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Photochemical Reactions of Benzophenone in Alcohols[1]

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Quantum yields of disappearance of $(C_6H_5)_2CO$ and formation of products were determined for the photolysis of solutions of $(C_6H_5)_2CO$ in isopropyl alcohol (IPA) at 25° and a variety of experimental conditions. Φ Acetone was 0.92 at 3660 Å., 0.99 at 3130 Å., and was independent of the amount of dissolved O_2 in solution. Φ Benzopinacol was 0.93 at 3660 Å. in O_2-free solutions but dropped to zero in O_2 saturated systems and H_2O_2 was formed. The following mechanism is proposed for the usual preparative conditions of benzopinacol where only traces of oxygen are present: $(C_6H_5)_2CO + h\nu \rightarrow (C_6H_5)_2CO^*$ (1); $(C_6H_5)_2CO^* + CH_3CHOHCH_3 \rightarrow (C_6H_5)_2\dot{C}OH + (CH_3)_2\dot{C}OH$ (2); $(CH_3)_2\dot{C}OH + (C_6H_5)_2CO \rightarrow (C_6H_5)_2\dot{C}OH + (CH_3)_2CO$ (3); $2(C_6H_5)_2\dot{C}OH \rightarrow (C_6H_5)_2COHCOH(C_6H_5)_2$ (4). Irradiation of $(C_6H_5)_2CO$ in $(-)CH_3C^*H(OH)CH_2CH_3$ gave no racemization of the residual alcohol. This rules out the previously proposed disproportionation reaction $2CH_3\dot{C}OHCH_2CH_3 \rightarrow CH_3CHOHCH_2CH_3 + CH_3COCH_2CH_3$. Photolyses of a solution of $(C_6H_5)_2CO$ and maleic acid in IPA, led to the ultimate isolation of terebic acid in a 50% yield. This is evidence for formation of $(CH_3)_2\dot{C}OH$ radicals in (2). Irradiation of oxygen-free solutions of $(C_6H_5)_2CO$ in IPA with high intensity 3660 Å. radiation gave, in addition to virtually quantitative yields of benzopinacol and acetone, a highly colored, oxygen sensitive "intermediate" (I). Spectroscopic and kinetic evidence suggest the free radical structure $(C_6H_5)_2\dot{C}OC(OH)(C_6H_5)_2$ for (I). "Intermediates" were observed with several alcohols and diisopropyl ether as solvents, and with 4,4′-substituted benzophenones, and $C_6H_5COCH_3$ in IPA. A modified mechanism involving I is proposed for the photolysis in oxygen-free systems.

Introduction

Photochemical pinacolization reactions of non-enolizable ketones have been the subject of many investigations[3] since the original discovery of Ciamician and Silber[4] that the action of sunlight on a solution of benzophenone in ethanol gave a good yield of benzopinacol. To date most of the work has been directed toward synthetic applications of these photo-reductions, since the yields in many cases are good, and the products more readily prepared than by the usual non-photochemical routes. The "classic" example is the photolysis of benzophenone in isopropyl alcohol which gives virtually a quantitative yield of pure benzopinacol.[5] Of the rather few studies dealing with over-all reaction mechanisms two of the more definitive include the acetophenone–butyl alcohol system by Weizmann, Bergmann and Hirshberg[6] and the photoreduction of benzophenone in toluene and diphenylmethane by Baker and Hammond.[7]

The present research deals with a rather long term series of experiments designed to assist in the elucidation of the mechanism of the photoreduction of benzophenone in isopropyl alcohol and to reveal the effect of oxygen on this mechanism.

Materials, Apparatus and Methods

Materials.—In the series of experiments in "nitrogen-flushed" systems, the isopropyl alcohol was dried over potassium carbonate, then over calcium and distilled in a nitrogen atmosphere. The fraction boiling at 92° (uncor.) was collected. Subsequently, Eastman Kodak "spectro-grade" isopropyl alcohol, as well as acetone and other solvents were employed.

Eastman Kodak white label benzophenone was recrystallized from absolute ethanol and from petroleum hexane, m.p. 48–48.5° (uncor.). Nitrobenzophenone was prepared by the method of Schroeter,[8] recrystallized twice from chloroform (Norit A) and dried at 60°.

Photochemical Apparatus.—Several types of apparatus and experimental procedures were employed. When the formation of the "intermediate" was studied, high intensities and deoxygenated solutions were required. No significant quantity of "intermediate" could be detected in the low intensity runs of long duration. It was found that a Hanovia type A medium pressure mercury arc operating at 3.5 amperes and placed 5 to 8.5 cm. from the solution was intense enough to produce the "intermediate." Inserted between the arc and the reaction vessel was a filter cell consisting of 1 cm. of water contained within two 4 mm. thick Pyrex plates. In runs at 3660 Å., a 3 mm. thick Corning #5840 red ultra filter was added. Maximum transmission of the filter was 55% at 3600 Å.

Two different procedures were used when spectra of irradiated solutions were studied. In the "nitrogen-flushed" system the solutions to be irradiated were placed in 1.00 cm. silica spectrophotometer cells equipped with glass stoppers. The cells were flushed with nitrogen before filling and then sealed with parawax. After prescribed periods of illumination the cells were transferred to a Beckman D.U. spectrophotometer having a cell holder thermostated at 25° and the absorbance determined.

For the experiments carried out in the "absence of oxygen," cells were made from 1.00 cm. square Pyrex tubing and 1.00 cm. diam. silica tubing. These were charged with material, then attached to a vacuum line and degassed several times before being sealed off and irradiated.

Quantum Yield Determinations.—In one series of experiments the quantum yield of disappearance of benzophenone was determined at 3130 Å. Absolute light intensities were determined by the procedure of Calvert and Rechen[9] using a 1.0×10^{-3} M solution of malachite green leucocyanide in absolute ethanol as an actinometer. The light source was a 500 watt Hanovia Type A mercury arc attached to a Farrand UV monochrometer. Reactions were carried out in 1.001 cm. square silica spectrophotometer cells set in a block thermostated at 25 ± 0.3°. Fractions of light absorbed were measured with an RCA 935 phototube and microammeter.

In the determination of the quanta per second passing through the reaction cell the following procedure was employed: 3.5 ml. of the 1×10^{-3} M malachite green leucocyanide solution, to which 0.02 ml. of 0.3 M hydrochloric acid was added, were placed in a spectrophotometer cell and

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[3] A. Schönberg and A. Mustafa, *Chem. Revs.*, **40**, 181 (1947).

[4] G. Ciamician and P. Silber, *Ber.*, **33**, 2911 (1900); **34**, 1541 (1901).

[5] W. E. Bachmann, "Organic Syntheses," Col. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 71.

[6] C. Weizmann, E. Bergmann and Y. Hirschberg, THIS JOURNAL, **60**, 1530 (1938).

[7] W. Baker and G. Hammond, Abstracts Div., of Physical and Inorganic Chem., Am. Chem. Soc., Page 31Q, Spring 1956.

[8] Schroeter, *Ber.*, **42**, 3360 (1909).

[9] J. G. Calvert and H. J. Rechen, THIS JOURNAL, **74**, 2120 (1952).

TABLE I

EFFECT OF DISSOLVED OXYGEN CONCENTRATION ON YIELD OF ACETONE FROM BENZOPHENONE–ISOPROPYL ALCOHOL PHOTOLYSIS AT 3660 Å

Expt. no.	Run no.	Treatment	Mg. acetone/g. isopropyl alc.
I	1	Completely degassed on vacuum line	0.44
	2	Completely degassed on vacuum line	0.37
			0.40 ± 0.03 av.
	3	Satd. with O_2 before irradiation	0.40
II		Higher light intensity than I	
	1	Contents deoxygenated by flushing with N_2	.68
	2	Contents deoxygenated by flushing with N_2	.68
	3	Contents deoxygenated by flushing with N_2	.75
	4	Contents deoxygenated by flushing with N_2	.80
			0.73 ± 0.05 av.
	5	Satd. with O_2 before and during irradiation	0.75

TABLE II

EFFECT OF OXYGEN ON YIELDS OF ACETONE, BENZOPINACOL AND HYDROGEN PEROXIDE IN PHOTOLYSES AT 3660 Å. AND 25° OF A 0.5 *M* SOLUTION OF BENZOPHENONE IN ISOPROPYL ALCOHOL

Run	Treatment of soln.	Acetone, moles × 10^4	Benzopinacol, moles × 10^4	Peroxide moles × 10^4	$\frac{\text{Moles benzopinacol}}{\text{moles acetone}}$	$\frac{\text{Moles peroxide}}{\text{moles acetone}}$	Quantum yield[b] benzopinacol
1	Degassed on vacuum line	1.60	1.69	0.00	1.03	0.00	0.95
2	Degassed on vacuum line	3.20	3.16	n.d.	0.99	n.d.	.91
3	Initially satd. with air	2.14	0.98	0.030	.45	0.014	.41
4	Initially satd. with air	1.79	.96	.019	.54	.011	.50
5	Continuously satd. with oxygen during irradiation	1.50	.00	.083	.00	.053	.00
6	Continuously satd. with oxygen during irradiation[a]	n.d.[c]	n.d.[c]	.083	.00	n.d.[c]	.00

[a] Run 6 was carried out under identical conditions with run 5 except that the peroxide analysis was performed directly on the irradiated solution instead of on the distillate as in runs 1 through 5. The agreement indicates that no appreciable amount of peroxide was lost in the distillation process and that the peroxide was probably hydrogen peroxide. [b] Based on a quantum yield of acetone formation of 0.92 at 3660 Å. (*cf.* Table IV). [c] n.d.—not determined.

TABLE III

QUANTUM YIELDS OF DISAPPEARANCE OF BENZOPHENONE IN THE PHOTOLYSIS OF A "NITROGEN FLUSHED" 1.32 × 10^{-2} *M* SOLUTION OF BENZOPHENONE IN ISOPROPYL ALCOHOL

Exposure time, min.	% Light absorbed	Log I_0/I at 3350 Å.[a]	Molec. $(C_6H_5)_2CO$ reacting/sec. × 10^{-15}	Intensity, quanta/sec. × 10^{-15}	Quantum yield[b]
185	95.3	1.386	0.76	1.20	0.66
210	92.6	0.980	1.18	1.20	1.06
120	94.8	1.275	1.43	1.20	1.29
120	94.4	1.225	1.52	1.20	1.37
120	86.9	0.880	0.90	1.12	0.93

[a] The molar extinction coefficient = 1.49 × 10^2 at 3350 Å. [b] Lack of precision is primarily due to residual oxygen present which, as is seen in Table II, reduces the quantum yield of benzopinacol to about 0.5 in these "nitrogen flushed" systems. In a completely degassed system $\Phi(C_6H_5)CO$ should approach 2 since Φ benzopinacol is unity under these conditions.

TABLE IV

QUANTUM YIELDS OF ACETONE FROM IRRADIATION AT SEVERAL WAVE LENGTHS AT 25° OF A 0.5 *M* SOLUTION OF BENZOPHENONE IN DEGASSED ISOPROPYL ALCOHOL

Wave length, Å.	Monochromator slit width, mm.	Quanta abs./sec. × 10^{-15}	Molec. acetone/sec. × 10^{-15}	Quantum yield
3660	(Filter system)	4.81	4.39	0.91
	5	1.46	1.34	0.92
3130	5	1.18	1.18	1.00
	5	1.09	1.05	0.97
2654	2	0.0888	0.117	1.31
2537	2	0.160	0.206	1.29

irradiated with 3130 Å. radiation for 60 seconds. The solution was then allowed to stand in the dark for three to five minutes. The absorbance of the irradiated solution was measured at 6200 Å. using a cell full of unirradiated solution as a blank. A constant rate of stirring was accomplished by passing nitrogen, saturated with solvent, through a capillary into the cell. Because this particular actinometer dye functions best at low intensities, a neutral density filter with 11.9% transmission was inserted in the light beam just following the exit slit of the monochromator (during the actual photolysis of the benzophenone–isopropyl alcohol solution this neutral density filter was removed). The fraction of light absorbed by the dye during exposure was 0.989. The average of seven experiments gave an absorbance of 0.382 (measured against the blank of unirradiated dye). Since the molar extinction coefficient ϵ (defined by absorbance $= A = \log I_0/I = \epsilon bc$ where c is in moles/liter) is 9.49 × 10^4 at 6200 Å., the average intensity was 1.20 × 10^{15} quanta/sec. in the 3.5-ml. volume. A second set of experiments on absolute light intensities, carried out after four quantum yield runs were made gave a value of 1.12 × 10^{15} quanta per second through the reaction cell. This is in good agreement with the previous value since the arc undoubtedly aged.

The determination of the molecules per second of benzophenone reacting on irradiation was carried out in essentially the same manner as the determination of the light intensity. The neutral density filter was removed and the irradiated solution was a 1.31 × 10^{-2} *M* solution of benzophenone in isopropyl alcohol. During the irradiation the fraction of light absorbed was determined and a weighted average was used in the calculation. After the exposure period the reaction cell was kept in the dark until the "dark" reaction of the intermediate (see Discussion) was completed. The absorbance of the solution was then measured at 3350 Å., where it previously had been determined that ϵ for benzophenone in isopropyl alcohol was 1.49 × 10^2. The results of this series of determinations are shown in Table III.

For quantum yield determinations at different wave lengths in the complete absence of air, a Bausch and Lomb grating monochromator was used. In these experiments silica cells for the Beckman D.U. spectrophotometer were again used as actinometer vessels. They were placed reproducibly in a holder clamped against the exit slit of the monochromator. The actual reaction cells were made of 1.00 cm. square Pyrex tubing for runs above 3000 Å. and

1.00 cm. i.d. silica tubing for shorter wave lengths. The cells were charged with solution, thoroughly degassed on a vacuum line and sealed off under vacuum.

The intensity output of the monochromator was determined with a uranyl oxalate actinometer. Oxalate decomposed was determined by adding excess ceric sulfate to the sample and the blank and estimating the difference spectrophotometrically.[10] Intensity measurements were performed immediately before and after each photolysis, using identical reaction cells placed in the same position.

Product Analyses.—If acetone only was to be determined, the photolyzed solution was distilled until no more distillate passed over below 85°. To 1.00 ml. of distillate was added 1 ml. of 45% aqueous KOH and 1 ml. of 5% salicylaldehyde in 95% ethyl alcohol. The solution was kept at 50° for 30 minutes, cooled and diluted to 10 ml. A Klett–Summerson photoelectric colorimeter with a green filter was used to compare the developed red color with that obtained from suitable standard solutions of acetone and a blank from the distillate of a similar non-irradiated solution. It was found that the measured absorbance varied linearly with acetone concentration, and unknown acetone concentrations could be found by interpolation. The presence of benzophenone in the distillate had no effect on the color developed.

For simultaneous analysis of all products the photolysis was performed in a tube with a side arm. A stopcock and standard joint enabled the tube to be connected back to the vacuum line, *via* a trap, after photolysis. The isopropyl alcohol, acetone and any peroxide formed were allowed to distil from the reaction tube at room temperature, under vacuum to the trap cooled at −80°. When distillation ceased, the reaction tube was immersed in a boiling water-bath, and the unchanged benzophenone distilled out and condensed in the side arm cooled at 0°. The reaction tube was then broken open and the benzopinacol washed with acetone into a weighing bottle, the acetone evaporated and the benzopinacol weighed. Tests showed that this procedure gave a quantitative isolation. The acetone in a portion of the distillate was estimated colorimetrically as before, and the peroxide in another portion estimated by titrating liberated iodine with dilute sodium thiosulfate.

Experimental Results

Effect of Oxygen on Products of Benzophenone–Isopropyl Alcohol Reaction.—Benzopinacol and acetone were formed in 95% yield when a ten weight per cent. solution of benzophenone in isopropyl alcohol was deoxygenated with a stream of nitrogen and irradiated for several days with light in the region 3200–3800 Å. When dissolved oxygen was not displaced from the solution, the yield of benzopinacol dropped and a peroxide, probably hydrogen peroxide, was detected.

As a more quantitative check on the effect of oxygen on the yields of acetone, portions of a solution of benzophenone in isopropyl alcohol were placed in several tubes containing various concentrations of oxygen, and the solutions irradiated, at the same intensity, for 1 hr. with 3600 Å. radiation. The yields of acetone, in arbitrary units of mg. acetone/g. isopropyl alcohol are shown in Table I. It is evident that the presence of dissolved oxygen did not affect significantly the yield of acetone.

In another series of runs, Table II, the yields of benzopinacol, acetone and peroxide at 3600 Å. were determined in solutions of benzophenone in isopropyl alcohol that contained different amounts of oxygen. The absolute yields of each product cannot be compared because of variations in light intensity and positioning of the tubes, but the large differences in the ratios, mole benzopinacol/mole acetone and moles peroxide/mole acetone are highly significant. Clearly the yields of benzopinacol and of peroxide are strongly dependent upon the amount of dissolved oxygen in the system, in contrast with the virtual independence of the acetone yield, as shown in Table I. The volatility and general behavior of the peroxide (compare runs 5 and 6) indicate it is predominantly, if not completely, hydrogen peroxide. The values of the ratio hydrogen peroxide/acetone are probably low due to decomposition of some of the peroxide during the separation and analysis; however, the extent of loss is not known.

Quantum Yields.—Quantum yields at 3130 Å. and 25° for the disappearance of benzophenone in "nitrogen flushed" isopropyl alcohol solutions containing some dissolved oxygen are given in Table III. The average of five determinations is 1.06 ± 0.2. Lack of precision results from differences in the amount of residual oxygen in the solutions and from the difficulty of obtaining reproducible spectrophotometric analyses for residual benzophenone in the irradiated solutions, because of interferences by traces of the strongly absorbing "intermediate" formed in the photolysis (see section on absorption spectra). It is evident from the data in Tables II and IV that the quantum yield of benzopinacol is about 0.5 at 3660 Å. in systems containing dissolved oxygen. This is compatible with a quantum yield of about unity for benzophenone disappearance at 3130 Å. in a similar system (Table II). In completely degassed systems the quantum yield of benzopinacol rises to unity and presumably Φ $(C_6H_5)_2CO$ would approach two.

Quantum yields of acetone formation as a function of wave length at 25° are given in Table IV for a 0.5 *M* solution of benzophenone in isopropyl alcohol. In this case the light intensity was determined with a uranyl oxalate actinometer. A highly sensitive spectrophotometric procedure was used to determine the amount of decomposed oxalate.[10]

Radiation at 2537 A. caused strong blue fluorescence in both the benzophenone solution and the actinometer solution. When the slits were 2 mm. apart and centered at 2654 Å., there was a significant contribution from the 2537 Å. line. This resulted in appreciable fluorescence in the run at 2654 Å., even though it was absent when the slits were narrowed and "pure" 2654 Å. radiation was tested.

It is interesting that the quantum yields at 2654 and 2537 Å. apparently exceed unity by about 30% when the effect of fluorescence in the benzophenone alcohol solution presumably would be to drop the value below one. The explanation may involve an intensity effect which more than counteracted loss of effective radiation from fluorescence. On the other hand, fluorescence of the uranyl oxalate solution at 2537 Å. might have led to a low value for quanta/sec. which in turn would lead to a high value for the quantum yield of acetone. At any rate, there is little doubt that at 3130 Å. the quantum yield of acetone formation is close to unity. At 3660 Å. Φ acetone is a little less than one and at 2654 and 2537 Å. it may be of the order of 1.3. Since the ratio (moles benzopinacol/moles acetone) is unity (*cf.* Table II) at 3660 Å. in degassed solution, the quantum yield of formation of benzopinacol is also 0.92 at that wave length. No experimental checks were made to determine the effect of wave length on the ratio (moles benzopinacol/moles acetone), it seems likely that the ratio is unity at 3130 Å. and thus that Φ benzopinacol is probably 1.0 at 3130 Å., in degassed solutions.

One semi-quantitative series of runs was made to determine approximately the effect of light intensity on the acetone yield at 3660 Å. Aliquots of a stock solution of 10 g. of benzophenone dissolved in 100 ml. of isopropyl alcohol were transferred to identical cells placed at various distances from the light source. After irradiation for various times, the acetone yield was determined in the usual manner. A plot of log (relative intensity) *vs.* log (acetone concentration) was linear with a slope of 0.9. This indicates that at 3660 Å. in solutions of this concentration the rate of formation of acetone is directly proportional to the first power of the light intensity.

Effect of Olefins on Benzophenone–Isopropyl Alcohol Reaction.—With 1-octene present benzopinacol formation was delayed at least 7 hr. whereas in the control solution precipitation started within 2 hr. and was complete 40 minutes later. Under similar conditions cyclohexene seemed to be completely effective in retarding benzopinacol formation. The control solution of benzophenone in isopropyl alcohol again showed a precipitate of benzopinacol in 2 hr.; however, no precipitate was observed after 95 hr. of irradiation of the solution containing benzophenone dissolved in a solvent made up of equal volumes of cyclohexene and isopropyl alcohol.

An attempt to isolate the product or products resulting from addition of radicals to cyclohexene was unsuccessful; however, isolation experiments involving maleic acid as a trap were successful. With small amounts of maleic acid the formation of benzopinacolone (the final product in acid

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[10] J. N. Pitts, Jr., J. D. Margerum, R. P. Taylor and W. Brim, This Journal, **77**, 5499 (1955).

solution) was inhibited and the period of inhibition was approximately proportional to the amount of maleic acid in solution. With large amounts of maleic acid no benzopinacolone was formed. From a reaction in which equimolar amounts of benzophenone and maleic acid were irradiated in isopropyl alcohol, was obtained a 50% yield of terebic acid (γ,γ-dimethyl-γ-butyrolactone-β-carboxylic acid). Subsequent to the completion of this work,[1] Schenck and coworkers[11] independently reported a high yield for the same reaction. This reaction is good evidence for the presence of $(CH_3)_2\dot{C}OH$ in the photolysis mixture.

Reaction of Benzophenone with (–) 2-Butanol.—Eight grams (0.04 mole) of benzophenone was dissolved in 10 ml. of (–)2-butanol,[12] $[\alpha]^{25}\text{D}$ $-3.98°$, and the solution was irradiated for 6 hr. The percentage completion of the reaction was determined by diluting 0.1 ml. of the final irradiated solution to 10 ml. with *dl*-2-butanol and determining the absorbance of benzophenone at 335 mμ; $A_{335} = 0.215$, $\epsilon = 1.49 \times 10^2$. The reaction went 96.5% to completion. The remainder of the irradiated solution was distilled and the fraction boiling at 97–97.2° (2.9 ml.) was collected. The rotation was $[\alpha]^{25.5}\text{D}$ $-3.98°$. In a duplicate experiment $[\alpha]^{25}\text{D}$ $-3.95°$. Therefore, when the pinacolization reaction was carried out to 96% completion in (–)2-butanol, the recovered alcohol showed *no racemization*. This is excellent evidence that methyl ethyl ketone is *not* formed in a disproportionation reaction (see Discussion).

Effect of Irradiation on Absorption Spectra of Solutions of Benzophenones.—An unexpected result of this research was the discovery that irradiation of deoxygenated solutions of carefully purified benzophenone in isopropyl alcohol with *high* intensity 3660 Å. radiation produces a large *increase* in the absorbance of the solution in the region 3000–4200 Å. This is contrary to the expectation that the absorbancy at 3600 Å. should decrease since the products, benzopinacol and acetone, do not absorb appreciably beyond 3300 Å., Fig. 1. Apparently high purity of the benzophenone is important to get a good yield of the substance responsible for this increased absorption.

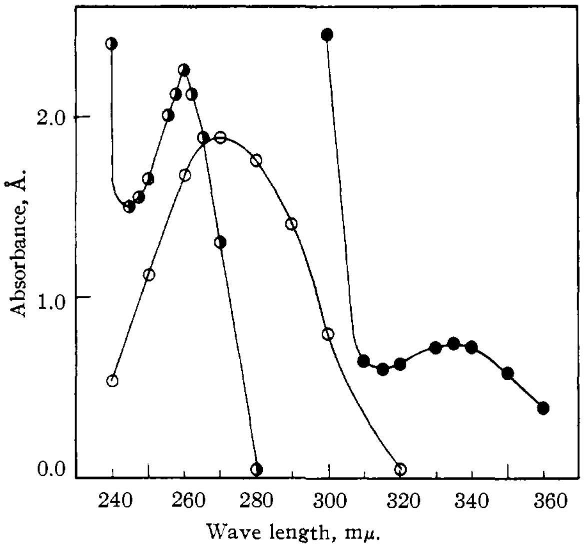

Fig. 1.—Absorption spectra of starting material, benzophenone (4.6×10^{-3} *M*, filled circles) and products, benzopinacol (2.0×10^{-3} M, half-filled circles), and acetone (0.136 *M*, open circles). All are dissolved in isopropyl alcohol.

Conditions under which the increase in absorbance was first observed were as follows: a 1.000 cm. silica cell for a Beckman D.U. spectrophotometer was flushed with nitrogen and filled with a 1.01×10^{-2} *M* solution of benzophenone in isopropyl alcohol. The solution was irradiated 15 minutes with a Hanovia quartz-mercury arc (110 v. d.c., 4 amp., 5 mm. Corning glass filter to isolate 3660 Å. line) placed 5 cm. from the cell. Absorption spectra taken immediately after irradiation and again after the cell had been 1.5 hr. in the dark, are shown in Fig. 2.

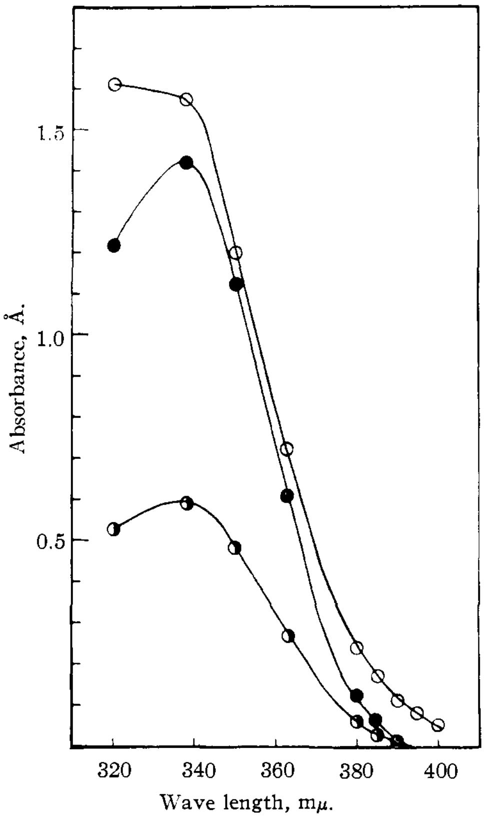

Fig. 2.—Effect of irradiation of 3660 Å. on absorption spectrum of 1.01×10^{-2} *M* solution of benzophenone in isopropyl alcohol. Nitrogen atmosphere but some dissolved O_2 in solution. Filled circles, initial; open circles, 15 min. irradiation; half-filled circles, spectrum after the 15 min. irradiation and 1.5 hr. in the dark.

It is clear that the irradiation initially produced a significant increase in the absorbance of the solution and extended the long wave length limit to about 4200 Å. Furthermore, the pronounced dark reaction that ensued when the light was shut off resulted in a sharp drop in the over-all absorbance of the solution until it reached a value about one half of that of the original non-irradiated solution.

Thus, it appears that intense irradiation results in a highly colored intermediate that reacts rapidly with traces of oxygen. Numerous experiments were conducted to learn more about this "intermediate" and the results can be summarized as follows.

(a) **Irradiation of Oxygen-free Solutions.**—The sharp-decrease in absorbance on standing in the dark, Fig. 2, indicated that dissolved oxygen might be destroying the colored "intermediate." Thus, a series of experiments were conducted in which the irradiated solutions were thoroughly degassed on a high vacuum line. To avoid contact with air the absorption cells were of 1.00 cm.^{2} square Pyrex or 1 cm. diameter silica tubing which could be attached directly to the vacuum line. These cells were filled and the solutions degassed, sealed off under vacuum and placed directly in the spectrophotometer.

Use of high vacuum techniques to degass the solutions led to strong enhancement of the unexpected absorption increase, as is shown in Fig. 3. Thus, after 15 minutes irradiation of a 3.6×10^{-3} *M* solution of benzophenone in isopropyl alcohol, the absorbance *A* at 3300 Å. rose from 0.54 initially (curve 1, Fig. 3) to 2.09 (curve 2, Fig. 3). Continued irradiation for 15 minutes at 3600 Å. (actually the 3100–3900 Å. region was isolated by the filter) apparently

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[11] G. O. Schenck, G. Koltzenburg and H. Grossmann, *Angew. Chem.*, **69**, 1177 (1957).

[12] The (–)2-butanol was kindly furnished by Professor R. L. Burwell.

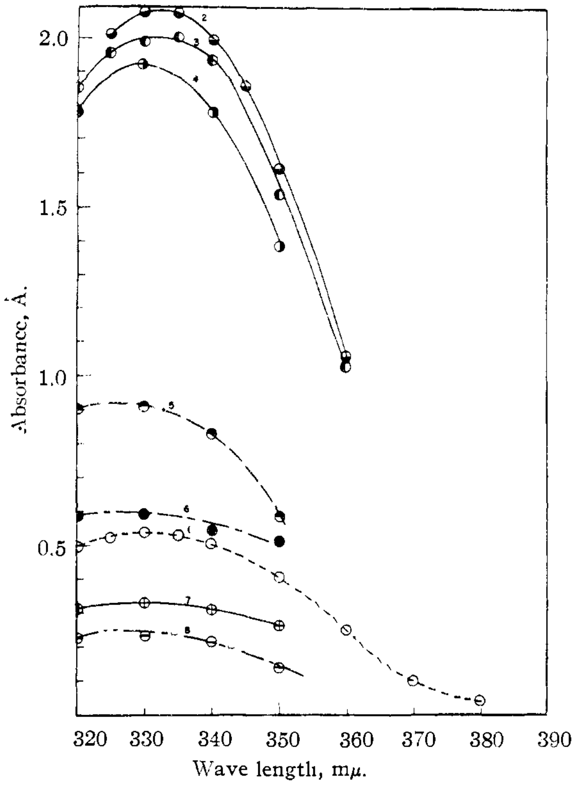

Fig. 3.—Effect of 3660 Å. radiation on absorption spectrum of a degassed 3.6 × 10^{-3} *M* solution of benzophenone in isopropyl alcohol: curve 1, initial; 2, 15 min. irradiation; 3, 30 min. total irradiation; 4, 30 min. total irradiation and 20 hr. in dark; 5, 30 min. irradiation + 20 hr. in dark + 5 minutes after shaking sample with air; 6, 7 and 8 are 27 min., 3 hr. and 40 min., and 20 hr. after shaking the sample with air.

destroyed some of the highly colored substance as the absorbance dropped slightly to 1.99 (curve 3, Fig. 3). Although only the range 3200–3600 Å. is shown in Fig. 3, other studies showed that this increase in absorbance paralleled that shown in Fig. 2; however, it was much more pronounced. It extended out to 4200 Å., at least 300 Å. beyond the upper limit of absorption of benzophenone.

Substantiation of the idea that oxygen rapidly destroys the colored intermediate is shown in curves 4 and 5 of Fig. 3. Curve 4 is the absorption spectrum after a total of 30 minutes irradiation and 20 hr. in the dark. The slight drop from curve 3 to curve 4 represents the total dark reaction in 20 hr. After 20 hr. in the dark the tip was broken off the sample tube and the contents shaken with air. Five minutes later the absorbance dropped to 0.81 at 3300 Å. and after 20 hr. it was only 0.22, less than half that of the initial value before irradiation. It therefore appears that the rapid "dark reaction," of the colored intermediate (Fig. 2) results from dissolved oxygen which is still present in the solution under the conditions of that experiment (cells simply flushed with nitrogen gas).

Direct visual confirmation of the colored intermediate was obtained by irradiation of more concentrated, thoroughly degassed solutions of benzophenone in isopropyl alcohol. Irradiation of a 10% solution produced a yellow color that persisted for several days at room temperature but disappeared within a few minutes after the tip was broken off the sample tube and air admitted to the system.

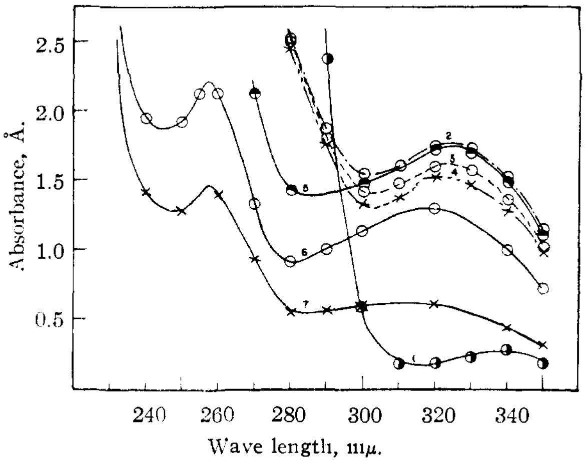

Fig. 4.—Effect of prolonged irradiation on degassed 1.08 × 10^{-3} *M* solution of benzophenone in isopropyl alcohol: curve 1, initial; curve 2, 5 min. irradiation; curve 3, 5 min. total irradiation and 1 hr. in dark; curve 4, same as 3 but 27.5 hr. in dark; curve 5, reirradiation of solution 10 min.; curves 6 and 7, further irradiation for 30 and 60 minute intervals, respectively.

The destruction of the colored intermediate by prolonged irradiation is shown in Fig. 4. After five minutes irradiation with radiation in the 3100–3900 Å. region, the absorbance at 3300 Å. of a degassed 1.08 × 10^{-2} *M* solution of benzophenone in isopropyl alcohol rose from 0.23 (curve 1) to 1.72 (curve 2). Following a total of 27.5 hr. in the dark the absorbance dropped to about 1.47 (curve 4). This was probably due to reaction with the last traces of oxygen left in the solution. Reirradiation for ten minutes brought the absorbance back to 1.72 (curve 5). Further irradiation began to destroy the "intermediate" and *A* dropped to 1.20 (curve 6) and 0.60 (curve 7) after successive intervals of 30 and 60 minutes exposure to light.

A solution of acetophenone in isopropyl alcohol, approximately 3 × 10^{-3} *M*, degassed on a high vacuum line showed a similar increase in absorbance when irradiated with light in the 3100–3600 Å. region. As is shown in Fig. 5, after 15 minutes irradiation the absorbance at 3600 Å. rose from 0.000 to 0.085 and the long wave length limit of absorption shifted from 3600 Å. to about 3900 Å. As was the case with thoroughly degassed benzophenone–isopropyl alcohol solu-

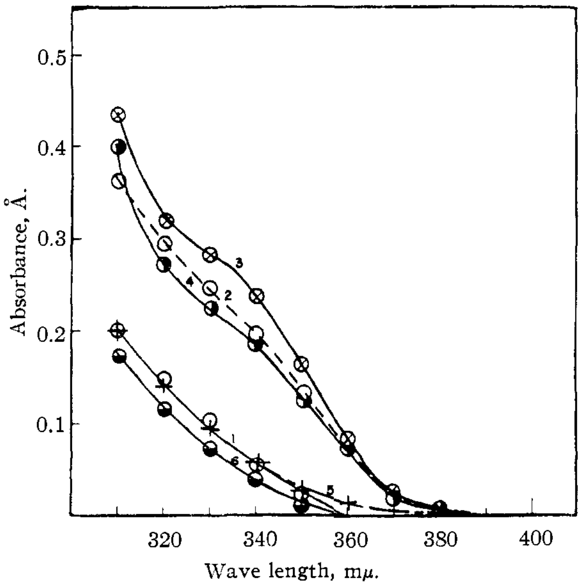

Fig. 5.—Effect of irradiation on absorption spectrum of a 3 × 10^{-3} *M* solution of acetophenone in isopropyl alcohol: curve 1, initial; curves 2 and 3, total of 5 min. and 20 min. irradiation, respectively; curve 4, spectrum after total of 20 min. irradiation and 5.5 hr. in dark; curves 5 and 6, 5 min. and 12 hr. after shaking with air.

tions, the absorbance of the irradiated solution at 3600 Å. dropped only slightly after 5.5 hours in the dark, (from 0.085 to 0.075) but after five minutes shaking with air it fell to 0.015. Presumably the enhanced absorption is due to a highly colored oxygen-sensitive intermediate similar to that formed in the benzophenone–isopropyl alcohol system.

(b) **Irradiation of "Nitrogen-flushed" Systems.**—The formation of highly absorbing, oxygen-sensitive intermediates was found to be quite general. Increases in absorbance in the region 3000–4200 Å. and bathochromic shifts of absorption spectra were noted in photolyses with various solvents and several substituted benzophenones under conditions similar to those employed to obtain the data for Fig. 2. These include flushing flasks, pipets and absorption cells with high purity dry nitrogen, and, after filling with solution, sealing the cells with parawax. It is important to note that while precautions were taken to remove oxygen in the atmosphere above the solution, the solutions themselves, in this series of runs, contained dissolved oxygen (in contrast to the series described above in which the solutions were degassed on a high vacuum line). Thus, after irradiation, all nitrogen flushed systems with alcohol solvents showed appreciable dark reactions (in contrast to the results shown in Figs. 3, 4 and 5), and it seems likely that this was due in part to destruction of the intermediates by reaction with residual oxygen. The results of these photolyses involving "nitrogen-flushed" solutions are summarized in the following paragraphs.

A number of kinetic studies were run on these "dark reactions" by following the decrease in absorbance with time at 4000 Å. With benzophenone in both isopropyl alcohol and absolute ethanol the dark reaction appeared to be second order for about the first 20 minutes, changing over to first order during the later period of the reaction. Thus, plots of $1/A$ *vs.* time were linear in the initial stages of the dark reaction, with log A *vs.* time becoming linear after about 20 minutes had elapsed. (Duplicate runs gave widely differing slopes for these plots, probably because of differences in residual oxygen concentrations in the solutions.)

Irradiation of solutions of benzophenone in ethanol, 2-butanol and isopropyl ether at 25° and 3660 Å. resulted in an increase in absorption between 3000 and 4200 Å. which faded rapidly on contact with air. The solution with isopropyl ether as a solvent showed a particularly large enhancement of absorption compared to the alcohol solutions.

No "intermediate" formation was observed when cyclohexene and benzene were solvents. Thus, with pure cyclohexene as a solvent, the benzophenone absorption peak at 3350 Å. decreased on irradiation. On the other hand, traces of cyclohexene did affect the absorption spectra of irradiated solutions of benzophenone–isopropyl alcohol. For example, in one experiment a 4.64×10^{-3} M solution of benzophenone in isopropyl alcohol was prepared and placed in two 1.00 cm. Beckman D.U. silica cells which had previously been flushed with nitrogen. Cell 1 was sealed and used as prepared. To cell 2 four drops of cyclohexene were placed side by side and irradiated for 30 minutes at 3660 Å. and 25°, then allowed to stand 10 minutes in the dark. The absorption spectra of the samples taken before irradiation were virtually identical, but it is evident from Fig. 7 that addition of a small amount of cyclohexene to the isopropyl alcohol greatly enhances the degree of absorption by the irradiated solution over the entire range from 3200 to 4000 Å. and results in a shift toward the red. Similar enhancements of absorption and bathochromic shifts of the spectra were obtained when small amounts of other free radical traps such as diethyl maleate or maleic acid were added to solutions of benzophenone in isopropyl alcohol and these were irradiated at 3660°. This effect may be due to the formation of a highly absorbing complex between the "intermediate" and the unsaturated compound, or possibly, to trapping by the olefin of some reaction species which can destroy the intermediate.

Solutions of 4,4'-dimethylbenzophenone, 4,4'-dimethoxybenzophenone and 4,4'-dichlorobenzophenone in isopropyl alcohol showed pronounced bathochromic shifts indicative of "intermediate" formation on irradiation at 25° and 3660 Å. Figure 6 shows the effect on 4,4'-dimethylbenzophenone. The photolyses were carried out in one cm. absorption cells which were flushed with nitrogen, filled and sealed with parawax. "Dark" reactions (probably chiefly involving residual oxygen) leading to destruction of the intermediate occurred in each case. Irradiation of 4-nitrobenzophenone in isopropyl alcohol gave an increase in absorbance, but the resulting absorption spectrum did not change with time or shaking the solution with air; apparently some stable compound had formed. With 4,4'-diphenylbenzophenone and with Michler's ketone no change in the absorption spectrum was observed on irradiation under similar conditions.

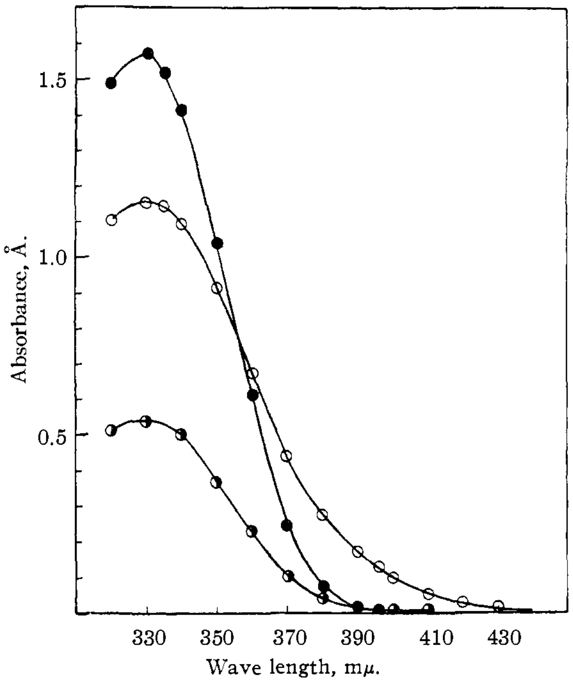

Fig. 6.—Effect of irradiation at 3660 Å. on absorption spectrum of a 6.7×10^{-3} M solution of 4,4'-dimethylbenzophenone in isopropyl alcohol (nitrogen atmosphere but some dissolved O_2 in the solution): Solid circles, initial; open circles, 20 min. irradiation + 282 min. in the dark; half-filled circles, total of 20 min. irradiation and 1226 min. in dark.

If we *arbitrarily* define the yield of intermediate in terms of the enhancement of the absorbance at 4000 Å. on irradiation (the validity of this assumption depends upon the relative magnitudes of the extinction coefficients of the various "intermediates"), then it seems from our data that the nature of the *para* substituent plays an important role in determining the yield of intermediate. Thus, in photolyses under roughly comparable conditions of concentration of solution, quanta absorbed per sec., time of run, etc., 4,4'-dimethylbenzophenone gave a much larger yield of "intermediate" after 20 minutes of irradiation at 3660 Å. and 282 minutes in the dark than did the 4,4'-dichloro analog for a similar irradiation period but only ten minutes in the dark. The 4,4'-dimethoxy derivative also seems to give a much higher quantum yield of "intermediate" than benzophenone itself or its 4,4'-dichloro derivative. However, this series of photolyses were primarily of a qualitative nature and accurate comparison between yields for the several compounds is impossible in view of the fact that different amounts of dissolved oxygen may have been present in each run. Accurate comparisons await studies in completely deoxygenated systems.

In an attempt to generate the "intermediate" in another type of system, solutions of benzohydrol in acetone were irradiated in the region where acetone absorbs, that is, below 3200 Å., and the absorption spectra studied after various periods of illumination. No trace of an "intermediate" similar to that found in the benzophenone–isopropyl alcohol system was observed. Furthermore, in apparent conflict with the results of Schönberg and Mustafa,[13] and their suggested mechanism, no benzopinacol was found.

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(13) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 276 (1943).

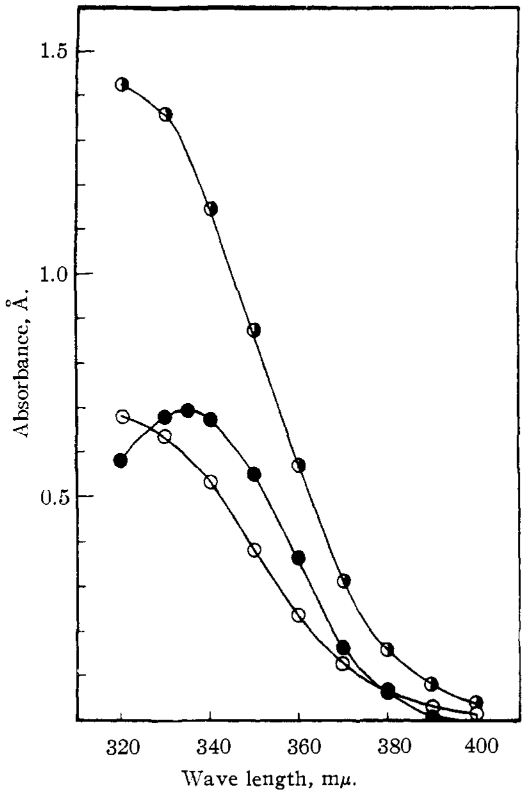


Fig. 7.—Effect of trace of olefin on absorption spectrum of irradiated solution of benzophenone in isopropyl alcohol: solid circles, absorption spectrum of 4.64 × 10^{-3} *M* solution of benzophenone in isopropyl alcohol (solution 1) and of same solution to which 4 drops of cyclohexene were added (solution 2); half-circles, solution 2 after 30 min. irradiation and 10 min. in dark; open circles, solution 1 after 30 min. irradiation and 10 min. in dark.

Discussion of Results

The following sequence of reactions appears to afford a satisfactory explanation of the mode of formation of products of the photoreduction of benzophenone in isopropyl alcohol under the usual experimental conditions designed to give a maximum preparative yield of benzopinacol.[5] These include illumination at relatively low intensities (*e.g.*, sunlight) and exclusion of air during the course of the photolysis, except for a small amount initially present in the reaction flask.

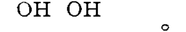
Primary process

$$(C_6H_5)_2CO + h\nu \longrightarrow (C_6H_5)_2CO^* \qquad (1)$$

Secondary reactions

$$(C_6H_5)_2^* + (CH_3)_2CHOH \longrightarrow (C_6H_5)_2\dot{C}OH + (CH_3)_2\dot{C}OH \qquad (2)$$

$$(CH_3)_2\dot{C}OH + (C_6H_5)_2CO \longrightarrow (C_6H_5)_2\dot{C}OH + (CH_3)_2CO \qquad (3)$$



$$2(C_6H_5)_2\dot{C}OH \longrightarrow (C_6H_5)_2\underset{OH}{\underset{|}{C}}-\underset{OH}{\underset{|}{C}}(C_6H_5)_2 \qquad (4)$$

The Primary Process.—Since 3660 Å. radiation is effective in promoting this reaction, it is clear that the primary photochemical process must involve absorption of radiation by the benzophenone (*cf.* Fig. 1), rather than excitation of the alcohol which is transparent above about 2200 Å. It seems reasonable, particularly on the basis of the results of Hammond and Baker[7] for the photolysis of benzophenone–toluene systems, that the sole chemically reactive excited state of benzophenone shown in (1) is a triplet. However, the results of the present research do not permit an unequivocal judgement of the relative chemical effectiveness of excited singlet and triplet states of benzophenone. It is clear, however, that since the quantum yields of products are close to unity over a wide wave length range (Table IV), deactivation of the excited benzophenone, whatever the state involved, by fluorescence or internal degradation must be slow relative to reaction 2.

Secondary Reactions.—The reaction sequence 2, 3 and 4 gives the observed quantum yields close to unity for both benzopinacol and acetone in degassed systems, and in contrast to a similar mechanism previously proposed by Weizmann, Bergmann and Hirschberg,[6] this satisfactorily accounts for the fact that no mixed pinacol is formed by combination of $(C_6H_5)_2\dot{C}OH$ and $(CH_3)_2\dot{C}OH$ radicals if we assume 3 to be fast relative to the combination reactions. Evidence for each of the steps can be summarized as follows:

Reaction (2).—The need for the solvent to furnish a hydrogen atom was demonstrated by Bowen and de la Praudieré who found that irradiation of molten benzophenone, or benzophenone in carbon tetrachloride, yielded no benzopinacol.[14] However, benzopinacol was formed in solvents from which hydrogen could be abstracted, and Cohen[15] reported that for a series of alcohols the yield of pinacol increased with increasing ease of removal of the hydrogen from the carbon atom holding the hydroxyl group.

Ethers as well as alcohols serve as hydrogen donors in the pinacolization reaction.[16a] Thus Bergmann and Fujise[16b] irradiated a solution of benzophenone in benzhydryl methyl ether and obtained benzopinacol and the dimethyl ether of benzopinacol. No monomethyl ether of benzopinacol was isolated. These facts, coupled with bond strength considerations and the inactivity of -butyl alcohol as a solvent for pinacolization, observed in the present research, are good evidence that the hydroxyl hydrogen is not abstracted by the photoactivated benzophenone.

The formation of $(C_6H_5)_2\dot{C}OH$ radicals in reaction 2 is proposed primarily because in the absence of oxygen benzopinacol is formed with a quantum yield close to unity and it is difficult to postulate a suitable mechanism that does not involve these radicals. Supporting, but also indirect, evidence is the fact that irradiation of acetophenone in cyclohexanol gave both diasteromeric pinacols[5] (and cyclohexanone in 80% yield) which strongly suggests the formation of $C_6H_5\overset{OH}{\underset{\cdot}{\overset{|}{C}}}CH_3$ radicals in a reaction analogous to (2).

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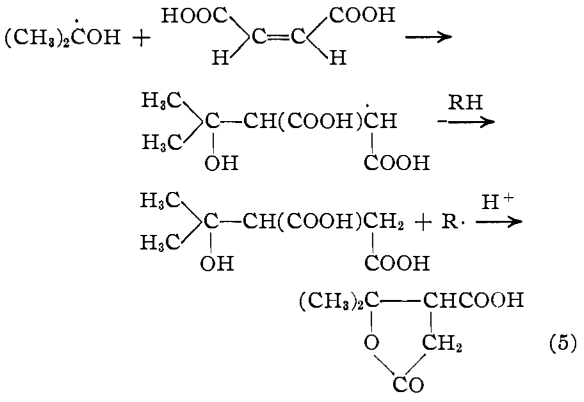
(14) E. J. Bowen and E. L. de la Praudieré, *J. Chem. Soc.*, 1503 (1934).

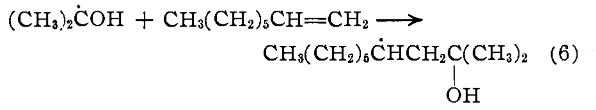
(15) W. D. Cohen, *Rec. trav. chim.*, **39,** 243 (1920).

(16) (a) G. Ciamician and P. Silher, *Ber.*, **44,** 1514 (1911); (b) E. Bergmann and S. Fujise, *Ann.*, **483,** 65 (1930).

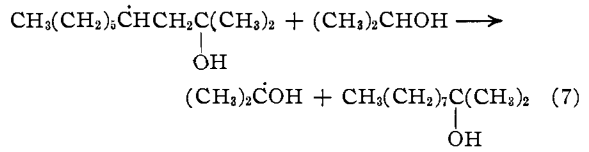
Perhaps the most direct evidence for the formation of $(CH_3)_2\dot{C}OH$ radicals in the photolysis is the isolation of terebic acid from irradiated solutions of benzophenone and maleic acid in isopropyl alcohol (see Results). It seems likely that this paraconic acid results from reactions 1 and 2 followed by the reaction sequence 5. Other mechanisms involving radicals more complex than $(CH_3)_2\dot{C}OH$ can be devised to explain the formation of terebic acid, but 5 is perhaps preferable on the basis of its being more direct and the simplest of several possible explanations.


(5)

It is interesting to speculate on the nature of RH, the hydrogen atom donor in the above sequence. In the alcohol–olefin system used by Urry and co-workers,[17] the alcohol serves as the hydrogen donor and good yields of the 1:1 adduct are obtained, as in the 1-octene–isopropyl alcohol system. In the benzophenone–maleic acid–isopropyl alcohol system, however, several observations point to the possibility of RH being, to a large extent, the $(C_6H_5)_2\dot{C}OH$ radical. First, no benzopinacolone precipitates out while excess maleic acid is still present in the solution, and the question arises as to the fate of $(C_6H_5)_2\dot{C}OH$ radicals. They could also add to the double bond in maleic acid, but no product corresponding to the diphenyl analog of terebic acid was isolated. Second, if irradiation is terminated before the precipitation of benzopinacolone, significant amounts of terebic acid are obtained, but most of the benzophenone can be recovered unchanged. The yield of benzophenone was only an estimate and must be redetermined in more quantitative experiments; however, if, as it now seems, benzophenone can be recovered virtually quantitatively, then it would appear that a substantial fraction of the reaction would follow the path 8.



$$(CH_3)_2\dot{C}OH + CH_3(CH_2)_5CH{=}CH_2 \longrightarrow CH_3(CH_2)_5\dot{C}HCH_2\underset{OH}{\underset{|}{C}}(CH_3)_2 \quad (6)$$



$$CH_3(CH_2)_5\dot{C}HCH_2\underset{OH}{\underset{|}{C}}(CH_3)_2 + (CH_3)_2CHOH \longrightarrow (CH_3)_2\dot{C}OH + CH_3(CH_2)_7\underset{OH}{\underset{|}{C}}(CH_3)_2 \quad (7)$$

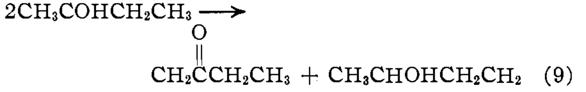
$$(C_6H_5)_2\dot{C}OH + (CH_3)_2COHCH(COOH)\dot{C}HCOOH \longrightarrow (C_6H_5)_2CO + (CH_3)_2COHCH(COOH)CH_2COOH \quad (8)$$

As pointed out in Results, cyclohexene and 1-octene both strongly inhibit the formation of benzopinacol in irradiated olefin–benzophenone–isopropyl alcohol systems. It seems likely that $(CH_3)_2\dot{C}OH$, and possibly $(C_6H_5)_2\dot{C}OH$, radicals add to these olefins but preliminary attempts to isolate the adducts were unsuccessful.

Reaction 3.—This process is postulated to account for the following facts:

a. In the absence of oxygen benzopinacol is formed in virtually quantitative yields. The absence of pinacol, mixed pinacols and benzohydrol indicates that $(CH_3)_2\dot{C}OH$ radicals react very soon after they are formed in reaction 2 but not in recombination or disproportionation processes with $(C_6H_5)_2\dot{C}OH$ radicals. The hydrogen transfer to form the more stable free radical $(C_6H_5)_2\dot{C}OH$ would appear to be rapid, and in view of the strongly reducing nature of the $(CH_3)_2\text{-}\dot{C}OH$ radical,[18,19] quite reasonable.

b. Prolonged irradiation of benzophenone in optically active *sec*-butyl alcohol did not change the rotation of the alcohol remaining after complete precipitation of the pinacol. This fact rules out the disproportionation reaction 9 in this solvent since formation of the planar radical would destroy the optical activity and lead to racemization of the remaining alcohol. By analogy it would seem that this evidence also rules out the disproportionation reaction 10 proposed in the mechanism of Weizmann and co-workers.[6] Reaction 3 in the present mechanism is, however, compatible with the stereochemical results.



$$2CH_3\dot{C}OHCH_2CH_3 \longrightarrow CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3 + CH_3CHOHCH_2CH_2 \quad (9)$$

$$2(CH_3)_2\dot{C}OH \longrightarrow (CH_3)_2CO + (CH_3)_2CHOH \quad (10)$$

It is interesting that Weizmann, Bergmann and Hirschberg irradiated acetophenone in optically active phenylmethylcarbinol.[6] They remark in a footnote, "It is noteworthy that part of the carbinol recovered unchanged from the experiment shows practically the original rotation." This observation also tends to eliminate reaction 10.

Reaction 4.—This reaction has been included in the more definitive studies[6,7] on the mechanism of the photoreduction of benzophenone in various solvents and is the simplest way to explain the virtually quantitative yield of benzopinacol in the usual synthetic procedure and the quantum yield close to unity at 3660 Å. in the absence of oxygen. It also explains the quantum yield of reaction of benzophenone being close to unity at 3130 Å. in "nitrogen-flushed" systems. Under similar conditions the quantum yield of benzopinacol is about 0.5 at 3660 Å. and probably close to that

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(17) W. H. Urry, F. W. Stacey, E. S. Huyser and O. O. Juveland, THIS JOURNAL, **76**, 450 (1954).

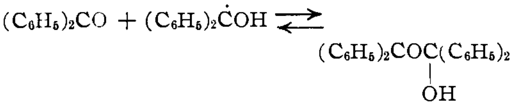
(18) J. H. Merz and Wm. A. Waters, *J. Chem. Soc.*, 5 (1949).

(19) Alan Y. Drummond and Wm. A. Waters, *ibid.*, 3119 (1953).

at 3130 Å. Since each molecule of benzopinacol formed corresponds to removal of one photoactivated and one non-photoactivated benzophenone molecule from the system, a quantum yield of about unity is reasonable. Reaction 4 is strongly inhibited by the presence of oxygen, as is shown in Table II, presumably because the oxidation of $(C_6H_5)_2\dot{C}OH$ radicals competes with their dimerization. An alternate scheme for formation of benzopinacol which does not involve this simple dimerization has some merit, particularly in oxygen-free systems, and it will be discussed subsequently.

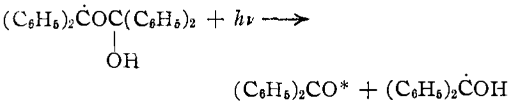
Mechanism in Total Absence of Oxygen.—An interesting result of this research was the discovery that a highly absorbing compound, with an absorption maximum at about 3350 Å. and an upper limit of absorption shifted several hundred Angstroms beyond that of benzophenone, is formed when thoroughly degassed solutions of benzophenone in isopropyl alcohol are irradiated with high intensity 3660 Å. light. As previously described in Results, prolonged irradiation or exposure to oxygen destroys this colored "intermediate." Formation of similar intermediates was observed with various alcohols, several substituted benzophenones and with benzophenone in diisopropyl ether as a solvent. The only literature reference found that described a similar effect in photopinacolization reactions was that of Böeseken who, in 1921, irradiated terephthalophenone in cyclohexanol and observed a visibly colored "photosubstance" that was destroyed by intense illumination or by shaking with oxygen.[20]

On the basis of the evidence accumulated to date in this research the following sequence of reactions is tentatively proposed to account for the formation of the "intermediate" and its thermal and photochemical reactions in the absence of oxygen

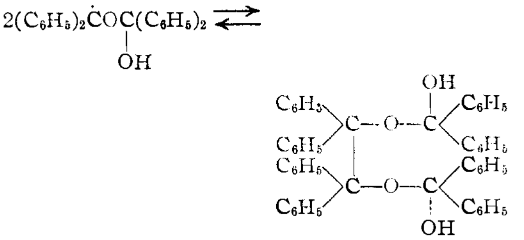


$$(C_6H_5)_2CO + (C_6H_5)_2\dot{C}OH \rightleftarrows (C_6H_5)_2CO\underset{\substack{|\\ OH}}{C}(C_6H_5)_2 \quad (11)$$

I

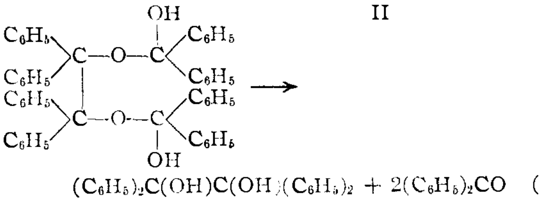


$$(C_6H_5)_2\dot{C}O\underset{\substack{|\\ OH}}{C}(C_6H_5)_2 + h\nu \longrightarrow (C_6H_5)_2CO^* + (C_6H_5)_2\dot{C}OH \quad (12)$$



(13)

II



(14)

In this mechanism it is proposed that the "intermediate" observed is actually the free radical $(C_6H_5)_2\dot{C}OC(OH)(C_6H_5)_2$ (I).[21] This would be expected to behave in a manner somewhat analogous to the triphenylmethyl radical: *i.e.*, it would be relatively stable, absorb strongly in the region 3000 to 4000 Å. (with the upper wave length limit shifted beyond that of benzophenone), and it would react rapidly with oxygen.

Perhaps the best evidence for the intermediate *not* being $(C_6H_5)_2\dot{C}OH$ radicals (or some impurity or side product), as well as the reason for postulating reaction 12 is the fact that the quantum yield of benzopinacol is close to unity in oxygen free systems where the intermediate is absorbing a large share of the incident 3660 Å. radiation. Thus, to avoid acting as an "inner filter" and reduce the quantum yield, the intermediate must absorb a quantum and then dissociate into products such that an over-all quantum yield of benzopinacol of unity is still maintained. It is difficult to see how such a material balance can be achieved if the intermediate is the $(C_6H_5)_2\dot{C}OH$ radical. On the other hand, if I is assumed to be the intermediate, the sequence 11, 12, followed by the usual reactions 2, 3 and 4, will permit an over-all quantum yield of unity.

Photolyses at 3660 Å. of samples of 1.22×10^{-3} and 2.07×10^{-3} M solutions of benzophenone in isopropyl alcohol showed that, after correcting for differences in quanta absorbed, the maximum yield of intermediate was, within ±15%, proportional to the initial concentration of benzophenone. Although the uncertainty is rather large, probably because of differences in the residual dissolved oxygen present in the nitrogen-flushed system, this result is compatible with reaction 11 and the proposed structure of the intermediate, I. Thus, if the intermediate were the $(C_6H_5)_2\dot{C}OH$ radical, zero order dependence in benzophenone would have been expected.

Reaction 13, the dimerization of the intermediate to give the hemiketal II is pictured as proceeding very rapidly, but not entirely to completion as is the usual case in most radical combinations. Thus, 13 is shown as an equilibrium, analogous to the hexaphenylethane–triphenylmethyl radical system, in which there is sufficient concentration of radical I left in oxygen-free systems to account for the strong residual absorption in the 3300-4000 Å. range.

Reactions 11 and 13 are analogous to those proposed by Rust, Seubold and Vaughn to explain the radical induced decomposition of benzaldehyde.[22]

Compound II is somewhat similar in structure to tetraphenyldiphenoxyethane. Bowden[23] reports that the latter compound dissociates slightly into the free radicals $(C_6H_5)_2\dot{C}OC_6H_5$ according to

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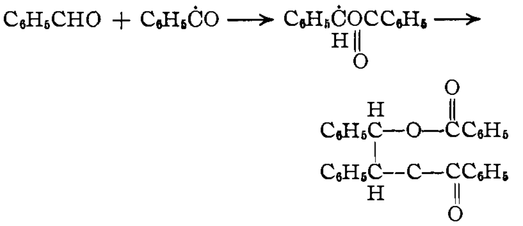
[20] J. Böeseken, *Rec. trav. chim.*, **40**, 433 (1921).

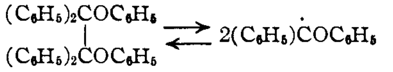
[21] The "intermediate" could also be $(C_6H_5)_2\dot{C}OC(OH)(CH_3)_2$. As the reactions of this radical would be analogous to those of I (*e.g.*, 12, 13 and 14), they will not be discussed further here. Data on the relative tendency of $(\dot{C}H_3)_2COH$ to (a) donate H· and (b) add to $(C_6H_5)_2CO$ are not presently available.

[22] F. F. Rust, F. H. Seubold and W. E. Vaughn, THIS JOURNAL, **70**, 3258 (1948).

[23] S. T. Bowden, *J. Chem. Soc.*, 26 (1939).


(15)

reaction 16. In this connection, also, it may be noted that oxygen reacts readily with $(C_6H_5)_2C$-$(CH_3)C(CH_3)(C_6H_5)_2$, presumably, because this ethane dissociates into free radicals.[24]



$$\begin{array}{c}(C_6H_5)_2COC_6H_5\\ |\\ (C_6H_5)_2\dot{C}OC_6H_5\end{array} \rightleftarrows 2(C_6H_5)\dot{C}OC_6H_5 \qquad (16)$$

Reaction 14 merely represents the dissociation of a hemiketal and would provide an alternate route to benzopinacol from II.

Mechanism of Photoöxidation in the Presence of Benzophenone.—It is evident from the results in Table II that the acetone yield is independent of the oxygen concentration in the system but the yield of benzopinacol is reduced from about unity in an oxygen free system to zero when the solution is saturated with oxygen and irradiated. In the latter case significant yields of hydrogen peroxide are also obtained, but the benzophenone in the system apparently is not used up in the reaction. Apparently the $(C_6H_5)_2\dot{C}OH$ radicals are being destroyed by the oxygen, and the following mechanism seems to afford a reasonable explanation

$$(C_6H_5)_2CO + h\nu \longrightarrow (C_6H_5)_2CO^* \qquad (1)$$

$$(C_6H_5)_2CO^* + CH_3CHOHCH_3 \longrightarrow (C_6H_5)_2\dot{C}OH + CH_3\dot{C}(OH)CH_3 \qquad (2)$$

$$(C_6H_5)_2\dot{C}OH + O_2 \longrightarrow HO_2 + (C_6H_5)_2CO \qquad (17)$$

$$CH_3\dot{C}(OH)CH_3 + O_2 \longrightarrow H\dot{O}_2 + CH_3COCH_3 \qquad (18)$$

$$H\dot{O}_2 + CH_3\dot{C}(OH)CH_3 \longrightarrow H_2O_2 + CH_3COCH_3 \qquad (19)$$

$$H\dot{O}_2 + (C_6H_5)_2\dot{C}OH \longrightarrow H_2O_2 + (C_6H_5)_2CO \qquad (20)$$

This phase of the problem was not studied in detail; hence it seems appropriate simply to point out that this mechanism is merely one sequence of reactions compatible with an over-all quantum yield of unity for acetone, zero for benzopinacol and an intermediate value for hydrogen peroxide. Qualitatively these products agree with those found by Bäckström for irradiation of a benzophenone-isopropyl alcohol oxygen system at 3660 Å. However, he reports almost quantitative yields of both acetone and hydrogen peroxide.[25]

In the present research, no attempt was made to achieve quantitative yields of the peroxide so that the differences in reported ratios of peroxide and ketone may be only an apparent anomaly. Furthermore, it is clear from the qualitative agreement between Bäckström and these authors that the reports of earlier investigators of photoöxidations,[20,26] in this system, one of whom reported a chain length of 18 for the oxidation[26] and water as a product (but no H_2O_2), warrant critical examination.

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[24] K. Ziegler, R. B. Whitney and P. Herte, *Ann.*, **551**, 187 (1942).

[25] H. Bäckström, "The Svedberg" (Memorial Volume), 1944, p. 45.

[26] A. Berthoud, *Helv. Chim. Acta*, **16**, 592 (1933).

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Formation of Hydrogen Peroxide by Ultrasonic Waves: Free Radicals

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In order to study the role of free radicals in chemical reactions caused by ultrasonic waves, the ultrasonic yield of hydrogen peroxide has been measured in water which contained radical scavengers in various concentrations and also was saturated with either oxygen or argon. The scavengers used were acrylamide, formic acid and allylthiourea. The results provide evidence that OH radical is an intermediate in the sonochemical production of H_2O_2. Further, it was observed that a radical scavenger may be efficient even though relatively unvolatile and therefore present in low concentration inside the cavitation bubble. Some differences between sonochemistry and radiation chemistry are pointed out, particularly that the destruction of hydrogen peroxide by back reaction with H or OH radicals is less important than in radiation chemistry. The experiments were carried out by treating 50 ml. of liquid in a 32 × 200 mm. Pyrex cell with 20 watts of acoustic energy at a frequency of 400 kilocycles/sec.

Introduction

Attempts to understand the mechanism by which intense ultrasonic waves cause chemical changes in liquid systems[1-9] have led to a variety of hypotheses. One of these, which has recently attracted much support,[10-14] attributes the sono-

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[1] A. Weissler, H. W. Cooper and S. Snyder, THIS JOURNAL, **72**, 1769 (1950).

[2] A. V. M. Parke and D. Taylor, *J. Chem. Soc.*, 4442 (1956).

[3] A. I. Virtanen and N. Ellfolk, *Acta Chem. Scand.*, **4**, 93 (1950).

[4] A. Weissler, *J. Acous. Soc. Am.*, **25**, 651 (1953).

[5] I. E. El'piner and A. V. Sokol'skaya, *Biofizika*, **2**, 225 (1957).

[6] V. Bellavita, F. A. Levi and N. Cagnoli, *Ann. Chim. (Rome)*, **45**, 248 (1955).

[7] A. Weissler, *J. Appl. Phys.*, **21**, 171 (1950).

[8] A. Henglein, *Z. Naturforsch.*, **10b**, 20 (1955); *Makromol. Chem.*, **14**, 15 (1954).

[9] R. O. Prudhomme, D. Picard and R. G. Busnel, *J. chim. phys.*, **50**, 107 (1953).

[10] O. Lindstrom, *J. Acous. Soc. Am.*, **27**, 654 (1955).

[11] P. Alexander and M. Fox, *J. Polymer Sci.*, **12**, 533 (1954).

[12] R. O. Prudhomme, *J. chim. phys.*, **54**, 332 (1957).

[13] M. A. Khenokh and E. M. Lapinskaya, *Zhur. Obshchei Khim.*, **26**, 2439 (1956).

[14] E. C. Steiner and J. Karpovich, paper K8 presented at the October 1957 meeting of the Acoustical Society of America, Ann Arbor, Michigan.