

Studies of Spectral Changes in Connexion with the Photoreduction of Benzophenone and 4,4'-Dialkylbenzophenones by Alcohols. II

HANS L. J. BÄCKSTRÖM and RUNE J. V. NIKLASSON*

Institutionen för fysikalisk kemi, Chalmers Tekniska Högskola, Göteborg, Sweden

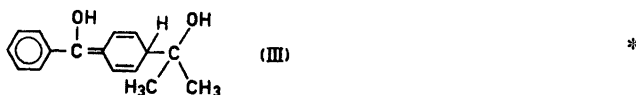
One of the reaction products formed in the photoreduction of benzophenone and substituted benzophenones by alcohols is characterized by an absorption band in the long-wave UV. We have irradiated very dilute oxygen-free solutions ($c_0 < 10^{-4}$ M) of benzophenone, 4,4'-dimethylbenzophenone (DMB), and 4,4'-di-*t*-butylbenzophenone (DBB) in methanol, ethanol, and isopropanol (IPA) with short-wave UV light (λ 253.7 nm) until the recorded spectral changes indicated, that the reaction had gone to completion. The results showed that position and intensity of the long-wave absorption band depend both on the ketone and on the alcohol. The primary reaction products are two free radicals, $\text{Ph}_2\dot{\text{C}}\text{OH}$ and $\text{Me}_2\dot{\text{C}}\text{OH}$ in the case of benzophenone in IPA. It was concluded that these radicals react with each other to form a mixture in constant proportions of the corresponding mixed pinacol and different isomers of the mixed isopinacol, the latter being responsible for the long-wave band. The structural formulas of the *para*- and *ortho*-isomers of the mixed isopinacol formed by benzophenone in IPA are shown on pp. 2590 and 2597.

In three cases short-wave irradiated solutions were further irradiated with long-wave UV light. This led to the gradual disappearance of the long-wave band and, presumably, to complete conversion of mixed isopinacol into mixed pinacol *via* dissociation into the primary radicals. In two cases (benzophenone in IPA and DMB in ethanol) difference spectra revealed the presence of two isomers, with values of λ_{max} differing by *ca.* 20 nm. The isomers with the higher values of λ_{max} are assumed to be the *ortho*-isomers, which agrees both with the structural formulas and with the fact that in DBB+IPA only one isomer is formed, with a high value of λ_{max} . — Values of molar extinction coefficients of mixed isopinacols were obtained by combining the results of such irradiation experiments with the results of acidolysis experiments.

* Present address: The Axel Johnson Institute for Industrial Research, S-149 01 Nynäshamn, Sweden.

Early investigations of the photoreduction of benzophenone by alcohols indicated that the only reduction product formed in this reaction is benzopinacol. However, later investigations have revealed that the reaction is considerably more complex than suggested by these early results. Thus it was shown by Schenck¹ and by Pitts² that irradiation of oxygen-free solutions of benzophenone in alcohols, as well as in other solvents that may serve as hydrogen donors, also results in the formation of small quantities of a substance characterized by a strong long-wave absorption band (λ_{\max} ca. 325 nm). Furthermore it has been found by Göth, Cerutti and Schmid,³ that if benzophenone is irradiated in relatively dilute methanol solution (ca. 0.02 M), the main reaction product is not benzopinacol, $\text{Ph}_2\text{C}(\text{OH})\cdot\text{C}(\text{OH})\text{Ph}_2$, but the mixed pinacol, $\text{Ph}_2\text{C}(\text{OH})\cdot\text{CH}_2(\text{OH})$.

In a previous paper under the same title,⁴ we presented some preliminary results of a study of spectral changes in connexion with the photoreduction of benzophenone and of two different 4,4'-dialkylbenzophenones by isopropanol and methanol. It is now generally agreed that the primary products formed in the reaction between, *e.g.*, a photoactivated molecule of benzophenone and a molecule of isopropanol are the radicals $\text{Me}_2\dot{\text{C}}\text{OH}$ (I) and $\text{Ph}_2\dot{\text{C}}\text{OH}$ (II).⁵ Our preliminary results, together with the results of earlier quantum efficiency determinations,⁶ seemed to show, that the final products formed in extremely dilute solutions are in this case the mixed pinacol, $\text{Ph}_2\text{C}(\text{OH})\cdot\text{C}(\text{OH})\text{Me}_2$, and a quinoid isomer (III), formed by *para* attack of radical I on radical II and responsible for the long-wave absorption band.



The principal results reported in the present paper have been obtained by studying the spectral changes taking place when solutions, containing the quinoid isomers, are irradiated with long-wave UV light, absorbed only in their long-wave absorption bands. The number of reductants has been increased by using also ethanol as solvent. The number of systems studied more in detail is small. The investigation is therefore mainly of an orienting nature.

EXPERIMENTAL

Apparatus and procedure. The apparatus used for irradiation experiments with light of wavelength 253.7 nm was essentially the same as that described in an earlier paper.⁸ The principal changes were a more stable mounting of the different parts of the system, better arrangements for excluding unwanted light, and an improved optical system. The housing for the reaction cell was kept close to 20°C by means of circulating water from a thermostat. The intensity of the exciting light entering the cell was in the same range as in the earlier work (ca. 9 micro-einstein $\text{l}^{-1}\text{min}^{-1}$).

* It had escaped our attention that already in 1965 it had been pointed out by Matthias⁷ that certain of his experimental results might be explained by assuming the formation of this "mixed isopinacol" in a reaction between radicals I and II. In his doctoral dissertation, Matthias gave reasons for considering this reaction as improbable, but in a recent paper by Schenck, Czieśla, Eppinger, Matthias and Pape⁸ it is included among the reactions that may be expected to take place in an irradiated solution of benzophenone in isopropanol.

In certain experiments a degassed solution of an aromatic ketone in an alcohol, which had first been irradiated with light of wavelength 253.7 nm, was then subjected to further irradiation with UV light of longer wavelengths. The light source was a Luma 250 W mercury lamp, surrounded by a Pyrex glass cooling jacket. The light was filtered through 6 mm of Red Purple Corex glass and 2 mm of Uviol glass. On the basis of information obtained from the lamp manufacturers and of published transmission data, the quantum composition of the transmitted UV light was estimated at 94 % 366 nm, 2.6 % 334 nm, 3.2 % 313 nm, and 0.2 % 302 nm. In experiments with di-*t*-butylbenzophenone in isopropanol the Uviol glass was replaced by window glass, which should have given *ca.* 98 % 366 nm, 1.5 % 334 nm, and 0.5 % 313 nm.

Acidolysis experiments on solutions that had been irradiated were performed in the absence of actinic light. After filling the space above the magnetically stirred solution with pure nitrogen, a small quantity of a 0.4 mM solution of HCl in isopropanol was added, using a current of nitrogen to prevent contact with air. During the experiment the spectrum was recorded at suitable intervals. The volume of HCl-solution added was generally 0.5 ml, giving a concentration of HCl = 15 μ M.

Materials. 4,4'-Dimethylbenzophenone, Eastman White Label, was recrystallized three times from aqueous methanol. 4,4'-Di-*t*-butylbenzophenone was prepared by the reaction of *t*-butylbenzene with CCl_4 in the presence of AlCl_3 , followed by hydrolysis of the dichloride. (*Cf.* the preparation of other substituted benzophenones by Cooper, Nauta, Ernsting and Faber.⁹) It was recrystallized from ethanol and finally purified by vacuum sublimation. M.p. 133.5–134.5°. (Larner and Peters,¹⁰ m.p. 133–134°.) 1,1-Dimethyl-2,2-diphenylethanediol was prepared according to Meerwein,¹¹ and purified by recrystallizations from ligroin + benzene and from aqueous methanol. Benzopinacol was prepared by exposing a solution of benzophenone in isopropanol to sunlight. It was recrystallized first from benzene and then from isopropanol. Isopropanol, Baker's Analyzed, and methanol, Merck *p.a.*, were fractionally distilled using a column corresponding to 15 theoretical plates. Only the middle fractions were used. Spectrograde ethanol was used without further purification. Other chemicals used were purified or prepared as described earlier.⁸

RESULTS AND DISCUSSION

Irradiation experiments with light of wavelength 253.7 nm

In a previous paper by Bäckström, Appelgren and Niklasson,⁶ the results of experiments were presented where oxygen-free benzophenone solutions in isopropanol of concentrations $< 10^{-4}$ M were irradiated with light of wavelength 253.7 nm and of known absolute intensity. The changes in absorbance at this wavelength and at 334 nm were recorded during the experiments. Calculations based on the changes in absorbance at 253.7 nm showed that the quantum yield for benzophenone consumption (ϕ_B) decreased with decreasing benzophenone concentration, and indicated a limiting value of unity at infinite dilution. The increase in ϕ_B is undoubtedly connected with the formation of benzopinacol, which is the dominating reaction at high concentrations.

In a solution of benzophenone in isopropanol, absorption of a light quantum by a benzophenone molecule results in the formation of a dimethylhydroxymethyl radical (I) and a diphenylhydroxymethyl radical (II). In the two different mechanisms proposed by Schenck¹ and by Pitts² to explain the formation of benzopinacol and acetone, the initiating step is in both cases a reaction between a radical I and a benzophenone molecule, *i.e.*, a reaction which will raise the value of ϕ_B , in the limiting case to the value 2.

The increasing light absorption at 334 nm resulting from the irradiation gave a measure of the development of the long-wave absorption band. The absorbance ultimately reached a maximum value, which was denoted by A_u .

Table 1. Results of irradiation experiments with degassed solutions of benzophenone and substituted benzophenones in isopropanol (IPA), ethanol (EtOH) and methanol (MeOH).

(1) Substituents	(2) Alcohol	(3) λ_{\max} nm	(4) A_u/c_0d $M^{-1}cm^{-1}$	(5) Approx. yield of mixed isopinacol	(6) k_i/k_p
None	IPA	322	5200	0.42	0.71
None	EtOH	319	4000	0.32	0.47
None	MeOH	315	1300	0.10	0.12
4,4'-dimethyl	IPA	332	4200	0.34	0.51
4,4'-dimethyl	EtOH	318	1900	0.15	0.18
4,4'-dimethyl	MeOH	— ^a	(700) ^b	(0.06) ^b	—
4,4'-di- <i>t</i> -butyl	IPA	349	3800	0.30	0.44
4,4'-di- <i>t</i> -butyl	EtOH	345	1500	0.12	0.14
4,4'-di- <i>t</i> -butyl	MeOH	323	600	0.05	0.05

^a In this system the absorbance in the long-wave absorption band did not reach a maximum, but the curves showed an inflexion point in the region 300–305 nm. ^b A_u measured at 300 nm.

On prolonged irradiation the absorbance again decreased, but this was a relatively slow process. A plot of A_u/c_0d vs. c_0 , where c_0 represents the initial benzophenone concentration and d the layer thickness in cm, showed that the yield of the substance with the long-wave absorption band increased with decreasing concentration. Extrapolation gave a value of ca. 4800 $M^{-1}cm^{-1}$ for A_u/c_0d at zero benzophenone concentration.

The results seemed to show that the substance, responsible for the long-wave absorption band, must be a compound formed in a reaction between radicals I and II, and possessing a molar extinction coefficient (ϵ) of ca. 4800 $M^{-1}cm^{-1}$ at 334 nm. Our present interpretation is that what is formed in the reaction is in reality a mixture in constant proportions of the mixed pinacol and one or more of its quinoid isomers. For these quinoid isomers we shall adopt the term mixed isopinacols, used by Matthias.⁷

Table 1 summarizes the results of all irradiation experiments of the kind described that have been made. Here λ_{\max} is the wavelength in nm of the maximum in the long-wave absorption band. The values of A_u/c_0d given in the table refer to λ_{\max} and are limiting values, corresponding to $c_0=0$, obtained by graphical extrapolation.

As appears from the table, the values of λ_{\max} obtained in irradiation experiments with a given ketone in the three different alcohols show considerable differences, particularly in the case of the substituted benzophenones. These differences are much too large to be ascribed to mere solvent effects.* They prove, therefore, that different quinoid isomers are formed in the different alcohols, as postulated above. Confirmatory evidence is furnished by the considerable variations in the values of A_u/c_0d . As will be shown in a later section (p. 2596), there is reason to believe that the values of ϵ_{\max} for the

* According to Fieser and Fieser,¹² no significant displacements of absorption bands of conjugated dienes and polyenes due to solvents have been observed. In solvents as closely related as the three alcohols used in the present work, displacements exceeding 1 nm seem highly improbable. — Fieser and Fieser also state that the effect of solvent on the extinction coefficient is negligible.

different quinoid isomers are approximately equal. With a mean value of $12\,500\text{ M}^{-1}\text{ cm}^{-1}$ for ϵ_{max} , the yields of quinoid isomers are obtained that are listed in column 5. Further discussion of these values will be postponed to the concluding discussion.

Post-irradiation with long-wave UV light and related experiments

Benzophenone in isopropanol. In a previous paper we presented the results of some experiments where deaerated solutions of benzophenone in isopropanol were subjected to prolonged irradiation with light of wavelength 253.7 nm .⁶ In the present investigation we have studied the spectral changes taking place when an alcoholic solution of benzophenone or a substituted benzophenone, which has been irradiated with light of 253.7 nm to approximately constant absorbance (*cf.* Ref. 6, p. 1557), is subjected to further irradiation with light of longer wavelengths, absorbed only in the long-wave band of the quinoid isomer. This results in the gradual disappearance of the long-wave absorption band as well as in other spectral changes. During the experiments the spectrum was recorded at suitable intervals until no further absorption changes were observed. With decreasing absorption of the exciting light the rate becomes lower and lower, which made the experiments very time-consuming. Filling the space above the deaerated solutions with pure nitrogen was therefore found to be a necessary precaution against the development of leaks.

Results obtained in experiments of this kind, using $20.1\ \mu\text{M}$ solutions of benzophenone in IPA, are shown graphically in Fig. 1 a, where absorbance values at a layer thickness of 3 cm are plotted *vs.* the wavelength in nm. Curve 1 (open circles) represents the final absorbance (A_{f}) of the short-wave irradiated solution. Curve 2 (filled circles) shows the residual absorbance of the same solution after irradiation with long-wave UV light for a sufficient length of time.

As we have shown earlier,⁴ addition of a small quantity of HCl to an irradiated solution of 4,4'-di-*t*-butylbenzophenone (DBB) in IPA leads to the gradual disappearance of the long-wave absorption band and the reappearance of the spectrum of DBB, which indicates that the quinoid isomer is decomposed with re-formation of the ketone and the alcohol. Under the conditions used, the reaction is complete in less than 1 h. In Fig. 1 b, the upper curve (3) shows the result of a corresponding experiment with a short-wave irradiated $20.1\ \mu\text{M}$ solution of benzophenone in IPA. The absorbance values have been corrected for the dilution caused by the addition of the acid. The curve has its maximum at 254 nm , which is close to the maximum in the absorption spectrum of benzophenone in IPA, 253 nm . If the A -values of curve 3 at different wavelengths are divided by the values of the molar extinction coefficient of benzophenone at the same wavelengths it becomes evident, however, that there are large systematic deviations between curve 3 and the absorption spectrum of benzophenone. This was to be expected since Fig. 1 a indicates the presence in the solution of other light absorbing substances than the quinoid isomer.

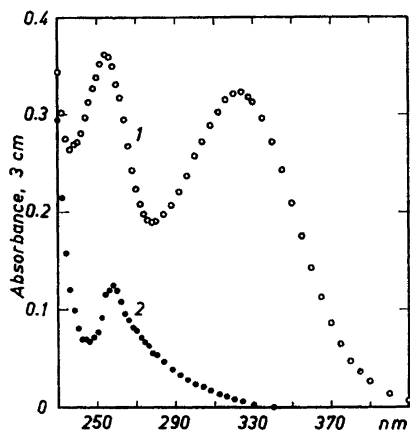


Fig. 1 a. Curve 1, open circles, absorbance of $20.1 \mu\text{M}$ solution of benzophenone in IPA after irradiation with short-wave UV light. Curve 2, filled circles, same solution after further irradiation with long-wave UV light. Curves 1–3 are averages from two experiments.

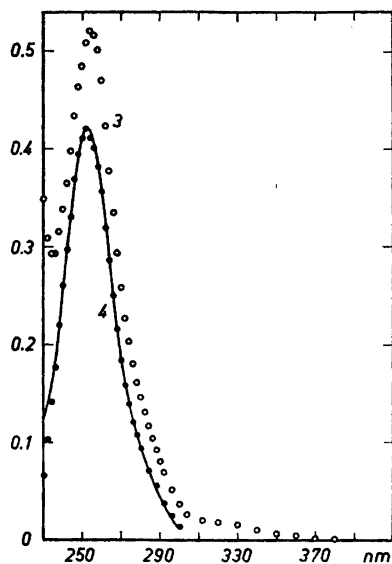


Fig. 1 b. Curve 3, open circles, solution irradiated as in curve 1 and then subjected to acidolysis. Filled circles, difference between curves 3 and 2. Full-drawn curve 4, calculated absorbance of $7.82 \mu\text{M}$ solution of benzophenone in IPA.

The filled circles in diagram 1 b represent the difference between curves 3 and 2. Except at wavelengths below 236 nm they fall, within limits of error, on the full-drawn curve 4 which represents the absorbance at wavelengths $< 300 \text{ nm}$ of a $7.82 \mu\text{M}$ solution of benzophenone in IPA.

The disappearance of the long-wave absorption band as the result of irradiation with long-wave UV light may be understood if it is assumed that light absorption causes the quinoid isomer to dissociate into the radicals from which it has been formed. These will then recombine to form either the mixed pinacol or its quinoid isomer.* Since the exciting light is absorbed by the quinoid isomer but not by the mixed pinacol, the final result should be the complete conversion of the former into the latter. Accordingly curve 2 cannot exactly represent the absorbance due to non-quinoid substances in the solution which has been subjected to acidolysis instead of to long-wave irradiation. The absorbance of the mixed pinacol formed during the latter process has to be subtracted. The spectrum of this pinacol, 1,1-dimethyl-2,2-diphenylethanol, is shown in Fig. 2, together with the spectrum of benzopinacol. Its concentration should be equal to that of the benzophenone formed

* As the solution does not contain unreacted benzophenone, conditions are unfavourable for the formation of benzopinacol.

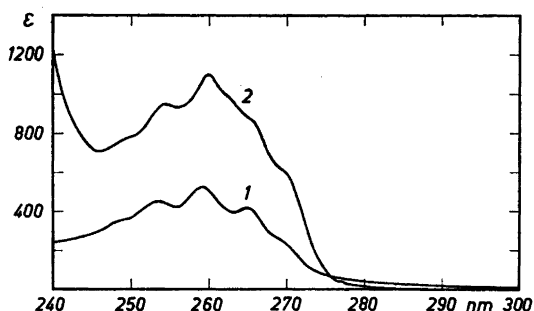


Fig. 2. Molar extinction coefficient (ϵ) vs. wavelength in nm of 1,1-dimethyl-2,2-diphenyl-ethanediol (curve 1) and benzopinacol (curve 2) in IPA.

on acidolysis, *ca.* 8 μM . Applying this small correction leads to even slightly better agreement with a benzophenone curve, with $A_{\text{max}}=0.434$ corresponding to a benzophenone concentration of 8.04 μM .

In the present case, the residual absorbance after the irradiation with long-wave UV light (Fig. 1 a, curve 2) by far exceeds the absorption to be expected if all the benzophenone originally present had been converted to the mixed pinacol or benzopinacol. The absorbance at the maximum, 258 nm, corresponds to a molar extinction coefficient of 2070 $\text{M}^{-1}\text{cm}^{-1}$, calculated per mole of benzophenone originally present in the solution. The highest maximum in the spectrum of the mixed pinacol is at 259 nm, with $\epsilon=520 \text{ M}^{-1}\text{cm}^{-1}$; similarly for benzopinacol, $\lambda_{\text{max}}=260 \text{ nm}$, $\epsilon/2=550 \text{ M}^{-1}\text{cm}^{-1}$. The residual absorption curve also extends farther toward the visible than the spectra of any of these two substances. Evidently, therefore, the solution whose absorption spectrum is given by this curve must have contained some other substance with considerably stronger light absorption and a different spectrum.

We have come to the conclusion that this substance or these substances are probably formed toward the end of the irradiation with light of wavelength 253.7 nm, as the result of light absorption by the pinacols formed. A number of facts support this view.

Thus it was found that if a solution, which has been subjected to long-wave irradiation until the quinoid band has disappeared, is again irradiated with light of wavelength 253.7 nm, this leads to increased light absorption. Two such experiments were made, starting with benzophenone in IPA and with 4,4'-dimethylbenzophenone (DMB) in ethanol. The result of the irradiation was in both cases a general increase in absorption, beginning at 390–400 nm and rising gradually to 320 and 300 nm, respectively. Below this limit it was approximately constant down to *ca.* 250 nm. Especially the results with DMB in ethanol showed clearly that there was no formation of a quinoid band. The long-wavelength limit before the irradiation was in both cases 340 nm.

Solutions of benzopinacols in alcohols have been irradiated by Matthias,⁷ using unfiltered light from a mercury arc. From a diagram, illustrating the resulting spectral changes with *p,p'*-dichlorobenzopinacol in IPA, it is evident that the main effect was a general increase in absorption, extending beyond 385 nm. In a recent paper,¹³ Mauser *et al.* report that irradiation of benzopinacol in methanol solution with light of wavelength 254 nm leads to a rapid increase in absorption in the whole region between 400 nm and 240 nm. We have irradiated a deaerated $6 \times 10^{-4} \text{ M}$ solution of the above-men-

tioned mixed pinacol in IPA with light of the same wavelength and obtained similar results. The limit of measurable absorption was 410 nm. The absorbance curve exhibited a shoulder at *ca.* 290 nm.

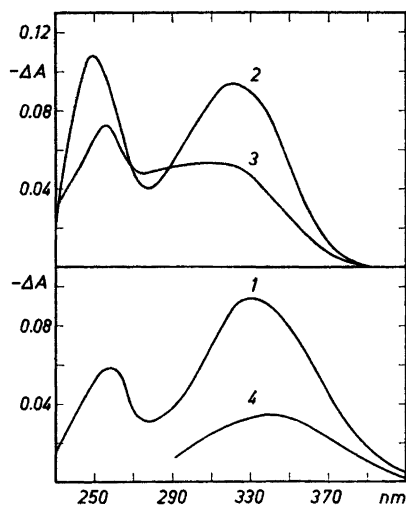
From Fig. 1 a it is evident that the quinoid isomer absorbs light not only in the long-wave band but also at shorter wavelengths. On prolonged irradiation of a solution of benzophenone in IPA with light of wavelength 253.7 nm, the absorbance in the long-wave band, after rising to a maximum, therefore again decreases as the result of the same process that takes place under the action of long-wave UV. In an experiment of this kind with a 20.1 μM solution, the irradiation was stopped when the absorbance at 323 nm had dropped to 50 % of its maximum value, and the solution was then subjected to acidolysis. The absorbance at 254 nm of the corrected acidolysis curve was found to be only 0.344, as against 0.521 in curve 3, Fig. 1 b. As expected, the partial decomposition of the quinoid isomer therefore resulted in a considerably reduced formation of benzophenone on acidolysis. The acidolysis curve also showed, however, that the absorbance at wavelengths > 306 nm, where the absorption of the benzophenone formed could be neglected, was nearly 3 times as high as in curve 3.

The molar extinction coefficients of the quinoid isomers. The results presented in the preceding section may be used to calculate the molar extinction coefficients of the quinoid isomers. Curves 1 and 2 in Fig. 1 thus show, that the disappearance of the quinoid isomer under the action of long-wavelength UV radiation resulted in a decrease in absorbance at the maximum in the long-wave band (323 nm) of 0.317. On the other hand, on the basis of one molecule of benzophenone formed on acidolysis from one molecule of the quinoid isomer, curve 4 indicates that the concentration of the latter was *ca.* 7.82 μM . A correction for the absorbance of the mixed pinacol formed in the former process raised this value to 8.04 μM . Since the layer thickness was 3 cm, these two values of the concentration correspond to ϵ_{323} for the quinoid isomer of 13 500 and 13 100 $\text{M}^{-1}\text{cm}^{-1}$, respectively.

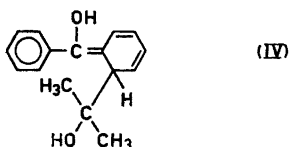
The former of these figures may be compared with the value of ϵ_{max} obtained by similar experiments on two other systems, where a correction for pinacol absorption could not be applied owing to lack of data. For the quinoid isomer formed in the system DBB in IPA, $\epsilon_{349}=12\ 000$; for the one formed by DMB in ethanol, $\epsilon_{318}=12\ 500$. The differences between the three values are not large, but are probably outside the limits of error. One source of error is that two different irradiated solutions have to be used for the determination of the residual-absorption curve and for the acidolysis experiment.

Results of irradiation experiments, showing that the long-wave absorption band formed by benzophenone in IPA is due to a mixture of isomers. From the spectral diagrams recorded in the course of a post-irradiation experiment with long-wave UV light, difference curves may be calculated, giving $-\Delta A$ as a function of λ during different stages of the process. In an experiment of this kind on a short-wave irradiated 20.1 μM solution of benzophenone in IPA, these curves showed very clearly that the long-wave quinoid band must, in this case, be due to at least two substances with different spectra. In the difference curve representing the spectral changes during the first 5 min of irradiation, $-\Delta A$ had its long-wave maximum at *ca.* 340 nm, as against 322 nm in the total difference spectrum. In later $-\Delta A$ -curves, the corresponding maximum was gradually displaced toward shorter wavelengths. The lower limit seemed to be *ca.* 321 nm.

Fig. 3. Curves 1—3, difference spectra from an experiment where a short-wave irradiated 20.1 μM solution of benzophenone in IPA was subjected to further irradiation with long-wave UV light. Curve 4, difference spectrum from an experiment where the short-wave irradiated solution was allowed to react with O_2 . For further explanations, see text.



The preferential decomposition of the substance with the higher value of λ_{max} must be due to the fact that, as mentioned earlier, the exciting light was mainly of wavelength 366 nm and was therefore more strongly absorbed by this substance than by the other. These two substances must be assumed to be the *ortho*- and *para*-isomers of the mixed isopinacol. As shown by the structural formula of the *para*-isomer (III, p. 2590) the three double bonds in this case form a cross-conjugated system. In the *ortho*-isomer, on the other hand, they form a linear-conjugated system (IV). This isomer should therefore have a higher value of λ_{max} . Further evidence supporting the view, that the substance absorbing at longer wavelengths must be the *ortho*-isomer, is furnished by certain experimental results that will be presented in a later section.



The $-\Delta A$ curve for the first 20 min of irradiation, Fig. 3, curve 1, shows a second, weaker absorption band with λ_{max} ca. 260 nm. In curve 2, which represents the spectral changes between 41 and 140 min of irradiation, this second band has increased considerably in strength, and its λ_{max} has been displaced to 249 nm. At the same time, the maximum in the long-wave band has been displaced from ca. 331 to 321 nm. The decrease in the relative ΔA values ($\Delta A/\Delta A_{\text{max}}$) at longer wavelengths seems particularly striking; at 370 nm, e.g., from 0.48 to 0.14.

The conclusion seems justified that curve 2 cannot be far from representing the spectrum of the pure *p*-isomer, whereas curve 1 represents the spectrum

of a mixture of the two isomers. Comparison of the position and shape of the short-wave bands in the two curves seems to show that also the spectrum of the *o*-isomer must possess a short-wave band, with λ_{\max} ca. 260 nm. The maximum in its long-wave absorption band cannot be far from 340 nm.

Whereas the spectral changes during the first 140 min of irradiation seem possible to account for as the result of the decomposition of only the above-mentioned two isomers, this is definitely not the case for the changes taking place on continued irradiation (140–350 min, curve 3). In curve 2, the two maxima are separated by a rather deep minimum (λ_{\min} 276 nm). This minimum has almost completely disappeared in curve 3. Besides remaining *p*-isomer, a new substance must have been decomposed, with considerable absorption in this wavelength region. On the other hand, from the fact that its decomposition takes place at such a late stage of the irradiation, it may be concluded that it possesses only relatively weak absorption at the wavelengths > 300 nm present in the exciting light. Its spectrum must therefore be very different from the spectra of the two isomers.

We have no suggestion to make regarding the structure of this substance (or mixture of substances). Possibly its formation may have had to do with the fact that the short-wave irradiated solution used in the experiment undoubtedly was somewhat over-irradiated, *i.e.*, it had received too large a dose of 253.7 nm radiation. However, the available material is insufficient for a discussion of this point.

Benzophenone in IPA. Spectral changes in the long-wave absorption band accompanying the reaction of the quinoid isomers with oxygen. In a previous paper we described some experiments where short-wave irradiated solutions of 4,4'-di-*t*-butylbenzophenone in IPA were saturated with oxygen or air.⁴ This led to the gradual disappearance of the long-wave absorption band and the reappearance of the spectrum of the ketone. A similar experiment was made with an irradiated 20.1 μM solution of benzophenone in IPA. It was not noticed at the time that in this case the reaction with oxygen not only resulted in decreasing absorbance in the long-wave absorption band, but also in a displacement of its maximum toward longer wavelengths. As shown by $-\Delta A$ curves, calculated from spectral diagrams recorded during the experiment, λ_{\max} remained constant and equal to 322 nm until ca. 77 % of the absorption band had disappeared, as measured by the decrease in absorbance at this wavelength. The two last difference curves for which $-\Delta A_{322}$ corresponded to 77–91 % and 91–100 % reaction, respectively, had $\lambda_{\max}=325$ nm and 340 nm. The latter of these curves is shown in Fig. 3, curve 4. Before saturation of the solution with air A_{322} was 0.317, at the end of the reaction 0.009.

The results show that both quinoid isomers react with oxygen, but the *ortho*-isomer much more slowly than the *para*-isomer. The percentage of the *ortho*-isomer was estimated at ca. 15.

The recorded absorption spectrum of the solution after completion of the reaction with oxygen could be directly compared with the corresponding curve after acidolysis, shown in Fig. 1, curve 3, since the value of c_0 was the same in both cases. The spectrum of the reaction products, as obtained by subtracting the residual-absorbance curve, Fig. 1, curve 2, in this case showed systematic deviations from a benzophenone spectrum, indicating that also another oxidation product had been formed, with maximum absorption at ca. 270 nm. The assumption that the absorbance of this oxidation product at wavelengths close to the maximum in the benzophenone spectrum could be neglected, gave a maximum value for the concentration of benzophenone = 6.7 μM . This shows

that at least 14 % less benzophenone had been formed in the reaction with O_2 than in the acidolysis experiments. It seems possible, therefore, that the reaction of the *ortho*-isomer with oxygen does not give benzophenone but a different oxidation product, with $\epsilon_{270} = ca. 10^4 M^{-1}cm^{-1}$.

No attempt will be made to discuss the mechanism of the reaction between the mixed isopinacols and O_2 . The experiment described above was the only one performed with an irradiated solution of benzophenone in IPA. The results of the experiments with 4,4'-di-*t*-butylbenzophenone in IPA indicated that the rate of oxidation was independent of the concentration of O_2 .*

4,4'-Di-*t*-butylbenzophenone in IPA. A short-wave irradiated 44 μM solution of DBB in IPA was subjected to post-irradiation with long-wave UV light for 343 min. The total difference spectrum obtained ($-\Delta A$ vs. λ in nm) is shown in Fig. 4a. From the long-wave maximum at 349 nm, $-\Delta A$ falls to a deep minimum at *ca.* 270 nm, with some indication of structure, and then rises to a second, much lower maximum at *ca.* 245 nm. There can be little doubt that this second maximum does not correspond to a maximum in the spectrum of the quinoid isomer. To obtain the absorbance of the quinoid isomer, the absorbance of the mixed pinacol, into which it is converted under the action of the light, has to be added to $-\Delta A$. The spectrum of this mixed pinacol is not known. However, the spectra of related compounds show that its absorption in the wavelength region in question may be expected to increase rapidly with decreasing wavelength. A rough estimate based on available data indicated that the short-wave maximum in the absorption spectrum of the quinoid isomer must be situated below 240 nm, and that its molar extinction

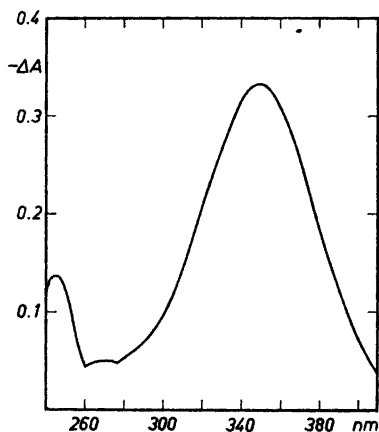


Fig. 4 a. Total difference spectrum from an experiment where a short-wave irradiated 44 μM solution of 4,4'-di-*t*-butylbenzophenone in IPA was subjected to further irradiation with long-wave UV light.

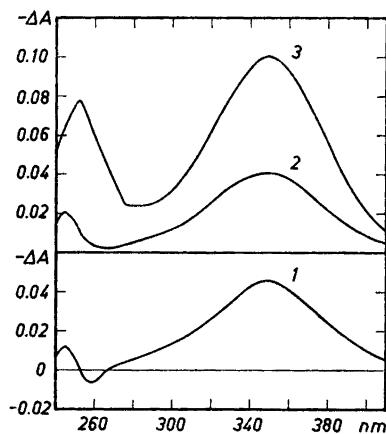


Fig. 4 b. Difference spectra from the same experiment, representing spectral changes during different stages of the irradiation with long-wave UV light.

* As shown by a calculation of the kind described in the preceding paragraph, dibutylbenzophenone was in this case the only light-absorbing oxidation product formed, within limits of error.

coefficient at the minimum (*ca.* 270 nm) should amount to about 1/6 of its value at 349 nm, *i.e.*, *ca.* 2000 M⁻¹cm⁻¹.

The spectral diagrams recorded in the course of the experiment gave no indication of the formation of more than one quinoid compound in this system. The long-wave absorption bands always had their maxima at 349 nm, within limits of error. The same applied to spectra recorded during previous experiments⁴ where a short-wave irradiated solution was allowed to react with oxygen. The reason why in this case only one quinoid compound is formed must be that the bulky substituents effectively prevent addition of dimethylhydroxymethyl radicals in the *para*-position. Also the high value of λ_{\max} indicates that it must be the *ortho*-isomer of the mixed isopinacol which is formed.

The spectral diagrams recorded during irradiation with long-wave UV light showed immediately that in this system there is no parallelism between the absorbance changes in the wavelength region around 260 nm and those in the long-wave absorption band. In Fig. 4 b, curve 1 represents the changes in absorbance during the first 10 min of irradiation. A decrease in A_{349} of 0.046 is here accompanied by an increase in absorbance in the region around 260 nm, amounting to 0.006 at the maximum. Similar difference curves were obtained until, after 70 min of irradiation, A_{349} had dropped to *ca.* 40 % of its original value, and the total increase in absorbance at the maximum (259 nm) was 0.016. Curve 2 represents the absorbance changes between 70 and 100 min, curve 3 the changes during the rest of the irradiation period. The strong decrease in absorbance in the region around 260 nm shown by curve 3 would seem to indicate that the substance, whose formation leads to increased absorbance in this region during the first stage of the irradiation, is made to disappear during the last stage.

A possible explanation of these results might be that, in the present case, the free radicals formed under the action of the light react with disproportionation to some extent. At a later stage of the irradiation the decrease in absorption by the quinoid isomer would enable the di-*t*-butylbenzophenone thus formed to compete for the exciting light, resulting in its disappearance by reaction with the alcohol. It is a question, however, whether this explanation is compatible with the relatively large difference between the maximum in the absorption spectrum of DBB in IPA (265 nm) and the observed maximum of the increase in absorbance shown by the first ΔA curves (259 nm). It is true that this increase represents the difference between the absorbance of the reaction products and that of the reactants, but the molar extinction coefficient of DBB is so high (23 400 M⁻¹cm⁻¹ at the maximum) that a shift in λ_{\max} of as much as 6 nm would hardly be expected.

4,4'-Dimethylbenzophenone in ethanol. Irradiation experiments of the kind described in the preceding section were made with 36 μ M solutions of DMB in ethanol. The results showed that in this system two quinoid isomers are formed. The $-\Delta A$ curves shown in Fig. 5 should approximately represent the spectra of the pure *ortho*- and *para*-isomers, respectively (curves 1 and 2). Compared to their analogues in the system benzophenone+

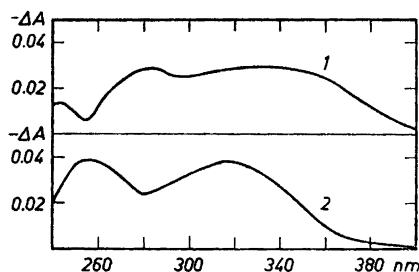


Fig. 5. Difference spectra from experiments where short-wave irradiated 36 μ M solutions of 4,4'-dimethylbenzophenone in ethanol were subjected to further irradiation with long-wave UV light.

IPA (*Cf.* p. 2596 and Fig. 3), both isomers have their long-wave maxima displaced 4–5 nm toward shorter wavelengths. Otherwise the spectra of the *para*-isomers are very similar, whereas the spectra of the *ortho*-isomers are quite different.

CONCLUDING DISCUSSION

As shown by Table 1, the values of λ_{\max} found for the mixed isopinacols formed by a given aromatic ketone in the three different alcohols increases in the order methanol, ethanol, isopropanol. The aliphatic free radicals formed as the result of light absorption by the ketone are in these alcohols $\text{H}_2\dot{\text{C}}\text{OH}$ (V), $\text{CH}_3\dot{\text{C}}\text{HOH}$ (VI) and $(\dot{\text{C}}\text{H}_3)_2\dot{\text{C}}\text{OH}$ (I). In the case of benzophenone, every methyl group introduced into V raises λ_{\max} by 3–4 nm. With 4,4'-di-*t*-butylbenzophenone, changing from ethanol to isopropanol produces a similar wavelength shift (4 nm). This indicates that in ethanol, just as in isopropanol, only the *ortho*-isomer of the mixed isopinacol is formed. With 4,4'-dimethylbenzophenone, on the other hand, the results are markedly different. The corresponding wavelength shift amounts to as much as 14 nm. Furthermore the value of λ_{\max} even in isopropanol is too low to be ascribed to the pure *ortho*-isomer, showing that also *para*-isomer must be formed to some extent. The alkyl substituents in the *para*-positions are in this case apparently not sufficiently bulky to prevent completely the addition in these positions even of radical I. Our experimental results in ethanol (*cf.* p. 2600) show that in this alcohol much more *para*- than *ortho*-isomer is formed. The low value of λ_{\max} observed with 4,4'-di-*t*-butylbenzophenone in methanol shows that the same probably applies also in this case. Addition of a hydroxymethyl radical (V) in a *para*-position seems to take place almost unhindered, in spite of the presence of the *t*-butyl groups.

From the extrapolated values of A_u/c_0d , listed in column 4, the yield of mixed isopinacol in extremely dilute solutions may be calculated, provided that its molar extinction coefficient at λ_{\max} is known. Experimental determinations of ϵ_{\max} were made only in three cases (p. 2596). In one of these cases (DBB in IPA) only the *ortho*-isomer of the mixed isopinacol is formed, in the other two mainly the *para*-isomer. The values found were approximately equal, the average being *ca.* $12\,500\text{ M}^{-1}\text{cm}^{-1}$. The yield figures listed in column 5 have been calculated on the basis of this value.

On the assumption that reactions between radicals I and II (or their equivalents in other systems) are the only reactions taking place in extremely dilute solutions, the yield of mixed isopinacol should be equal to $k_i/(k_i+k_p)$, where k_i and k_p are the rate constants for the formation of mixed isopinacol and mixed pinacol, respectively. Approximate values of the ratio k_i/k_p may therefore be calculated from the yield figures and are given in column 6. Evidently k_i is the sum of the rate constants for the formation of the *ortho*- and *para*-isomers.

A result of great interest is the strong dependence of the ratio k_i/k_p for a given ketone on the alcohol functioning as reductant. We shall not try to discuss the results in detail. Undoubtedly, the rates of both the competing reactions may be expected to be largely determined by both electronic and steric effects.

Not only reactions between unlike radicals but also between radicals of the same kind are of course possible. In irradiated solutions of, *e.g.*, benzophenone in the alcohols used, the aliphatic radicals would unite to form ethyleneglycol or methyl-substituted ethyleneglycols. These substances have no appreciable light absorption in the wavelength region investigated. Reactions between diphenylhydroxymethyl radicals (II), on the other hand, would lead to the formation of a mixture in constant proportions of benzopinacol and different quinoid isomers of benzopinacol. If these reactions were the only ones occurring, the same spectrum would therefore be obtained in the three alcohols, and also the extrapolated values of A_u/c_0d would be the same. From our experimental results with one and the same ketone in different alcohols the conclusion seems justified that reactions between radicals of the same kind were not taking place to a measurable extent.

As we have pointed out in an earlier paper, dealing with the photoreduction of benzophenone by isopropanol,⁶ the reaction between radicals I and II cannot be assumed to take place within the "cage" of solvent molecules in which they are formed.* From our results it may be concluded, therefore, that in the cases dealt with in the present paper the rate constants of the reactions between unlike radicals must be much higher than those of the corresponding reactions between like radicals. Similar results have been reported from studies of the kinetics of copolymerization reactions, where preferred interaction between unlike radicals has been observed in a considerable number of cases. In the system styrene—butyl acrylate the ratio of the cross-termination rate constant to the geometric mean of the rate constants for symmetric termination has been found to be as high as 150.¹⁵

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* In addition to the arguments presented in the paper cited, proving that the reaction is too slow to be a cage reaction, we may refer to an experimental study of a cage reaction by Waits and Hammond.¹⁴