CHEMICAL REVIEWS

PHOTOCHEMICAL REARRANGEMENT OF ARYL, VINYL, AND SUBSTITUTED VINYL ESTERS AND AMIDES OF CARBOXYLIC ACIDS

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CONTENTS

I. INTRODUCTION

It was established that upon irradiation with ultraviolet light the spectra of aryl esters are changed markedly and irreversibly (42, 54), and that the spectra of the products were similar to the spectra of *o-* and *p*-hydroxybenzophenones (24). The suggestion that these products were formed by a photoinitiated rearrangement of phenyl esters was made by several authors in connection with the use of aryl esters as ultraviolet absorbers in plastics (8, 56, 75).

In 1960, Anderson and Reese (4) irradiated an alcoholic solution of catechol monoacetate (I) with ultraviolet light and isolated the isomeric dihydroxyacetophenones (II, III) in fair yields. Later vinyl
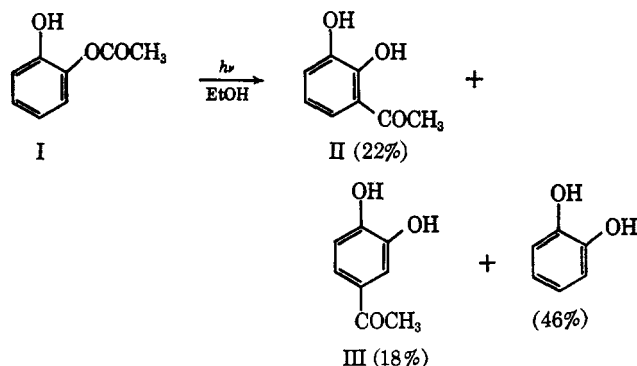
benzoate (IV) was found to undergo an analogous photochemical rearrangement (32) accompanied by a photochemical decarbonylation of the initial product (V).
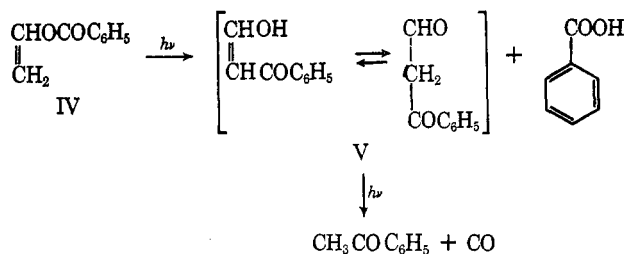

These photoinitiated rearrangements were found to occur with many aryl esters of carboxylic acids, vinyl and substituted vinyl esters, and N-arylamides. It is the purpose of this review to present a survey of the literature on these reactions through February 1966 and to discuss the mechanisms proposed.

## II. ARYL ESTERS

A. MONO AND DIARYL ESTERS

The photochemical rearrangement of aryl esters can be illustrated by the rearrangement of phenyl benzoate (Eq 1). If the phenolic moiety is unsubstituted, a mixture of *o-* and *p*-hydroxyphenones results. Di*ortho*-substituted phenyl esters give *para*-rearranged
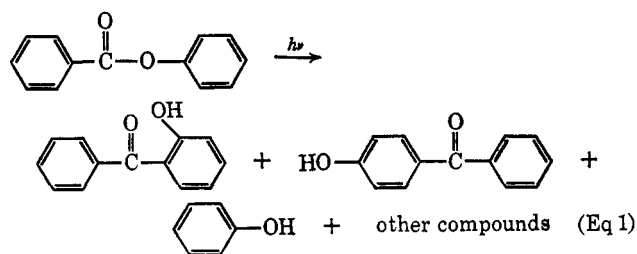
products; *para*-substituted phenyl esters give *ortho*-rearranged products. A certain amount of free phenol is always produced, and occasionally by-products can be identified. Numerous exceptions to the above rules will be discussed later.

Table I contains the aryl esters whose photochemical behavior has been studied. In this table and in the subsequent tables a plus sign indicates that the product was formed but the yield was not determined; a zero indicates that the substance was sought but not found; a negative sign indicates that the substance was not sought in the cited work; an X indicates that formation of the substance is not possible. Since the investigators used different reaction times, solvents, and sources of ultraviolet light, the listed yields of hydroxyphenones and by-products provide only approximate information. In only three cases were sources other than the 80–3000-medium- or high-pressure mercury arcs used. Diphenylolpropane dibenzoate rearranged upon irradiation with a Westinghouse Type RS sunlamp (52); phenyl salicylate and resorcinol monobenzoate rearranged under the effect of sunlight (56); and hydroquinone monoacetate was irradiated by a tungsten filament lamp (22). In order to determine quantum yields the required wavelengths were selected by filters from a high-pressure mercury arc source (46).

There is little information about the influence of the solvent on the photorearrangement of aryl esters. It becomes important when the resulting substances are sensitive to the effect of ultraviolet light. Thus *p-t-*butylphenyl formate (VI) (40) upon rearrangement in ethanol gave the following products.
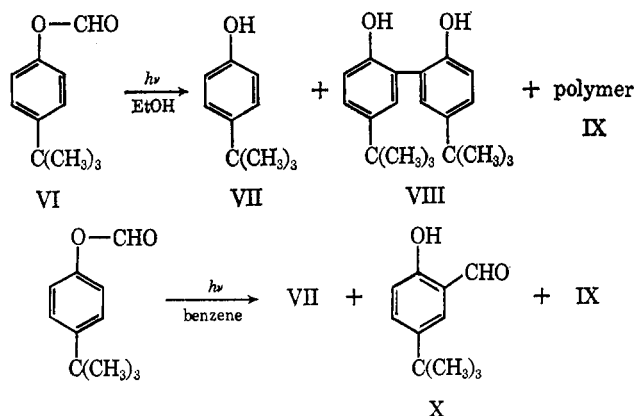

It seems probable that the initial product in ethanol was probably 2-hydroxy-5-*t*-butylbenzaldehyde (X), but it simultaneously decarbonylates and the phenyl radicals formed recombine to give 2,2'-dihydroxy-5,5'-di-*t*-butylbiphenyl (VIII). It is possible that in benzene solution decarbonylation is suppressed by absorption of shorter wavelengths of ultraviolet light. The solvent does influence the distribution of products of rearrangement of phenyl carbonates (Table II).

Only in the single case of the photolysis of 3,4-dihydrocumarin (XI) in ethanol was it established that the solvent reacts with the substance in a photoinitiated solvolysis (5).
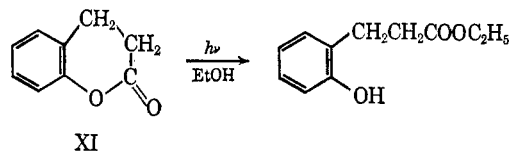
It was found that certain aryl esters do not rearrange to the *ortho* or *para* position of the phenolic moiety even though these positions are free. Thus no *para*-rearranged products were obtained upon irradiation of 3,5-di-*t*-butylphenyl acetate, benzoate (XII), and *p*-methoxybenzoate (33); upon irradiation of phenyl ferrocenoate (XIII; Fc = ferrocenyl), on the contrary, the sole product of rearrangement was *p*-hydroxybenzoylferrocene (XIV) (34).
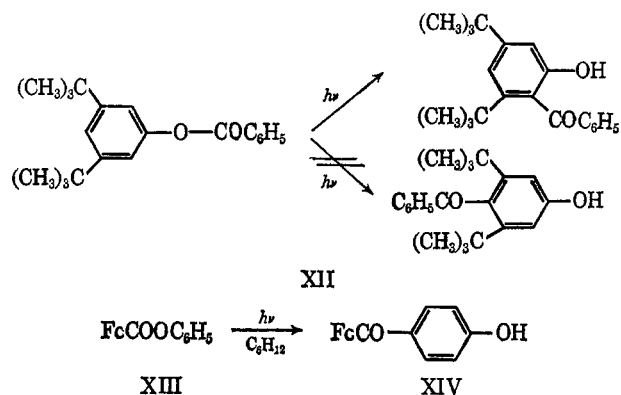
Migration or elimination of alkyl groups from the phenolic moiety, so characteristic for the ionic Fries rearrangement (48), has not been established for the photochemical rearrangement. However, it has been established that in contrast to the ionic Fries rearrangement, the photo Fries rearrangement proceeds also to an *ortho* position occupied by chlorine (Eq 2; see also compounds 36 and 37 in Table I) (46). Probably other *o*-halogen-substituted phenyl esters will behave in the same way.

(Eq 2)
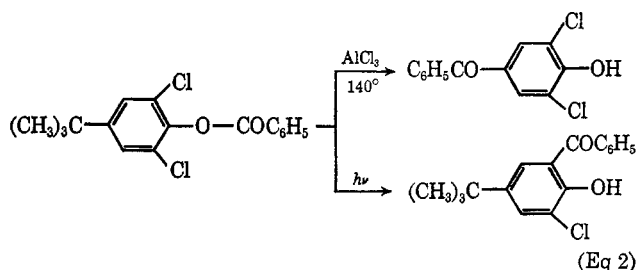
In rare cases the formation of *meta*-rearranged products was observed. Upon irradiation of phenyl acetate and after methylation of the reaction mixture, traces of *m*-methoxyacetophenone (<0.3%) were detected by

means of gas chromatography (5). Finnegan and Mattice (34), using a very intensive source of light, observed the rearrangement of 3,4-benzocumarin (XV), in which structural conditions determined the migration of the aroyl group to the *meta* position with regard to the phenolic oxygen atom, to 4-hydroxyfluorenone (XVI) with a yield of 0.08% of the initial XV. This exceptionally low yield confirms the general resistance to the formation of *meta*-rearranged products.

XV   XVI
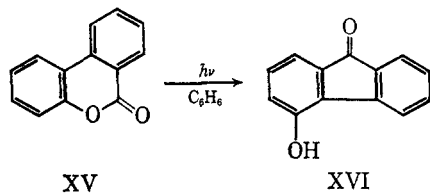
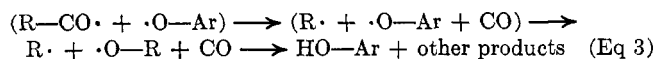Besides the main reactions 8a and 8b (see section II.C), the reverse recombination and the supposed diffusion of the radical pair from the solvent cage, leading to phenol formation and decarbonylation of the acyl radical in the solvent cage (or outside of it?), are also possible, leading to further reactions (Eq 3).

(R—CO· + ·O—Ar) ⟶ (R· + ·O—Ar + CO) ⟶
R· + ·O—R + CO ⟶ HO—Ar + other products   (Eq 3)

If R· represents an exceptionally stable radical (for example, triphenylacetyl, 9-xanthenyl, 9-fluorenyl), decarbonylation proceeds very easily to give fairly good yields of the corresponding phenols (Table III) (9, 10).

A further side reaction, occurring especially upon photolysis of phenyl esters with a high steric barrier, is decarboxylation. Though exact facts influencing the relation between rearrangement and decarboxylation are not known, it is obvious that photodecarboxylation can be useful for the preparation of certain biaryls and alkylaryls (33). Thus 2,4,6-tri-*t*-butylbiphenyl (XVII) can be prepared according to Eq 4; *o*-di-*t*-butylbenzene from *o*-*t*-butylphenyl pivalate (33), *p*-cresylferrocene from *p*-cresyl ferrocenoate (34),ᵉtc.


XVII (17%)
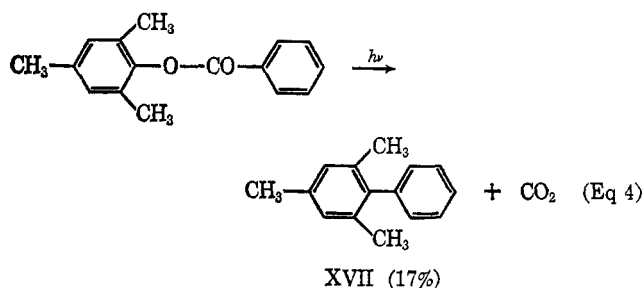
The last side reaction observed in the photolysis of phenyl esters is the formation of a carboxylic acid corresponding to the initial ester (Eq 5) (34, 49, 79). It is supposed (34) that an elimination reaction is involved analogous to the photolysis (20) and pyrolysis (67) of alkyl esters or vinyl esters (14) where acid and acetylene are formed.

R—CO—O—Ar ⟶ R—COOH + other products   (Eq 5)
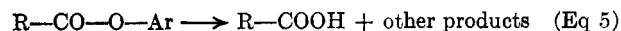
Extending this idea to the photolysis of aryl esters, formation of aryne intermediates has to be supposed; this is not absolutely absurd, as arynes are also produced photochemically in other systems (15–19, 43).

Many light-induced reactions between quinones (XVIII) and aldehydes (XIX) produce quinol monoesters (XX) and acylquinols (2,5-dihydroxyphenones, XXI) (44, 45, 71). Tetrasubstituted *p*-benzoquinones yield the corresponding quinol monoesters (55, 70, 76). It may be supposed that the formation of XX followed by a light-induced Fries rearrangement could be the normal path for all photoreactions of XVIII which yield XXI (Eq 6, steps a–c). In this case the work of

XVIII   XIX   XX   (Eq 6)
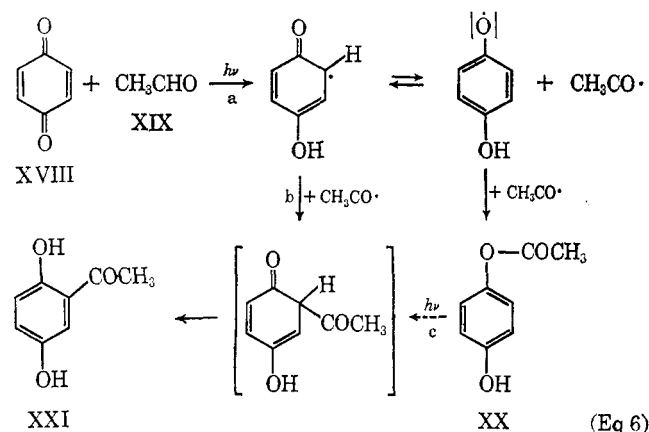
Klinger and Standke (44) would describe for the first time a reaction in which the photo Fries rearrangement occurs in a latent form. However, Bruce and Cutts (21, 22) have shown in a series of experiments involving irradiation of quinol monoacetate in acetaldehyde with or without benzoquinone that the photo Fries rearrangement (Eq 6, step c) does not contribute appreciably to formation of acetylquinol in the emission spectrum of a tungsten filament lamp or in the light from a medium-pressure mercury arc (Pyrex glass reactor).

B. POLYARYL ESTERS

The photochemical rearrangement of polyaryl esters is interesting from the practical (i) as well as from the theoretical (ii) point of view.

(i) The practical view makes possible the simple preparation of polymers with *o*- (*p*-) hydroxyphenone groups as part of the main (12, 52, 57) or side chain (57) which are, after the rearrangement of a certain number of ester groups, more resistant to further action of ultraviolet light ("self-stabilizing effect") and can be used as ultraviolet absorbers for other polymers (12).

(ii) Formation of *o*-hydroxyphenone structures with high absorptivity, noted for radiationless transformation of absorbed energy to heat, retards in a character-

TABLE I
PHOTOREARRANGEMENT OF ARYL ESTERS

No.	Ester of — Phenol	Ester of — Carboxylic acid	Hydroxyphenone, % yield[a] ortho	Hydroxyphenone, % yield[a] para	Phenol, % yield[a]	Other compounds, % yield[a]	Solvent[b]	Ref
				Monophenols and Monocarboxylic Acids				
1	Phenol	Formic	0	0	49	Polymer, 50	E	40
2		Acetic	+	+	+	+	E	4
			19	15	28	m-Hydroxyacetophenone, 0.3	E	5
3		Benzoic	20	28	14	—	E	5
			11	29	—	—	C	34
			13	23	—	—	D	34
			13	20	—	—	B	34
			47	42	12	—	E	40
4		p-Chlorobenzoic	49	6	—	—	C	34
			42	14	—	—	B	34
5		Salicylic	37	42	2	Polymer, 15	E	40
			+	—	—	—	AB	56
6		3,5-Di-t-butyl-4-hydroxybenzoic	+	—	—	—	I	27
7		Mesitoic	6	11	—	Mesitoic acid	H	34
			9	12	—	Mesitoic acid	B	34
8		Ferrocenoic	0	9	—	—	C	34
			0	44	—	—	C	34
9	p-Cresol	Benzoic	+	X	—	—	CH	12
			25	X	—	—	C	34
			20	X	—	—	D	34
			34	X	—	—	IP	34
			51	X	—	—	B	34
10		3,5-Di-t-butyl-4-hydroxybenzoic	+	X	—	—	I	27
11		Ferrocenoic	0	X	—	p-Cresylferrocene, 5; Ferrocenoic acid, 2	C	34
12	m-Cresol	3,5-Di-t-butyl-4-hydroxybenzoic	+	X	—	—	I	27
13	p-t-Butylphenol	Formic	0	X	80	Polymer, 12; 2,2'-Dihydroxy-5,5'-di-t-butylbiphenyl, 0.5	E	40
			9.4	X	73	Polymer, 11	B	40
14		Acetic	34	X	34	Polymer, 23	E	40
15		Benzoic	54	X	—	—	B	46
16		p-t-Butylbenzoic	60	X	—	—	B	46
17		p-Chlorobenzoic	72	X	—	—	B	46
			74	X	—	—	E	46
18		3,4-Dichlorobenzoic	58	X	—	—	B	46
19		p-Cyanobenzoic	71	X	—	—	B	46
20		p-Aminobenzoic	36	X	—	—	B	46
21		p-Nitrobenzoic	30	X	—	—	B	46
22		3,5-Dinitrobenzoic	10	X	—	—	B	46
23		1-Naphthoic	67	X	—	—	B	46
24		2-Furoic	30	X	—	—	B	46
25	p-Phenylphenol	3,5-Di-t-butyl-4-hydroxybenzoic	+	X	—	—	I	27
26	2,6-Dimethylphenol	Benzoic	X	33	—	—	IP	34
27	2,6-Diisopropylphenol	Benzoic	X	56	—	—	IP	34
28	3,5-Di-t-butylphenol	Acetic	+	0	88	3,5-Di-t-butyltoluene	B	33
29		Benzoic	29	0	42	3,5-Di-t-butylbiphenyl, 7; Benzoic acid, 4.7; Biphenyl, traces	B	33
30		p-Methoxybenzoic	16	0	36	p-Methoxybenzoic acid, 17; 3,5-Di-t-butyl-4'-methoxybiphenyl, 13	B	33
31	Mesitol	Benzoic	X	X	12	—	IP	34
			X	X	15	Phenylmesitylene, 17; Hydrocarbon $C_{18}H_{16}$, 5; Benzophenone, 1; Biphenyl, traces	B	33

TABLE I (Continued)

No.	Phenol	Carboxylic acid	Hydroxyphenone, % yield[a] ortho	para	Phenol, % yield[a]	Other compounds, % yield[a]	Solvent[b]	Ref
		─────Ester of─────						
32	4-Methyl-2-phenoxy-phenol	Acetic	16	×	—	Brown polymer	E	78
33	p-Chlorophenol	Benzoic	37	×	—	—	C	34
			29	×	—	—	IP	34
			51	×	—	—	B	34
34		3,5-Di-t-butyl-4-hydroxybenzoic	+	×	—	—	I	27
35	m-Chlorophenol	3,5-Di-t-butyl-4-hydroxybenzoic	+	—	—	—	I	27
36	2-Chloro-4-t-butyl-phenol	Benzoic	10; 31[c]	×	—	—	B	46
37	2,6-Dichloro-4-t-butylphenol	Benzoic	29[c]	×	—	—	B	46
38	3-Chloro-4,6-di-methoxyphenol	2-Methyl-4-hydroxy-6-methoxybenzoic	8	×	—	—	E	79
39	p-Cyanophenol	3,5-Di-t-butyl-4-hydroxybenzoic	+	×	—	—	I	27
40	m-Cyanophenol	3,5-Di-t-butyl-4-hydroxybenzoic	+	—	—	—	I	27
41	p-Nitrophenol	p-Nitrobenzoic	11	×	—	—	B	34
42	p-Carbethoxyphenol	3,5-Di-t-butyl-4-hydroxybenzoic	+	×	—	—	I	27
		Diphenols and Monocarboxylic Acids						
43	Pyrocatechol	Acetic (monoester)	22	18	46	—	E	4
44	Resorcinol	Benzoic (monoester)	+	?[d]	—	—	AB	56
			+	?[d]	—	—	CH	12
45	Hydroquinol	Acetic (monoester)	0	—	—	—	AC	22
46	2,2-Di(4-hydroxy-phenyl)propane	Benzoic	44[e]	×	+	Resin	B	52
		Monophenols and Dicarboxylic Acids						
47	Phenol	Oxalic	0	0	25	Polymer, 59	E	40
48	p-t-Butylphenol	Oxalic	0	0	49	Polymer, 46	E	40

[a] Always calculated on consumed ester = 100 minus recovered ester. [b] In this and further tables the following abbreviations will be used: E = ethanol, C = cyclohexane, D = dioxane, B = benzene, H = hexane, IP = isopropyl alcohol, CH = chloroform, I = isooctane, AB = sheet of cellulose acetate-butyrate, S = solid state, AC = acetaldehyde. [c] To the ortho position occupied by chlorine. [d] para position identical with ortho position. [e] 2-(3-Benzoyl-4-hydroxyphenyl)-2-(4-benzoxyphenyl)propane 4-mono-benzoate.

TABLE II

PHOTOARRANGEMENT OF ARYL ESTERS OF CARBONIC ACID

| No.	Carbonate	Product of rearrangement	Solvent	Yield,[a] %	Ref
1	Phenyl ethyl	Ethyl salicylate	Acetic acid	16	59
			Ethanol	17	
			Diethyl ether	8–10	
			Benzene, n-heptane	Traces	
		Ethyl p-hydroxybenzoate	Acetic acid	25	
			Ethanol	18	
			Diethyl ether	10	
			Benzene, n-heptane	Traces	
		Phenol	Acetic acid	7–8	
			Ethanol, diethyl ether	13	
		Polymer	Benzene, n-heptane	Main product	
2	Diphenyl	2,2'-Dihydroxybenzophenone	Ethanol	4	40
		2,4'-Dihydroxybenzophenone	Ethanol	11	
		Polymer	Ethanol	20	
3	Di(p-t-butylphenyl)	p-t-Butylphenyl(2-hydroxy-5-t-butyl)benzoate	Ethanol	2	40
			Benzene	No	
		2,2'-Dihydroxy-5,5'-di-t-butylbenzophenone	Ethanol	26	
			Benzene	36	
		2,2'-Dihydroxy-5,5'-di-t-butylbiphenyl	Ethanol	Traces	
			Benzene	No	
		Polymer	Ethanol	26	
			Benzene	15	

[a] On irradiated carbonate.

TABLE III

YIELDS OF PHENOLS UPON IRRADIATION OF EASILY
DECARBONYLATED ARYL ESTERS (9, 10)

No.	Aryl ester	Time of irradiation, hr	Material of irradiated vessel[a]	Phenol, %
1	2-Naphthyl benzoate	2	Q	4
2	2-Naphthyl o-iodobenzoate	4	Q	14
3	2-Naphthyl o-(phenylthiomethyl)benzoate	0, 5	Q	10
4	2-Naphthyl trichloroacetate	3	Q	22
5	2-Naphthyl triphenylacetate	1	Q	39
6	2-Naphthyl fluorene-9-carboxylate	4	P	60
7	p-Cresyl fluorene-9-carboxylate	2	Q	58
8	Guaiacyl fluorene-9-carboxylate	2	Q	58
9	2-Naphthyl xanthene-9-carboxylate	4	P	60

[a] Q = quartz, P = Pyrex.

istic way the photolytic cleavage of the polymer chain. This phenomenon has been investigated with poly(2,2′-propane-4-phenyl carbonate) (XXII), where from ultraviolet and infrared spectra and on the basis of products of alkaline hydrolysis (13) a gradual photo-rearrangement (Eq 7; $x > m > n =$ chain length) of polycarbonates (XXII) through a polymer with phenyl salicylate structures (XXIII) to a polymer containing 2,2′-dihydroxybenzophenone structures (XXIV) was established.

XXII

XXIII

XXIV
                  (Eq 7)
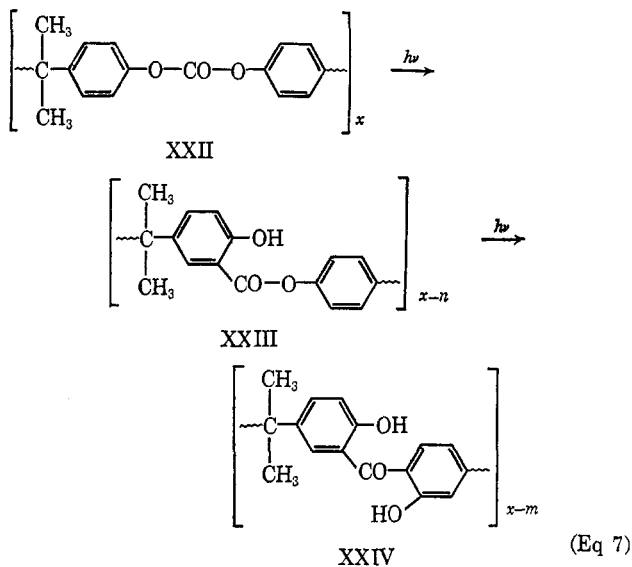
The incident quanta of polychromatic radiation are distributed among the absorbing structures. The relative probability that photons ($\lambda_1 < \lambda < \lambda_2$) will be absorbed by the jth-type group is

$$n_j \int_{\lambda_1}^{\lambda_2} \frac{\epsilon_j(\lambda)}{\sum_i n_i \epsilon_i(\lambda)}\, d\lambda$$

where ϵ_i is molar absorptivity at wavelength λ, and n_i is the concentration of the corresponding structure absorbing ultraviolet radiation. It is obvious that the rate of quantum absorption by carbonate structures will decrease since the numerator decreases only slightly whereas the denominator increases continuously.

The plot of the well-known dependence for the degradation process $(1/M_{n(t)}) - (1/M_{n(0)}) = kt$ (where $M_{n(0)}$ and $M_{n(t)}$ are the number molecular weights before and after irradiation in the time t; k is a constant) is curved in contradistinction to the photolysis of other random-scissioned polymers.

It can be supposed that the rearranged phenyl ester groups are statistically randomly distributed in the polymer chain. Spectral data of hypothetic polymers are not known so that the rearrangement can be interpreted only approximately by means of analogous structures of low molecular weight models. Maerov (52), investigating the rearrangement of a thin film of poly(4,4′-diphenylolpropane isophthalate), used the spectral data of 2,2′-bis(3-m-carboxybenzoyl-4-hydroxyphenyl)propane and observed the following rates of formation of o-hydroxybenzophenones: xenon lamp, rate $= 3.9 \times 10^{-2}$ mole l.$^{-1}$ hr^{-1}; carbon arc lamp, rate $= 3.8 \times 10^{-3}$ mole l.$^{-1}$ hr^{-1}; sunlight in April 1960, Florida, rate $= 1.5 \times 10^{-2}$ mole l.$^{-1}$ hr^{-1}. By titration of free carboxyl groups a photolysis rate of 9.5×10^{-3} mole l.$^{-1}$ hr^{-1} was determined, that is, 2.5 times more than the rate of photorearrangement with the same carbon arc lamp. Upon irradiation of the same thin layer with a high-pressure mercury arc having spectral bands in the range of 275–285 mμ the quantum yield $\varphi_{or} = 0.016$ was established (47). For interpretation, spectral data of 2,2′-bis(3-benzoyl-4-hydroxyphenyl) propane were used. The measured quantum yield is remarkably lower than those determined upon rearrangement of low molecular weight esters in solution.

A survey of hitherto irradiated polyesters is given in Table IV. In all irradiated polymers o-hydroxyphenone groups in rearranged repeat units and carboxylic and phenolic groups on the ends of scissioned repeat units act as chromophoric groups with a consequent shift of light absorption to higher wavelengths and yellowing of polyesters. Upon rearrangement in solution no cross-linking of polymers was observed in contradistinction to the ionic Fries rearrangement (12, 57).

C. MECHANISM OF THE REARRANGEMENT

The rearrangement is initiated by ultraviolet light in the absorption region of an ester or N-arylamide. The rate of rearrangement markedly decreases with time because the products of the rearrangement have a higher absorption, as a rule, in the effective region than the original ester. The nature of the solvent proved to be decisive in the rearrangement of phenyl esters of formic acid (40) and carbonic acid (40, 59). Quantum yields were determined only in two cases (46, 52).

Owing to a formal analogy to the Fries rearrangement, the photochemical rearrangement of phenyl esters is sometimes called the photo Fries rearrangement. In contradistinction to the ionic Fries rearrangement (53),

TABLE IV
PHOTOREARRANGEMENT OF POLYARYL ESTERS

No.	Polyaryl ester	ν_{ester} cm^{-1}	$\nu_{CO\cdots HO}$,[a] cm^{-1}	λ_{max}, mμ	Solvent[b]	Ref
1	Poly(p-cresyl acrylate)	1755	1640	350	D, S	57
2	Poly-2,2-propanebis(4-phenyl isophthalate coterephthalate)	1740	1635	350	D, S	57
3	Poly-2,2-propanebis(4-phenyl isophthalate)	—	1639	350	S	52
4	Poly(1,3-phenylene adipate)	1757	1638	322	CH	12
5	Poly-2,2-propanebis(4-phenyl adipate)	1756	1647	337	CH	12
6	Poly-2,2-propanebis(4-phenyl 3-thiapimelate)	1734	1656	335	CH	12
7	Poly-1,3-phenylene-co-2,2-propanebis(4-phenyl isophthalate) (70:30)	1752	1638	333	CH, KBr[c]	12
8	Poly-2,2-propanebis(4-phenyl carbonate)	1780	1635	355–362	CH, S, D	13

[a] After rearrangement. [b] See Table I for abbreviations. [c] In KBr pellet.

it is supposed that the photochemical rearrangement of phenyl esters proceeds intramolecularly *via* a radical mechanism. The intramolecular character of the rearrangement was proved by an experiment in which an equimolar mixture of phenyl *p*-chlorobenzoate and *p*-chlorophenyl benzoate (34) was irradiated. From the reaction mixture only monochlorohydroxybenzophenones were isolated as products of intramolecular rearrangement. Neither dichlorinated "crossover" nor unchlorinated products could be detected.

There are two opinions about the proper mechanism of photorearrangements. Anderson and Reese (5) presume that the photorearrangement of phenyl esters proceeds through bicyclic diradical intermediate products XXV and XXVI. From these, dienones result which upon enolization give aromatic *o*- and *p*-hydroxy


XXV   XXVI
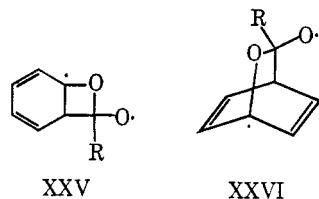
ketones, respectively. An intermediate product to XXV, except for being a dipole instead of diradical, has been supposed (2) in the pyrolytic rearrangement of vinyl benzoate to benzoylacetaldehyde. Although structures XXV and XXVI can not be rejected, at present preference is given to the mechanism according to Kobsa which will be described later. The photorearrangement of esters of 2-naphthol could provide clearer evidence of the validity of this rearrangement mechanism through structures XXV and XXVI. It is difficult to imagine eventual formation of 6-hydroxy-2-naphthophenones through an intermediate bridge structure of type VI between the amphi positions of naphthalene.

According to the view of Kobsa (46) the rearrangement starts with a photodissociation of the ester into a pair of radicals (acyl-oxygen fission). It should be emphasized that hitherto there is no information on the multiplicity of the excited state of phenyl esters; also lacking are data on the influence of wavelength and

sensitizers (22) on the rearrangement. It is supposed that upon absorption of a light quantum a molecule of the ester XXVII dissociates (Eq 8) with quantum yield φ_d to an acyl radical (XXVIII) and a phenoxy radical (XXIX) which can exist in resonance structures XXIX, XXX, and XXXI.

XXVII
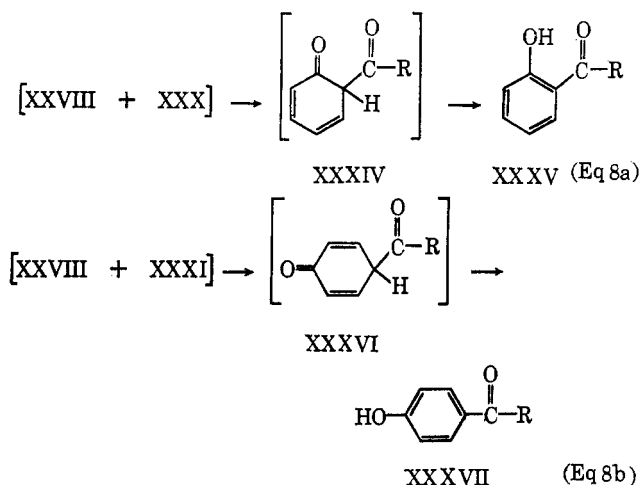

XXVIII   XXIX   XXX   XXXI   (Eq 8)
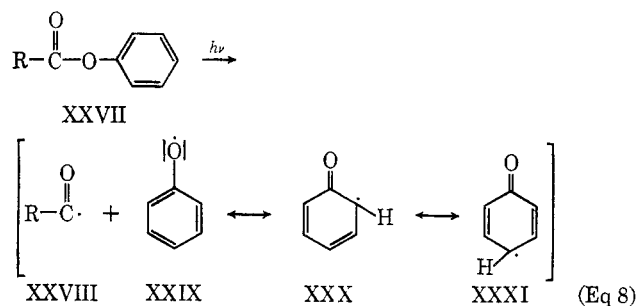
The formation of acyl radicals, analogous to XXVIII, had been often supposed in related photolytic reactions (72, 73) and was recently proved by the esr method in the photolysis of acyl bromides at 77°K (74). In the photorearrangement of alkyl aryl carbonates the primary process of photohomolysis (Eq 8) and the formation of alkoxycarbonyl radicals (XXXII) instead of XXVIII is supposed (59). In order to rigorously
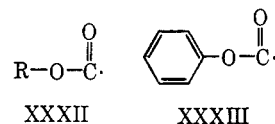
XXXII   XXXIII

explain the photorearrangement of compounds 2 and 3 from Table II according to Kobsa's scheme, the formation of aryloxycarbonyl (XXXIII) radicals has to be supposed, analogous to the primary step of the sequential rearrangement of carbonate → phenyl salicylate → 2,2'-dihydroxybenzophenone. In this article, when the reaction of acyl radicals is discussed, XXXII and XXXIII also might be understood in special cases of the rearrangement of aryl carbonates. The formation of alkoxycarbonyl radicals upon photolysis of similar compounds is supposed by several authors (7, 20, 58, 60).

Radicals XXVIII and XXIX, enclosed in the solvent cage, recombine upon collision either to form the

original molecule of ester, or the acyl radical recombines with the radical XXX in quantum yield φ_{or} with the formation of a 2-acyl-3,5-cyclohexadienone (XXXIV), followed by isomerization to a 2-hydroxyphenone (XXXV). Analogously, the formation of 4-hydroxyphenones (XXXVII) is supposed in quantum yield φ_{pr}.

$$[\text{XXVIII} + \text{XXX}] \rightarrow \left[\text{XXXIV} \right] \rightarrow \text{XXXV} \quad (\text{Eq 8a})$$

$$[\text{XXVIII} + \text{XXXI}] \rightarrow \left[\text{XXXVI} \right] \rightarrow$$

$$\text{XXXVII} \quad (\text{Eq 8b})$$

If radicals diffuse from the solvent cage, separated products are formed. From phenoxy radicals abstraction of hydrogen from the solvent results most probably in a phenol which could be always observed in products of photolysis of phenyl esters in solution. In certain investigations formation of phenoxy radicals was traced by photochemical methods (51, 69, 84), but the behavior of the phenoxy radical is not described in detail in these papers. The fate of the free acyl radical is not known. Most probably it is a constituent of a polymer deposit on the wall of the irradiated vessel which hitherto could not be identified closer (46). Upon irradiation of mesityl benzoate in benzene, the formation of benzophenone with a 1% yield was observed (33). However, it is hard to judge from this experiment whether the interaction of the benzoyl radical with the solvent or recombination of the benzoyl radical with the phenyl radical resulting from decarbonylation of another benzoyl radical was involved.

With p-t-butylphenyl benzoate a decrease in the quantum yield of phenyl ester to $\varphi_{d,obsd} = 0.65$ was observed (46). The primary quantum yield of photodissociation of these phenyl esters, φ_d, has to be considered higher than 0.65, owing to the validity of Eq 9 where $\varphi_{d,obsd}$ is the observed quantum yield of ester decrease, k_{or} and k_{pr} are the rate constants of rearrangement respectively to the *ortho* or *para* position, k_{df} is the rate constant of formation of free phenol (diffusion from the cage), and k_{rec} is the rate constant of reverse recombination, the magnitude of which is certainly greater or very close to the sum of k_{or} and k_{pr}. This is in accordance with the total absence of fluorescence or phosphorescence in solutions of these esters (45).

$$\varphi_{d,obsd} = \varphi_d \frac{k_{or} + k_{pr} + k_{df}}{k_{or} + k_{pr} + k_{df} + k_{rec}} \quad (\text{Eq 9})$$

Kobsa (46) tried to correlate for different derivatives of p-t-butylphenyl benzoate, substituted in position 4 of the benzoyl moiety, the rate constant of formation of o-hydroxybenzophenone, k_{or}, with values of σ. He calculated k_{or} from Eq 10 where α is the fraction of the consumed ester converted to o-hydroxybenzophenone.

$$k_{or} = k_{df} \frac{\alpha}{1 - \alpha} \quad (\text{Eq 10})$$

$$\log \frac{\alpha}{1 - \alpha} = 0.105 + 0.391\sigma \quad (\text{Eq 11})$$

He obtained Eq 11 with a standard deviation of $s = \pm 0.142$, and correlation coefficient $r = 0.828$. When calculating the regression curve he applied the method of Jaffé (41). The relatively high value of the standard deviation probably reflects variations of k_{df} for different esters which was considered constant in the calculation.

Both in Anderson and Reese's and in Kobsa's scheme the formation of intermediate dienones XXXIV and XXXVI is supposed. Up to this time no evidence of their real existence was obtained, not even upon irradiation of mesityl benzoate (34). In this latter case dienones, should they appear, could not isomerize. The only products obtained by this reaction were mesitol and the initial ester.

The rate of photorearrangement markedly decreases with time. o- and p-hydroxyphenones, in most cases the main products of the rearrangement, show greater absorption in the ultraviolet region of the spectrum than the initial ester and they are photochemically exceptionally stable. With 2-hydroxyphenones no fluorescent or phosphorescent spectra appear even at room temperature or in solid solutions. In these compounds there occurs a transformation process of absorbed energy to heat, consisting of transition from the excited singlet state, having a π–π^* character, to the ground state. This transition is preferred to other transitions (11). Pitts (63) and Hammond (38) deduce from the analogy to proved photoenolization of 2-alkylbenzophenones (81, 83) that in the excited state a fast reversible photoenolization of 2-hydroxybenzophenones sets in, whereby the absorbed energy is radiationlessly dissipated. The inactivity and stability of the 2-hydroxyphenones can, for example, be explained also by low quantum yields of their photopinacolization (10^{-3}–10^{-4}) (11) and by their resistance to photodestruction (62, 80). Although with 4-hydroxyphenones in solid solution a strong phosphorescence occurs, they are also photochemically stable (11, 63). The unreactivity of their excited state entails charge transfer from the electron donor OH group to the electron acceptor C=O group (36, 64–66).

TABLE V

PHOTOREARRANGEMENT OF VINYL AND SUBSTITUTED VINYL ESTERS

| No.	Ester	Product of rearrangement, % yield	By-product, % yield	Solvent	Ref
1	Vinyl benzoate	Acetophenone, 4	Benzoic acid, 15	D, SSB[a]	32
		Benzoylacetaldehyde, 6	—	B	32
		Acetophenone, traces			
2	Isopropenyl benzoate	Benzoylacetone, ?[b]	—	C	31
3	Cyclohexen-1-yl benzoate	—	1-Benzoylhex-5-en-2-one,?[b]	C	31
4	6-Methylcyclohexen-1-yl benzoate	—	1-Benzoyl-3-methylhex-5-en-2-one, ?	C	31
5	Others (various steroid vinyl acetates and benzoates)			C	31, 37, 82

[a] Skellysolve B. [b] Yield of products and by-products upon rearrangement of compounds 2, 3, and 4 indicated only generally as 10–30%.

Derivatives of 2-hydroxyphenones, particularly of 2-hydroxybenzophenones, are largely used as ultraviolet absorbers for plastics (25, 26, 39), dyes (35), textiles (77), varnishes (61), etc. because of their high absorption capacity and photochemical stability.

Phenols, the third main product of the rearrangement, in an inert medium are also relatively stable against further effects of ultraviolet radiation.

### III. VINYL AND SUBSTITUTED VINYL ESTERS

There is relatively little information on the photo-initiated rearrangement of vinyl esters (Table V). β-Dicarbonyl compounds are products of such a rearrangement (Eq 12, step b), in contrast to products of rearrangement of phenyl esters sensitive to the effects of ultraviolet light, and their further fate depends on the character of the solvent, as can be demonstrated from the photolysis of vinyl benzoate (XXXVIII) (32).


traces XXXIX   (Eq 12)
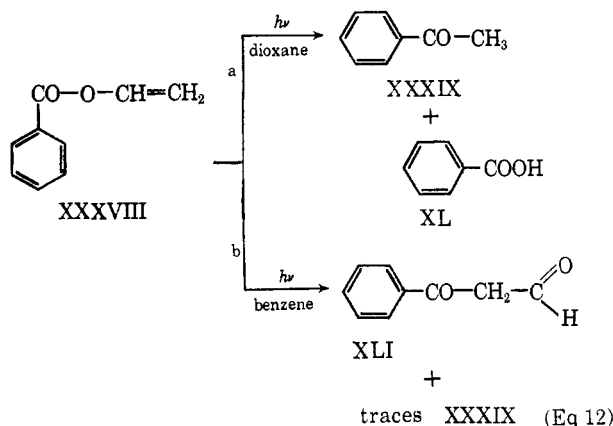
An analogous behavior was discussed in connection with the rearrangement of phenyl formate (VI). Benzoylacetaldehyde (XLI), the primary product of the rearrangement, decarbonylates in transparent solvents with the formation of acetophenone (XXXIX). Photochemical decarbonylation of aldehydes is a well-known process (1, 23). XXXIX, XL, and XLI result also from the thermal rearrangement of XXXVIII (2, 68).

The mechanism of the rearrangement is similar to that of the rearrangement of phenyl esters (Eq 8, 8a,

and 8b where the phenoxy radical is replaced by a vinyloxy radical in two resonance structures XLII and XLIII).

$$\cdot O{-}CH{=}CH_2 \longleftrightarrow O{=}CH{-}CH_2\cdot$$

XLII   XLIII
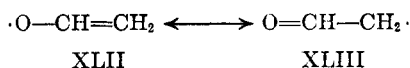
A different mechanism is supposed in the rearrangement of cyclic vinyl esters (XLIV, R = H or CH₃) where the ring is opened (31). It is supposed that in


XLVI   (Eq 13)
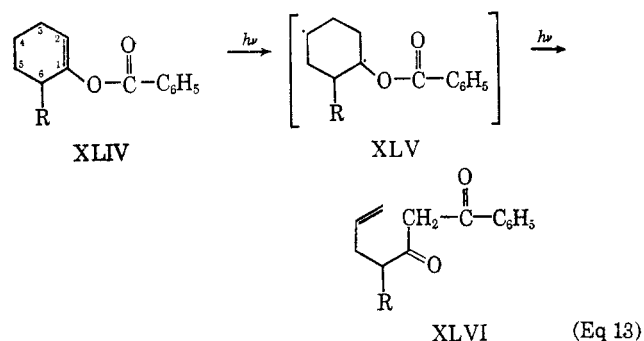
the excited state a hydrogen atom is shifted from position 4 to 2, followed by cleavage of the C_2-C_3 bond. Only then does the excited system dissociate into a pair of radicals giving, upon recombination, α-benzoyl ketone. According to the "normal" rearrangement mechanism, α-benzoylcyclohexanone (XLVII) should have resulted from the rearrangement of XLIV. However, upon irradiation of XLVII no XLVI was obtained, which excluded its presence in the rearrangement according to Eq 13 (31). XLVII results, however, from the pyrolysis of XLIV (3).
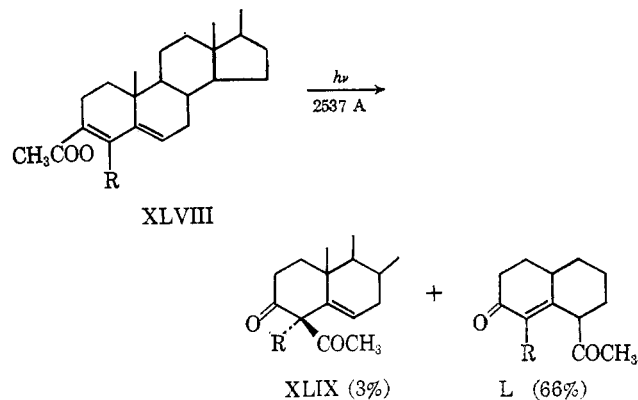
Upon irradiation of steroid vinyl benzoates and vinyl acetates with monochromatic light no cleavage of the ring was observed (31, 82). The acetate of type XLVIII (R = H or CH$_3$) rearranges to XLIX and L, representing thus far the only example of a rearrangement to the second conjugated double linkage in an aliphatic system (37).

IV. N-ARYLAMIDES

It was established by Elad (29) that upon photolysis of N-arylamides (LI) of carboxylic acids a migration of acyl groups to the *ortho* and *para* positions (LII and LIII) of the aromatic moiety with simultaneous formation of free aniline (LIV) takes place. Whereas from
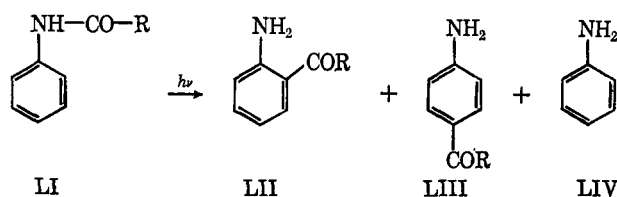

the rearrangement of N-acylanilides catalyzed by aluminum chloride, LIII and only traces of LII result (6, 28, 50), the distribution of *ortho* and *para* products from the photoinitiated rearrangement is almost identical (Table VI).

TABLE VI
PHOTOREARRANGEMENT OF N-ACYLANILIDES

No.	Anilide	Aminophenone, % yield, ortho	para	Aniline, % yield	Solvent	Ref
1	Acetanilide	14	12	6	E	30[b]
		20	25	18	E	29[b]
2	Propionanilide	13	10	7	E	30
		22	25	17	E	29
3	Butyranilide	17	23	20	E	29
4	Benzanilide	14	22	Traces[a]	E	30

[a] Benzoic acid with a yield of 27% was isolated. [b] In all experiments according to ref 30 a 550-w high-pressure Hanovia mercury arc and 3-day irradiation periods were used; in ref 29 a Hanau Q-81 high-pressure mercury arc and 8-18-hr irradiation periods were used.

The mechanism of the rearrangment is presumably the same as that for phenyl esters (Eq 8), where the phenoxy radical is replaced by an aniline radical in three resonance structures LV, LVI, and LVII, though certain preliminary experiments show that the mechanism is probably much more complex (29, 30).
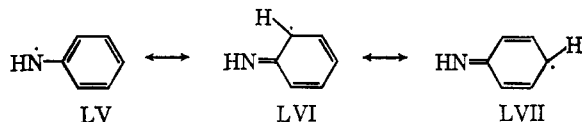
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