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Rearrangement of Aromatic Esters by Ultraviolet Radiation

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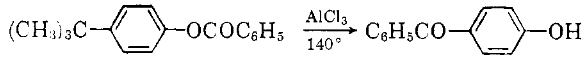
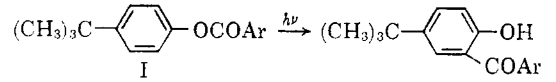
Twelve different substituted phenyl aromatic esters were converted to *o*-hydroxybenzophenones in yields up to 55% by irradiation with ultraviolet light (245–330 mμ) in benzene or ethanol solution. The high quantum yields, $\phi_{ester} \cong 0.65$, give this reaction preparative value for the synthesis of some otherwise difficultly accessible *o*-hydroxybenzophenones. It is shown that the photochemical rearrangement proceeds by a different mechanism and frequently leads to different products than the Fries rearrangement. A free radical mechanism is proposed.

Some time ago, we observed that irradiation of *p*-*t*-butylphenyl benzoate in benzene or ethanol solution with ultraviolet light of 245–330-mμ wave length gave good yields of 2-hydroxy-5-*t*-butylbenzophenone. This reaction was of considerable interest both as a preparative method and for its theoretical implications, since our previous attempts at preparing various 2-hydroxy-5-*t*-butyl substituted benzophenone derivatives by the Fries rearrangement of the corresponding esters had been largely unsuccessful: The aluminum chloride-catalyzed rearrangement always resulted in complex reaction mixtures in which the 4-hydroxybenzophenone derivative obtained by elimination of the *t*-butyl group predominated, *e.g.*



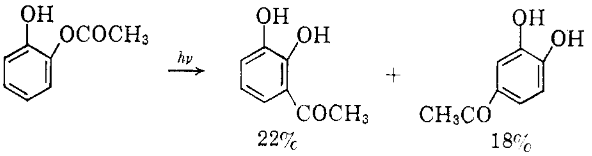
In the light-catalyzed rearrangement, however, no loss of *t*-butyl groups occurred and the only benzophenone derivatives formed were those resulting from the migration of the acyl group into the *ortho* position.



I II (1)

This suggested a fundamental difference in reaction mechanism between the light-catalyzed rearrangement and the Fries rearrangement. Our objectives in this work were to (1) determine the scope and the limitations of the light-catalyzed rearrangement of aryl esters and (2) cast some light on the mechanism of this reaction.

After this work was essentially completed, Anderson and Reese[1] reported that irradiation of catechol monoacetate in alcoholic solution with ultraviolet light leads to the formation of a mixture of dihydroxyacetophenones.



Similarly, phenyl acetate was found to give a mixture of *o*- and *p*-hydroxyacetophenone.

Results and Discussion

In order to explore the scope of the light-catalyzed rearrangement, we first prepared a series of *p*-*t*-butylphenyl esters of various substituted benzoic acids as well as α-naphthoic acid and α-furoic acid. These esters were irradiated in benzene solution with ultraviolet light of 245–330-mμ wave length. The reaction mixtures were separated by chromatographic techniques and quantitatively analyzed for unchanged starting material and for the 2-hydroxy-5-*t*-butylbenzophenone formed according to reac-

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[1] J. D. Anderson and C. R. Reese, *Proc. Chem. Soc.* (London), 217 (1960).

TABLE I

YIELDS OF 2-HYDROXY-5-*t*-BUTYLBENZOPHENONES (II) FROM IRRADIATION OF *p*-*t*-BUTYLPHENYL ESTERS (I)[a]

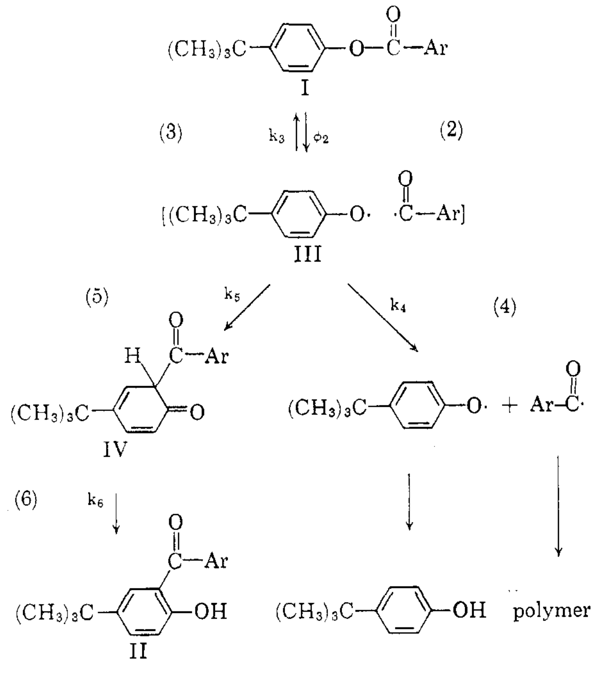
Ar	Incident energy (Einstein)	% recovered starting material	% conversion	% yield
Phenyl	0.316	17	54	45
p-*t*-Butylphenyl	.336	21	60	48
p-Chlorophenyl	.336	29	68	48
p-Chlorophenyl	1.14	24	72	55
p-Chlorophenyl[b]	0.592	35	74	48
3,4-Dichlorophenyl	.285	37	58	37
p-Cyanophenyl[c]	.307	32	71	48
p-Aminophenyl[d]	.269	67	36	12
p-Nitrophenyl	.900	67	30	10
3,5-Dinitrophenyl	.269	32	10	7
α-Naphthyl	.325	34	67	44
α-Furyl	.316	69	30	9

[a] Unless otherwise noted, all experiments were carried out with 0.05 molar solutions in benzene. [b] In ethanol. [c] 0.02 molar solution. [d] 0.04 molar solution.

tion 1. The results are summarized in Table I. From a preparative point of view, reaction 1 was found to be quite satisfactory in all cases where the Ar group was either an unsubstituted aromatic residue or a phenyl ring substituted with alkyl, halogen, or cyano groups. Yields were much lower with amino or nitro groups or when the aryl group was a furane ring. In the case of the nitro compounds, complex reaction mixtures were formed and it appears quite likely that photochemical reactions involving the nitro groups were taking place independently of and in competition with reaction 1.

We propose to show that these and other results to be presented below are consistent with the following reaction mechanism.

Upon absorption of a light quantum, the ester molecule (I) dissociates (reaction 2) with a quantum yield ϕ_2 into a pair of radicals (III). These two radicals are formed in a solvent cage and will tend to remain in close proximity to each other for a sufficient length of time to permit a large number of collisions between them. These collisions can either lead to a reversal of the dissociation reaction (reaction 3) or to addition of the aroyl radical to one of the *ortho* positions of the phenoxy radical (reaction 5) resulting in the formation of the cyclohexadienone (IV), which will eventually rearrange (reaction 6) to the *o*-hydroxybenzophenone (II). Alternatively, the radicals may escape from the solvent cage (reaction 4) and diffuse to give separate products. The *p*-*t*-butylphenoxy radical is most likely to wind up as *p*-*t*-butylphenol, and this compound has indeed been isolated from all irradiated samples in amounts sufficient to account, together with recovered starting material and the hydroxybenzophenone produced in the reaction, for substantially 100% of the *p*-*t*-butylphenol residues in the charge. The fate of the aroyl radicals, on the other hand, is not known. All attempts at isolation of additional products failed, although trace amounts of aromatic aldehydes were detected by their odor. Most likely, the aroyl radicals were the precursors of the polymeric deposits which were found to build up on the front surface of the irradiation vessel. However, attempts to characterize these polymeric deposits did not yield satisfactory results, presumably because of extensive secondary photochemical decomposition.



The quantum yield for the disappearance of starting material was measured in a number of cases and found to be approximately 0.65. The primary quantum yield must be larger than that if the back reaction 3 occurs at all.

$$-\phi_{\text{ester}} = \phi_2 \frac{k_4 + k_5}{k_3 + k_4 + k_5}$$

If, as we believe, k_3 is as large as or larger than k_4, ϕ_2 must be very close to unity. This is consistent with the total absence of fluorescence or phosphorescence in solutions of these esters. If the sequence of events depicted by equation 2 were very fast, no measurable emission from the excited state (or states) could occur.

In those cases, where the irradiation was carried out in benzene solution, a certain fraction of the light was undoubtedly absorbed by the solvent rather than the solute. However, examination of the ultraviolet absorption spectra revealed that this fraction became appreciable only for wave lengths less than about 270 mμ. Since the emission of our light source was relatively weak at these shorter wave lengths, the portion of the incident light which was absorbed by the solvent was only a minor fraction of the total intensity. Moreover, in the relatively concentrated solutions which were investigated in this work, energy transfer from the solvent to the solute is likely to be very efficient so that it may be assumed that light absorbed by the solvent

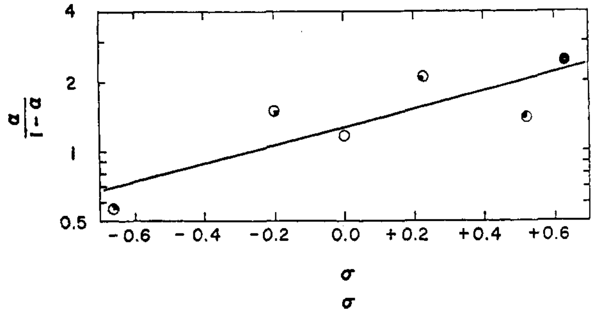


Fig. 1.— $\frac{\alpha}{1-\alpha}$ *vs.* σ for the photorearrangement of *p-t*-butylphenyl esters: ○, benzoate; ◔, *p*-aminobenzoate; ◑, *p-t*-butylbenzoate; ◐, *p*-chlorobenzoate; ◕, 3,4-dichlorobenzoate; ●, *p*-cyanobenzoate.

contributed to the photorearrangement of the solute. Indeed, quantum yields measured in benzene and ethanol solution were found to be almost equal within the limits of error.

In order to simplify the analysis of our data, we assumed that the rate constant k_4 would be sensibly the same for all compounds under consideration. While this is certainly not strictly true, the variations should be relatively minor, at least when comparing the effects of various substituent groups of small size.

Designating the fraction of consumed starting material converted to the *o*-hydroxybenzophenone (II) by α, we obtain $k_5 = k_4 \frac{\alpha}{1-\alpha}$. If, as we assumed, k_4 is a constant, the Hammett equation should be applicable and therefore

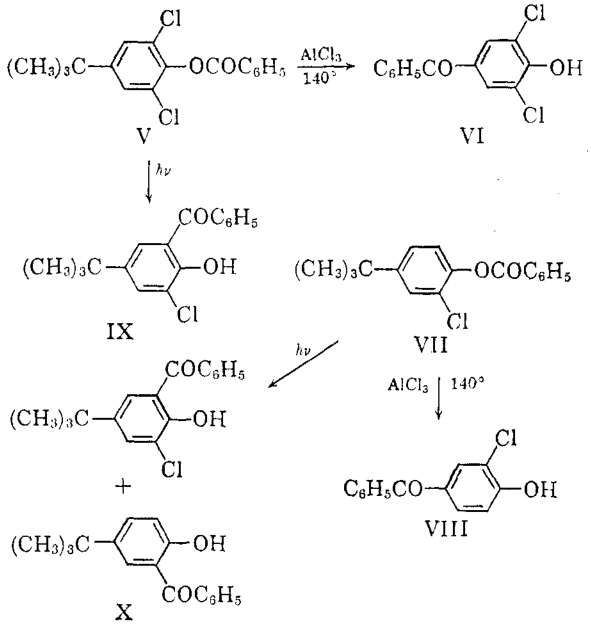
$$\log \frac{\alpha}{1-\alpha} = \text{const.} + \sigma\rho \qquad (7)$$

Figure 1 shows a plot of equation 7 based on the data in Table I. The nitro compounds were excluded for the reasons given above. Further, the α-naphthoate and the α-furoate had to be omitted since the Hammett equation does not apply to these compounds. The values used in plotting Fig. 1 were those given by Jaffé.[2] The regression

$$\log \frac{\alpha}{1-\alpha} = 0.105 + 0.391\ \sigma \qquad (8)$$

line was computed by Jaffé's procedure (standard deviation: $s = \pm 0.142$; correlation coefficient $r = 0.828$). The calculated value of +0.39 for ρ is not unreasonable for reaction 5. Jaffé lists two reactions in which aroyl radicals are being *formed* (reactions no. 189 and 190 in Table II, *loc. cit.*); these have ρ values of −0.488 and −1.668, respectively. In reaction 5, aroyl radicals are being *consumed;* moreover, the activation energy for this reaction is certainly very small. It follows that a small, positive value of ρ would be expected. The relatively large value of the standard deviation probably reflects variations in k_4 as well as experimental errors.

In order to establish further the fundamental difference between the mechanism of the Fries reaction and the mechanism of reaction 1, we next turned to an ester in which the two *ortho* positions in the phenolic part had been substituted with chlorine. It is well known that alkyl substituents do not block the Fries rearrangement. Blatt[3] lists numerous examples of the successful application of the Fries reaction to 2,4,6-trisubstituted phenols; these reactions proceed with elimination of an alkyl group. In our experience, elimination of a *p-t*-butyl group may occur even when free *ortho* positions are available and some examples for such rearrangements are given in this paper. On the other hand, we are not aware of a single case where a Fries rearrangement has been reported to proceed with elimination of a chlorine substituent. Therefore, it was not at all surprising that treatment of the ester (V) with aluminum chloride at 140° resulted in elimination of the *t*-butyl group and gave the *p*-hydroxybenzophenone (VI) as the sole isolated reaction product. Even the monochloro ester (VII) with one free *ortho* position rearranged largely in this fashion: The *p*-hydroxybenzophenone (VIII) was the major product. However, in the light-catalyzed rearrangement, the reaction took an entirely different course. Here chlorine substituents were eliminated with comparative ease whereas no products resulting from migration of the acyl group into the *para* position with concomitant elimination of the *t*-butyl group could be detected. The detailed results are presented in Table II.



We believe that the photorearrangement of compounds V and VII takes exactly the same course as

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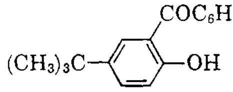
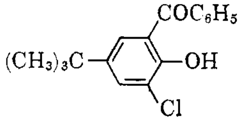
[2] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

[3] A. H. Blatt, *Org. Reactions*, **1**, 342 (1942).

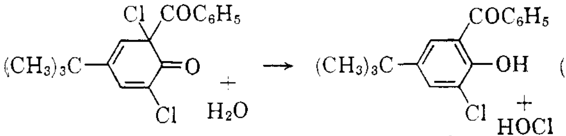
TABLE II

YIELDS OF HYDROXYBENZOPHENONES FROM BENZOATES OF CHLORINE-SUBSTITUTED PHENOLS[a]

Phenol	Incident energy (Einstein)	% recovered starting material				
			% conv.	% yield	% conv.	% yield
p-*t*-Butylphenol	0.316	17	54	45	..	..
2-Chloro-4-*t*-butylphenol	0.467	31	31	21	10	7
2,6-Dichloro-4-*t*-butylphenol	1.27	60	..	..	29	12

[a] All experiments were carried out with 0.05 molar solutions in benzene. The reported results are typical of a large number of runs.

that of compounds I, except that reaction 6 is replaced by reactions such as



XI XII (9)

or

$$\text{XI} + \text{RH}_2 \longrightarrow \text{XII} + \text{R} + \text{HCl} \qquad (10)$$

where RH_2 is a reducing agent. While we were unable to isolate XI in pure form because of the very unstable nature of this compound, we succeeded in obtaining considerable circumstantial evidence for both reactions 9 and 10 by carrying out appropriate experiments with freshly irradiated solutions of V.

The results of the irradiation of these esters of chlorine-substituted phenols provided a further check on the kinetic scheme proposed above. In the photochemical rearrangement of *p*-*t*-butylphenyl benzoate, we can write

$$k_5 = 2k_H$$

since there are two equivalent unsubstituted *ortho* positions to which the benzoyl radical may attach itself. Therefore,

$$\frac{2k_H}{k_4} = \frac{\alpha}{1 - \alpha} = 1.17$$

$$k_H = 0.59\ k_4$$

Similarly, in the photorearrangement of V

$$k_5 = 2k_{Cl}$$

or

$$\frac{2k_{Cl}}{k_4} = 0.40$$

$$k_{Cl} = 0.20\ k_4$$

These results can now be used to predict the results from the photorearrangement of VII. Conversion to IX should be

$$\frac{k_H}{k_H + k_{Cl} + k_4} = 0.33$$

and conversion to X

$$\frac{k_{Cl}}{k_H + k_{Cl} + k_4} = 0.11$$

This is in very good agreement with the experimental values of 0.31 and 0.10, respectively.

It will be interesting to find out what effects *o*-substituents other than chlorine have on the rate of the addition reaction 5.

Experimental

Preparation of Esters.—Most esters were prepared by reacting equimolar portions of acid chloride and *p*-*t*-butylphenol in pyridine. The reaction mixture was diluted with water, the ester filtered, dried, and recrystallized from alcohol until no further improvement in melting point was observed. Benzoyl chloride, *p*-nitrobenzoyl chloride, 3,5-dinitrobenzoyl chloride, 1-naphthoyl chloride, and furoyl chloride were Eastman reagent grade. *p*-*t*-Butylbenzoyl chloride, *p*-chlorobenzoyl chloride, 3,4-dichlorobenzoyl chloride, and *p*-cyanobenzoyl chloride were synthesized from the corresponding acids by reaction with thionyl chloride in the presence of catalytic amounts of *N*,*N*-dimethylformamide.[4]

p-*t*-Butylphenyl *p*-aminobenzoate was prepared by catalytic reduction of *p*-*t*-butylphenyl *p*-nitrobenzoate in the presence of Raney nickel using absolute ethyl alcohol as the solvent. The ester was separated from the catalyst residues and precipitated from acetone solution as the hydrochloride. The hydrochloride was recrystallized from tetrahydrofuran and reconverted to the free base.

As a final purification step, all esters were chromatographed on a 400 × 50 mm. column of aluminum oxide (Woelm), neutral, activity grade I. Petroleum ether was used as the eluent whenever possible, but with some of the more highly substituted esters it was necessary to add various amounts of benzene to achieve solubility. This procedure was frequently found to raise the melting point.

Irradiation Procedure.—A specially designed 3000-watt mercury arc manufactured by the Hanovia Chemical and Manufacturing Co. was employed as the light source. The arc was surrounded by a double-walled quartz jacket through which an aqueous solution containing 600 g./l. of nickel sulfate hexahydrate and 100 g./l. of copper sulfate heptahydrate was pumped. This filter solution removed radiation outside the wave length region 245–330 mμ. Preliminary studies had shown that all wave lengths within this region are photochemically active. Radiation of longer wave length is not sufficiently absorbed by some of the esters. The solutions of the esters were contained in large square-cross-section quartz cells which were accurately positioned along-

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[4] British Patent 820.444 [*Chem. Abstr.*, **54**, 16371f (1960)].

TABLE III

ANALYTICAL DATA FOR SUBSTITUTED BENZOPHENONES PREPARED BY PHOTOREARRANGEMENT OF ESTERS

		Calcd. Found				
Compound	M.p.	C	H	Cl	N	Mol. wt.[b]
5-*t*-Butyl-2-hydroxybenzophenone	67	80.3	7.13			
		80.0	7.10			
5,4′-Di-*t*-butyl-2-hydroxybenzophenone	Oil[a]	81.3	8.44			
		81.4	8.48			
5-*t*-Butyl-2-hydroxy-4′-chlorobenzophenone	92–94	70.7	5.94	12.3		
		70.3	5.93	12.1		
5-*t*-Butyl-2-hydroxy-3′,4′-dichlorobenzophenone	110–111	63.2	4.99	21.9		
		63.1	5.11	21.6		
5-*t*-Butyl-2-hydroxy-4′-cyanobenzophenone	103–104	77.4	6.14		5.02	
		77.3	6.29		4.90	
5-*t*-Butyl-2-hydroxy-4′-nitrobenzophenone	102–103	68.2	5.73		4.68	
		68.2	5.90		4.68	
5-*t*-Butyl-2-hydroxy-3′,5′-dinitrobenzophenone	133–134	59.3	4.68		8.14	
		59.2	4.70		8.18	
5-*t*-Butyl-2-hydroxy-4′-aminobenzophenone	98–100	75.8	7.11		5.20	
		75.3	7.18		4.90	
—Hydrochloride				11.6	4.58	
				10.9	4.65	
5-*t*-Butyl-2-hydroxyphenyl 1-naphthyl ketone	104–105	82.9	6.62			304.4
		82.5	6.64			308.0
5-*t*-Butyl-2-hydroxyphenyl 2-furyl ketone	68–69	73.8	6.60			244.3
		73.8	6.86			239.0
5-*t*-Butyl-3-chloro-2-hydroxybenzophenone	55–59	70.7	5.93	12.3		
		70.3	5.98	12.7		

[a] B.p. 150° at 2×10^{-3} mm. [b] Cryoscopic in benzene.

side the arc. The whole assembly was submerged in a water thermostat maintained at 30.00 ± 0.05°.

The light intensity incident on the samples was monitored by a calibrated Eppley thermopile connected to a Liston-Becker Model 14 breaker amplifier the output of which was fed to a strip-chart recorder. An automatic shutter in front of the thermopile eliminated drift effects.

In all preparative work, the ester (usually 0.05 mole) was dissolved in 1 l. of dry, thiophene-free benzene or absolute ethyl alcohol. The solution was placed in the cell and dissolved oxygen was removed by bubbling a slow stream of pure, dry nitrogen through the solution. This also served to keep the solution stirred during irradiation. Irradiation was started by opening a shutter and stopped after the desired number of quanta had been absorbed by the solution.

For kinetic measurements, more dilute solutions (0.01 molar) were employed. Small samples were withdrawn from time to time and analyzed by ultraviolet spectroscopy.

Isolation of Products.—After irradiation, the solvent was evaporated in a slow stream of air at room temperature and the crude mixture chromatographed on a 400 × 50 mm. column of aluminum oxide (Woelm), neutral, activity grade III. In general, unchanged starting material was eluted with a mixture of 1 part benzene and 4 parts petroleum ether. The hydroxyphenone was then obtained by switching to pure benzene or ethyl ether. A third fraction consisting of *p*-*t*-butylphenol came off the column either before or behind the hydroxyphenone. Representative examples are given below.

5-*t*-Butyl-2-hydroxybenzophenone.—A solution of 12.72 g. (0.05 mole) of *p*-*t*-butylphenyl benzoate in benzene was irradiated with 0.316 Einstein, and worked up as described above. Elution with 3 l. of benzene–petroleum ether (1:4) gave 2.10 g. of white crystals which were identified as unchanged starting material by their infrared spectrum, melting point, and mixed melting point with an authentic sample (m.p. 82–83°). Further elution with ethyl ether yielded 5.78 g. of a yellow material which, after distillation had a melting point of 67° compared with a literature value[5] of 67–68° for 5-*t*-butyl-2-hydroxybenzophenone. The infrared spectrum was identical with a previously published spectrum[6] for this compound. Additional analytical results are given in Table III.

5,4′-Di-*t*-butyl-2-hydroxybenzophenone.—A solution of 15.52 g. (0.05 mole) of *p*-*t*-butylphenyl *p*-*t*-butylbenzoate in benzene was irradiated with 0.336 Einstein and worked up as described above. Elution with 3 l. of benzene–petroleum ether (1:4) gave 3.19 g. of white crystals which were identified as starting material by their infrared spectrum, melting point, and mixed melting point with an authentic sample (m.p. 124–125°). Further elution with ethyl ether yielded 7.44 g. of a yellow oil which distilled at 150°/2×10^{-3} mm. The infrared spectrum of 5,4′-di-*t*-butyl-2-hydroxybenzophenone has not been published. However, a comparison of the infrared spectrum (1% carbon tetrachloride solution *vs.* pure carbon tetrachloride) of fraction 2 with that of 5-*t*-butyl-2-hydroxybenzophenone showed common bands at 3.4, 6.1, 6.2, 6.5, 6.7, 7.1, 7.3, 7.5, 7.7, 7.9, 8.0, 8.2, 8.3, 8.6, 8.9, 9.0, and 10.4 μ. This was taken as sufficient proof for the assigned structure.

5-*t*-Butyl-3-chloro-2-hydroxybenzophenone.—A solution of 16.16 g. (0.05 mole) of 2,6-dichloro-4-*t*-butylphenyl benzoate in benzene was irradiated with 1.27 Einstein and worked up as described above. Elution with 5 l. of benzene–petroleum ether (1:20) gave 9.70 g. of white crystals which were identified as unchanged starting material by their infrared spectrum, melting point, and mixed melting point with an authentic sample (m.p. 106–107°). Continuing elution with a mixture of benzene and ethyl ether (9:1) yielded 1.67 g. of yellow crystals which, after distillation at 150°/0.2 mm., exhibited a melting point of 55–59°. The infrared spectrum of this fraction was very similar to the infrared spectra of the other 5-*t*-butyl-2-hydroxybenzophenones prepared in this work. The most significant differences were in the positions of two bands: The band usually found at 6.7 μ was shifted to 6.9 μ, and the 10.4 μ band was shifted to 10.2 μ. The ultraviolet absorption spectrum was also very similar to the absorption spectrum of 5-*t*-butyl-2-hydroxybenzophenone: In benzene solution, the

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(5) M. Kulka, *J. Am. Chem. Soc.*, **76**, 5469 (1954).

(6) Sadtler Infra Red Spectrogram #6778.

present compound exhibited an absorption maximum at 355 mμ, a minimum at 305 μ, and a second, stronger maximum at 280 mμ; the corresponding wave lengths for 5-*t*-butyl-2-hydroxybenzophenone are 347, 300, and 258 mμ, respectively. Introduction of chlorine substituents into 2-hydroxybenzophenones is known to produce bathochromic shifts of about that magnitude.

Fries Rearrangement of 4-*t*-Butyl-2-chlorophenyl Benzoate.—4-*t*-Butyl-2-chlorophenyl benzoate (18 g.) and aluminum chloride (10.5 g.) were intimately mixed in a flask fitted with a reflux condenser and slowly heated by means of a metal bath until the temperature of the reaction mass rose to 140°. This temperature was maintained for approximately 10 min. The reaction mixture was cooled and decomposed with a mixture of ice, dilute hydrochloric acid, and ethyl ether. The ether layer was separated, washed with water, and dried. Evaporation of the ether left a residue which was extracted with carbon tetrachloride. The carbon tetrachloride-insoluble part was recrystallized from ethanol, then from benzene. This procedure gave colorless needles, melting point 179–180°. The melting point of 3-chloro-4-hydroxybenzophenone has been reported by Hayashi[7] to be 180–181°. The ultraviolet absorption spectrum, λ_{max} (log ϵ) = 353 mμ (3.36), 285 mμ (4.04), 235 mμ (4.09), and the infrared spectrum, λ_{max} = 3.0 (s), 6.0 (s), 6.2 (s), 6.3, 6.6, 6.9, 7.1, 7.7 (s), 8.6, 9.5, 10.3, 10.5, 11.1, 12.0, 12.5, 13.5, 14.2 (s), 14.7 μ, were consistent with this structure; yield, 4.0 g., (28%).

Anal. Calcd. for $C_{13}H_9ClO_2$: C, 67.1; H, 3.90; Cl, 15.24; O, 13.75. Found: C, 67.0; H, 3.94; Cl, 15.22; O, 13.86. Molecular Weight Calcd.: 232. Found: 239.

Dinitrophenylhydrazone, m.p. 240°. *Anal.* Calcd. for $C_{19}H_{13}ClN_4O_4$: N, 13.58. Found: N, 13.38.

The carbon tetrachloride solution was evaporated and the tarlike residue was distilled under reduced pressure. The material distilled over a very broad range 80–240°/0.05 mm., and could not be separated into clean fractions even on redistillation of individual cuts. The infrared spectra of some fractions showed some indication of the presence of 2-hydroxybenzophenones, but no pure compound could be isolated.

In another attempt to obtain 5-*t*-butyl-3-chloro-2-hydroxybenzophenone by Fries rearrangement of 4-*t*-butyl-2-chlorophenyl benzoate, 18 g. of the ester was dissolved in 100 ml. of carbon disulfide. The solution was cooled to 0° and saturated with boron trifluoride. The solution was allowed to stand for 3 days and then worked up. Unchanged 4-*t*-butyl-2-chlorophenyl benzoate was recovered quantitatively. Several other experiments showed the same negative result: No reaction occurred under mild conditions; under forcing conditions, a substantial fraction of the *t*-butyl groups were lost and complex mixtures were obtained. Other *t*-butyl substituted phenyl esters behaved in a substantially similar fashion.

Acknowledgment.—The author is indebted to Dr. R. G. Beaman of this laboratory for helpful advice and discussions.

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[7] V. M. Hayashi, *J. prakt. Chem.* [2], **123**, 293.

Tetraphenylcyclobutadiene Derivatives. III. Preparation of Precursors and Some Preliminary Investigations

H. H. FREEDMAN

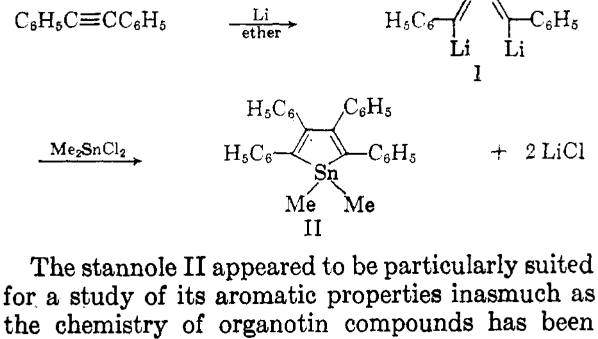
The Dow Chemical Company, Eastern Research Laboratory, Framingham, Massachusetts

Received March 6, 1962

Details are given for the behavior of 1,1-dimethyl-2,3,4,5-tetraphenylstannole (II) toward electrophiles, particularly halogen. The resulting stannole dihalides were converted to 1,4-dihalo-*cis,cis*-1,2,3,4-tetraphenylbutadienes and their utility as intermediates in the synthesis of tetraphenylcyclobutadiene was investigated. A new preparation of 1,2,3-triphenylazulene isreported.

In a previous communication,[1] we have reported that tetraphenylcyclobutadiene derivatives may be conveniently prepared by the thermolysis of (4-bromo-1,2,3,4-tetraphenyl-*cis, cis*-1,3-butadienyl)dimethyltin bromide (IV); we wish to record here the details of the preparation and chemistry of IV and its homologs and to describe some of our early attempts to convert these compounds to cyclobutadiene derivatives.

A secondary objective of this communication (and one from which this research originally stemmed) is the presentation of some evidence bearing on the potential aromaticity of 1,1-dimethyl-2,3,4,5-tetraphenylstannole (II), a member of an unusual new group of metal heterocycles originally prepared by other workers in this laboratory.[2] The stannole II was prepared by modifications of the previously reported[2] technique involving the lithium dimerization of diphenylacetylene to 1,4-dilithio-1,2,3,4-tetraphenylbutadiene (I) and the reaction of I with dimethyltin dichloride.



The stannole II appeared to be particularly suited for a study of its aromatic properties inasmuch as the chemistry of organotin compounds has been extensively explored and any modification of the ex-

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(1) For parts I and II, see H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2194, 2195 (1961).

(2) F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternas, and D. S. Lehman, *ibid.*, **82**, 5099 (1960).