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Hydrogen Donating Solvent Participation in the Photochemistry of Benzaldehyde and Deoxybenzoin: A ^{13}C CIDNP Study

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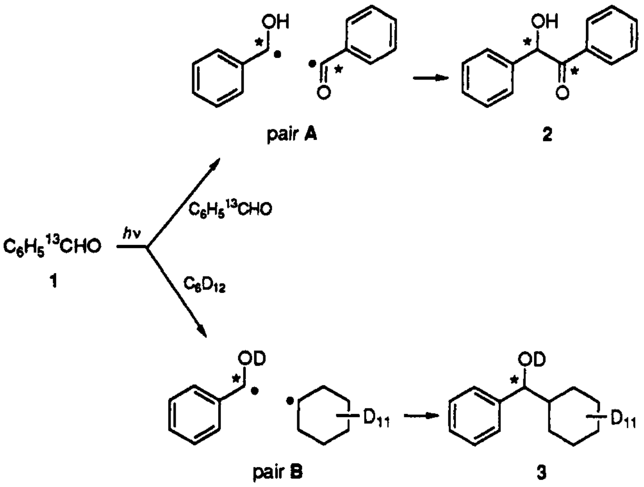
Photolysis of benzaldehyde (1; 90% $^{13}C{=}O$) in cyclohexane-d_{12} results in the formation of benzaldehyde-*h* and -*d* with emissive CIDNP for the $^{13}C{=}O$ function. This observation requires a secondary encounter of a free benzoyl radical with either phenylhydroxymethyl or cyclohexyl-d_{11} radicals. Photolysis of deoxybenzoin (5; 99% $^{13}C{=}O$) and *p*-chloro-5 (99% $^{13}C{=}O$) in cyclohexane-d_{12} also generates benzyldehyde-*h* and -*d* with the same emissive CIDNP for the $^{13}C{=}O$ function. These observations are rationalized in terms of a previously unreported primary intermolecular deuterium abstraction by photoexcited deoxybenzoin from the (deuterated) solvent. This assignment is supported by the significantly decreased measured lifetime of triplet deoxybenzoin in cyclohexane-*h* and -*d* (429 and 724 ns, respectively) compared to the lifetime in benzene (847 ns).

Introduction

The photochemistry of benzaldehyde (1) in homogeneous solutions has been studied in detail by analysis of the product distribution[1] and by spectroscopic techniques, such as ^1H chemically induced dynamic nuclear[2] or electron polarization[3] (CIDNP/CIDEP), or dynamic nuclear polarization (DNP).[4] In cyclohexane-d_{12} photoexcited benzaldehyde undergoes H-abstraction either from ground-state benzaldehyde or from the solvent to generate two different radical pairs, **A** and **B**, respectively.[2d,e]



Coupling of pair **A** generates benzoin (2) which shows emissive polarization at the carbonyl and enhanced absorption at the hydroxyl carbon.[2d–f] Coupling of pair **B** produces phenylcyclohexylmethanol (3). The emissive polarization observed for the methine proton of 3 was shown to be suppressed for the ^{13}C-labeled species as the result of the interaction with the large hyperfine coupling constant at the hydroxyl carbon.[2f,5] Hydroxybenzyl radicals which escape from pair **A** may transfer a hydrogen atom to ground state 1, thereby generating 1 with emissive ^1H polarization as well as an unpolarized hydroxybenzyl radical.[2a] Pair **A** can also be generated by photolysis of benzoin and displays similar ^1H CIDNP.[2b–d]

In this report, we describe the ^{13}C CIDNP observed upon irradiation of benzaldehyde (90% $^{13}C{=}O$), deoxybenzoin (99% $^{13}C{=}O$), and *p*-chlorodeoxybenzoin (99% $^{13}C{=}O$) in cyclohexane-d_{12} solution. These experiments demonstrated the unexpected formation of benzaldehyde-*d* with emissive $^{13}C{=}O$ polarization in all three cases. The results are rationalized in terms of intermolecular hydrogen (deuterium) abstraction by the photoexcited ketones from solvent molecules, and a disproportionation process following a secondary encounter of cage-escaped radicals.

Experimental Section

All CIDNP experiments were executed in a Bruker 250-MHz FT NMR spectrometer. The collimated beam of an Oriel 1000-W high-pressure Hg lamp was filtered through 1 M $NiSO_4$ solution and guided into the NMR probe by a quartz light pipe. Details of the setup have been described previously.[2e] Typical samples contained 0.02–0.04 M ketone in cyclohexane-d_{12}. The samples were degassed by purging with argon gas for 5 min immediately before irradiation. Benzaldehyde-$^{13}C{=}O$ (90% $^{13}C{=}O$) was purchased from Merck Isotopes and used as received. Deoxybenzoin-$^{13}C{=}O$ (99% $^{13}C{=}O$) and *p*-chlorodeoxybenzoin-$^{13}C{=}O$ (99% $^{13}C{=}O$) were synthesized as described previously.[2e]

The rate constants for the decay of the triplet deoxybenzoins were determined in argon-deaerated solutions by conventional laser flash photolysis with a Lambda Physics EMG 101 excimer laser at an excitation wavelength of 308 nm and a pulse width of ~10 ns.[6]

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(3) Atkins, P. W.; Frimston, J. M.; Frith, P. G.; Gurd, R. C.; McLauchlan, K. A. *J. Chem. Soc., Faraday Trans. 2* **1973,** *69,* 1542.

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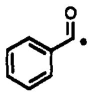
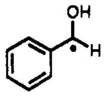
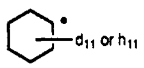
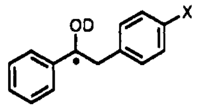
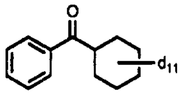
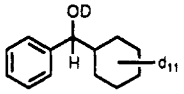
Table 1: Electron and Nuclear Magnetic Resonance Parameters for Free Radicals and Diamagnetic Products Generated by Photoexcited Benzaldehyde and Deoxybenzoin

parameter	g	$A_{^{13}C}$ (G)	A_H (G)	$^1J_{H,C}$ (Hz)	$^1J_{D,C}$ (Hz)	$^3J_{H,C}$ (Hz)
structure						
	2.0008[a]	130[b]				
	2.0031[c]	23[d]	−14.9[d]			
	2.0026[e]					
	2.0031[c]	23[d]				
C_6H_5CHO				170.9		5.0
C_6H_5CDO					26.3	5.0
						13.1
				140.7		

[a] Reference 8b. [b] Reference 8c. [c] Reference 8a. [d] Reference 2d. [e] Reference 9.

The irradiation of the samples for product analysis were conducted under conditions similar to those for the CIDNP experiments, i.e., with a 1000-W high-pressure Hg lamp through a 1 M $NiSO_4$ filter solution. The solutions were deoxygenated with argon prior to photolysis. The photolyses were carried to 10–60% conversion. The products were characterized by comparison of their GC/MS and GC traces with those of authentic samples.

Results and Discussion

A. Irradiation of Benzaldehyde in Cyclohexane. The CIDNP effects observed during the photoreactions of the three ketones investigated here are net effects, which can be interpreted on the basis of the net effect sign rule formulated by Kaptein.[7] The polarization of the recombination product benzoin can be explained as follows, on the basis of the magnetic parameters given in Table 1. The electronic g factor for the phenylhydroxymethyl radical is 2.0031,[8a] and the hyperfine coupling constant $A_{^{13}C(OH)} = +23$ G.[2d] The benzoyl radical has the magnetic parameters, $g = 2.0008$[8b] and $A_{^{13}C=O} = +130$ G.[8c] Given these data and the generation of the geminate pair from a well-established triplet precursor[2] ($\mu > 0$), Kaptein's rule[7] predicts emissive polarization ($\Gamma < 0$) for the carbonyls of the geminate product benzoin (A, $\epsilon > 0$; $\Delta g < 0$) and enhanced absorption ($\Gamma > 0$) for the hydroxy carbon of benzoin (A, $\epsilon > 0$; $\Delta g > 0$). The experimental results follow the predicted polarization pattern. Coupling of pair **A** produces benzoin with emission at the carbonyl carbon and absorption at the hydroxyl carbon, as expected for a geminate recombination product from a triplet precursor. Coupling of pair **B** produces cyclohexyl-d_{11}-phenylmethanol (**3**) with enhanced absorption at the hydroxyl carbon (doublet near 80 ppm, $^1J_{H,C} = 140.7$ Hz; $\Delta g > 0$, since $g_{cyclohexyl} = 2.0026$[9]), the predicted polarization for a geminate recombination product ($\epsilon > 0$).

In addition to the CIDNP of the geminate recombination products derived from pairs **A** and **B**, we also observe the formation of benzaldehyde-*h* as well as benzaldehyde-*d*, both with emissive $^{13}C{=}O$ polarization (Figure 1). The polarization of benzaldehyde-*h* (~189.5 ppm) shows a clear doublet-of-triplet pattern with $^1J_{H,C=O} = 170.9$ Hz and $^3J_{H,C=O} = 5.0$ Hz, ascribed to the protons in the ortho position. The benzaldehyde-*d* resonance shows a triplet-of-triplet pattern with $^1J_{D,C=O} = 26.3$ Hz ($J_H/J_D = 6.5$) and $^3J_{H,C=O} = 5.0$ Hz, due to coupling with the ortho protons. The deuterium causes a 0.3-ppm upfield shift in the adjacent $^{13}C{=}O$ as compared to the chemical shift of benzaldehyde-*h*, in line with related D-induced changes in chemical shift.[10] The magnitude of the $^{13}C{=}O$ polarization of benzaldehyde-*h* is about 3 times that of benzaldehyde-*d*. Neglecting any effect of the isotopes on the ^{13}C spin-lattice relaxation, this observation would indicate a 3-fold higher yield of benzaldehyde-*h* compared to benzaldehyde-*d*.

The emissive polarization of benzaldehyde-*h*-$^{13}C{=}O$ ($\Gamma < 0$) can be explained by one of two divergent mechanisms, either from the benzoyl radical by geminate disproportionation of pair **A** ($\Delta g < 0$; $\epsilon > 0$) or, alternatively, from phenylhydroxymethyl radicals, which escape and become diffusively separated from their counterradicals in either pair **A** or **B**, by H (D) transfer to another benzaldehyde molecule ($\Delta g > 0$; $\epsilon < 0$).[2a] Both pathways have been considered as an explanation for the ^1H polarization.[2b]

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(6) (a) Wang, J. F.; Doubleday, C. E., Jr.; Turro, N. J. *J. Phys. Chem.* **1989**, *93*, 4780. (b) Wang, J. F.; Rao, V. P.; Doubleday, C. E., Jr.; Turro, N. J. *J. Phys. Chem.* **1990**, *94*, 1144.

(7) Kaptein, R. *J. Chem. Soc., Chem. Commun.* **1971**, 732.

(8) (a) Wilson, R. *J. Chem. Soc. B* **1968**, 64. (b) Paul, H.; Fischer, H. *Helv. Chim. Acta* **1973**, *56*, 1575. (c) Krusic, P. J.; Rettig, T. A. *J. Am. Chem. Soc.* **1970**, *92*, 722.

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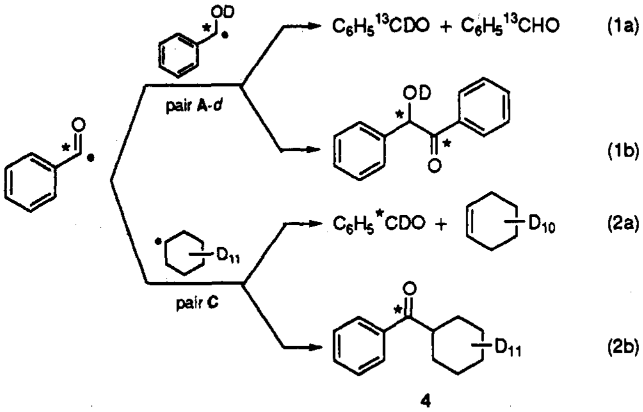
(10) Breitmeier, E.; Jung, G.; Voelter, W.; Pohl, L. *Tetrahedron* **1973**, *29*, 2485–2489.

Although benzaldehyde is a possible product of geminate pair disproportionation, such a pathway would lead to enhanced absorption (as found in the carbonyl carbon of benzoin), not the observed emission. Thus, the observed signal direction (E; $\Gamma < 0$) is inconsistent with geminate disproportionation of pair **A** as the predominant source of this polarization. Furthermore, the $^{13}C{=}O$ polarization of benzaldehyde-*d* cannot be explained via either of the disproportionation of pair **A** or the H-exchange pathway, because neither pathway provides a source for the deuterium atom at the formyl position of benzaldehyde. Clearly, a different pathway is required to explain both the sign of the polarization and the incorporation of deuterium in benzaldehyde-*d*.

One plausible explanation for the benzaldehyde-*d* polarization, and for a fraction of benzaldehyde-*h*, would invoke a "free" encounter of benzoyl radicals (escaped from pair **A**) with either phenylhydroxymethyl or cyclohexyl radical, both stemming from pair **B**. The resulting pairs, pair **A**-*d* and pair **C**, respectively, might couple or disproportionate. Coupling of pair **A**-*d* would generate benzoin-OD, with ^{13}C polarization as discussed above; coupling of pair **C** generates cyclohexyl phenyl ketone, (**4**; $^{13}C{=}O$, $\delta \sim 201$ ppm), which was identified by comparison with authentic material. Pathways 1a or 2a are expected to generate emissive polarization (μ, ϵ, $A > 0$, $\Delta g < 0$, $\Gamma < 0$) for benzaldehyde-*d*, whereas benzaldehyde-*h* from eq 1a would show enhanced absorption (μ, ϵ, A, $\Delta g > 0$, $\Gamma > 0$). The overall emission of benzaldehyde-*h* can be explained, as was the case for the ^{1}H polarization, if the absorptive polarization of benzaldehyde-*h* produced in step 1a is outweighed by the emissive polarization of benzaldehyde-*h* produced via H- or D-transfer from phenylhydroxymethyl radicals, escaped from pairs **A** or **B**, to ground-state benzaldehyde.



The hypothesis that (polarized) products can originate from the disproportionation of *secondary* random or free-radical pairs is not without precedent. For example, Closs and Miller observed microsecond time-resolved ^{1}H CIDNP effects during the photolysis of deoxybenzoin (**5**) and noted a significant rise of polarized **5** in the time range (0.1–1 μs) corresponding to secondary encounters of cage-escaped radicals.[11] Also, the ^{1}H-polarization for para-substituted benzaldehydes observed during the photolysis of several para-substituted benzils was ascribed to free-radical encounters of benzoyl and cyclohexadienyl radicals and subsequent disproportionation.[12] Finally, time-resolved CIDNP techniques have been applied to study the rates of hydrogen transfer from ketyl radicals to benzaldehyde, and between two ketyl radicals.[13] Again, the latter pair clearly is formed in a free-radical encounter. These findings combine to suggest that secondary encounters of cage-escaped radicals are of general importance for the course of photoreactions of ketones in homogeneous solutions. Of course, the observation of $^{13}C{=}O$ polarized benzaldehyde-*h* and -*d* discussed here elucidate the intricacies of this mechanism with special clarity. We have observed additional evidence for this reaction type during the photolysis of deoxybenzoin (**5**; 99% $^{13}C{=}O$) or its *p*-chloro derivative (99% $^{13}C{=}O$) in cyclohexane-d_{12}.

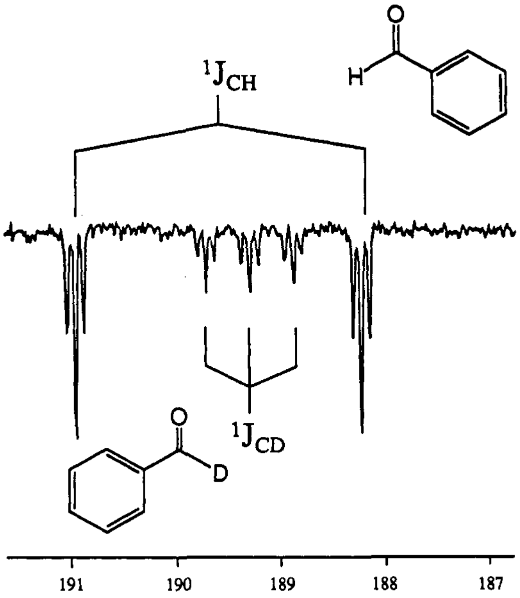
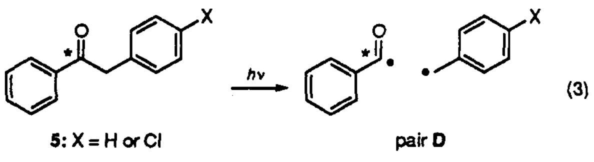


Figure 1. ^{13}C CIDNP of 20 mM benzaldehyde (90% $^{13}C{=}O$) in cyclohexane-d_{12} obtained from a Bruker 62.8-MHz FT NMR without proton decoupling. The rf pulse angle is 15° and eight FIDs were collected. The total data acquisition time is 12 s.

B. Photochemistry of Deoxybenzoin in Cyclohexane. Photoexcited **5** is well known to undergo Norrish type I α-cleavage, producing geminate triplet benzoyl-benzyl radical pairs (pair **D**).[14] Geminate recombination of this pair regenerates the starting material and is known to give rise to strong ^{1}H CIDNP effects;[2b] we have observed, in addition, an interesting feature of the ^{13}C polarization. Because the $^{2}J_{H,C}$ coupling constants for the benzylic and the benzoyl ortho protons are very similar, the $^{13}C{=}O$ signals of the un-decoupled spectrum appear as quintets at 195 and 194.5 ppm for **5** and *p*-chloro-**5**, respectively (Figure 2). If induced in pair **D** through geminate recombination, the $^{13}C{=}O$ signal is expected to show emission ($g_{benzyl} = 2.0025$;[8b] $\Delta g_{C=O} < 0$; ϵ, μ, $A > 0$), as was indeed observed.



Surprisingly, emissive ^{13}C polarization for both benzaldehyde-*h* and -*d* was also observed during the photo-

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(11) Closs, G. L.; Miller, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 3586.

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(14) Heine, H.-G.; Hartmann, W.; Kory, D. R.; Magyar, J. G.; Hoyle, C. E.; McVey, J. K.; Lewis, F. D. *J. Org. Chem.* **1974**, *39*, 691.

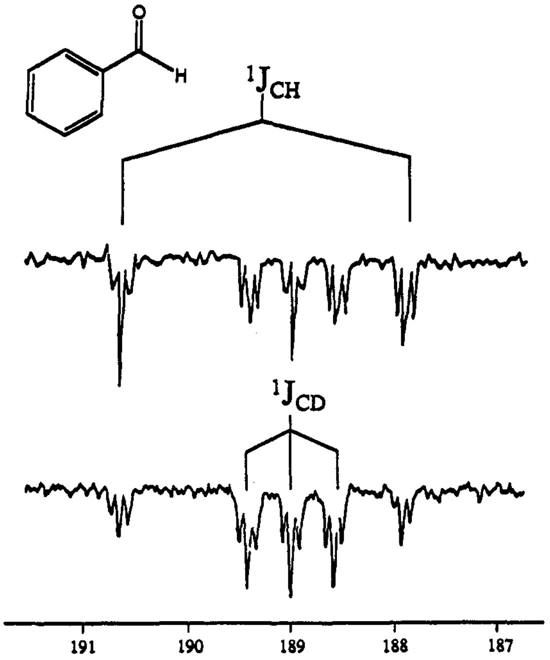
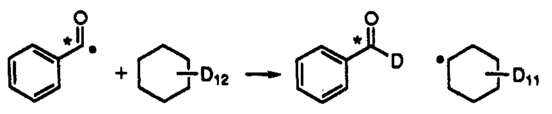


Figure 2. ^{13}C CIDNP effects (62.8 MHz; ^1H undecoupled) observed during the UV irradiation of 40 mM dexoybenzoin (99% $^{13}C{=}O$) in cyclohexane-d_{12} (top) and 40 mM p-chlorodexoybenzoin (99% $^{13}C{=}O$) in cyclohexane-d_{12} (bottom). The rf pulse angle is 10°; a total of 512 FIDs were accumulated with total acquisition time of 12 min 48 s. The spectral range of 193–202 ppm is shown.

reaction of **5** as well as p-chloro-**5** in cyclohexane-d_{12}; both **1**-*h* and **1**-*d* (Figure 3). The CIDNP enhancement ratio of **1**-*h* to **1**-*d* was about 1:1 for **5** and 1:2 for p-chloro-**5**. In addition, we also observed emission signals at the characteristic chemical shift of phenyl cyclohexyl ketone (**4**), which must be formed by free radical pairs. The intensity of the polarization observed for **4** is comparable to that of regenerated **5**. In the absence of major differences in the ^{13}C spin lattice relaxation times of the diamagnetic products, **4** and **5**, this finding also indicates the importance of the secondary encounters of cage-escaped "free" radicals.

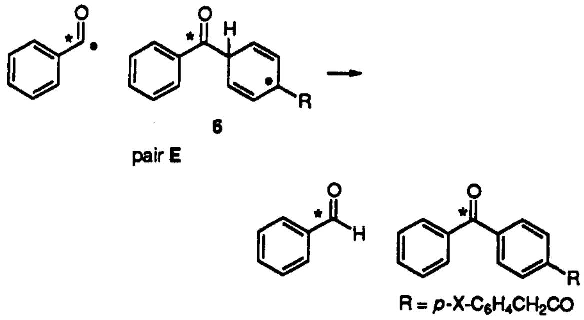
The observation of polarized **1**-*h* and -*d* was particularly unexpected, since the observed polarization (E; $\Gamma < 0$) suggested a geminate disproportionation mechanism ($\epsilon > 0$ with $A > 0$ and $\Delta g < 0$). The only logical source of benzaldehyde in this reaction is the benzoyl radical and the only possible deuterium source is the deuterated solvent. Hydrogen abstraction by free benzoyl radicals from n-hexane, a reaction generating **1**-*h*, has been proposed.[3] However, this process can only yield enhanced absorption (Δg, $\epsilon < 0$; μ, $A > 0$), a polarization that is opposite to the observed effect. In addition, this pathway is unlikely to retain any polarization in the benzaldehyde formed from the following argument. H-abstraction by benzoyl is relatively slow ($k_{C_6H_{14}} \sim 10^3$ M^{-1} s^{-1})[3] and D-abstraction should be significantly slower. Accordingly, the rate of D-abstraction (eq 4) in neat cyclohexane ($[C_6H_{12}] = 9.3$ M^{-1}; $k \times [C_6D_{12}] \leq 10^4$ s^{-1}) is expected to be much slower than the relaxation of the polarized benzoyl radical ($T_1 \approx 10^6$ s^{-1}).[15]



(4)

Clearly, polarized **1** from the photolysis of **5** must arise from secondary encounter free-radical pairs. The simplest such pair can be generated by free encounters of benzoyl radicals (from pair **D**) with cyclohexyl-d_{11} radicals. However, the resulting pair cannot be the exclusive source of the observed polarization, since it can generate only **1**-*d* (and **4**), but not **1**-*h*. Therefore, a reasonable source of H- and, very likely, a more efficient source of D-substituted radicals is required. We consider two such pathways, either the free-radical addition of benzoyl to **5** (or p-chloro-**5**), or a pathway initiated by intermolecular D abstraction by photoexcited deoxybenzoin from the solvent. The first reaction is a source of H only, whereas the other may account for **1**-*h* and **1**-*d*.

The addition of free radicals to the para position of aromatic rings is well supported. For example, CIDNP evidence suggests that pairs of benzyl radicals couple to yield semibenzenes;[16] the specific formation of cyclohexadienyl radicals has been invoked to account for the formation of oligomeric products in the photolysis of benzoin alkyl ethers.[17] Because of such precedent, the ^1H polarization of **1**-*h* observed during the photolysis of benzil was explained via the addition of benzoyl to benzil, free-radical encounter of the resulting cyclohexadienyl radical with a second benzoyl, and disproportionation.[12] Similarly, addition of benzoyl to **5** (or p-chloro-**5**) would give rise to a cyclohexadienyl species **6**, whose free-radical encounter with a second benzoyl (→ pair E) followed by disproportionation (eq 5) would generate **1**-*h* with the experimentally observed ^1H and ^{13}C polarization (^{13}C or ^1H: $\Delta g < 0$; μ, ϵ, $A > 0$; E). However, this pathway has serious mechanistic disadvantages, since it requires the involvement of two consecutive benzoyl radicals, whose concentration is certainly very limited at the comparatively low photon flux of the CIDNP experiments.



(5)

An alternative pathway to be considered involves D-abstraction by photoexcited deoxybenzoin from the solvent (→ pair F). Compared to the predominant α-cleavage of the deoxybenzoins, this pathway of reaction of triplet deoxybenzoins has been somewhat neglected previously with respect to α-cleavage, although there is a report that triplet-**5** can abstract hydrogen atoms from tetrahydrofuran.[18]

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(17) Adam, S.; Güsten, H.; Steenken, S.; Schulte-Frohlinde, D. *Liebigs Ann. Chem.* **1974**, 1831.

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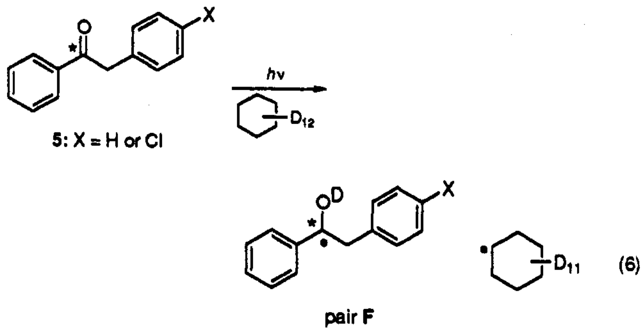
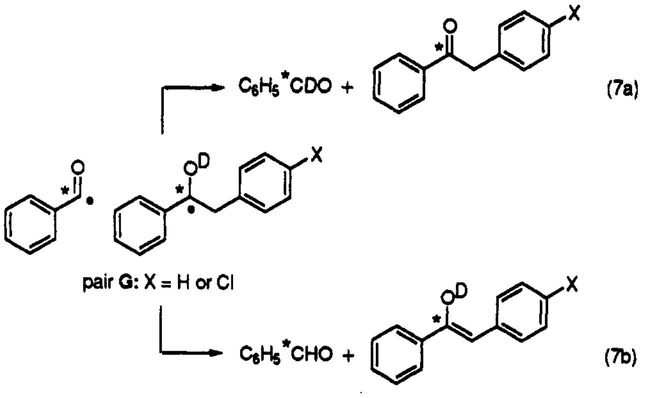


(6)

Following diffusive separation of pair **F**, free encounters of benzoyl radical (from pair **D**) with either of the radicals of pair **F** will generate pairs **C** and **G**. Pair **C** will produce cyclohexyl phenyl ketone (**4**; *E*; $\delta \sim 201$ ppm; Figure 2) by coupling and benzaldehyde-*d* by disproportionation (*vide supra*). An important feature of pair **G**, containing the ketyl radical derived from **5**, is that it can give rise to both **1**-*h* and **1**-*d*. Transfer of a benzylic H forms **1**-*h* along with the enol of **5** (eq 7b); **1**-*d* is formed, along with **5**, by D-transfer from the O–D function (eq 7a). The emissive ^{13}C polarization of **1**-*h* and -*d* formed via this mechanism follows from the polarization determining parameters (μ, ϵ, $A > 0$; $\Delta g < 0$). Support for the plausibility of the abstraction mechanism (eqs 6, 7a, and 7b) can be derived from the fact that the ^{13}C polarization of **1**-*h*, **1**-*d*, and **4** completely disappeared, when *p*-chloro-**5** (99% ^{13}C=O) was photolyzed in benzene-d_6. This finding suggests a crucial role of the solvent for the formation of all three products. Benzene-d_6 is a poor deuterium source; the suppression of the three products can be ascribed to the inability of the photoexcited ketones to abstract D from this solvent.



(7a)

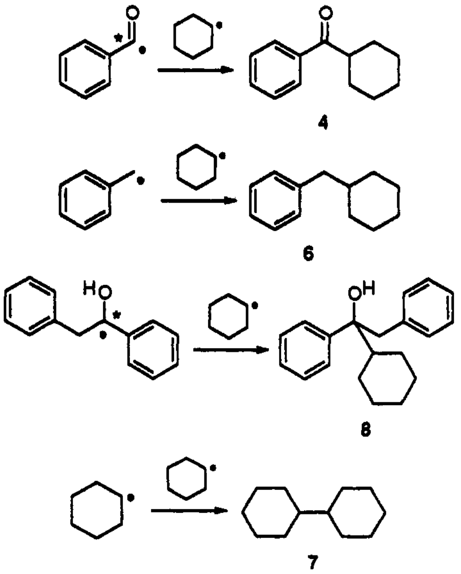
(7b)

C. Supporting Evidence. The data presented in this paper allow two mechanistic conclusions: (1) that hydrogen abstraction from solvents such as cyclohexane contributes significantly to the deactivation of photoexcited deoxybenzoin, and (2) that a significant fraction of the geminate pairs formed in this reaction diffuse apart and the resulting free radicals have secondary encounters, forming so-called F-pairs and leading to the formation of products. These conclusions are not based exclusively on the mere observation of the CIDNP effects, but they are supported by the additional evidence discussed below.

The fraction of products resulting from secondary encounters is not revealed directly in the product yields, because key products may be formed from either geminate or secondary pairs. In order to substantiate the significant involvement of secondary (free-radical) encounters in the systems discussed here, we offer two kinds of evidence: (a) the yields of products that cannot be formed from geminate encounters, and (b) the relative intensities of the CIDNP effects for products of secondary encounters versus those of geminate encounters.

The irradiation of benzaldehyde in cyclohexane gives rise to radical pairs **A** and **B**; the recombination of these pairs generates benzoin (**2**) and phenylcyclohexylmethanol (**3**). Other products formed in this reaction include dicyclohexyl (**7**), a product surely formed by a secondary encounter, in yields 2–3 times higher than those of **3**. Concerning the photochemistry of benzoin, the well-established α-cleavage leads to pair **D**, whereas hydrogen abstraction from the solvent generates pair **F**. Recombination of pair **D** does not lead to a detectable product, whereas recombination of pair **F** forms 1-cyclohexyl-1,2-diphenylethanol (**8**). At least four other products are formed from secondary encounters, including dicyclohexyl (**7**, in 10% yield), benzylcyclohexane (**6**, 3%), cyclohexyl phenyl ketone (**4**, 2%), and benzaldehyde (**1**, 4%). For comparison, product **8**, which can be formed from both geminate and secondary pairs, is obtained in 12% yield. Clearly, cage escape and secondary encounters are significant.

This conclusion is further supported by the intensities of the observed polarization. For example, the photolysis of deoxybenzoin (**5**) results in comparable intensities for cyclohexyl phenyl ketone (**4**) and regenerated **5**. Product **5** can be formed by the recombination of pair **D**, either as a geminate or as a secondary pair. Product **4**, on the other hand, is formed by recombination of pair **C**, which is clearly a secondary (free-radical encounter) pair. Unless the ^{13}C=O spin lattice relaxation times of the diamagnetic products, **4** and **5**, are significantly different, the comparable CIDNP intensities substantiate the importance of the secondary encounters.



The hydrogen abstraction mechanism is also supported by lifetime measurements. Triplet-**5** has a lifetime of 847 ns in benzene and significantly shorter lifetimes, 429 ns and 734 ns, in cyclohexane-h_{12} and cyclohexane-d_{12}, respectively. On the basis of the assumption that the lifetime in benzene is predominantly determined by α-cleavage, the rate constant of this process is computed to be 1.2×10^6 M^{-1} s^{-1}. From the assumption that the

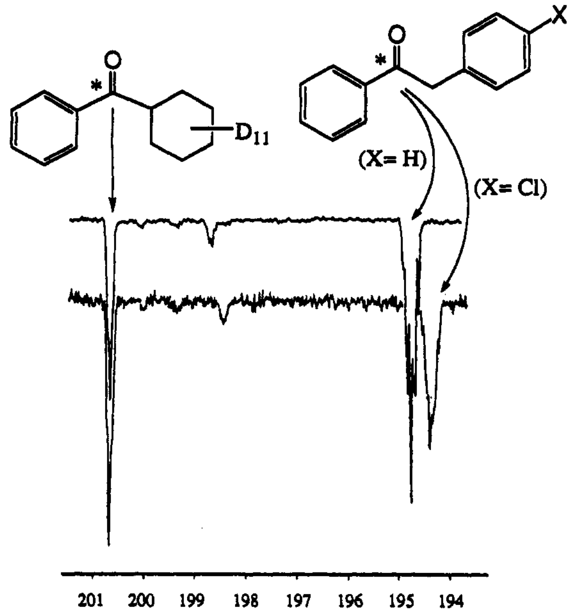


Figure 3. ^{13}C CIDNP effects of the identical samples used for Figure 2, measured under identical experimental conditions, except that the spectral range of 187–192 ppm is shown.

decrease in lifetime of triplet-**5** is determined by hydrogen-atom abstraction (and from the density of cyclohexane), the rate constants for hydrogen abstraction from cyclohexane-h_{12} and -d_{12} (assumed to have identical densities) are computed to be 2.1 × 10^5 and 3.9 × 10^4 M^{-1} s^{-1}, respectively. From the molarity of cyclohexane (~9.3 M) pseudo-first-order rate constants of 2 × 10^6 and 3.9 × 10^5 M^{-1} s^{-1} are calculated for H- and D-abstraction by triplet-**5**, respectively. Compared to typical rate constants for hydrogen abstraction from cyclohexane by various other photoexcited ketones (1 × 10^7 to 5 × 10^5 M^{-1} s^{-1})[18,19] hydrogen abstraction by triplet-**5** is somewhat slow. Nevertheless, its pseudo-first-order rate of hydrogen abstraction from neat cyclohexane-h_{12} (2 × 10^6 M^{-1} s^{-1}) is faster than α-cleavage (1.2 × 10^6 M^{-1} s^{-1}), whereas its rate of deuterium abstraction (3.9 × 10^5 M^{-1} s^{-1}) is still competitive with the rate of α-cleavage. The deuterium isotope effect of about 5 has the correct magnitude for a primary isotope effect.[19] The lifetime measurements support the involvement of ketyl radicals in the photochemistry of deoxybenzoin in cyclohexane-d_{12}.

Conclusion

On the basis of the observation of $^{13}C{=}O$ CIDNP for benzaldehyde-*h* and -*d* during the photolysis of **5** and *p*-chloro-**5**, we have concluded that photoexcited deoxybenzoin can abstract hydrogen as well as deuterium from appropriate solvents. This conclusion is supported by triplet lifetime measurements. Hydrogen abstraction from neat cyclohexane-h_{12} is faster than α-cleavage, whereas deuterium abstraction is competitive with α-cleavage. The observed polarization supports the conclusion[11,12] that a major portion of recombination as well as disproportionation products are derived by secondary encounters of cage-escaped radicals.

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