

## PHOTOCHEMISTRY OF KETONES IN SOLUTION LVIII: MECHANISM OF PHOTOREDUCTION OF BENZOPHENONE BY BENZHYDROL

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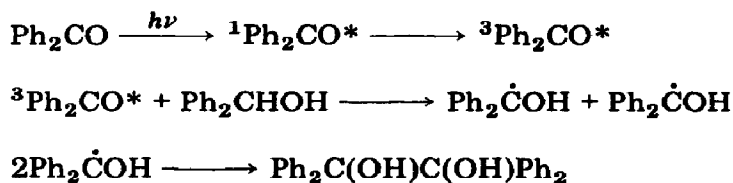
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### Summary

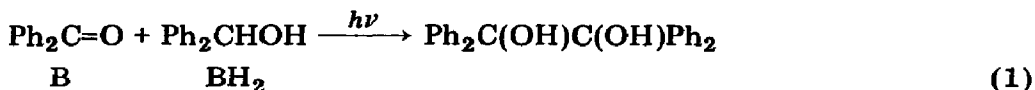
New studies of the mechanism of photoreduction of benzophenone by benzhydrol are reported. They demonstrate conclusively that the primary photochemical act involves hydrogen abstraction from benzhydrol by the  $n,\pi^*$  uncomplexed triplet state of benzophenone to give a triplet radical pair which does not couple to a measurable extent within the solvent cage. Escape of the radicals from the cage is followed by a series of hydrogen transfer reactions with ground state ketone, leading to scrambling of label when either the ketone or the hydrol is labeled initially. The competition between coupling and disproportionation of  $\text{Ph}_2\dot{\text{C}}\text{OH}$  and  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$  is contrasted and rationalized, as is the virtual absence of in-cage reaction in the benzophenone-benzhydrol system and the moderately efficient in-cage reactions in the benzophenone-isopropyl alcohol system. Thus, textbook descriptions of this prototype photoreduction should reflect the fact that the initially produced pair of radicals do not couple directly, but undergo a series of hydrogen transfers prior to coupling outside the initial solvent cage.

### 1. Introduction

Reference should be made to Part LVII [1]. The reduction of benzophenone (B) to benzpinacol by UV irradiation in the presence of secondary alcohols such as benzhydrol ( $\text{BH}_2$ ), as depicted in eqn. (1), is generally considered to be one of the best understood organic photochemical reactions.

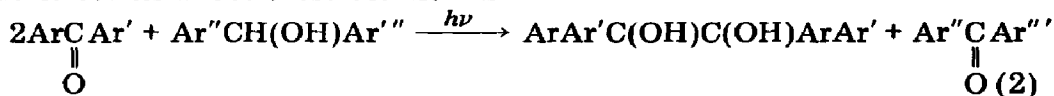


Scheme 1.



Scheme 1 gives the mechanism for this reaction, as presented in most standard photochemistry texts [2] and in some seminal papers in this field [3 - 7]. This mechanism clearly implies that the pair of radicals Ph<sub>2</sub>C $\dot{\text{O}}\text{H}$  (BH $\dot{\text{C}}$ ) generated in the initial photochemical act, as a result of hydrogen atom abstraction from the carbinol carbon of the alcohol by the triplet excited state of benzophenone (<sup>3</sup>B\*), couple to give benzpinacol. Labeled B or BH<sub>2</sub> should give half-labeled pinacol derived from combination of labeled and unlabeled BH $\dot{\text{C}}$ , assuming only minor isotope and substituent effects on the rates of radical coupling.

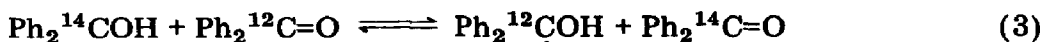
However, there are a series of reports dating originally from 1920 which indicate serious discrepancies with this mechanistic prediction. Over fifty years ago, Cohen [8] and Boeseken [9] measured the chlorine content of the pinacol product from the photoreduction of benzophenone by *ortho*- and *para*-chlorobenzhydrol, and demonstrated that unchlorinated pinacol was the exclusive reduction product in the first case and that it was a major product in the second reaction. *ortho*-Chlorobenzophenone and BH<sub>2</sub> gave dichlorinated benzpinacol as a major product. At that time the exact distribution of products was not determined. The results were generalized [8] in terms of eqn. (2), which represents the dominant and sometimes exclusive course of events under these conditions:



Given this reaction course, the composition of the pinacol product should change as the reaction proceeds, since the newly generated ketone Ar'' $\overset{\text{O}}{\parallel}{\text{C}}$ Ar'' competes for the incident light. This condition can be simulated

by varying the ketone:hydrol ratio of the starting material. Many years later Cziesla and Pape [10] verified the original observations using the systems *p*-Cl-B-BH<sub>2</sub> and B-*p*-Cl-BH<sub>2</sub>, and indeed found that the chlorine content of the pinacol was a sensitive function of the ketone:hydrol ratio. At high ratios of ketone to hydrol the initially formed pinacol was almost entirely derived from the ketone, in agreement with eqn. (2) and in conflict with the mechanism of Scheme 1.

To determine if some unexpected substituent effect might have influenced the reaction course in these systems [8, 9], Franzen [12] investigated the photoreduction of B by <sup>14</sup>C-labeled BH<sub>2</sub>. He found that the <sup>14</sup>C content of the pinacol after irradiation for 24 h in benzene and acetonitrile decreased as the B:BH<sub>2</sub> ratio increased. Although the predominant radical reaction appeared to involve coupling of the initially formed radical pair to give half-labeled pinacol (*i.e.* the extent of <sup>14</sup>C labeling was not consistent with eqn. (2)), the data were interpreted as providing evidence for a "redox reaction" involving hydrogen transfer:



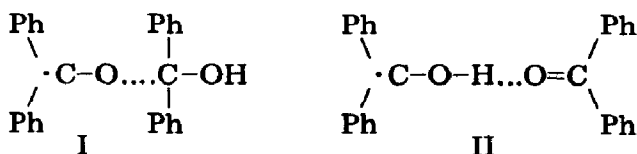
However, the exact distribution of pinacols containing 0, 1 or 2 atoms of  $^{14}\text{C}$  was not determined, nor was the time course of label incorporation. When a much more active sample of  $^{14}\text{C}\text{-BH}_2$  was used [10], the results were in much better accord with Cohen's [8] formulation. The activity of the pinacol was quite small at short conversions and at high ratios of  $\text{B}:\text{BH}_2$ , and increased with longer photolysis time and decreased  $\text{B}:\text{BH}_2$  ratios. Thus it was evident that the absence of coupling of the initial radical pair generated in the hydrogen abstraction step and the formation of pinacol predominantly (if not exclusively) from the ketone reactant, accompanied by oxidation of the hydrol to the corresponding ketone, are fundamental features of the photoreduction mechanism. Schenck and coworkers [11, 13] continually stressed the "trimolecular character" of the photoreduction, but did not otherwise provide a detailed mechanistic elaboration.

Further confirmation came from studies [11, 13] of the photoreduction of  $\text{B-d}_{10}$  by  $\text{BH}_2\text{-d}_0$ , in which the distribution of pinacols with 0, 10 and 20 deuteriums could be easily and precisely determined by mass spectrometry. After 10 min of irradiation the pinacol produced was 74.0%  $\text{d}_{20}$ , 22.8%  $\text{d}_{10}$  and 3.2%  $\text{d}_0$ , whilst after 1 h the distribution was 40.2%  $\text{d}_{20}$ , 40.4%  $\text{d}_{10}$  and 19.4%  $\text{d}_0$ , closer to the statistical distribution (1:2:1). The amount of  $\text{B-d}_0$  gradually increased to 72.3% after 1 h, but it was significant that there was no measurable formation of  $\text{BH}_2\text{-d}_{10}$  at any time. This indicates that radical disproportionation does not occur under these conditions, *i.e.*



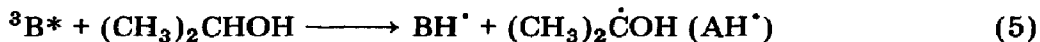
This observation is consistent with reports [4, 7] that photoreduction of  $\text{B}$  in optically active aliphatic secondary alcohols does not result in even partial racemization of the alcohol, although appreciable racemization results when optically active ethers (*e.g.* methyl 2-octyl ether) are used as reducing agents [14].

Franzen [12] has postulated that the hydrogen transfer of reaction (3) occurs through a ketone- $\text{BH}^\cdot$  complex in which electron transfer to give a ketyl radical anion  $\text{Ar}_2\ddot{\text{C}}\text{O}^-$  and the cation  $\text{Ar}_2\ddot{\text{C}}\text{OH}^+$  precedes proton transfer. This suggestion was based on a single observation that isotope scrambling occurs to a slightly greater extent in acetonitrile than in benzene as solvent, a finding that was not reproduced in the study of Cziesla and Pape [10]. Based on the finding that isotopic exchange occurs on generation of  $\text{BH}^\cdot$  by heating benzpinacol at  $140^\circ\text{C}$  in anisole in the presence of  $\text{B-d}_{10}$ , as shown by the formation of  $\text{B-d}_0$  as well as labeled and unlabeled  $\text{BH}_2$ , Schenck *et al.* [13] have suggested two types of radical complexes (I and II)



that might be involved in the hydrogen transfers occurring under these conditions. Charge separation was considered to be insignificant in these complexes. Electron spin resonance spectra of irradiated benzene solutions of B and BH<sub>2</sub> at sufficiently high ketone concentrations were subsequently found [15] to be consistent with hydrogen-bonded complexes of type II, and not consistent with the corresponding ketyl radical anion [16].

The hydrogen transfer reaction depicted in eqn. (3) is well substantiated between aromatic ketones and dialkylhydroxymethyl radicals (for an example involving a ketotriazole and benzhydrol, see ref. 17). Thus, the observation that the quantum yield for photoreduction of benzophenone by isopropyl alcohol approaches 2.0 at high ketone concentrations was explained twenty years ago [4, 18] in terms of the following sequence of reactions:



This sequence involves hydrogen abstraction from the carbinol carbon by  ${}^3\text{B}^*$ , followed by hydrogen transfer from AH $^\cdot$  to a second ground state ketone molecule, and then coupling of BH $^\cdot$  to give benzpinacol. This pathway was substantiated [19, 20] by generation of AH $^\cdot$  and related radicals thermally by decomposition of di-*t*-butyl peroxide in secondary alcohols in the presence of aryl ketones ArCOR, giving the dialkyl ketone and products (pinacol and hydrol) clearly derived from the radical ArR $\dot{\text{C}}\text{OH}$ . In at least one case [20] the intermediacy of a ketyl radical anion was ruled out by independent generation of this species, which led to a different set of products. In the benzophenone-isopropyl alcohol system the absence of cross coupling products ArRC(OH)C(OH)(CH<sub>3</sub>)<sub>2</sub> and pinacol (CH<sub>3</sub>)<sub>2</sub>C(OH)-C(OH)(CH<sub>3</sub>)<sub>2</sub> was a matter of concern, and it has only recently been resolved (see Section 3).

Thus it seems reasonably clear that hydrogen transfer (eqns. (3) and (6)) is an important general feature of aryl ketone photoreduction by secondary alcohols, typified by the benzophenone-benzhydrol system. Our curiosity was piqued by the fact that this has continued to be ignored by most writers of photochemistry texts and monographs, with the apparent exceptions only of Neckers and of Cowan and Drisko [21]. Also there is no complete account of the recent work on this problem [10, 11] in the standard refereed literature, suggesting that perhaps there is more to this problem than meets the eye. Considering that benzophenone photochemistry represents one of the foundations of organic solution photochemistry [2 - 7, 21, 22] and that several important aspects of this reaction are still not understood, at least to our satisfaction, we decided to investigate the benzophenone-benzhydrol reaction with the following goals in mind: (1) to verify the observations of Schenck and coworkers [11, 13] on the B-d<sub>10</sub>-BH<sub>2</sub> system; (2) to establish the molecularity of the basic photochemical step using flash techniques, which has never been reported; (3) to further probe the mechanism of the hydrogen transfer reaction, assuming the success of (1); (4) to determine the extent

of coupling of the initially formed radical pair within the solvent cage; (5) to attempt to devise a mechanistic scheme for this and related reaction systems which is consistent with all the data.

## 2. Results

The triplet lifetime  $\tau_T$  of benzophenone in benzene in the presence of benzhydrol was directly determined using nanosecond flash photolysis by procedures described previously [22]. The lifetime of  $^3B^*$  was independent of the concentration of B over the range  $10^{-4}$  -  $5 \times 10^{-2}$  M and decreased as the concentration of  $BH_2$  increased. The value of the hydrogen abstraction rate constant  $k_a$ , determined directly from the slope of a linear plot of  $1/\tau_T$  versus  $[BH_2]$ , was  $4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ . This is in excellent agreement with a previous indirect determination [6, 23] of  $k_a$  (approximately  $5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) from quenching of steady state irradiations assuming diffusion-controlled quenching rate constants, and with a value of  $2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  obtained from early relatively imprecise microsecond flash studies [24]. It is clear from these kinetic results that the key photochemical step involves interaction of a single uncomplexed ketone triplet with one molecule of benzhydrol, and that the second ketone molecule becomes involved only at a later stage of reaction.

To probe the dynamics of the system with respect to product formation, aliquots of B- $d_{10}$  and  $BH_2$ - $d_0$  were irradiated for varying lengths of time using the method of Roselius [11]. The pinacol product was isolated and subjected to mass spectrometric analysis after quantitative rearrangement to benzpinacolone. Recovered benzophenone was also analyzed mass spectrometrically. The results summarized in Table 1 clearly demonstrate that the proportions of B- $d_0$  (relative to total B) and of pinacol- $d_{10}$  and pinacol- $d_0$  (relative to total pinacol) increase with time, whilst the relative amount of

TABLE 1

Isotopic distributions in the product and the recovered starting material from photolysis of benzophenone- $d_{10}$  and benzhydrol- $d_0$  in benzene<sup>a</sup>

Time (min)	Pinacol			Benzophenone	
	$d_{20}$ (%)	$d_{10}$ (%)	$d_0$ (%)	$d_0$ (%)	$d_{10}$ (%)
0	—	—	—	—	99.98
15	85	9	6	10.5	89.5
30	77	15	8	28	72
45	55	33	12	37	63
60	40	35	25	45	55

<sup>a</sup>Irradiation with a 450 W Hanovia lamp through Corning 7-37 filters to cut off light below 300 nm. The solutions in quartz test tubes were purged with argon prior to irradiation. The tubes were topped with serum caps and irradiated in a carousel apparatus.

pinacol- $d_{20}$  steadily decreases. These data are in total agreement with the earlier findings of Roselius [11] on this system. At no time does the distribution of deuterated pinacols correspond either to random (*i.e.* statistical) coupling of  $BH^\cdot$  or to coupling of the radical pair formed directly upon hydrogen abstraction.

The effect of light intensity on the distribution of deuterated pinacols and on the yield of B- $d_0$  is shown in Table 2. The light intensity was systematically varied using wire mesh screens and the time of irradiation was adjusted so that the total quanta of incident light was constant from sample to sample. It is obvious that the lower the light intensity, the more the product distribution resembles that expected from eqn. (2). Increased light intensity should result in higher steady state concentrations of  $^3B^*$  and  $BH^\cdot$ , enhancing radical-radical reactions (coupling and disproportionation) at the expense of radical-molecule reactions such as the hydrogen transfer reaction of eqn. (3). Therefore, if B- $d_0$ , pinacol- $d_{20}$  and pinacol- $d_0$  arise as a result of hydrogen transfer reactions, the formation of these products relative to pinacol- $d_{10}$  should increase as the light intensity decreases. The results in Table 2 confirm this expectation with the exception of the data for pinacol- $d_0$  (see Section 3). It should be noted that in Table 1 the yield of pinacol- $d_{10}$  is greater than that of pinacol- $d_0$ , consistent with the trend observed earlier by Roselius [11], but the proportions are reversed in the runs reported in Table 2. We have no explanation for this discrepancy which seems to be beyond the limits of experimental uncertainty. The sensitivity of the product distribution to the light intensity is quite small in absolute terms, however, suggesting that the rate of hydrogen transfer is probably quite large and the energy barrier quite small. Schenck *et al.* [15] have suggested that  $E_{act} \gtrsim 7 \text{ kcal mol}^{-1}$  whilst for the related benzaldehyde-benzyl alcohol

TABLE 2

Effect of light intensity on the isotopic distributions in the product and the recovered starting material from photolysis of benzophenone- $d_{10}$  and benzhydrol- $d_0$  in benzene<sup>a</sup>

$I^0$ ( $\times 10^{-15} \text{ quanta s}^{-1}$ )	$I_{tot}$ ( $\times 10^{-15} \text{ quanta}$ )	Pinacol			B
		$d_0$ (%)	$d_{10}$ (%)	$d_{20}$ (%)	$d_0$ (%)
<i>Run I</i>					
2.2	1980	10.4	7.5	81.6	10.2
0.66	1972	8.5	7.0	84.5	12.6
0.15	1990	8.0	6.2	85.8	16.8
<i>Run II</i>					
2.0	1800	10.1	7.3	82.6	10.4
0.6	1974	8.4	6.8	84.8	12.7
0.14	1816	7.8	5.8	86.4	17.0

<sup>a</sup>Irradiation of argon-purged solutions on an optical bench using an Osram HBO 200 W light source and a Corning 7-51 filter to cut off light below 300 nm. The intensity of the incident radiation was varied using wire screens of different mesh sizes. Actinometry was carried out using 0.15 M potassium ferrioxalate.

system, Closs and Paulson [25] have estimated the rate constant for hydrogen transfer to be  $8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  from chemically induced dynamic polarization (CIDNP) data.

We also repeated the experiment [11] in which benzpinacol is decomposed thermally in the presence of B-d<sub>10</sub>, and obtained sizable quantities of BH<sub>2</sub>-d<sub>10</sub> which was identified mass spectrometrically. This result implies that unlabeled BH' derived from the pinacol transfers hydrogen to B-d<sub>10</sub> to form BH'-d<sub>10</sub>, which undergoes disproportionation.

Finally, the extent of combination of BH' to give benzpinacol within the initial solvent cage was determined from photoreductions carried out in the presence of camphorquinone(III) (Fig. 1) which is known [26] to be an excellent scavenger of "free" BH' radicals which have escaped from the solvent cage. For example, Weiner [27] has shown that, when benzophenone is irradiated in isopropyl alcohol at 350 nm in the presence of III (all light absorbed by benzophenone), the formation of benzpinacol is completely suppressed but benzhydrol and the mixed pinacol Ph<sub>2</sub>C(OH)C(OH)(CH<sub>3</sub>)<sub>2</sub> are still formed. In the B-d<sub>10</sub>-BH<sub>2</sub> system, the following questions were examined: (1) is any benzpinacol formed by coupling of radicals in the initial solvent cage; (2) if so, is it exclusively pinacol-d<sub>10</sub>; (3) is there any measurable radical disproportionation in the solvent cage, as indicated by formation of BH<sub>2</sub>-d<sub>10</sub>. In the event, no benzpinacol could be detected chromatographically and spectroscopically when the irradiation was carried out in the presence of III, and no benzpinacolone could be detected gas chromatographically after treatment of the photolysate under conditions used routinely to convert benzpinacol to benzpinacolone. Thus, it must be concluded that all benzpinacol is formed from BH' radicals which have escaped from the initial solvent cage. It should be noted that a detectable amount of BH<sub>2</sub>-d<sub>10</sub> was formed in this experiment, presumably the result of a very minor disproportionation reaction occurring within the solvent cage.

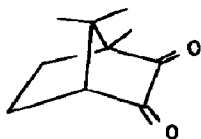
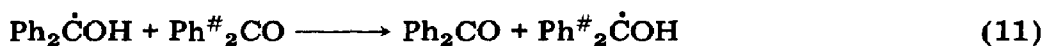
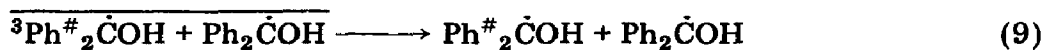
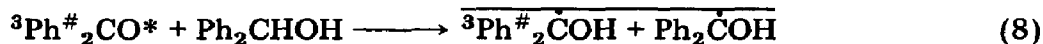
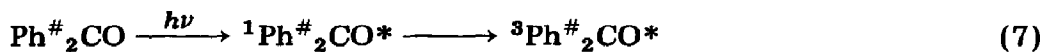


Fig. 1. The structure of III.

### 3. Discussion

The mechanism outlined in Scheme 2 for photoreduction of benzophenone (B) by benzhydrol (BH<sub>2</sub>) in an inert solvent such as benzene satisfactorily accounts for the reproducible findings pertaining to this reaction obtained in this study and in the previously cited studies back to 1920. In-cage reactions of the initially produced radical pair are negligible in this system, except perhaps for a very small amount of disproportionation



Scheme 2 (# represents some positional or isotopic label).

which becomes detectable when reactions of radicals which escape from the cage are suppressed by camphorquinone. Since the initial radical pair is generated from reaction of the  $n,\pi^*$  triplet state of benzophenone with ground state benzhydrol, the radical pair is born as a triplet pair with parallel spins of the two odd electrons. This triplet radical pair has no readily available mechanism for conversion to a singlet radical pair, a necessary step prior to coupling or disproportionation within the solvent cage, since the two  $\text{BH}^\cdot$  radicals are identical (except for isotopic substitution) and necessarily possess the same  $g$  values. A change of spin state of a radical pair from triplet to singlet (and vice versa) can still occur as a consequence of nuclear hyperfine interactions, but generally this is not as rapid or efficient as the mechanism resulting from loss of spin correlation due to the difference in  $g$  values of the partners in an initial radical pair [28]. Thus, in the photoreduction of benzophenone by isopropyl alcohol, where the two radicals produced as a result of hydrogen abstraction are different, the efficiency of cage reaction to form cross-coupled pinacol and disproportionation products has been determined by Weiner [27] to be  $0.11 \pm 0.02$ , in sharp contrast with the benzophenone–benzhydrol system. In both systems all benzpinacol formation occurs outside the initial solvent cage, although *a priori* this would not have been necessary in the B– $\text{BH}_2$  system if spin flip to give a singlet pair were competitive with diffusion out of the solvent cage. This is clearly not the case.

The  $\text{BH}^\cdot$  radicals which escape from the initial cage eventually encounter one another in solution, producing a singlet radical pair with a statistical probability of 25%. In the meantime, each radical has had several opportunities to encounter a ketone ground state molecule and to transfer a hydrogen by reactions (10) and (11) during the encounter. The resulting enhancement in the concentration of  $\text{BH}^\cdot$  radicals derived from the ketone at the expense of those derived from the hydrol becomes manifest in the composition of the pinacol product. The one surprising finding is that the relative yield of pinacol- $\text{d}_0$  decreases as the light intensity is decreased, an effect that we believe is beyond the limits of experimental uncertainty. High light intensity



should enhance radical-radical reactions, specifically coupling of  $\text{BH}^\cdot$ , at the expense of the hydrogen transfer reaction. (A mechanistically related reaction has been described previously [29].) Pinacol- $\text{d}_0$  is derived from undeuterated  $\text{BH}^\cdot$  originating either from  $\text{BH}_2$  or from labeled  $\text{BH}^\cdot$  which has transferred hydrogen to  $\text{B-d}_0$ , itself formed via hydrogen transfer. Formation of pinacol- $\text{d}_0$  via  $\text{BH}^\cdot$  derived only from  $\text{BH}_2$  should increase in importance as the light intensity increases and should be less likely than coupling of a labeled  $\text{BH}^\cdot$  with an unlabeled  $\text{BH}^\cdot$ , consistent with the relative proportions of pinacol- $\text{d}_0$  and pinacol- $\text{d}_{10}$  in Table 1 but inconsistent with the product ratios in Table 2. The pathway leading to pinacol- $\text{d}_0$  via hydrogen transfer should decrease in importance as the light intensity is increased, resulting in a trend in yield of pinacol- $\text{d}_0$  parallel to that observed for pinacol- $\text{d}_{20}$ , *i.e.* a decrease relative to the yield of pinacol- $\text{d}_{10}$ . This is not observed. The experimental finding might reflect the operation of some kinetic isotope effect on the coupling reaction (*i.e.* slightly faster coupling of unlabeled  $\text{BH}^\cdot$  compared with labeled  $\text{BH}^\cdot$ ) but this seems unlikely considering the magnitude of the rate constant for coupling, measured as  $1.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  in isopropyl alcohol [27]. More extensive studies of the effect of the light intensity in this and related systems might resolve this remaining anomaly.

Finally, some comments on the disproportionation of the radicals  $\text{R}_2\dot{\text{C}}\text{OH}$  are in order, comparing  $\text{R} = \text{Ph}$  with  $\text{R} = \text{CH}_3$ . The failure to observe measurable quantities of  $\text{BH}_2\text{-d}_{10}$  starting with  $\text{B-d}_{10}$  and unlabeled  $\text{BH}_2$ , in accord with earlier findings [11, 13], clearly demonstrates that the rate of coupling of such radicals when  $\text{R} = \text{Ph}$  is much larger than the rate of disproportionation. Exactly the opposite is the case for  $\text{R} = \text{CH}_3$ , as shown by studies [30] of the photochemistry of acetone in 2-propanol, where  $(\text{CH}_3)_2\text{-C}(\text{OH})\text{C}(\text{OH})(\text{CH}_3)_2$  is formed with relatively low quantum efficiency ( $0.105 \pm 0.005$  at  $25^\circ\text{C}$  and  $300 \text{ nm}$ ). The major reaction between  $(\text{CH}_3)_2\text{-COH}$  radicals is disproportionation by transfer of a  $\beta$  hydrogen to give the enol  $\text{CH}_2=\text{CH}(\text{OH})\text{CH}_3$  (which subsequently tautomerizes to acetone) and  $(\text{CH}_3)_2\text{CHOH}$ , *i.e.* the starting materials are regenerated. This reaction has been clearly demonstrated by Laroff and Fischer [31] using the CIDNP technique, and the ratio of disproportionation to coupling has subsequently been found to be  $7.8 \pm 1.5$  [30] (the efficiency of initial radical production is  $0.92 \pm 0.19$ ). Since this disproportionation reaction involves breaking and making of C-H bonds, it should be roughly thermoneutral and proceed with a low activation energy. Disproportionation of  $\text{Ph}_2\dot{\text{C}}\text{OH}$ , involving breaking an O-H bond and making a C-H bond, should be endothermic by at least  $10 \text{ kcal mol}^{-1}$  (see ref. 27 for a discussion and primary references), resulting in a much higher activation energy. Thus disproportionation of  $\text{Ph}_2\dot{\text{C}}\text{OH}$  should occur at a much lower rate than for  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ , whilst the rates of coupling to give pinacols should be similar in the two cases. The fact that  $\text{BH}_2\text{-d}_{10}$  is found on thermal decomposition of pinacol- $\text{d}_0$  in the presence of  $\text{B-d}_{10}$  is not inconsistent with this analysis. Presumably most  $\text{BH}^\cdot$  radicals, labeled and unlabeled, couple to give pinacol, whose isotopic content was not assayed in this experiment. The small fraction which leads

to  $\text{BH}_2\text{-d}_{10}$  (from either two labeled radicals or from reaction of a labeled with an unlabeled radical) is readily detected, since there is no  $\text{BH}_2$  in the system at the beginning of the reaction.

From studies [32] of the photochemical behaviour of  $(\text{CD}_3)_2\text{CO}$  in  $(\text{CH}_3)_2\text{CHOH}$ , we have measured the extent of exchange of deuterium in recovered acetone using nuclear magnetic resonance and mass spectra, and have shown that exchange of all the deuteriums for protons is much faster than exchange of only one or two protons. The former process almost certainly occurs via hydrogen transfer reactions analogous to reaction (11), whereas the latter could be the result of radical disproportionation. Thus, as in the case of  $\text{Ph}_2\dot{\text{C}}\text{OH}$ , hydrogen transfer to ground state ketone in the acetone system is much faster than radical-radical reactions. The difference is that, with acetone, the radical-radical reactions predominantly result in disproportionation whereas, in the benzophenone system, such interactions result in coupling.

#### 4. Conclusion

The photoreduction of benzophenone by benzhydrol is usually discussed from a mechanistic viewpoint in photochemistry textbooks as a prototypic ketone photoreduction reaction. However, the mechanisms as usually written [2] imply that the pair of radicals initially generated by hydrogen abstraction couple to give pinacol, which is totally incorrect. In fact there is no detectable coupling within the solvent cage, presumably because there is no available mechanism for spin flip to give a singlet radical pair which is sufficiently rapid to compete with diffusion of radicals out of the cage. Once outside, the radicals undergo many hydrogen transfers to ketone ground state molecules; this leads to scrambling of isotopic and substituent labels, originally present in one or other reactant, prior to radical coupling. Disproportionation on interaction of  $\text{Ph}_2\text{COH}$  radicals is expected to be slow relative to coupling, in contrast with the situation with dialkylhydroxymethyl radicals where disproportionation involves C—H rather than O—H bond cleavage. The description of these reactions in textbooks should reflect these facts, which are fundamental consequences of the spin states of the reactive ketone excited state and of the radical pair initially produced in the photochemical act.

#### 5. Experimental procedures

All solids were recrystallized and all liquids and solvents were redistilled prior to use. Mass spectra were recorded on a Varian Associates M-66 double focusing cycloidal path mass spectrometer and on a DuPont Model 21-292B mass spectrometer.

A typical photolysis and analytical procedure was as follows. A stock solution containing 0.01 M benzophenone- $\text{d}_{10}$  (Merck) and  $10^{-2}$  M benzhydrol in purified benzene was prepared. Aliquots of this solution were

degassed on a vacuum line through several freeze-pump-thaw cycles and were then irradiated with a 450 W Hanovia lamp for varying lengths of time in Pyrex tubes. The benzene was removed using a rotary evaporator while heating the sample in a tepid water bath, and the residue was washed several times with petroleum ether at 40 °C. The undissolved benzpinacol was separated, and was rearranged quantitatively to benzpinacolone by dissolution in acetic acid and heating at reflux for 5 min in the presence of a trace of iodine [33]. After removal of the bulk of the acetic acid, this sample was submitted for mass spectral analysis. Since the molecular ion was of low intensity under the conditions of the analysis, the peaks at  $m/e$  243 ( $\text{Ph}_3\text{C}^+$ ) through 258 ( $\text{Ph}_3\text{C}^+ \text{-d}_{15}$ ) were used to determine the deuterium content of the sample. The benzophenone in the petroleum ether solution was separated from benzhydrol by derivatization with freshly prepared 2,4-dinitrophenylhydrazine solution, and the hydrazone derivative was submitted for mass spectral analysis. Residual benzhydrol was then obtained by removal of the solvent and extraction.

Other experimental details are given in Tables 1 and 2 and in Section 2.

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