because of excess thermal energy, and therefore less likely to react with a cyclohexyl radical (Scheme II).

(4) The azine **1** does not react with benzene at 170°. However, if cyclohexane is added, the benzene does react and 1,1-bis(trifluoromethyl)norcaradiene is formed. This reaction of the diazo compound **4** with benzene to give a norcaradiene has been previously demonstrated.[3] It is likely that the benzene is intercepting some of the diazo compound **4** (or the carbene derived from it) that was formed from the reaction of the azine with cyclohexane.

Experimental Section

Reactions of Hexafluoroacetone Azine with Cyclohexane. The reactants listed in Table I were sealed in glass tubes and heated as indicated in an oil bath. The reaction products were identified and analyzed by glc and ^{19}F nmr and ir spectroscopy. All products were compared with authentic[1] samples for positive identification. The azine used in these experiments was prepared by photolysis of *N*-bromohexafluoroacetone imine.[4]

Polymerization of Acrylonitrile with Hexafluoroacetone Azine. A mixture of 400 μl of acrylonitrile and 40 μl of hexafluoroacetone azine was sealed in a glass tube and heated at 95° for 17 hr. A hard, solid block of white polymer formed. No change occurred to a control sample of acrylonitrile that contained no azine but was also heated at 95° for 17 hr.

2-Chloro-2-(trichloromethyl)-1,1,1,3,3,3-hexafluoropropane. A mixture of 50 ml of carbon tetrachloride and 20 g of bis(trifluoromethyl)diazirine was heated at 150° for 12 hr in a 400-ml stainless steel tube. The tube was cooled and vented, and the contents were distilled to give 8.65 g of 2-chloro-2-(trichloromethyl)-1,1,1,3,3,3-hexafluoropropane as a colorless liquid, bp 134–135°, that solidified upon cooling: mp 100–101° (sealed capillary); ^{19}F nmr (CCl_3F) δ 64.5 ppm from CCl_3F (s).

Anal. Calcd for $C_4Cl_4F_6$: C, 15.81; Cl, 46.67; F, 37.52. Found: C, 16.19; Cl, 47.01; F, 37.32.

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(3) D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Amer. Chem. Soc.*, **88**, 3617 (1966).

(4) W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, **30**, 1398 (1965).

The Behavior of Photochemically Generated Ketyl Radicals. A Modified Mechanism for Benzophenone Photoreduction

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Abstract: The photoreductions of benzophenone by isopropyl alcohol and of acetone by benzhydrol produce both benzpinacol and $(C_6H_5)_2C(OH)C(OH)(CH_3)_2$. In isopropyl alcohol solution, the latter product can only arise from a cage reaction. The fraction of cage reaction, *a*, has been measured to be 0.11 ± 0.02. This value demonstrates that electron spin flipping in a caged radical pair is fast compared with diffusive destruction of the cage.

While the photoreduction of benzophenone in isopropyl alcohol solution has been studied intensively, the exact mechanism is still a matter of controversy.[1-3] One of the most perplexing aspects is the failure to detect the mixed pinacol, $(C_6H_5)_2C(OH)C(OH)(CH_3)_2$ (I), in the reaction mixture. Analogous cross-coupled products have been reported in the photoreduction of benzophenone in toluene and cumene solutions,[1] and in methanol and ethanol solutions.[4] Furthermore the statistical distribution of these products was taken to mean that the products were not formed from the initial caged species. However, more recently the absolute termination constants of benzophenone ketyl, cumyl, and benzyl radicals have been measured.[5,6] The very high values obtained for these constants would seem to demand a cage reaction in these systems.

Despite the intense interest in photoreductions, very little work has been done on the system of benzhydrol in acetone solution. Earlier workers reported that the products were benzpinacol and isopropyl alcohol[7] while later workers said the reaction was not repeatable.[2] These reports are equally disturbing. If the reaction goes at all, one would expect compound I as a product even if there were no cage reaction. This comes about because there is no benzophenone in the solution to serve as a trap for the acetone ketyl radical, $(CH_3)_2\dot{C}(OH)$. Consequently, one would expect statistical product distribution unless the ketyl radicals disproportionated. Accordingly, it was decided to take a closer look at this system and at benzophenone in isopropyl alcohol solution in an attempt to shed some light on the seemingly odd behavior of ketyl radicals generated under these conditions.

Experimental Section

All solvents were Matheson Coleman Bell spectroscopic grade and were used as received except for isopropyl alcohol which was distilled from magnesium turnings. Benzophenone, benzhydrol, and benzpinacol were recrystallized from ethanol. Camphorquinone was recrystallized from hexane. The melting points were in agreement with literature values.

1,1-Diphenyl-2-methyl-propane-1,2-diol (I) was synthesized by the addition of excess methylmagnesium bromide to an ether solution

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(1) G. S. Hammond, W. P. Baker, and W. M. Moore, *J. Amer. Chem. Soc.*, **83**, 2795 (1961).

(2) J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patterson, and R. B. Martin, *ibid.*, **81**, 1068 (1959).

(3) N. Filipescu and F. L. Minn, *ibid.*, **90**, 1544 (1968).

(4) H. Mauser and V. Bihl, *Z. Naturforsch. B*, **22**, 1077 (1968).

(5) G. S. Hammond and S. A. Weiner, *Intra-Sci. Chem. Rep.*, **3**, 241 (1969).

(6) R. D. Burkhart, *J. Amer. Chem. Soc.*, **90**, 273 (1968).

(7) A. Schönberg and A. Mostafa, *J. Chem. Soc.*, 276 (1943).

of methyl benzilate.[8] The excess Grignard reagent was destroyed by addition of water. The ether solution was dried and then stripped with a rotary evaporator. The resultant yellow oil was triturated with pentane yielding a white precipitate. The solid was recrystallized from ethanol–water and dried over phosphorus pentoxide in a vacuum dessicator. The purified solid melted at 92–93.5° (lit.[8] mp 88–89°). Spectral data were ir (Nujol) strong 3470, 3305, 2920, and 2860 cm^{-1}; nmr (CCl_4) τ 2.32 (m, 3.3 H, arom), 2.77 (m, 6.5 H, arom), 7.47 (s, 0.7 H, OH), 8.05 (s, 0.7 H, OH), and 8.65 (s, 6.0 H, CH_3). On addition of a trace of D_2O the singlets at τ 7.47 and 8.05 disappeared. Gel permeation chromatography in *p*-dioxane yielded a molecular weight in the range 240–270.

Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.3; H, 7.49. Found: C, 78.9, 79.1; H, 7.47, 7.57 (Spang Laboratories).

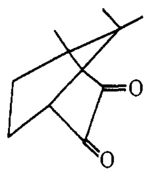
All photolyses were run on samples in Pyrex tubes which were degassed by several freeze–thaw cycles. The photolyses were run in a Rayonet RPR-100 photochemical reactor using the Model MGR-100 Merry-Go-Round and either the RPR-3000 or RPR-3500 Å lamps. After approximately 20% of the starting material had been consumed the tubes were opened and absorption spectra taken. The product analyses were then carried out on a Beckman GC4 chromatograph with a logarithmic scale recorder and an Infotronics digital readout system, Model CRC-114SB/42. The identification of 1,1-diphenyl-2-methylpropane-1,2-diol as a reaction product was shown by identical retention times with an authentic sample on 2-ft columns of 1.5% Carbowax 20M on Gas Chrom Q, 1.5% Ucon-H.B. 2000 on Gas Chrom Q, and 1.5% polyphenyl ether on Gas Chrom T varying both the flow rates and the column temperatures.

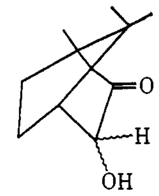
Under all conditions, benzpinacol decomposed to benzophenone and benzhydrol on the injector block while compound I was stable. Consequently, it was necessary to devise a different scheme for quantitative analysis. The reaction mixtures were evacuated on a rotary evaporator and then refluxed in a solvent of 15% concentrated sulfuric acid–85% glacial acetic acid to yield the rearrangement products $(C_6H_5)_3CCO(C_6H_5)$ from benzpinacol,[9] and $(C_6H_5)_2(CH_3)CCO(CH_3)$ and $(CH_3)_2(C_6H_5)CCO(C_6H_5)$ from I.[10] The latter two compounds overlapped somewhat on the Carbowax column used for the analysis while benzpinacolone had a much longer retention time. A series of standard solutions containing pure benzpinacol and compound I were made up in acetone solution and the above procedure followed. A plot of initial pinacol ratios *vs.* counts of the pinacolone ratios from the digital readout gave a good straight line. This plot was used to determine the ratio of benzpinacol to I in the photolyzed solutions. The appearance of the pinacolones in the photolysates treated in this manner is further proof that compound I is formed in the reaction.

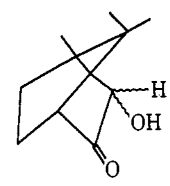
Attempts were made to cleave thermally compound I in solution at 160° in the presence of camphorquinone, a known scavenger of ketyl radicals. No decrease in the camphoquinone concentration was noted after 1 week. Using a Perkin-Elmer differential scanning calorimeter, compound I melted at 89–92° but the onset of decomposition was at 249°. Accordingly, evacuated solutions of I in benzene with and without camphorquinone were thermally decomposed at 250° for 3 days. All attempts to carry this out in isopropyl alcohol solution resulted in explosion.

Results

Thermolysis of 1,1-Diphenyl-2-methylpropane-1,2-diol (I). When an evacuated solution of I in benzene was heated at 160° for 5 days, no benzophenone was detected. The procedure was repeated with a sample containing both I and camphorquinone, II, a known scavenger of ketyl radicals.[11,12] Again benzophenone was not produced nor was there any loss of II or production of dihydrocamphorquinones, IIIa, b. The results of the thermal decomposition of I in benzene solution at 250° in the presence and absence of II are shown in eq 1 and 2, respectively. In the absence of


II


IIIa


IIIb

$$\underset{\text{I}}{(C_6H_5)_2C(OH)C(OH)(CH_3)_2} \xrightarrow[C_6H_6]{250^\circ} (C_6H_5)_2CO + (C_6H_5)_2CHOH + (CH_3)_2CO + (CH_3)_2CHOH + 7\text{ other products} \quad (1)$$

$$\text{I} + \text{II} \xrightarrow[C_6H_6]{250^\circ} \text{IIIa, b} + (C_6H_5)_2CO + (CH_3)_2CO + 7\text{ other products} \quad (2)$$

scavenger, II, the major products included benzophenone, benzhydrol, acetone, and isopropyl alcohol.[13] When the decomposition was carried out in the presence of camphorquinone, II, benzophenone and acetone were produced but not benzhydrol or isopropyl alcohol. Furthermore, camphorquinone was reduced to dihydrocamphorquinone, IIIa, b, demonstrating that I undergoes homolytic cleavage to yield two ketyl radicals, IV and V, as shown in eq 3. These radicals reduce II to IIIa, b. For the purposes of later discussion, the

$$\text{I} \xrightarrow[C_6H_6]{250^\circ} \underset{\text{IV}}{(C_6H_5)_2\dot{C}(OH)} + \underset{\text{V}}{(CH_3)_2\dot{C}(OH)} \xrightarrow{\text{II}} \text{IIIa, b} + (C_6H_5)_2CO + (CH_3)_2CO \quad (3)$$

important point is that at temperatures of 160° and below, compound I is thermally stable.

Photochemical Stability of Compound I. Two Pyrex tubes were irradiated in parallel at 300 nm for 150 min. The first tube contained a 0.016 *M* solution of I in isopropyl alcohol solution. The second tube held a solution in isopropyl alcohol which was 0.020 *M* in I and 0.058 *M* in benzophenone. The tubes were opened and the samples injected into the chromatograph. No loss of I occurred in either tube. Absorption spectra were run on both samples. The spectrum from the first tube indicated no absorption above 3400 nm. The solution in the second tube had turned yellow. The absorption spectrum agreed well with that published in the literature. The literature spectrum was obtained in the absence of I and assigned to an isopinacol.[3] A third tube consisting of a solution in acetone of benzhydrol (0.06 *M*) and I (0.021 *M*) was irradiated at 300 nm for 150 min. After photolysis, the concentration of I was reduced to 0.85 of its initial value while the concentration of benzhydrol dropped to 0.92 of its initial value.

$$(C_6H_5)_2CHOH + (C_6H_5)_2C(OH)C(OH)(CH_3)_2 \xrightarrow[(CH_3)_2CO]{300\text{ nm}} 15\%\text{ loss of I} \quad (4)$$

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[8] T. I. Temnikova and N. Almashi, *Dokl. Akad. Nauk SSSR*, **81**, 211 (1951); *Chem. Abstr.*, 47, 3818*e* (1953).

[9] "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 73.

[10] W. M. Schubert and P. H. LeFevre, *J. Amer. Chem. Soc.*, **91**, 7746 (1969).

[11] B. M. Monroe, S. A. Weiner, and G. S. Hammond, *ibid.*, **90**, 1913 (1968).

[12] B. M. Monroe and S. A. Weiner, *ibid.*, **91**, 450 (1969).

[13] Other workers have shown that the thermal decomposition of I also produces $(C_6H_5)_2C(CH_3)CO(CH_3)$, $(CH_3)_2C(C_6H_5)CO(C_6H_5)$, and 1,1-diphenyl-2,2-dimethyl-1,2-epoxyethane.[14–16]

[14] T. I. Temnikova, *J. Gen. Chem. USSR*, **15**, 514 (1945).

[15] I. W. Parry, *J. Chem. Soc.*, **99**, 1169 (1911).

[16] I. W. Parry, *Proc. Chem. Soc.*, **27**, 141 (1911).

This solution also was noticeably yellow. The absorption spectrum had the same shape as that of the solution in the second tube. No loss in intensity was observed in the absorption spectrum of the acetone solution after standing in air for 1 week. The product analyses of the photolysates demonstrate that compound I is photochemically stable in isopropyl alcohol solution with and without benzophenone. Also, it seemed likely that in acetone solution I could well be stable in low concentration.[17]

Production of I in the Photolysis of $(C_6H_5)_2CO$ in Isopropyl Alcohol and of Acetone Containing $(C_6H_5)_2CHOH$. The results of parallel irradiation at 300 nm of a 0.10 *M* solution of benzophenone in isopropyl alcohol and a 0.10 *M* solution of benzhydrol in acetone are shown in Table I and eq 5 and 6. The ratio of I relative to benzpinacol was determined by converting the pinacols to the corresponding pinacolones and measuring the ratio of pinacolones by glc. As it is well known that benzpinacol is stable to the photolytic conditions,[1-3,7] the fact that the ratio of I to benzpinacol was constant over the time period involved shows that I also is not lost under these conditions. At the end of the irradiation both solutions are visibly yellow. When the tubes were opened, the solutions were diluted and absorption spectra were obtained. The spectra were identical and agreed with that previously published by Filipescu and Minn.[3] The spectrum obtained from the acetone solution is shown in Figure 1. A similar spectrum was obtained from a solution of 20 g of benzhydrol in 100 ml of acetone which was exposed to sunlight for 2 months. A product analysis of this solution gave essentially the same results as were reported by Schönberg and Mostafa.[7] We could not detect any $(C_6H_5)_2C(OH)C(OH)(CH_3)_2$. A solution of benzophenone in isopropyl alcohol containing camphorquinone was irradiated at 350 nm under conditions where benzophenone absorbed all the light. While most of the benzophenone triplets are quenched by II, this quenching is not complete and some benzophenone triplets do abstract hydrogen atoms from the solvent.[11,12] Camphorquinone also serves to scavenge all of the free ketyl radicals in solution, preventing the formation of benzpinacol.[11,12] Under these conditions, compound I was detected in the product mixture along with benzhydrol. The ratio of benzhydrol to I was 0.8 ± 0.2.

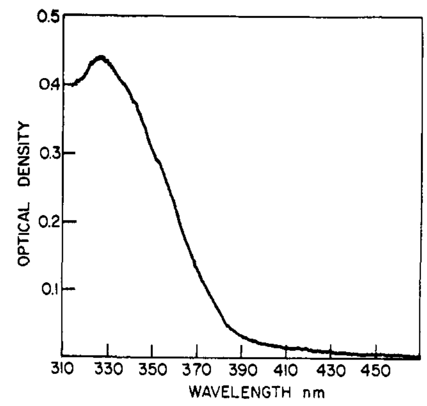

Figure 1. The absorption spectrum of a solution of benzhydrol in acetone after photolysis at 300 nm. The spectrum has previously been assigned to an isopinacol.[3]

Table I. The Ratio of $(C_6H_5)_2C(OH)C(OH)(CH_3)_2$ to $(C_6H_5)_2C(OH)C(OH)(C_6H_5)_2$ Formed on Photolysis

	System	
Time, min	$(C_6H_5)_2CO$ in $(CH_3)_2CHOH$	$(C_6H_5)_2CHOH$ in $(CH_3)_2CO$
40	0.066 ± 0.007	
122		0.33 ± 0.02
922	0.070 ± 0.007	0.34 ± 0.01

$$\underset{}{(C_6H_5)_2CO} \xrightarrow[(CH_3)_2CHOH]{300\ \text{nm}} \underset{1.000}{(C_6H_5)_2C(OH)C(OH)(C_6H_5)_2} + \underset{0.068}{\text{I}} \qquad (5)$$

$$(C_6H_5)_2CHOH + (CH_3)_2CO \xrightarrow{300\ \text{nm}} \underset{1.00}{(C_6H_5)_2C(OH)C(OH)(C_6H_5)_2} + \underset{0.34}{\text{I}} \qquad (6)$$

$$(C_6H_5)_2CO + (CH_3)_2CHOH \xrightarrow[\text{II}]{350\ \text{nm}} \underset{0.8}{(C_6H_5)_2CHOH} + \underset{1.0}{\text{I}} \qquad (7)$$

Discussion

Mechanism of Benzophenone Photoreduction in Isopropyl Alcohol. The fact that compound I is produced under conditions where all the acetone ketyl radicals, $(CH_3)_2\dot{C}(OH)$, are scavenged demands that I result from a cage reaction. The photolysis in the presence of camphorquinone produced both I and benzhydrol. Accordingly, the photolysis is best explained by the following sequence where overlines indicate a caged species. Analysis of this reaction scheme leads to eq

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(17) *A priori* there are two ways to account for the loss of I in the photolysis of a solution of I and benzhydrol in acetone solution. One is to assume that the acetone triplet abstracts a hydrogen atom from I according to reaction i or ii. The other is to assume that the abstraction is done by a ketyl radical, R = CH_3, C_6H_5. While reactions i and ii are exothermic as written, it would seem that the benzophenone

$$(CH_3)_2CO^3 + \text{I} \longrightarrow (C_6H_5)_2CO + 2(CH_3)_2\dot{C}(OH) \qquad \text{(i)}$$

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

$$R_2\dot{C}(OH) + \text{I} \longrightarrow R_2CHOH + (C_6H_5)_2CO + (CH_3)_2\dot{C}(OH) \qquad \text{(iii)}$$

$$R_2\dot{C}(OH) + \text{I} \longrightarrow R_2CHOH + (CH_3)_2CO + (C_6H_5)_2\dot{C}(OH) \qquad \text{(iv)}$$

triplet state should also possess enough energy to abstract a hydrogen atom from I. However, we have already shown that this does not occur. Furthermore, it is known that the benzophenone triplet state does not interact with benzpinacol.[1-3] These observations serve to rule out reaction i. However, reaction ii can be regarded as reaction i followed by an exothermic hydrogen atom transfer from acetone ketyl to benzophenone. Thus, it too is ruled out. If benzophenone ketyl, R = C_6H_5, could induce the decomposition of I, then I should also be lost when benzophenone is photolyzed in isopropyl alcohol containing a high concentration of I. But this did not occur. On the basis that acetone ketyl, R = CH_3, transfers a hydrogen atom readily to benzophenone, the loss of I in acetone, but not in isopropyl alcohol, is best accounted for by reaction iii and/or iv with R = CH_3. While we cannot distinguish between reaction iv and reaction iii followed by an exothermic hydrogen atom transfer, it is easy to show both iii and iv are exothermic as written since I is unstable relative to the corresponding ketone and alcohol. The slower loss of I at 250° in the presence of camphorquinone relative to the unscavenged sample is now easily explained. The scavenger reacts with the ketyl radicals, preventing reaction iii and/or iv. The induced reaction is slow enough that, at 25° in the absence of high concentrations of I, it cannot compete with the other reactions available to the acetone ketyl radical.

$$(C_6H_5)_2CO^3 + (CH_3)_2CHOH \longrightarrow \underbrace{(C_6H_5)_2\dot{C}(OH) + (CH_3)_2\dot{C}(OH)}_{VI} \quad (8)$$

$$VI \xrightarrow{k_9} \underset{I}{(C_6H_5)_2C(OH)C(OH)(CH_3)_2} \quad (9)$$

$$VI \xrightarrow{k_{10}} (C_6H_5)_2CHOH + (CH_3)_2CO \quad (10)$$

$$VI \xrightarrow{k_{11}} (C_6H_5)_2\dot{C}(OH) + (CH_3)_2\dot{C}(OH) \quad (11)$$

$$(CH_3)_2\dot{C}(OH) + (C_6H_5)_2CO \longrightarrow (CH_3)_2CO + (C_6H_5)_2\dot{C}(OH) \quad (12)$$

$$2(C_6H_5)_2\dot{C}(OH) \xrightarrow{k_{13}} (C_6H_5)_2C(OH)C(OH)(C_6H_5)_2 \quad (13)$$

14 and 15. The amount of cage reaction, a, is equal to

$$[I]/[(C_6H_5)_2C(OH)C(OH)(C_6H_5)_2] = k_9/k_{11} \quad (14)$$

$$[(C_6H_5)_2CHOH]/[I] = k_{10}/k_9 \quad (15)$$

$(k_9 + k_{10})/(k_9 + k_{10} + k_{11})$. The value of a calculated from the results in Table I is equal to 0.11 ± 0.02.[18]

The measured value of $a = 0.11$ is in sharp contrast with the earlier assumptions that $a = 1$[3] or $a = 0$.[1,2] Because the excited state of benzophenone which abstracts the hydrogen atom is a triplet, at the moment of formation the pair of radicals which constitutes VI must have parallel electron spins. Elementary energy considerations demand that before reactions 9 and 10 can occur, one radical must reverse its spin.[24] There is no such restraint on reaction 11. Consequently the nonzero value of a demands that, in at least some pairs, VI, spin flipping must occur prior to diffusion out of the solvent cage. If we knew the value of a for systems in which VI was generated thermally, then we would be able to relate quantitatively the rate of spin flipping to diffusion. As we shall show later, such a value can be calculated.

Mechanism of Benzhydrol Photooxidation in Acetone. The photolysis of benzhydrol in acetone solution is best explained by eq 16–23.[26] Using standard steady-state treatment, analysis of this scheme leads to eq 24–27. Alegebraic manipulation of these equations leads to the complex expression (28) for the ratio of I to benzpinacol.

$$(CH_3)_2CO^3 + (C_6H_5)_2CHOH \longrightarrow VI \quad (16)$$

$$VI \xrightarrow{k_{17}} I \quad (17)$$

$$VI \xrightarrow{k_{18}} (C_6H_5)_2CHOH + (CH_3)_2CO \quad (18)$$

$$VI \xrightarrow{k_{19}} (C_6H_5)_2\dot{C}(OH) + (CH_3)_2\dot{C}(OH) \quad (19)$$

$$2(C_6H_5)_2\dot{C}(OH) \xrightarrow{k_{20}} (C_6H_5)_2C(OH)C(OH)(C_6H_5)_2 \quad (20)$$

$$2(CH_3)_2\dot{C}(OH) \xrightarrow{k_{21}} \text{nonradical products} \quad (21)$$

$$(CH_3)_2\dot{C}(OH) + (C_6H_5)_2\dot{C}(OH) \xrightarrow{k_{22}} I \quad (22)$$

$$(CH_3)_2\dot{C}(OH) + (C_6H_5)_2\dot{C}(OH) \xrightarrow{k_{23}} (C_6H_5)_2CHOH + (CH_3)_2CO \quad (23)$$

$$dI/dt = k_{17}(VI) + k_{22}[(CH_3)_2\dot{C}(OH)][(C_6H_5)_2\dot{C}(OH)] \quad (24)$$

$$d(\text{benzpinacol})/dt = k_{20}[(C_6H_5)_2\dot{C}(OH)]^2 \quad (25)$$

$$k_{13}(VI) = 2k_{21}[(CH_3)_2\dot{C}(OH)]^2 + (k_{22} + k_{23})[(CH_3)_2\dot{C}(OH)][(C_6H_5)_2\dot{C}(OH)] \quad (26)$$

$$[(CH_3)_2\dot{C}(OH)] = (k_{20}/k_{21})^{1/2}[(C_6H_5)_2\dot{C}(OH)] \quad (27)$$

$$[I]/[\text{benzpinacol}] = (k_{17}/k_{19})[2 + (k_{22} + k_{23})/(k_{20}k_{21})^{1/2}] + k_{22}/(k_{20}k_{21})^{1/2} \quad (28)$$

If there is not much difference in radical reactivity on going from isopropyl alcohol to acetone solution, then $(k_{17}/k_{19}) = (k_9/k_{11})$ and $(k_{16}/k_{17}) = (k_{10}/k_9)$. Assuming that spin flipping is fast relative to diffusion, $(k_{23}/k_{22}) = (k_{18}/k_{17})$. With these assumptions and the experimental value of the ratio of I to benzpinacol, one derives the result that $k_{22} = 0.2(k_{20}k_{21})^{1/2}$. It should be stressed that k_{22} is the rate constant for cross termination, and $(k_{20}k_{21})^{1/2}$ is the geometric mean of the rate constants for self-coupling of the acetone and benzophenone ketyl radicals. Under conditions where there are no "special" interactions between a pair of dissimilar radicals, the cross-coupling rate constant is assumed to be twice the geometric mean of the self-coupling rate constants.[27]

Let us assume that the low value of the cross-coupling constant obtained in acetone solution applies to isopropyl alcohol solution.[28] The measured value of k_{20} in this system is $1.1 \times 10^8\ M^{-1}\ \text{sec}^{-1}$.[5] Assuming reaction 21 is diffusion controlled, *i.e.*, $k_{21} = 2 \times 10^9\ M^{-1}\ \text{sec}^{-1}$, $k_{22} = 1 \times 10^8\ M^{-1}\ \text{sec}^{-1}$. According to simple cage theory, $k_{22} = ak_D$, where k_D is the bulk encounter constant and is estimated at $2 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ for isopropyl alcohol.[29] These estimates lead to a cal-

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[18] If eq v is added to the reaction scheme, then this value is a lower limit of a. However, there are several grounds on which eq v can be eliminated. Under certain conditions, the quantum yield for disappearance of benzophenone in isopropyl alcohol is 2.[2] If reaction v were occurring, then the overall photoreaction cannot be this efficient. While the overall heats of reactions 10 and v are identical[19,20] it is unlikely that the activation energies and entropies for the two reactions are equivalent. In reaction 10, benzophenone ketyl radical, $(C_6H_5)_2\dot{C}(OH)$, is abstracting a hydrogen atom from acetone ketyl radical. In reaction v, the reverse is occurring. However, the O–H bond strength in $(C_6H_5)_2\dot{C}(OH)$ is 35 kcal/mol[21] while that of the O–H bond in $(CH_3)_2\dot{C}(OH)$ is 20 kcal/mol.[22] It has been shown that a good model for methyl hydrogen atoms is the hydroxyl hydrogen and *vice versa*.[22,23] Thus acetone ketyl can be looked on as having seven "equivalent" hydrogen atoms compared to only one in $(C_6H_5)_2\dot{C}(OH)$. For these reasons, it is felt that reaction v is negligible compared with reaction 10.

$$VI \longrightarrow (C_6H_5)_2CO + (CH_3)_2CHOH \quad (v)$$

[19] G. S. Parks, J. R. Mosley, and P. V. Peterson, Jr., *J. Chem. Phys.*, **18**, 152 (1950); G. S. Parks, K. E. Manchester, and L. M. Vaughan, *ibid.*, **22**, 2089 (1954).

[20] N. A. Lange, "Handbook of Chemistry," 9th ed, McGraw-Hill, New York, N. Y., 1956, p 1631.

[21] C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, **87**, 3361 (1965).

[22] R. Walsh and S. W. Benson, *ibid.*, **88**, 3480 (1966).

[23] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

[24] The energy available to VI is on the order of 80 kcal/mol, 68.5 kcal/mol from the triplet state of benzophenone,[22] and 11 kcal/mol from converting a C–H bond to an O–H bond.[22,23] But the triplet states of acetone, benzhydrol, and I all lie above 80 kcal/mol.[25]

[25] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965.

[26] In this system there is no direct evidence for reactions 18 and 23. These reactions are included because it is felt that the species involved behave identically in acetone and isopropyl alcohol solutions.

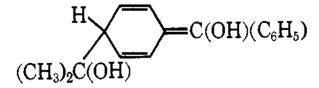
[27] W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 15.

[28] This assumption is consistent with the observation that the self-coupling rate constants for aromatic ketyl radicals in isopropyl alcohol solution fit a Hammett σ–ρ plot with a ρ value of -1.06.[6]

culated value for a of 0.05. This value has been calculated for thermally generated free radicals. Within the rather large errors associated with such a calculation, the agreement with the experimental value of 0.11 ± 0.02 for photolytically generated radicals is acceptable. This agreement provides support for the idea that spin flipping is fast compared with free-radical diffusion out of a solvent cage. This is equivalent to saying that the caged radical pair, VI, behaves identically whether generated photochemically (triplet state) or thermally (singlet state).

The Significance of the Yellow Color Assigned to an Isopinacol. In a recent paper, a mechanism for benzophenone photoreduction was proposed which assigned the yellow color to the key intermediate, VII.[3] The

$$\underset{\text{VI}}{(C_6H_5)_2\dot{C}(OH) + (CH_3)_2\dot{C}(OH)} \longrightarrow$$



VII (29)

$$\text{VII} + (C_6H_5)_2CO \longrightarrow (CH_3)_2CO + 2(C_6H_5)_2\dot{C}(OH) \quad (30)$$

mechanism is shown in eq 29 and 30. It was assumed that VI was quantitatively converted to VII and that, in a subsequent slow, dark reaction (30), VII reacted with benzophenone to produce two benzophenone ketyl radicals and acetone. Since we have detected I in the product mixture, VI cannot quantitatively produce VII. The photooxidation of benzhydrol in acetone also produces VI. If the yellow color is due to VII, then it is also formed in acetone. Accordingly, the key step in acetone solution should be reaction 31, the analogy to reaction 30. However, this

$$\text{VII} + (CH_3)_2CO \longrightarrow (CH_3)_2CO + (CH_3)_2\dot{C}(OH) + (C_6H_5)_2\dot{C}(OH) \quad (31)$$

reaction is merely the reverse of reaction 29 and thus should be negligible if reaction 29 were quantitative.[30] Finally, in our hands, the yellow color was found to be stable for at least 1 week. Thus while the yellow color might be due to the presence of compound VII, the yellow "intermediate" cannot go on to products at a rate consistent with the results of this and earlier studies.[1-3]

Conclusion

The present work has demonstrated that there are cage reactions in the benzophenone–isopropyl alcohol system. Other workers have assumed that there are no cage reactions in this system[1-3] and in the benzophenone–toluene[1,31] and benzophenone–cumene systems.[1] Interestingly, one of the first papers on benzophenone photoreduction in isopropyl alcohol reported that the ratio of benzpinacol formed to benzophenone lost was 0.39. No comment was made on this deviation from an expected value of 0.5, assuming no cage reaction.[32] A value of 0.39 would indicate a value of $a = 0.2$ for benzophenone–isopropyl alcohol. This is in fair agreement with our value of 0.11. The argument for no cage reactions in the photoreduction of benzophenone in the hydrocarbon systems was based on product studies and the idea that the more stable radical, cumyl, should lead to a lower amount of cross-product than the benzyl radical if the crossed product were formed in the cage. The fact that the yield of crossed product was higher in cumene was taken to mean that there was no cage effect. The latter reasoning was based on the assumption that the more stable cumyl radical terminates more slowly than the benzyl radical.[1] Recent work has shown this to be untrue.[6,33] The self-termination constant for cumyl radical is $8 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ [33] while that for benzyl is $4 \times 10^9\ M^{-1}\ \text{sec}^{-1}$.[6] As for the product studies, a reexamination of the original paper showed that in the benzophenone–toluene system the yields of isolated product based on benzophenone consumed were benzpinacol (0.51), benzyldiphenyl carbinol (0.43), and no bibenzyl.[1] It is clear that this product ratio is nowhere near the statistical distribution expected in the absence of a cage effect. In the benzophenone–cumene system, the isolated product yields were benzpinacol (24%), crossed product (48–60%), and bicumyl (24%).[1] Here the product ratio is the expected 1:2:1. However, this ratio is predicted only if the cross-termination constant is twice the geometric mean of the self-termination constants. In benzene solution, the termination constant for benzophenone ketyl radical is $1.1 \times 10^9\ M^{-1}\ \text{sec}^{-1}$.[4,5] Assuming the cross-termination constant is twice the geometric mean leads to a value of $6 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ for the cross-coupling rate constant. Using the formula, $a = k_{\text{cross}}/k_D$, with $k_D = 10^{10}\ M^{-1}\ \text{sec}^{-1}$,[29] $a = 0.6$. This is in serious disagreement with the conclusion that $a = 0$. This disagreement can be reconciled if the cross-coupling constant is less than twice the geometric mean and the cross-coupled product is also formed in the initial cage. For example, if the cross-coupling constant is equal to the geometric mean, a 1:2:1 product ratio would be obtained if $a = 0.2$. Thus the data on ketone photoreductions are consistent with the idea that spin flipping is fast compared to radical diffusion and that the cross-coupled products are, in part, formed from the initial caged pair of radicals.

Acknowledgment. I would like to thank Drs. L. R. Mahoney and H. C. Heller for many helpful suggestions during the course of this work.

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(29) H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

(30) It should also be pointed out that reaction 31 is some 13 kcal/mol less exothermic than reaction 30.[21,22]

(31) M. B. Rubin, *Tetrahedron Lett.*, 3931 (1969).

(32) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, **83**, 2789 (1961).

(33) S. A. Weiner and G. S. Hammond, *ibid.*, **91**, 986 (1969).