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Photochemistry of Some Deoxybenzoins in Micellar Solutions. Cage Effects, Isotope Effects, and Magnetic Field Effects

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Abstract: The photolyses of 1,2-diphenyl-2-methyl-1-propanone (**1**) and its D-, ^{13}C-, and alkyl-substituted derivatives **2–5** in various micellar solutions have been investigated. It was found that the extent of cage disproportionation to yield benzaldehydes **6** and α-methylstyrenes **7** is enhanced by a factor of about 10 compared to the photolyses in homogeneous organic solvents. The advantage of using micelles rather than homogeneous solutions to enhance the magnitude of magnetic isotope and magnetic field effects on cage disproportionation is demonstrated. The results are interpreted in terms of a mechanism involving the competition between hyperfine-induced intersystem crossing of a triplet radical pair ($^3\overline{\mathrm{RP}}$) to form a singlet radical pair ($^1\overline{\mathrm{RP}}$) and escape of $^3\overline{\mathrm{RP}}$ from the micelle.

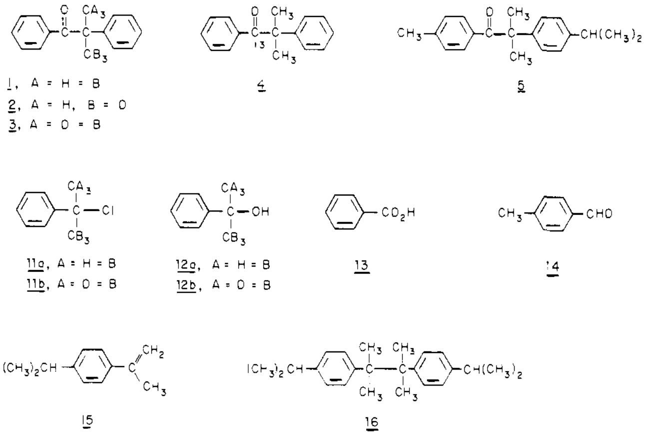
Enhanced solubility of hydrophobic compounds in water can be observed by addition of detergents to the aqueous solution and is due to the formation of micelles by the detergent molecules above the critical micelle concentration (cmc).[1] The model of a micelle usually presented is such that the interior contains the hydrophobic chain part of the amphiphiles while the charged head groups are located at the surface, forming a charged electrical double layer in contact with the surrounding water.[1]

Despite the fact that micelles are not static species but rather exist in a dynamic equilibrium with detergent monomers,[1–4] they can be employed to organize organic substrates. This is plausible because from the point of view of solubilization, micelles are rather static entities:[2] the breakup of formation of a micelle occurs[2] with rates of ~10–10^3 s^{-1}, whereas, for example, entrance rates of neutral arenes are nearly diffusion controlled,[5] and exit rates[5] are of the order of 10^4–10^6 s^{-1}. For detergent monomers the dissociation rate constants[1,2] are generally of the order of 10^4–10^8 s^{-1}. However, the rate of exchange of monomers seems not to affect the general organizational qualities of micelles as demonstrated in numerous investigations.[6]

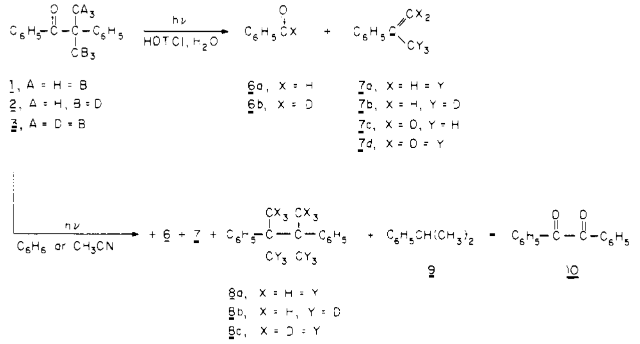
The selectivity of photoreactions in micellar solutions involving radical pairs (in particular, the recombination of those radical pairs photochemically generated from dibenzyl ketone) has been reported recently from this laboratory and has led to an efficient method of separation of ^{13}C and ^{12}C isotopes by utilizing the magnetic ^{13}C-isotope effect.[7] One other important reaction of radical pairs is the disproportionation to form molecules.[8] It is well-known that deoxybenzoins mainly undergo α cleavage to benzoyl and benzyl radicals, which in homogeneous solution suffer free-radical reactions,[9,10] that is

$$\mathrm{ArCOCXYAr'} \xrightarrow{h\nu} \mathrm{Ar\dot{C}O\ \dot{C}XYAr'} \rightarrow \text{products} \qquad (1)$$

Scheme I



Scheme II



In the case of suitable substitution (e.g., X = Y = CH$_3$) one possible reaction of the radical pair is disproportionation to yield an aldehyde and a styrene derivative. This disproportionation, also observed in homogeneous solution (but to a very small extent),[9,10] exhibits a substantial enhancement in micellar solutions.[11] In view of our interest in cage effects, isotope effects, and magnetic field effects on the reactions of radical pairs, we have undertaken a detailed investigation of the photochemistry of **1** and its D- and ^{13}C-labeled and alkyl-substituted derivatives **2–5** (Scheme I).

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(2) E. A. G. Aniansson, S. N. Wall, M. Almgren, H. Hoffmann, I. Kielmann, W. Ulbricht, R. Zana, J. Lang, and C. Tondre, *J. Phys. Chem.*, **80**, 905 (1976).

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

(10) F. D. Lewis, R. T. Lauterbach, H. G. Heine, W. Hartmann, and H. Rudolph, *J. Am. Chem. Soc.*, **97**, 1519 (1975).

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Table I. Chemical and Quantum Yields of the Photolysis of 1 and 5 in Benzene and Acetonitrile[a]

			6 or 14		7 or 15		8 or 16		10	
ketone	solvent	ketone[b] ϕ	%	ϕ	%	ϕ	%	ϕ	%	ϕ
1	C_6H_6	0.87	15	0.13	3.4	0.03	21	0.18	8	0.07
	CH_3CN	0.95	10	0.10	3.3	0.03	18	0.17	9	0.09
5	C_6H_6	0.72	*c*		<14	<0.1	22	0.16		
	CH_3CN	0.68			<15	<0.1	32	0.22		

[a] Concentration of 1 or 5 is 5 mM. Chemical yields are related to the disappearance of the ketones = 100%. 9 is only formed in traces (see ref 11). No attempt was made to identify the cumene and benzil derivatives resulting from photolysis of 5. [b] Quantum yields for disappearance of ketone. Error limits less than ± 20%. [c] The quantitative measurement of formation of 14 was not reproducible because of its instability under VPC conditions. However, the largest values were of the order of magnitude as those for the formation of 15.

Table II. Chemical and Quantum Yields of the Photolysis of 1–5 in Aqueous HDTCl Solutions[a]

	ketone[b]	6 or 14		7 or 15		8 or 16		9	
ketone	ϕ	%	ϕ	%	ϕ	%	ϕ	%	ϕ
1[c]	0.71	30	0.21	30	0.21	2.0	0.014	1	0.006
2[d]	0.7	27	0.19	27	0.19	2.0	0.014	1	0.006
3[d]	0.7	23	0.16	23	0.16	2.2	0.015	1	0.006
4[d]	0.7	41	0.29	41	0.29	1.4	0.010	0.7	0.005
5[c]	0.53	*e*		66	0.35	0.4	0.002		

[a] Concentrations of ketones 1–5 are 5 mM. Micellar solutions contain 150 mM hexadecyltrimethylammonium chloride (HDTCl) in water. The chemical yields are related to the disappearance of the ketones = 100%. Error limits ± 20% of the number quoted. [b] See footnote *b* of Table I. [c] Quantum yields were measured by using valerphenone in *tert*-butyl alcohol as actinometer. [d] The quantum yields of the photolyses of the ketones 2–4 were measured by using the disappearance of 1 in aqueous HDTCl as actinometer. The average deviation was ± 8% in these experiments. [e] See footnote *c* of Table I.

Results

Chemical Products and Quantum Yields. Irradiation of 1,2-diphenyl-2-methyl-1-propanone (**1**) in homogeneous organic solvents (benzene, acetonitrile, methylene chloride) results mainly in the formation of the dibenzyl derivative **8a** and benzaldehyde (**6a**), together with smaller amounts of benzil (**10**) and α-methylstyrene (**7a**), and traces of cumene (**9**) (see Table I and Scheme II). In addition to the products previously reported by Heine et al.,[9] we have found trace yields ($\phi \lesssim 0.01$) of benzophenone, 2,2-diphenylpropane, and biphenyl are formed in benzene solution.[12] Irradiation of **5**, a derivative of **1**, in organic solvents yields analogous products, but a higher yield of the corresponding styrene **15** is found (Table I).

On the contrary, in aqueous HDTCl solutions the major products of photolysis of **1–4** are **6** and **7** (Scheme II). In the case of **5**, analogous products (**14** and **15**) are formed in 66% yield. Small amounts of **8** and **9** or **16**, respectively, were also detected by VPC analysis (Table II). For ketones **1–4**, neither **10** nor the trace products of photolysis in benzene (see above) were found. Photolyses of **1** in various cationic, anionic, and nonionic micellar solutions yield similar results.[11] The products were identified by comparison of VPC retention times and spectral properties (GC–MS) with those of authentic samples and in the case of **14**, **15**, and **16** by isolation and comparison with authentic samples or comparison with literature data (Experimental Section). No evidence was found for the formation of an isomer of **1** such as isopropylbenzophenone. By comparison of the data of Table I and Table II, the following aspects are noteworthy: in aqueous HDTCl solution, (1) the yields of **6** and **7** are identical; (2) the yields of **8** especially (important product in homogeneous solutions) and also **10** are nearly negligible; (3) D labeling leads to a decrease in the formation of disproportionation products, whereas ^{13}C labeling and alkyl substitution lead to an increase.

Scavenging Experiments. Micellar Cage Effects. Table III presents the results that are obtained from the photolysis of **1** and **3** in the presence of Cu(II), which serves as a selective scavenger of radicals that enter the aqueous phase. It is noted that (1) the quantum yields for disappearance of **1** and **3** are found to be nearly unchanged in comparison to those observed in the absence of Cu(II); (2) the yields for formation of **6** and **7** in the presence and absence of Cu(II) are experimentally identical; (3) the minor products **8** and **9** are completely absent at sufficiently high concentrations of Cu(II) (ketone:$CuCl_2$ = 1:5); (4) three new products, **11**, **12**, and **13**, are formed in the presence of Cu(II). The mass balance of the photolysis of **1** for the α,α-dimethylbenzyl part is 79%, whereas for the benzoyl part it is 62%. On the basis of results of this laboratory that Cu(II) as a free-radical scavenger[13] only reacts with radicals which escape from the micelles into the surrounding water phase,[14] we calculate the "cage effects" for HDTCl micelles as 30% for **1** and 23% for **3**, i.e., the cage effect is equal to the absolute yield of **6** (or **7**) relative to the ketone reacted (Table III). Thus, **6** and **7** as **14** and **15** appear to be formed exclusively in micelles from reactions of geminate pairs, i.e., cage disproportionation of the geminate radical pair is much faster than radical escape from the micelle.

In order to prove that **6** and **7** indeed are formed by a cage disproportionation of the α,α-dimethylbenzyl–benzoyl radical pairs, we investigated the photolysis of **3** in aqueous HDTCl solution. Within the experimental accuracy of ^1H NMR, it was found that deuteriobenzaldehyde (**6b** X = D) and also pentadeuterio-α-methylstyrene (**7d**, X = Y = D) were the only detectable products, confirming the conclusion that **6** and **7** are cleanly produced via cage disproportionation of the geminate radical pair generated by photolysis of **1** (or of **3**).

Isotope Effects on Quantum Yields and Cage Efficiency. Table II demonstrates the influence of D and ^{13}C substitution on yields of the photolysis products in micellar solution. From the data in Table III cage effects may be computed. Figure 1 shows how the cage effect varies with the application of an external field and with D and ^{13}C substitution. It is of particular note that (1) D substitution decreases the "cage effect" from 30% (**1**) and 27% (**2**) to 23% (**3**); (2) ^{13}C substitution at the carbonyl carbon increases the "cage effect" to 41% (**4**). In order to check the possibility of a kinetic isotope effect for the atom transfer in the disproportionation reaction, an investigation of the photolysis of **2** in aqueous HDTCl solution was undertaken. It was found within the accuracy of NMR analysis that both benzaldehyde and α-methylstyrene exhibit a signal ratio, which is expected from 1:1 probability of H/D abstraction from the α,α-dimethylbenzyl radical by the benzoyl radical (**6a**:**6b** = 1:1; **7b**:**7c** = 1:1).

The origin of the substantial D and ^{13}C isotope effects on the extent of cage reaction may be ascribed to a competition of diffusion of radicals out of the micelle cage and intersystem crossing of a triplet radical pair to a singlet radical pair, followed

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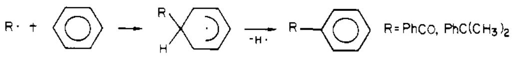
[12] Analogous to results of an investigation of phenyladamantyl ketone (N. J. Turro and C. H. Tung, *Tetrahedron Lett.*, **21**, 4321 (1980)), we assume that benzene is the source for the side products benzophenone and 2,2-diphenylpropane:



This reaction could also be the source for the relatively high yield of benzaldehyde in benzene solution.

[13] J. Kochi, "Free Radicals", Wiley, New York, 1973.

[14] N. J. Turro, M.-F. Chow, C.-J. Chung, and G. Weed, *J. Am. Chem. Soc.*, **102**, 4843 (1980).

Table III. Quantum and Chemical Yields of the Photolysis of 1 and 3 in Aqueous HDTCl Solutions in the Presence of Various Concentrations of $CuCl_2$[a]

	1 + $CuCl_2$					3 + 25 mM $CuCl_2$	
compd	ϕ (2 mM)[d]	ϕ (10 mM)[d]	ϕ (20 mM)[d]	ϕ (25 mM)[d]	yield, %	ϕ	yield, %
6	0.19	0.20	0.20	0.20	29	0.15	22
7	0.21	0.19	0.20	0.21	30	0.16	23
8	0.015	0.010	Tr				
9	0.006	0.004	Tr				
11[b]				0.18	26	0.20	29
12[b]				0.16	23	0.17	24
13[c]				0.23	33		

[a] See footnote *a* of Table II. Unless otherwise specified, the listed numbers are quantum yields. Yield means chemical yield. The disappearance of the ketones 1 and 3, respectively, remained nearly unchanged compared to those values in the absence of $CuCl_2$ ($\phi = 0.7$). Error limits less than ±20%. [b] The yields of formation of α,α-dimethylbenzyl chloride (11) and α,α-dimethylbenzyl hydroxide (12) were only measured at the highest $CuCl_2$ concentration. [c] 13 was analyzed as its ethyl ester. The yield reported here is a minimum yield. [d] Concentration of $CuCl_2$.

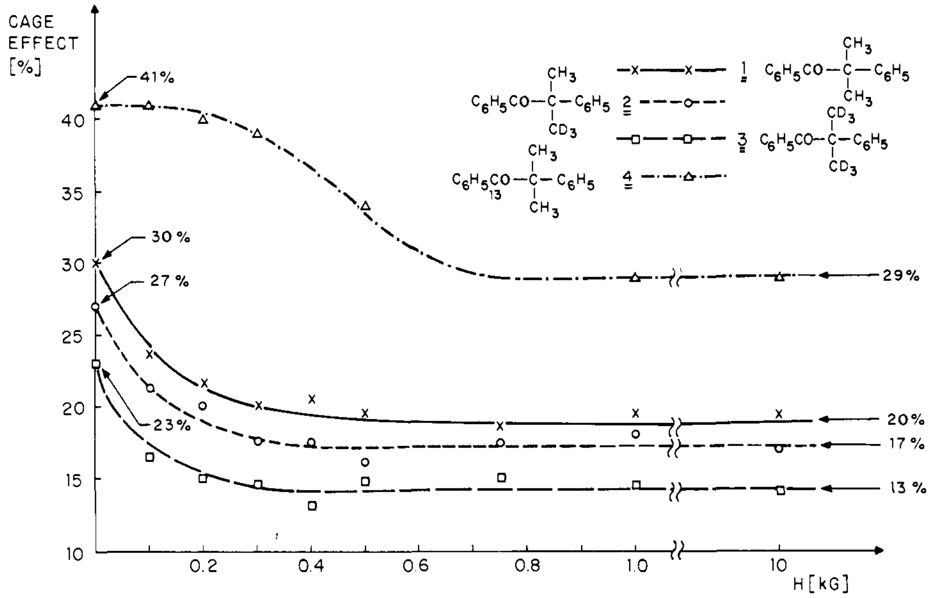


Figure 1. Cage effect as a function of field strength.

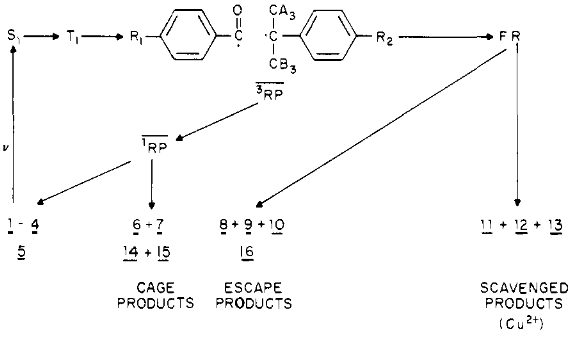
by disproportionation. This postulate allows the conclusion that the measured cage effects will be sensitive to the application of laboratory magnetic fields. Thus, a study of the cage effects of **1–4** as a function of external magnetic field strength was undertaken.

Magnetic Field Effects on Cage Effects. Figure 1 presents data which confirm the expectation mentioned above: (1) the cage effects for the ketones **1–3** are decreased to an extent of ca. 35% by applying an external magnetic field of at least 200–300 G; (2) further increase in field strength to 10 000 G does not result in a further substantial decrease; (3) the ^{13}C-labeled ketone **4** shows a somewhat smaller reduction of the cage effect (ca. 30%) with the onset of the effect occurring at higher fields (400–600 G).

Discussion

The products observed upon irradiation of the ketones **1–5** in micellar solutions can be accounted for in terms of a general mechanism shown in Scheme III. On the basis of the results of the photolysis of deoxybenzoins in benzene solution reported by Heine et al.,[9] we assume that α cleavage is the only important primary photochemical process after excitation of the ketones. The same authors demonstrated that α cleavage occurs exclusively from the lowest $^3n,\pi^*$ excited state.[9] The competition between hyperfine-induced intersystem crossing of the triplet radical pairs ($^3\overline{RP}$) to yield singlet radical pairs ($^1\overline{RP}$) and escape of the radical pairs from the micelles into the surrounding water phase result in a sorting of the disproportionation products **6** and **7** (or **14** and **15**) from the free radical products **8** and **9** (or **16**). Scavenging and isotopic labeling experiments are consistent with this interpretation.

Scheme III



The very small portion of cage reactions in homogeneous solution (see Table I and also ref 9) is due to the rapid loss of spin correlation in radical pairs, a consequence of rapid (~10^{-10} s) diffusive separation.[15] It has been demonstrated that entrapping the reactive species in micelles inhibits such diffusive escapes.[7]

Enhanced cage effects of radical pairs have been observed by substituting at least one radical center with ^{13}C.[7,14] The magnetic isotope (^{13}C) effect[16] operates on the reactivity of ($^3\overline{RP}$) by influencing the rate of isc via nuclear–electronic hyperfine interaction to yield ($^1\overline{RP}$), which undergoes recombination to the starting

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(15) B. Kraeutler and N. J. Turro, *Chem. Phys. Lett.* **70**, 270 (1980) and references therein.

(16) A. L. Buchachenko, *Russ. J. Phys. Chem.*, **51**, 1445 (1977); A. L. Buchachenko et al., *Dokl. Akad. Nauk. SSSR*, **228**, 379 (1976).

ketone or disproportionation to **6** and **7**. For **4** the consequences are higher quantum yields in the formation of the cage products and lower yields in the formation of escape products, i.e., a higher cage effect compared to **1** (Figure 1). D substitution (**2** and **3**) causes the reverse effects (Table II and Figure 1).

The concept of magnetic isotope effects further implies a dependence of the quantum yields for cage reactions on the application of an external magnetic field photolysis.[17] Qualitatively, the lowered cage effect (see Figure 1) is ascribed to partial or complete removal of the degeneracy of the T_+ and T_- sublevels of the triplet radical pair. As a consequence, the $T_\pm \rightarrow S$ isc is inhibited when the strength of the applied field is greater than the hyperfine interaction. Figure 1 presents further data which confirm this expectation. The strong influence of ^{13}C (in **4**) relative to the influence of protons is also reflected by the observation that higher external magnetic field strengths are necessary to inhibit the $T_\pm \rightarrow S$ isc compared to those required for **1**; this result is expected from the large hyperfine coupling constant of ^{13}C in the benzoyl-α-^{13}C radical, i.e., $a \sim 128$ G.[18] Furthermore, the contribution of the methyl protons of the α,α-dimethylbenzyl radical to the hfc in the radical pair is comparable, although somewhat smaller: $a \sim 16$ G per proton.[18,19] Therefore, D substitution (**2**, **3**) leads to a less efficient hfc in the radical pair (generally $a < 1$ G per deuterium in the α position of α,α-dialkylbenzyl radicals[18]). See Table I and Figure 1.

Experimental Section

Electronic absorption spectra were recorded on a Cary-17 or a Gilford 250 spectrometer; ^{1}H NMR spectra were recorded on Varian A-60 and Perkin-Elmer R 32 spectrometers, using Me_4Si as internal standard, or on a Bruker WP 80 spectrometer. Vapor phase chromatography (VPC) analyses were performed on a Varian Model 3700 (flame ionization detector), using a Minigrator (Spectra Physics) for evaluation. For preparative VPC the Varian Aerograph Model 90-P (thermal conductivity detector) was employed.

General. Solvents and Detergents. Water was doubly distilled (first distillation from $KMnO_4$); organic solvents (Fischer Scientific Co., "Spectroanalyzed") were used without further purification. The detergents used, hexadecyltrimethylammonium chloride (HDTCl), hexadecyltrimethylammonium bromide (HDTBr), dodecyltrimethylammonium chloride (DDTCl), all from Eastman Kodak Co., and sodium dodecyl sulfate ($NaDodSO_4$) from Bio-Rad Laboratories, were recrystallized from ethanol/ethyl ether and dried at 0.01 torr at room temperature. The nonionic detergent polyoxyethylene (**23**) lauryl ether (Brij 35) from Aldrich Chemical Co. was used without further purification.

Chemical Compounds. Unless otherwise specified, the materials for synthesis and comparisons were used as commercially available in highest purity. Iodomethane-d_3 (minimum isotopic purity, 99.5 atom % D) and phenylacetonitrile-*1*-^{13}C (90 atom % of ^{13}C), both from Merck Sharp & Dohme Canada, were used without further purification (this may explain the relatively low chemical yield in the synthesis of **4**). 2,3-Dimethyl-2,3-diphenylbutane (**8a**) was prepared according to Raley et al.;[20] the isopropylbenzophenones (compounds to check the possibility of a photochemical isomerization of **1**) were synthesized by using Bergmann's procedure.[21]

Ketones. 1,2-Diphenyl-1-propanone (starting material for **1** and **2**) was prepared in 63% yield by reaction of phenylmagnesium bromide with α-methylbenzyl cyanide, according to Newman and Linsk:[22] bp 110–111 °C (0.25 mm); mp 51–52 °C; ^{1}H NMR ($CDCl_3$) δ 1.53 (d, $J = 7$ Hz, 3 H), 4.66 (q, $J = 7$ Hz, 1 H), 7.20–7.50 (m, 8 H), 7.90–8.05 (m, 2 H). On methylation[22,23] this α-methyldeoxybenzoin was converted into 1,2-diphenyl-2-methyl-1-propanone (**1**): mp 46 °C; yield 81%; ^{1}H NMR ($CDCl_3$) δ 1.59 (s, 6 H), 7.05–7.50 (m, 10 H).

1,2-Diphenyl-2-trideuteriomethyl-1-propanone (**2**) was synthesized from 1,2-diphenyl-1-propanone, using trideuterioiodomethane as alkylation reagent, by the same method as above:[22,23] yield 85%; mp 46–47 °C (recrystallized from pentane); ^{1}H NMR ($CDCl_3$) δ 1.58 (s, 3 H), 7.10–7.55 (m, 10 H).

Deoxybenzoins 3, 4, and 5 (labeled and substituted) were prepared by the modification method of Brodhag and Hauser.[24]

α,α-Bis(trideuteriomethyl)phenylacetonitrile. Di(methyl-d_3)phenylacetonitrile was synthesized in one step. Phenylacetonitrile (2.6 g, 22 mmol) in 50 mL of dry ethyl ether was metalated with sodium amide (2.6 g, 66 mmol) under nitrogen atmosphere by cooling with water (15-min stirring). Then the sodionitrile was methylated with trideuterioiodomethane (12.1 g, 83 mmol), first at 0 °C for 30 min and then for 2 h at room temperature. After workup, a yield of 2.8 g (81%) of α,α-bis(trideuteriomethyl)phenylacetonitrile was obtained and was used in the next step without further purification: ^{1}H NMR ($CDCl_3$) δ 7.20–7.55 (m); no absorption at δ 3.6 (phenylacetonitrile) and δ 1.5 and 3.8 (α-methylphenylacetonitrile).

1,2-Diphenyl-2-trideuteriomethyl-3,3,3-trideuterio-1-propanone (**3**). α,α-Bis(trideuteriomethyl)phenylacetonitrile (2.8 g, 18 mmol) was refluxed with a xylene suspension of phenylmagnesium bromide (prepared from 36 mmol of bromobenzene and magnesium in ether) for 15 h. While being cooled, the addition complex was decomposed with diluted hydrochloric acid (1:1) and again refluxed for 5 h. Usual workup yielded 4.1 g of crude **3**, which gave, after recrystallization from pentane, 3.2 g of **3** (63% overall yield starting from phenylacetonitrile): ^{1}H NMR ($CDCl_3$) δ 7.05–7.60 (m); no absorption at $\delta \sim 1.5$.

α,α-Dimethylphenylacetonitrile-*1*-^{13}C was prepared by starting from phenylacetonitrile-*1*-^{13}C (2.7 g, 23 mmol, 90 atom % ^{13}C) and using iodomethane as alkylation reagent in accordance with the procedure described for the synthesis of **3**. Crude α,α-dimethylphenylacetonitrile-*1*-^{13}C (3.1 g, 92%) was obtained and used without further purification: ^{1}H NMR ($CDCl_3$) δ 1.61 (d, $J = 5$ Hz, 6 H), 7.15–7.55 (m, 5 H).

1,2-Diphenyl-2-methyl-1-propanone-*1*-^{13}C (4). Reaction of 3.1 g of crude α,α-dimethylphenylacetonitrile-*1*-^{13}C with phenylmagnesium bromide, hydrolysis of the imine, and purification of the resulting ketone by column chromatography on silica gel with benzene/petroleum ether (bp 35–60 °C) (1:4) yielded 2.3 g of **4** (44% overall yield starting from phenylacetonitrile-*1*-^{13}C): mp 45–47 °C (after recrystallization from pentane): ^{1}H NMR ($CDCl_3$) δ 1.54 (d, $J = 4$ Hz, 6 H), 7.05–7.55 (m, 10 H).

α,α-Dimethyl(4-isopropylphenyl)acetonitrile. (4-Isopropylphenyl)acetonitrile[25] was methylated as described above to give crude α,α-dimethyl(4-isopropylphenyl)acetonitrile in 94% yield: ^{1}H NMR ($CDCl_3$) δ 1.21 (d, $J = 7$ Hz, 6 H), 1.65 (s, 6 H), 2.86 (h, $J = 7.5$ Hz, 1 H), 7.15–7.45 (m, 4 H).

1-(4-Tolyl)-2-(4-isopropylphenyl)-2-methyl-1-propanone (5). Reaction of 4-tolylmagnesium bromide with the foregoing substituted phenylacetonitrile analogous to the synthesis of **3** yielded **5** as a highly viscous oil (70% of crude product): bp 125–127 °C (0.25 torr). Even after further purification by column chromatography on silica gel with benzene/petroleum ether, **5** did not crystallize: ^{1}H NMR ($CDCl_3$) δ 1.22 (d, $J = 6.5$ Hz, 6 H), 1.54 (s, 6 H), 2.21 (s, 3 H), 2.81 (h, $J = 6.5$ Hz, 1 H), 6.70–7.40 (m, 8 H); UV (CH_3CN) λ (ϵ) 254 (12600), 319 (212), 330 nm (194); UV (cyclohexane) λ (ϵ) 252 (12800), 319 (175), 333 nm (160).

General Procedures for Irradiations, Analyses, and Quantum Yields. Irradiations at $H = 0$ G (Earth's Magnetic Field). Unless otherwise specified, generally both preparative irradiations and the mechanistic studies, including quantum yield determinations and scavenging studies, were carried out by using a "merry-go-round" apparatus[26] immersed into a thermostated bath (20–25 °C). A 450-W medium-pressure Hanovia Hg lamp was employed as the light source; 313-nm light was selected by using aqueous 0.27 g/L potassium chromate–1 g/L sodium carbonate[27] and Corning 7-54 filters.[27] For absolute quantum yield measurements, a valerophenone/*tert*-butyl alcohol actinometer ($\phi = 1.0$)[28] was used. Generally, 4-mL sample solutions containing 5 mM ketone and eventually definite amounts of copper chloride in 150 mM detergent/water (solutions were prepared by shaking or stirring for several hours) or

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organic solvents were placed in Pyrex tubes, deoxygenated by inert gas bubbling (nitrogen or argon),[29] and then stoppered tightly.

Prepatative Irradiations of 5. For preparation of the cage products **14** and **15**, a 100-mL solution of **5** (35 mM) in aqueous HDTCl (450 mM) was irradiated as described above (ca. 80% conversion within 2 h). The combined samples were diluted with water (because of relatively high HDTCl concentration), provided with sodium sulfate, and extracted with ether several times. **14** and **15** were isolated by preparative gas chromatography at 130 °C, using a 10% SE 30 column.

***p*-Tolualdehyde (14).** **14** was isolated as the cage product with the smaller retention time in 96% purity as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3 H), 7.33 and 7.78 (AB, $J = 8$ Hz, 4 H), 9.95 (s, 1 H). **14** is identical with an authentic sample. **4-Isopropylisopropenylbenzene (15).** **15** was obtained as a colorless liquid in 98.6% purity: ^{1}H NMR ($CDCl_3$) δ 1.25 (d, $J = 6.4$ Hz, 6 H), 2.14 (broad s, 3 H), 2.89 (h, $J = 6.4$ Hz, 1 H), 5.05 (m, 1 H), 5.35 (broad s, 1 H), 7.20 and 7.42 (AB, $J = 8$ Hz, 4 H).

2,3-Di-*p*-cumyl-2,3-dimethylbutane (16). A solution of 2 g of **5** in 75 mL of benzene was irradiated in a photochemical reaction vessel under atmosphere by using a Hg lamp and light filters as described above. After complete conversion (6 h), the solvent was evaporated. The residue crystallized within a few hours, and the white crystals were filtered and washed with either: 0.1 g; mp 132 °C (lit. mp 134–135 °C);[30] ^{1}H NMR ($CDCl_3$) δ 1.15–1.30 (m, 24 H), 2.88 (h, $J = 7$ Hz, 2 H), 7.04 (s, 8 H).

Measurements of Quantum Yields and Cage Effects. After irradiation the samples were extracted with calibrated volumes of methylene chloride or ethyl ether[31] containing an internal standard (generally biphenyl; for the analysis of **16**, 9-methylanthracene was used as the standard) and quantitatively analyzed by VPC, using a 10% SE 30 column. In the case of organic solvents, it is sufficient only to add the standard solution. VPC analyses of the actinometer solutions were carried out by using a 10% Carbowax column and also biphenyl as the internal standard. In all cases, the starting concentrations of the ketones were checked by analyzing the unirradiated samples. In order to get not more than 10–20% conversion, the irradiation time usually was limited to 10 min. At least two samples were prepared for each measurement and analyzed by VPC several times. Only the averages of these analyses were used to calculate either quantum yields or cage effects. Escaped benzoyl radicals were detected by scavenging with copper chloride as ethyl benzoate (after esterification of benzoic acid with ethanol, already in the presence of biphenyl as the internal VPC standard).

Irradiations with Variable Laboratory Magnetic Fields. Magnetic field experiments were performed in a Model 4600/4 Adjustable Electromagnet, Alfa Scientific, Inc., Oakland, Cal. Calibration was done with a gaussmeter, Bell Model 640. Fields employed were in the range of 0 G to 10 kG. For photolyses, the Pyrex tubes containing the samples (see above) were placed into the center of the gap of the electromagnet and irradiated with a 1000-W Oriel xenon–mercury lamp. Analyses especially to measure cage effects were carried out as described above.

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[29] Photolyses of the ketones in aqueous detergent or organic solvents after vacuum degassing (0.01 Torr, −40 °C) show no difference to those only degassed by inert gas bubbling.

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Cyanation of Aromatic Compounds in a Gaseous Plasma

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Abstract: Aromatic compounds are directly cyanated by passing cyanogen and the respective compounds through a radio-frequency generated and inductively coupled glow discharge zone. Benzene and a wide variety of substituted benzenes (C_6H_5X: X = CH_3, *t*-Bu, CF_3, OH, F, Cl, Br, CHO) are cyanated providing a good yield of ortho-, meta-, para-, and ipso-substituted products. The relative amount of ipso product increases as the carbon–X bond dissociation energy decreases. The ratio of ortho to meta to para cyanated products demonstrates a slight preference for substitution on electron-rich positions. A plot of the meta/para yield ratio against $\sigma_m - \sigma_p$ gives a ρ value of −0.5. It is proposed that electron impact on cyanogen produces $CN\cdot$, which in turn attacks the aromatic, causing substitution.

This study is part of an effort to understand the fundamentals and develop the utility of plamsa chemistry.[1] We report here a unique reaction which produces preparatively useful amounts of cyano aromatics. The observed reactions are also of interest with regard to prebiotic chemistry[2] and might be used for surface modification.[3]

The experiments described below were performed using an inductively coupled, radio-frequency discharge. This approach has previously been used to perform a number of organic reactions.[1a] One advantage of this electrodeless discharge is that corrosion of the metallic electrodes and undesired side reactions caused by them can be eliminated. The experiments are carried out by passing the gaseous reactants through the discharge zone. Material in this zone is partially ionized and reactions are induced by electron impact. The method involves a flowing system which requires no heating, solvent, or catalysts. The power required is normally about 50 W and more than 5 g of products can be obtained in 30 min.

A preliminary communication described the reaction of cyanogen with aromatic compounds using this method.[4] This paper provides details and a discussion of some of the results. The cyanation of aromatics in a plasma was first reported by Kikkawa and co-workers using acetonitrile as the cyano source.[5] This

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