether, 9:1, gave a mixture of unreacted esters and *o*-hydroxyketones. Continued elution provided no more than a trace of 4-hydroxy-4′-chlorobenzophenone, recognized by its IR spectrum, and 0·66 g of apparently polymeric products which could not be further purified. The mixture of esters and *ortho*-isomers mentioned above was further resolved by rechromatography on alumina. In this way, 7·63 g (76%) of combined starting esters were obtained along with 0·60 g (25%) of a mixture of 2-hydroxy-5-chlorobenzophenone and 2-hydroxy-4′-chlorobenzophenone. This latter mixture was identified by comparison of its IR spectrum with that of an artificial mixture; furthermore, the individual components were separated by fractional crystallization and compared with authentic samples.

Irradiation of phenyl ferrocenoate. A solution of 0·82 g phenyl ferrocenoate, m.p. 124–124·5°, in 750 ml cyclohexane was irradiated for 2 hr in the type C apparatus at 37°. A small amount of precipitate was noted which was subsequently combined with a product obtained by chromatography (silica) and shown to be *p*-hydroxybenzoylferrocene, 0·123 g, 44%. A quantity of starting material (0·54 g, 66%) was also obtained from this chromatography. The hydroxyketone was identified by its m.p. and by m.m.p. (undepressed), IR, and UV spectral comparisons with an authentic sample prepared as follows: *p*-Anisoylferrocene (0·5 g) m.p. 81–82°, (Lit.[47] m.p. 82–83°) was refluxed in benzene with $AlCl_3$ (0·4 g) for 40 min. After being cooled, the mixture was poured onto ice and stirred for 5 min. The organic layer was washed with water and reduced to about $\frac{1}{5}$ volume (*in vacuo*) before it was extracted with 20 ml 5% KOHaq. The solid which formed upon acidification

TABLE 2. MPS, APPARATUS, AND WORK UP PROCEDURES

Starting material	m.p.	lit. m.p.	Ref.	Apparatus Type[a]	Work up
Phenyl benzoate	69–70°	70°	33	A	*b*
p-Tolyl benzoate	73·5–74	71	34	A	*b*
p-Chlorophenyl benzoate	89–90	87	33	A	*b*
2,6-Dimethylphenyl benzoate	42–42·8	40·5–41	35	B	*c*
Phenyl *p*-chlorobenzoate	104·5–105	100	33	A	*b*
2,6-Diisopropylphenyl benzoate	73·6–74·5	70–72	42	B	*c*
Phenyl mesitoate	35–36[d]	37	43	modified C	*c*
				modified B	*c*
p-Nitrophenyl *p*-nitrobenzoate	162·5–163·5[d,e]	160–161	45	modified C	*c*
Mesityl benzoate	62–64[d]	62	46	C	*c*
Products					
o-Hydroxybenzophenone	36·5–37	39–40	36		
p-Hydroxybenzophenone	132	134	37		
2-Hydroxy-5-methylbenzophenone	79–82	84	38		
2-Hydroxy-5-chlorobenzophenone	93·7–95	94	39		
3,5-Dimethyl-4-hydroxybenzophenone	139–141·6	142–142·5	35		
2-Hydroxy-4′-chlorobenzophenone	75–76	74–75	40		
4-Hydroxy-4′-chlorobenzophenone	172·5–173·8	175–176	41		
3,5-Diisopropyl-4-hydroxybenzophenone	113·5–114[f,g]				
2,4,6-Trimethyl-2′-hydroxybenzophenone	81–83[d]	81–82	44		
2,4,6-Trimethyl-4′-hydroxybenzophenone	167–168[d,h,i]				
2-Hydroxy-5,4′-dinitrobenzophenone	189[d,e,j,k]				

[a] See description in general procedure section.

[b] Steam distillation method; see general procedure section.

[c] Chromatography; see general procedures section.

[d] M.p. was determined on a Fisher-Johns block and is uncorrected.

[e] We are happy to acknowledge the execution of this experiment by D. Knutson.

[f] A phase change occurred at 98·5°.

[g] $\lambda_{\max}^{\text{cyclohexane}}$ 233, 282 mμ; $\nu_{\max}^{\text{KBr}}$ 3328, 2942, 1600, 1588, 1460, 1438, 1290, and 723 cm^{-1}. (Found C, 80·70; H, 7·76; O, 11·11; $C_{19}H_{22}O_2$ requires: C, 80·82; H, 7·85; O, 11·33%).

[h] $\lambda_{\max}^{\text{EtOH}}$ 222 (shoulder), 282 mμ (log e, 4·25, 4·25), $\lambda_{\max}^{\text{EtOH}}$-NaOH 214, 246, 346 m$\mu$ (log e, 4·19, 3·23, 4·50); $\nu_{\max}^{\text{KBr}}$ 3247, 1642, 1603, 1567, 1284, 1239, 1168, 1133, 917 and 847 cm^{-1}. (Found C, 79·76; H, 6·78; $C_{16}H_{16}O_2$ requires: C, 79·97, H, 6·71%.) The NMR spectrum (CCl_4) showed a singlet (weight 6) at 7·95τ (2 equiv. methyls), a singlet (wt 3) at 7·72τ (the *p*-methyl group), a singlet (wt. 2) at 3·18τ (hydrogens on the alkylated ring), an AB quartet (wt. 4) (J = 9 c/s) with one doublet centered at 2·35τ and the other at 3·20τ (protons on the phenolic ring), and a singlet (wt. 1) at 1·02τ assigned to the hydroxyl proton.

[i] A product, m.p. 318–320° (sublimes), $\nu_{\max}^{\text{KBr}}$ 3450, 1751, 1255, 1244, 1163, 1079 and 847 cm^{-1}, was also obtained. (Found C, 80·43; H, 7·56; Mol. wt., 277.)

[j] $\lambda_{\max}^{\text{EtOH}}$ 271 and 305 (shoulder) mμ (log e, 4·30, 4·12); $\lambda_{\max}^{\text{EtOH}}$-NaOH 268 and 397 m$\mu$ (log e 4·20, 4·30); $\nu_{\max}^{\text{KBr}}$ 3300–2500, 3120, 3100, 1630, 1624, 1580, 1535, 1520, 1470, 1340 cm^{-1}. (Found: C, 54·10; H, 2·74; N, 9·65; Mol. wt., 278; $C_{13}H_8N_2O_6$ requires: C, 54·18; H, 2·80; N, 9·72%; Mol. wt., 288.)

[k] Although a careful search was made, no dinitrobiphenyl was found.

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Refs. continued at foot of opposite page.

was dissolved in ether, dried ($CaCl_2$) and chromatographed on silica. Recrystallization from an ether–pet. ether mixture provided the product, *p*-hydroxybenzoylferrocene, m.p. 190–191°, ν_{max}^{KBr} 3175, 1613, 1450, 1290, 1163, 854, 833 and 773 cm^{-1}; $\lambda_{max}^{cyclohexane}$ 223, 271 and 352 mμ, (Found: C, 67·09; H, 4·58; $C_{17}H_{14}FeO_2$ requires: C, 67·30; H, 4·64%.)

In a second experiment (Table 1), 0·78 g phenyl ferrocenoate in cyclohexane was irradiated for 26 hr in the type B set-up. Chromatography on silica afforded 0·55 g (71%) starting ester and only 0·02 g (9%) *p*-hydroxybenzoylferrocene. In both experiments, some polymeric black material remained at the top of the column.

Irradiation of o-*hydroxybenzoylferrocene*. *o*-Hydroxybenzoylferrocene (0·72 g) m.p. 87–88°, (Lit.[48] m.p. 87·5–88·5°) in 750 ml cyclohexane was irradiated for 24 hr at 35° in the type C apparatus. Chromatography (silica) provided 0·64 g (89%) recovered starting material. No other materials were eluted although some dark material remained at the top of the column.

Irradiation of p-*tolyl ferrocenoate*. A solution of 2·66 g *p*-tolyl ferrocenoate, m.p. 97–97·5°, in 750 ml cyclohexane was irradiated for 24 hr at 35° employing the type C apparatus. A small amount (4 mg) solid precipitated during the course of the reaction which appeared to be polymeric since it did not melt or soften at temps up to 280° and was insoluble in strong alkali. Chromatography of of the reaction mixture on silica afforded in the pet. ether–benzene eluates, 0·06 g (5%) of an orange crystalline product, m.p. 135–136°, which was identified as *p*-tolylferrocene (Lit.[49] m.p. 140–142°) by comparison of its IR spectrum with that of an authentic sample,[49] m.p. 138–139°;[50] m.m.p. with the photo-product, 136–139°.[50] Continued elution gave 1·31 g (49%) unchanged starting material, followed by a series (total, 0·15 g) of dark, tarry, nonphenolic materials which could not be purified. Finally, after long elution with ether–ethyl acetate mixtures, there was obtained 0·02 g (2%) ferrocenoic acid identified by IR and m.m.p. comparisons with an authentic sample, m.p. 224–225°, which was available in the laboratory.

Irradiation of 3,4-*benzocoumarin*. A solution of 2·0 g 3,4-benzocoumarin,[51] m.p. 92·5–94°[50] (Lit.[52] m.p. 94·5°) in 100 ml benzene was irradiated[53] for 119 hr at temps between 60 and 75° in a type A apparatus. Periodic examination of aliquots showed no change in the IR spectra of the recovered samples all of which melted between 91 and 93°.[50] Chromatography of the reaction mixture on alumina resulted in the recovery of 90% of the starting material.

A second irradiation[54] of 10·324 g 3,4-benzocoumarin, m.p. 93·5–94·5°, in 4800 ml benzene was carried out in the modified type C apparatus for 45 hr at refluxing temp. Chromatography of the product on alumina resulted in the recovery of 9·469 g starting material and the obtention of 0·087 g

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[50] See footnote *d* to Table 2.

[51] This material was prepared by oxidation of 9 fluorenone with peroxytrifluoroacetic acid and purified by chromatography on alumina by J. E. Burcsu and A. M. Bachmann.

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[53] We thank Miss A. M. Bachmann for conducting this experiment.

[54] See footnote *e* in Table 2.

(10%) crude 4-hydroxyflourenone. After recrystallization from water, this substance had m.p. 253°,[50] (Lit.[55] m.p. 250–251°) alone or admixed with an authentic sample which had been obtained commercially (Aldrich Chemical Co.) and similarly recrystallized. The IR as well as the UV spectra of these 2 samples were indistinguishable.

2,4,6-*Trimethylbenzyl mesitoate*. 2,4,6-Trimethylbenzyl alcohol (1·289 g) (α^2-isoduryl alcohol), m.p. 85–89°,[60] (Lit.[56] m.p. 86·5–87·5°) which had been prepared by LAH reduction of mesitoic acid, was dissolved in 5 ml pyridine with 3·156 g crude mesitoyl chloride and allowed to stand at room temp for 1 hr. Ether was added and the mixture was washed successively with water, HClaq, NaOHaq and finally with water before it was dried ($MgSO_4$) and the solvent was stripped. The residue was purified by chromatography on alumina which provided 0·609 g white solid, m.p. 65–70°.[60] Three additional recrystallizations from isohexane gave 0·242 g of the ester with m.p. 69·5–72°,[60] ν_{max}^{KBr} 1715 cm^{-1}. (Found: C, 81·45; H, 8·24; Mol. wt. 307; $C_{20}H_{22}O_2$ requires: C, 81·04; H, 8·16%: Mol. wt., 296).

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