Both the photochemical and the thermal reaction mixtures did not contain peroxides in any significant amount as judged from the iodometric titrations.

Thermal Oxidation Reaction 2. Propylene (9.5 mL/min) and oxygen (10.7 mL/min) were bubbled through an acetonitrile solution (100 mL) of sulfur dioxide (3.60 g, 56.2 mmol) and potassium nitrite (0.548 g, ca. 85% pure, 5.47 mmol) at 26.0 °C. The formation of propylene oxide and the loss of sulfur dioxide were monitored by GLC analysis and the result is shown in Figure 1.

Thermal Oxidation Reaction 3. Potassium nitrite (1.0 g, 85% pure) was added to a mixture of sulfur dioxide (6.32 g, 98.6 mmol) and propylene (0.87 g, 20.7 mmol) in acetonitrile (100 mL) in a 300-mL flask connected to an oxygen reservoir. The reaction mixture was stirred with a magnetic stirrer at 23 °C for 8 h. The amount of oxygen absorbed during the reaction was 7.4 mmol. The reaction mixture was analyzed by GLC on a 3-m dioctyl sebacate column (10% on Diasolid S) at 40 °C. The amount of propylene oxide formed in the reaction was 5.95 mmol and the amount of sulfur dioxide reacted was 11.3 mmol. The amount of propylene which remained in the reaction mixture was 4.3 mmol. After filtration the solvent was removed from the reaction mixture. A viscous liquid (0.95 g) remained in the flask.

Reaction of the Nonvolatile Product with Pyridine. The viscous product (0.31 g) obtained from the thermal oxidation reaction was dissolved into pyridine (2 mL) at room temperature. Some solids precipitated over a month; the solution was filtered and washed with chloroform and then dried in a silica gel desiccator under vacuum. IR (KBr) 3400 (broad), 3050, 2980, 2940, 1635, 1595, 1450, 1200 (strong), 1030 (m), 790, 780, 750, 710, 680, 610, 570,545, 515; NMR (Me_2SO-d_6) δ 1.15 (d, 3 H, $J = 7$ Hz), 2.90–3.40 (m, 2 H), 4.72 (d, 1 H, $J = 7$ Hz), 7.85–9.22 (m, pyridine ring protons, 5 H).

Anal. Calcd for $C_3H_6O_3S \cdot C_5H_5N$: C 47.74; H, 5.50; N, 6.96; S, 15.93. Found: C, 47.42; H, 5.42; N, 6.85; S, 16.22.

Stability of Propylene Oxide under the Thermal Oxidation Conditions. Oxygen (7.7 mL/min) was bubbled through a stirred mixture of propylene oxide (1.68 g, 28.9 mmol), sulfur dioxide (6.75 g, 105 mmol), and potassium nitrite (1.0 g, 85% pure) in acetonitrile (200 mL) at 30 °C. After 6 h the reaction mixture was analyzed by GLC on a 3-m dioctyl sebacate column (10% on Diasolid S) at 40 °C. Most of the propylene oxide (92%) remained in the mixture. The amounts of sulfur dioxide and propylene oxide which were lost during the reaction were 10 mmol and 2.4 mmol, respectively, and were not significantly larger than those driven away by the oxygen stream. The reaction mixture was filtered and the solvent was removed from the filtrate by rotary evaporation. Only a small amount of a liquid (ca. 0.05 g) was obtained. The infrared spectrum (neat on KBr) showed strong characteristic absorptions at 1630 and 1280 cm^{-1} ($-ONO_2$). The NMR spectrum($CDCl_3$) showed a pair of methyl doublets at around δ 1.29 ($J = 6.5$ Hz).

Thermolysis of the Nonvolatile Product. The viscous liquid product (0.12 g) obtained in the photochemical oxidation reaction (chromatographed on a silica gel column) was placed in a glass container and heated under a nitrogen stream with a Bunsen burner. The gas evolved was absorbed in cold toluene. The GLC analysis of the toluene solution on a 3-m dioctyl sebacate column showed the presence of acetone (1.13 mmol per 1 g of the liquid), sulfur dioxide (2.16 mmol per 1 g of the liquid), and propylene (1.04 mmol per 1 g of the liquid). The formation of propylene and acetone was confirmed by the NMR spectrum of the benzene solution of the evolved gases.

The thermolysis of the liquid product obtained from the thermal oxidation reaction gave a similar result.

Acknowledgment. The author wishes to thank Mr. R. Ishioka for his encouragement during the study and Mr. T. Tsukamoto for technical assistance. The author is much indebted to Drs. R. Kurosawa and T. Ueshima for a gift of 6-cyanonorborn-2-ene.

Magnetic and Micellar Effects on Photoreactions. 1. ^{13}C Isotopic Enrichment of Dibenzyl Ketone via Photolysis in Aqueous Detergent Solution

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Abstract: The photolysis of dibenzyl ketone (DBK) in homogeneous organic solutions and in micelle-containing detergent solutions has been investigated from the standpoint of determining the extent and location of ^{13}C enrichment that occurs. In a series of experiments it is established that for incomplete conversions the residual, recovered DBK is enriched in ^{13}C relative to the initial unphotolyzed DBK. The efficiency of the $^{13}C/^{12}C$ separation is shown to be characterized by an isotope enrichment parameter, α, which is independent of the extent of conversion. A combination of mass spectrometry and nuclear magnetic resonance spectroscopy provides support for the primary location of the ^{13}C enrichment at C-1 (the carbonyl carbon) with a lesser but significant enrichment at C-2 (the methylene carbon). A very small but experimentally distinct enrichment of the aromatic rings is indicated by ^{13}C NMR analysis. An isomer of DBK, 1-phenyl-4′-methylacetophenone (PMAP) is formed as a minor product of photolysis in micellar solutions. PMAP, like the recovered, residual DBK, is found to be substantially enriched in ^{13}C relative to the starting DBK. The magnitude of α is found to be significantly influenced by the application of laboratory magnetic fields to the photolysis sample. The latter result, along with the unusually large magnitude of α, suggests that the mechanism involved in isotopic enrichment is not dominated by kinetic mass isotope effects but rather by nuclear magnetic moment and/or magnetic spin isotope effects.

Introduction

The photolysis of dibenzyl ketone (DBK) in homogeneous organic solvents has been shown to proceed via an initial homolytic α cleavage of the T_1 state, followed by decarbonylation and eventual coupling of benzyl radicals to yield 1,2-diphenylethane, DPE (eq 1).[1] A strong CIDNP spectrum is generated during the photolysis of DBK.[2] Theoretical analysis of these spectra leads to the conclusion that DPE is formed via free-radical combination and that some cage recombination of $C_6H_5CH_2\dot{C}O$ $\dot{C}H_2C_6H_5$ geminate radical pairs occurs. According to the radical pair theory of CIDNP,[3] when a cage reaction of a geminate pair

$$C_6H_5CH_2COCH_2C_6H_5 \xrightarrow{h\nu} S_1 \rightarrow T_1 \rightarrow C_6H_5CH_2\dot{C}O + C_6H_5\dot{C}H_2 \rightarrow C_6H_5CH_2CH_2C_6H_5 + CO \quad (1)$$

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[1] (a) Quinkert, G.; Opitz, K.; Wiersdorf, W. W.; Weinlich, J. *Tetrahedron Lett.* **1963**, 1863. (b) Engel, P. S. *J. Am. Chem. Soc.* **1970**, *92*, 6074. (c) Robbins, W. K.; Eastman, R. H. *Ibid.* **1970**, *92*, 6076, 6077.

[2] (a) Langhals, H.; Fischer, H. *Chem. Ber.* **1978**, *111*, 543. (b) Blank, B.; Mennitt, P. G.; Fischer, H. *Proc. 23rd Int. Congr. Pure Appl. Chem.* **1971**, *4*, 1.

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competes with escape from the solvent cage to form free radicals, it is possible that the competition will be influenced, or even controlled, by magnetic isotope effects.[4] In particular, if T_1 (eq 1), cleaves to produce a geminate triplet radical pair, $C_6H_5CH_2CO\uparrow\ \uparrow CH_2C_6H_5$ (^{3}RP), then intersystem crossing (ISC) to a geminate singlet radical pair may be the process that is rate limiting for cage recombination to regenerate DBK. In this case, ^{3}RP's that contain ^{13}C nuclei may undergo ISC *faster* than ^{3}RP's that do not. Indeed, for a given set of molecules containing a single ^{13}C nucleus, the rate of ISC will depend on the position of the ^{13}C atom in the molecule. The basis of these remarkable predictions resides in a magnetic isotope effect by which ISC rates are dependent on the occurrence or nonoccurrence of magnetic moments and magnetic spins of nuclei. In addition to the expectation that isotopes can be separated on the basis of isotopically competitive chemical reactions whose efficiencies depend on nuclear magnetic moments and nuclear spins, the CIDNP-derived theory of magnetic isotope effects predicts that the efficiency of separation will be dependent on the application of magnetic fields to the reaction system.

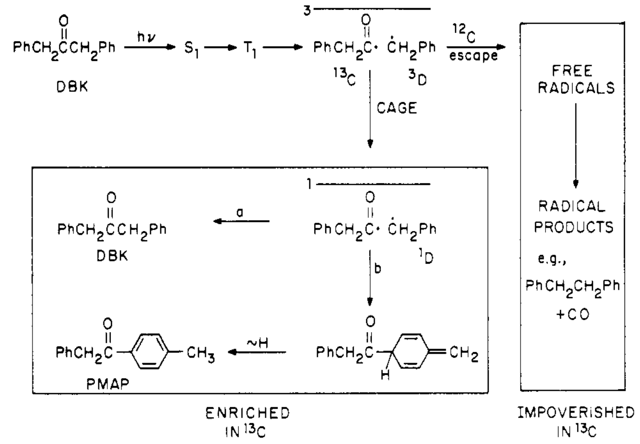
This report is concerned with the establishment of a convincing experimental demonstration that ^{13}C enrichment of residual DBK occurs when DBK is photolyzed to partial conversion under various conditions.[5] Establishment of convincing evidence that the mechanism of ^{13}C enrichment involves a magnetic isotope effect and a detailed study of magnetic field effects on the efficiency of separation are given in the following paper.

Results

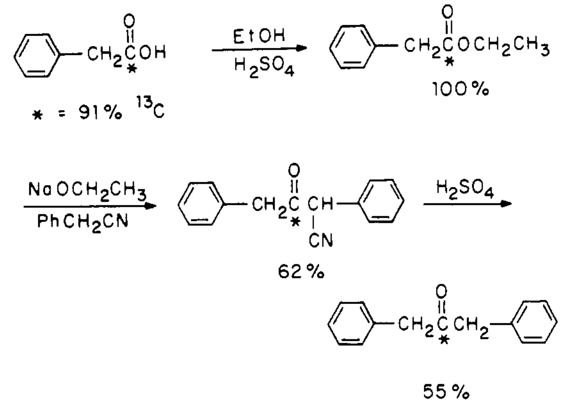
Preparative Photolysis of Dibenzyl Ketone (DBK): Identification of Products. The photolysis of DBK in deaerated (nitrogen purged) solutions in benzene, cyclohexane, or dodecane resulted in a clean, quantitative photodecarbonylation to diphenylethane (DPE), as reported earlier.[1] In cyclohexanol solution, besides DPE as the major product, minor amounts of photoproducts are also formed (VPC analysis: new products have shorter retention times than DBK). Photolysis of deaerated solutions of DBK in aqueous micellar hexadecyltrimethylammonium chloride (HDTCl) also leads to DPE as the predominant product,[6] but a small amount of a second photolysis product (with longer VPC retention time than DBK) was also isolated and identified (typical yield 5–10%) as 1-phenyl-4′-methylacetophenone (PMAP), an isomer of DBK. Experimentally, the formation of PMAP appears to require the existence of micelles and was found to be favored by low temperature and an excitation wavelength of about 300 nm.[7] Importantly for the kinetic analyses, it was found that in the absence of scavenger (i.e., molecular oxygen, oxidizing metal ions, etc.) the disappearance of DBK can be quantitatively accounted for by the two photoproducts, DPE and PMAP (Scheme I).

Experiments with DBK Synthetically Enriched in ^{13}C. Since we were concerned with an unambiguous demonstration that the partial photolysis of DBK occurs with concomitant ^{13}C enrichment of the DBK, experiments were conducted with DBK that was synthetically enriched to an extent that allowed accurate and precise ^{13}C analysis by several complementary methods. In order to obtain high accuracy and precision, it was decided to prepare DBK's that were synthetically enriched in ^{13}C at the 1-carbon (carbonyl) and at both of the 2- and 2′-carbons (methylene).

Scheme I

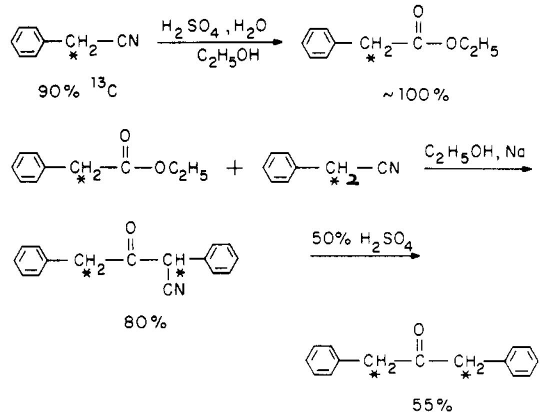


Dibenzyl ketone, 91% ^{13}C at the 1-carbon [DBK-*1*-^{13}C (91%)] was prepared[8] by the sequence given in eq 2. Dibenzyl ketone,



(2)

90% ^{13}C at both 2-carbons [DBK-*2,2′*-$^{13}C_2$ (90%)] was prepared by the sequence given in eq 3. In the first series of experiments, DBK-*1*-^{13}C (47.6%) (prepared by mixing appropriate weights of DBK-*1*^{13}C (91%) and natural abundance DBK) was used.



(3)

The DBK that was recovered from partial photolysis in aqueous deaerated micellar solutions of HDTCl (usually 0.05 M) was analyzed by several complementary methods (^{1}H NMR, GC/MS, and ^{13}C NMR). From mass spectrometric analysis of the recovered DBK (Figure 1), the fraction of mass 211 (M + 1 ion of DBK) increased progressively during the course of the photolysis of the detergent solution of DBK. After 91% conversion, the ^{13}C content in the carbonyl of the recovered DBK was determined to have increased from 47.6% to 63.7% (error limits ±2%). The assignment of the progressive increase of the fractional DBK with mass 211 (from mass spectrometric analysis) to the ^{13}C enrichment

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(6) The presence of air in the aqueous detergent solution had no significant effect of the ^{13}C enrichment in DBK, but the chemical yield of DPE was reduced in favor of lower molecular weight products.

(7) (a) Kraeutler, B.; Turro, N. J. *Chem. Phys. Lett.* **1980**, *70*, 266. (b) Turro, N. J.; Chow, M.-F.; Kraeutler, B. *Ibid.* **1980**, *73*, 545. (c) The ease of photofragmentation of deoxybenzoin in micellar detergent solutions suggests a secondary photolysis of PMAP to be a possible explanation for this wave length dependence.

(8) Coan, S. B.; Becker, E. I. "Organic Synthesis"; Rabjohn, NJ, Ed.; Wiley: New York, 1968; Collect. Vol. IV, pp 174, 176.

Table I. ^{13}C Enrichment in Recovered Residual Dibenzyl Ketone

initial DBK composn[d]	reaction conditions[a]	% conversion	initial DBK $(m + 1)/m$	recovered DBK $(m + 1)/m$	recovered DBK % ^{13}C for 1 carbon
DBK-*1*-^{13}C (47.6%)	0.05 M HDTCl	91	104.3/100	187.7/100	63.7
DBK-NA[c]	0.05 M HDTCl	93	16.5/100	18.47/100	3.34
DBK-NA[c]	0.05 MHDTCl	95	16.5/100	17.65/100	2.52
DBK-NA[c]	0.1 M DDTCl	95.5	16.5/100	18.76/100	3.63
DBK-NA[c]	0.1 M SDS	97.5	16.5/100	18.60/100	3.47
DBK-*1*-^{13}C (10.2%)	benzene	96	26.7/100	28.28/100	11.4
DBK-*1*-^{13}C (10.2%)	dodecane	92	26.7/100	28.20/100	11.4
DBK-*1*-^{13}C (10.2%)	cyclohexanol	86	26.7/100	29.51/100	12.4
DBK-$2,2'$-$^{13}C_2$ (20.5%)	0.05 M HDTCl	84	25.7/100[b]	33.13/100[b]	24.9

[a] Experiments run in the earth's magnetic field. See Experimental Section for details. [b] Calculated for $(m + 2)/m$. [c] NA = natural abundance. [d] Percent isotopic incorporation given in parentheses.

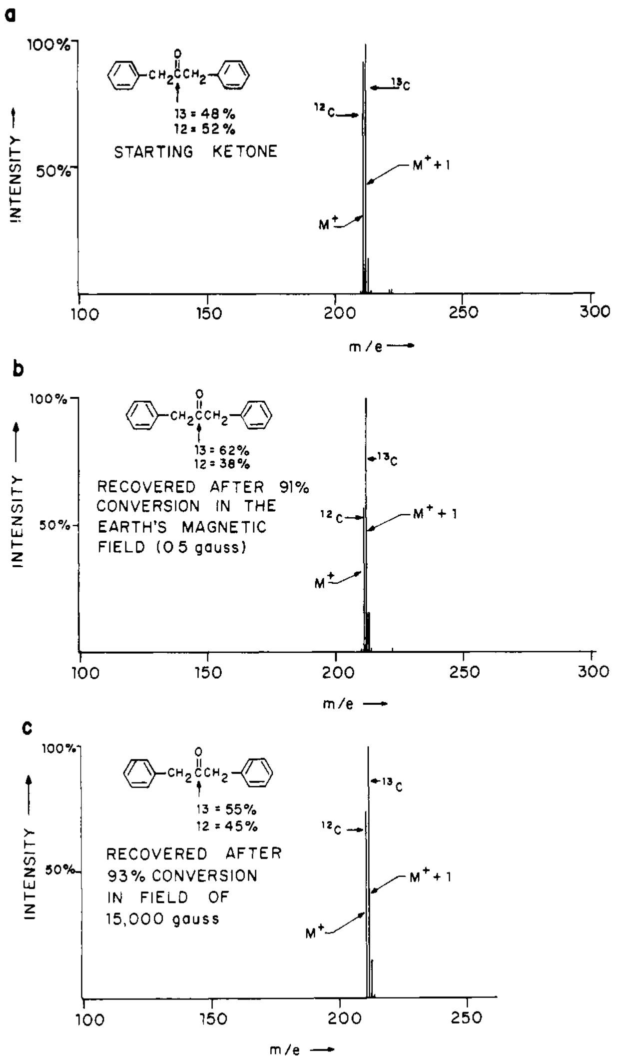

Figure 1. Mass spectra (molecular ion region only): (a) initial ketone before photolysis; (b) recovered residual ketone after 91% conversion from photolysis in the earth's magnetic field: (c) recovered residual ketone after 93% conversion from photolysis in a field of 15 000 G.

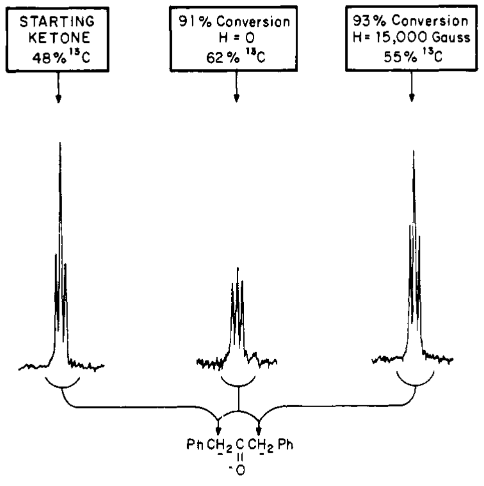

Figure 2. ^{1}H nuclear magnetic resonance spectra (methylene region only): left, initial ketone; middle, recovered residual ketone after 91% conversion from photolysis in the earth's magnetic field; right, recovered residual ketone after 93% conversion from photolysis in a field of 15 000 G. the spectra refer to material extracted from micellar solutions as described in the experimental section.

in the carbonyl of DBK is supported by complementary ^{1}H NMR analysis of the recovered DBK at several stages of this experiment. A very specific test for the ^{13}C enrichment of the carbonyl of DBK is available by the ^{13}C satellites in the ^{1}H NMR spectrum: the methylene protons of DBK (Figure 2) with a ^{12}C carbonyl are a singlet (at 3.66 ppm, $CDCl_3$, Me_4Si as internal reference), while a doublet centered at the same chemical shift with $J_{^{13}\mathrm{C,H}} = 6.5$ hz is caused by ^{13}C–proton coupling when ^{13}C is contained in the carbonyl. Integration over the singlet and doublet signals allows determination of the ^{13}C content of the carbonyl of DBK with good precision and accuracy. Thus, from the "satellite method", 62 ± 4% ^{13}C is computed in the recovered DBK (after 91% conversion). For the DBK recovered after 91% conversion, a *quantitative agreement exists between the mass spectrometrically determined mass increase and the ^{1}H NMR determined ^{13}C enrichment of the carbonyl of DBK.* These samples of DBK, after mass and ^{1}H NMR spectroscopic analysis were subsequently subjected to ^{13}C NMR analysis, which also established qualitatively that the predominant ^{13}C enrichment occurs in the carbonyl of DBK (the relative increase of the carbonyl signal corresponds to a 60 ± 5% ^{13}C content). A small ^{13}C enrichment of the methylene carbons was also apparent.

From the same experiment (DBK originally containing 47.6% ^{13}C in the carbonyl), the ^{13}C enrichment in the isomeric ketone, PMAP (preparative VPC), was also determined by mass and ^{1}H NMR (satellite method) spectroscopy as shown in Figure 3. Both analyses demonstrated an increased content of ^{13}C in the carbonyl of PMAP for a sample recovered after 91% conversion [mass spectral analysis (58.7 ± 2% ^{13}C) and ^{1}H NMR satellite analysis (57.5 ± 4% ^{13}C)]. Interestingly, only a small difference of the ^{13}C content of the carbonyl in PMAP is noticed when samples taken after 91% conversion (58.7 ± 2% ^{13}C) or after only 29% conversion (54.4 ± 3% ^{13}C) are compared.

To investigate the magnitude of ^{13}C enrichment in DBK at sites other than the carbonyl, we used DBK-$2,2'$-$^{13}C_2$ (^{13}C label at both methylene carbons) in enrichment experiments in deaerated aqueous 0.05 M HDTCl solutions. Incomplete photolysis of DBK-$2,2'$-$^{13}C_2$ (20.5%) and recovery of DBK, followed by mass spectroscopic analysis, established a substantial ^{13}C enrichment in the CH_2 carbon atoms (Table I). This result is in agreement with the expectation of enrichments of the CH_2 groups as indicated earlier by ^{13}C NMR.

Enrichment Experiments with Natural Abundance DBK. The strong increase of the ^{13}C content of the carbonyl of DBK during

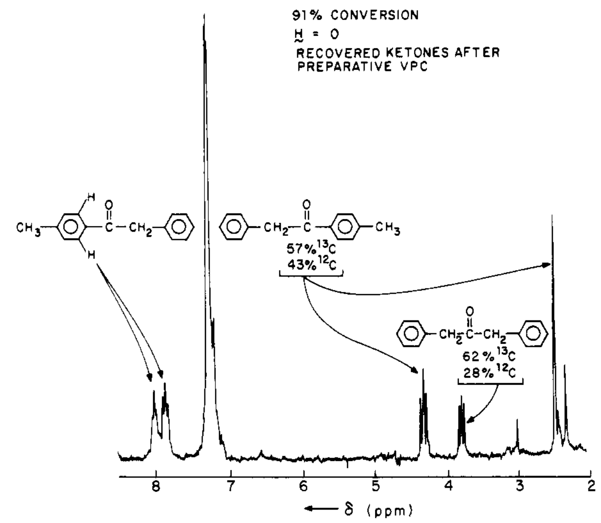

Figure 3. ^{1}H nuclear magnetic spectrum of residual ketones extracted from the photolysis of DBK-*1*-^{13}C (47.6%) after 91% conversion in the earth's field. the spectum refers to VPC purified material. See Experimental Section for details.

photolysis in deaerated aqueous solutions of 0.05 M HDTCl, as determined by photolysis of ^{13}C labeled DBK, encouraged an attempt to perform enrichment experiments with natural abundance DBK. DBK (natural abundance) was photolyzed in HDTCl solutions as described above. Analysis of the recovered DBK by mass spectroscopy showed a progressive increase of the ^{13}C content of the ketone (as determined from the increase of the isotopic peak corresponding to DBK of mass 211). Quantitative analysis of standardized ^{13}C NMR spectra showed considerable ^{13}C enrichment of the methylene carbons and also some ^{13}C enrichment of the ring carbons, although the main increase of ^{13}C content occurred in the carbonyl (Table I). The photolysis of natural abundance DBK in deaerated aqueous solutions of various detergents showed a similarity of the resulting enrichments. These results are clearly distinct from those of another series of photolysis experiments, where the influence of solvent viscosity in homogeneous solution was studied (vide infra). All experiments in homogeneous solutions starting with natural abundance or with synthetically enriched ^{13}C resulted in very low enrichments (Table I).

Effects of External Magnetic Fields on the ^{13}C Enrichment. Analysis of ^{13}C enrichment of recovered DBK from photolysis of partially ^{13}C-carbonyl-labeled DBK in micellar detergent solution (deaerated aqueous 0.05 M HDTCl) under the influence of an applied external magnetic field showed a marked dependence of the enrichment for a given extent of conversion on the strength of the applied magnetic fields. For comparable conversions the ^{13}C content of the carbonyl for a sample starting with DBK-*1*-^{13}C (47.6%) increased to 63.7% in the earth's magnetic field (~0.5 G) but to only 55% in a laboratory magnetic field of 15 000 G. A discussion of magnetic field effects on ^{13}C enrichment is deferred to the following paper in this series.

Isotopic Enrichment Parameter α. Since the ^{13}C enrichment depends on the extent of conversion, in order to discuss the results in a form that is both precise and mechanistically relevant, we now introduce the concept of a parameter, α, which is the single-stage isotope separation factor.[9] The magnitude of this parameter (1) allows a relevant comparison of the efficiency of isotope separation in terms of measurable quantities and (2) is not significantly dependent upon the extent of conversion, under appropriate conditions.

Bernstein[9] has shown that for competitive, first-order, isotopic reactions the residual unconverted starting material becomes exponentially enriched in the slower reacting isotope. As a result, if the isotope separation factor is substantial and if the reaction is run to high conversion, the recovered material may become significantly enriched in the slower reacting isotope. In the case of the photolysis of DBK, if we consider only the ^{12}C/^{13}C competitive isotope reactions, then residual, unconverted DBK will become enriched in ^{13}C, if molecules containing this isotope proceed to products at a slower rate than molecules that contain ^{12}C. The parameter α is defined as the single-stage separation factor and can be computed from the measurable quantities S, the overall separation factor, and f, the fractional conversion. The quantities are defined mathematically as shown in eq 4 and 5,

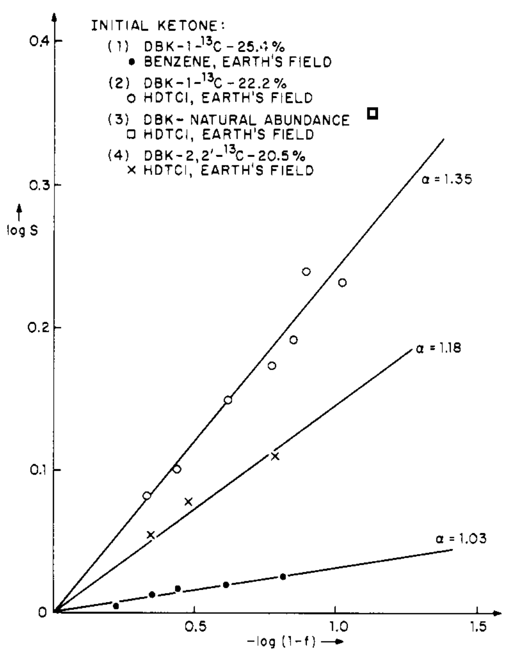

Figure 4. Plots of the separation factor S and the fraction conversion according to eq 6.

$$S = \frac{[{}^*\mathrm{DBK}][\mathrm{DBK}]_0}{[\mathrm{DBK}][{}^*\mathrm{DBK}]_0} \tag{4}$$

$$f = 1 - \frac{[\mathrm{DBK}] + [{}^*\mathrm{DBK}]}{[\mathrm{DBK}]_0 + [{}^*\mathrm{DBK}]_0} \tag{5}$$

where the zero subscript refers to the initial conditions and [*DBK] and [*DBK]$_0$ refer to the ^{13}C content in the residual recovered ketone and in the initial ketone. From the definitions of the measurable quantities S and f, the magnitude of α can be computed from eq 6, where R_0 = [*DBK]$_0$/[DBK]$_0$. For practical

$$\log S = \frac{\alpha - 1}{\alpha}\left[\log\left(\frac{1 + SR_0}{1 + R_0}\right) - \log(1 - f)\right] \tag{6}$$

cases eq 6 can be reduced to eq 7 as a good approximation. Thus,

$$\log S = [(\alpha - 1)/\alpha]\,[-\log(1 - f)] \tag{7}$$

from a plot of log S vs. −log $(1 - f)$ an experimental slope approximately (±5%) equal to $(\alpha - 1)/\alpha$ is obtained from which α may be computed.

Experimental Determination of Isotopic Enrichment Parameters. If eq 6 is followed experimentally, the occurrence of competitive first order isotopic reactions is confirmed, and the magnitude of α reflects the efficiency of the separation of ^{13}C from ^{12}C in a single stage of the competitive isotopic reaction. Measured vlaues of S and f were plotted in terms of eq 7, and the results are shown in Figure 4. The experiments were of the following types. (1) The initial ketone contained ^{13}C in natural abundance, and photolysis was conducted in 0.05 M HDTCl solution in the earth's magnetic field; a single-stage gross enrichment factor, α, was calculated from the mass spectrometrically determined value of S (calculation based on a single carbon atom enrichment). (2) The initial ketone was synthetically enriched in ^{13}C at the carbonyl

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[9] Bernstein, R. B. *J. Phys. chem.* **1952**, *56*, 893; Proceedings of the Symposium on Isotope Separation, Amsterdam, 1957, p 313.

Table II. Single Stage ^{13}C Isotopic Enrichment Parameters for Photolysis of Dibenzyl Ketone under Various Conditions

initial composn of ketone[b]	reaction conditions[a]	α^c
natural abundance	0.05 M HDTCl	~1.6
DBK-*1*-^{13}C (26.7%)	0.05 M HDTCl	1.37 ± 0.03
DBK-*2,2'*-$^{13}C_2$ (20.5%)	0.05 M HDTCl	1.18 ± 0.04
DBK-*1*-^{13}C (25.4%)	benzene	1.03 ± 0.001
DBK-*1*-^{13}C (10.2%)	benzene	1.04 ± 0.002
DBK-*1*-^{13}C (10.2%)	*n*-dodecane	1.05 ± 0.003
DBK-*1*-^{13}C (10.2%)	cyclohexanol	1.075 ± 0.002

[a] Experimental run at ~0 G (earth's magnetic field; see Experimental Section). [b] Percent isotopic incorporation given in parentheses. [c] Calculated from eq 6.

(DBK-*1*-^{13}C) or at the methylene carbon (DBK-*2,2'*-^{13}C), and the photolysis of 0.05 M HDTCl solutions was conducted in the earth's magnetic field. The corresponding single-stage enrichment factors $\alpha_{CO}{}^{DBK}$ (enrichment specifically at the carbonyl carbon of DBK) and $\alpha_{CH_2}{}^{DBK}$ (^{13}C enrichment specifically at the methylene carbons of DBK) were also calculated from mass spectrometrically determined values of *S*. The magnitude and selectivity of the ^{13}C enrichments were corroborated by quantitative analysis of ^{13}C content by the ^{13}C satellite method. (3) The initial ketone was synthetically enriched (as above) in ^{13}C, and the photolysis was conducted in homogeneous organic solvents or in water. The enrichment factor $\alpha_{CO}{}^{DBK}$ was computed as described above. The values of α computed from these experiments are listed in Table II.

Discussion

^{13}C Enrichment during the Photolysis of DBK. The quantitative correlation between mass, ^1H NMR (satellite method), and ^{13}C NMR spectroscopic analysis of the ^{13}C enrichment in the carbonyl of DBK recovered from photolysis (of 47.6% ^{13}C-labeled starting DBK) in 0.05 M deaerated, aqueous HDTCl solution leaves no doubt that a sizable and readily measurable ^{13}C enrichment in the carbonyl of DBK occurs under the conditions of photolysis at room temperature, with a single-stage enrichment factor of $\alpha_{CO}{}^{DBK} \approx 1.35 \pm 0.03$. Analogous photolysis in 0.05 M HDTCl solution of DBK partially labeled with ^{13}C at both methylene carbons confirms that considerable enrichment also occurs at these positions, with an enrichment factor $\alpha_{CH_2}{}^{DBK} \approx 1.18 \pm 0.04$. This enrichment pattern ($\alpha_{CO}{}^{DBK} > \alpha_{CH_2}{}^{DBK}$) agrees well with results obtained with the ^{13}C NMR spectra of recovered DBK from photolysis of natural abundance DBK. Indeed, the larger α values (~1.6) obtained for photolysis of natural abundance DBK in 0.05 M HDTCl solution (α is calculated for a singlet site of enrichment from mass spectrometric analysis) should be taken as representing the sum of enrichments at all carbon positions of the DBK molecule. The summation of individual values of α gives a reasonable correlation; i.e., $\alpha_{CO}{}^{DBK} \approx 1.35$ and $\alpha_{CH_2}{}^{DBK} \approx 1.18$. Enrichment at the other positions (in the aromatic rings) is certainly smaller and is not yet clearly established, although such enrichment is clearly indicated by the ^{13}C NMR spectra of the material recovered from photolysis of natural abundance DBK in micellar detergent solutions. The minor product, PMAP, produced in the photoreaction in aqueous detergent solution, also shows enriched ^{13}C content in the carbonyl (with respect to the original ^{13}C content of DBK starting material). Starting with a 47.6% ^{13}C label in the carbonyl of starting DBK, one observes that ^1H NMR and mass spectroscopic analyses are in quantitative agreement with respect to the extent of the enrichment, with a single-state enrichment factor $\alpha_{CO}{}^{PMAP} = 1.26 \pm 0.03$. The predominant site of enrichment is confirmed to be the carbonyl by the characteristic ^{13}C satellites of the CH_2 group (and the acetophenone ortho protons) of PMAP in the ^1H NMR spectrum (Figure 3). The structural identification of PMAP was performed by independent synthesis of the ketone from phenacetyl chloride and toluene.[10]

Effect of Micellar Aggregates and Viscosity on the Efficiency of ^{13}C Enrichment during Photochemistry of Dibenzyl Ketone. From earlier experiments with the unsymmetrical dibenzyl ketone derivative, 1-*p*-tolyl-3-phenylacetone (TPA), an efficient "micellar cage effect" on the photoreaction of this ketone was apparent.[11] An examination of the factors responsible for this cage effect in micellar detergent solutions is considered here in the context of the ^{13}C enrichment studies. Two main factors are specifically taken into consideration, first the topological "cage character" of the micelles and second, the viscosity of the micellar interior.[11] These were tested by examining the effect of various detergents and the effect of varying the solution viscosity in experiments with homogeneous solutions of DBK. These were tested by examining the effect of various detergents and the effect of varying the solution viscosity in experiments with homogeneous solutions of DBK. The effect of solution viscosity for homogeneous solutions is of minor importance (Table II). Nevertheless, a small effect of viscosity on the ^{13}C enrichment in DBK is still apparent,[12] since the single stage enrichment factor $\alpha_{CO}{}^{DBK}$ increase somewhat from α (benzene, $\eta = 0.6$ cP) = 1.04 to α (dodecane, $\eta = 1.36$ cP) = 1.05 and to α (cyclohexanol, $\eta = 60$ cP) = 1.08. Similar investigations, testing for the effect of homogeneous solution viscosity on the product formation from photolysis of unsymmetrically substituted dibenzyl ketones,[1c] have also shown no observable viscosity effect on the product ratios. Judged by these two criteria, product distribution and ^{13}C enrichment, the effect of homogeneous solvent viscosity on the relevant geminate caged lifetime of the pertinent radical pairs is small.

In contrast to the minor role of viscosity, the "topology" of the micellar detergent solutions is crucial for significant enrichments, i.e., the existence of micellar or other cages seems to be an important prerequisite for strong ^{13}C enrichment for photolysis of DBK in solution. In all of the detergent solutions tested (as 0.05 M, deoxygenated, aqueous solutions) ^{13}C enrichment in (natural abundance) DBK was found to be very similar and substantial: e.g., α values were 1.60 (for HDTCl), 1.66 (for dodecyltrimethylammonium chloride, DDTCl), 1.47 (for sodium dodecyl sulfate, SDS), and 1.41 (for hexadecyltrimethylammonium bromide, HDTBr). In the aqueous detergent solutions, α critically depended on the existence of the micelles, as was shown by a dilution series, for which α could be linearly correlated with a calculated concentration of the micelles and was found to be large only above the critical micelle concentration (cmc). Below the cmc the enrichment of ^{13}C in the carbonyl of DBK is small and similar to values achieved in other homogeneous solutions (α = 1.06 at 10^{-3} M HDTCl, a concentration below the cmc).[7a]

Micelles do not seem to be unique in furnishing suitable cages for a high ^{13}C enrichment in DBK: for example, preliminary experiments indicate photolyses of solutions of DBK impregnated in porous glass ($\alpha \approx 1.22$) and in polymethacrylate polymer films ($\alpha \approx 1.30$) give substantial ^{13}C enrichments as in the micellar detergent solutions.

In conclusion, we associate the major effect of the micellar detergent solution on the ^{13}C enrichment in the photolysis of DBK and other ketones with their ability to provide extended "cages", in which the probability for recombination of the radical pairs is high. In the following paper we report studies directed toward elucidation of the complete mechanism of the photolysis of DBK in micellar solution.

Experimental Section

Preparation and Purification of Ketones. Dibenzyl Ketone (DBK = natural abundance isotopic compositions; Aldrich Chemical Co.) was commercially available material and was sublimed at 10^{-1} torr (at ca. a 40 °C bath temperature) to give colorless crystals that were stored in the

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[10] Behagel, O.; Ratz, H. *Chem. Ber.* **1939**, *72*, 1257.

[11] (a) Turro, N. J.; Cherry, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 7431. (b) Turro, N. J.; Aikawa, M.; Yekta, A. *J. Am. Chem. Soc.* **1979**, *101*, 772.

[12] During the refereeing of this paper, a report appeared on the measurements of the viscosity dependence of ^{13}C enrichment of dibenzyl ketone in homogeneous solutions: Sterna, L.; Ronis, D.; Wolfe, S.; Pines, A. *J. Chem. Phys.* **1980**, *73*, 5493. The values of α for cyclohexanol and toluene (computed from Figure 5 of the latter paper) are ~1.1 and ~1.04.

dark at 0 °C under nitrogen. **Dibenzyl-*1*-^{13}*C* ketone** (90.9% ^{13}C in the carbonyl) was prepared[8] by using ^{13}C-labeled phenylacetic acid-$^{13}C_1$ (90% ^{13}C, Merck Sharp & Dohme) as starting material. The raw DBK-*1*-^{13}*C* (90.9%) obtained in 55% overall yield from phenylacetic acid, was sublimed and stored as described above for DBK. Selected data: ^{1}H NMR (90 MHz, $CDCl_3$, in parts per million vs. Me_4Si as internal standard) 3.66 (s, $H_2C^{12}C{=}O$) superimposed with 3.66 (d, $J_{^{13}C,H} = 6.5$ Hz; $H_2C^{13}C{=}O$) and with a ratio of satellite to central peak integrals corresponding to 89.5 ± 2% ^{13}C. ^{13}C NMR (13.2 MHz, $CDCl_3$, in parts per million vs. Me_4Si as internal standard, proton decoupled) 205.5 (s, $^{13}C{=}O$), 49.1 (d, $J_{^{13}C^{13}C} = 31$ Hz, $H_2{}^{13}C^{13}C{=}O$) superimposed with 49.2 (s, $H_2{}^{13}CC{=}O$) and with a ratio of integrals corresponding to 91.5 ± 5% ^{13}C; IR ($CHCl_3$) 1670 cm^{-1} (s, $^{13}C{=}O$); mass spectrum (chemical ionization), *m/e* (relative intensity) 211 (11.7, $M^+ + 1$), 212 (100, $M^+ + 2$), 213 (15.8, $M^+ + 3$), with a calculated ^{13}C content in the carbonyl of 90.0 ± 0.3% ^{13}C. **Dibenzyl-*2,2′*-$^{13}C_2$ ketone** (90% ^{13}C in each methylene of DBK) was also prepared by starting with phenylacetonitrile-α-^{13}*C* (Merck Sharpe & Dohme, 90% α-^{13}C) in an overall yield of 45% as shown in eq 2. Purification and storage were as described for DBK. Selected spectral data: ^{1}H NMR (90 MHz, $CDCl_3$, in parts per million vs. Me_4Si as internal standard) 3.66 (s, $H_2{}^{12}C^{12}CO$) superimposed with 3.66 (d, $J_{^{13}CH} = 130$ Hz, $^{13}C{-}^{12}CO$) and with a ratio of integrals (satellites to central peak) corresponding to 90.5 ± 2% ^{13}C at the 2,2′-positions; IR ($CHCl_3$) 1705 cm^{-1} (s, ^{12}CO); mass spectrum (chemical ionization) *m/e* (relative intensity) 212 (22.1, $M^+ + 2$), 213 (100, $M^+ + 3$), 214 (14.4, $M^+ + 4$), with a calculated ^{13}C content at the 2,2′-positions of 89.8 ± 0.5%.

Solvents and Detergents. Water was doubly distilled (first distillation from $KMnO_4$); benzene (Fisher, "spectroanalyzed"), cyclohexane (Fisher, "spectroanalyzed"), dodecane (Aldrich, 99%), and cyclohexanol (Fisher, reagent grade) were used without further purification. The detergents used, hexadecyltrimethylammonium chloride (HDTCl), hexadecyltrimethylammonium bromide (HDTBr), and dodecyltrimethylammonium chloride (DDTCl), were obtained from Eastman Co. and sodium dodecylsulfate (SDS) from Biolab. The detergents were recrystallized from ethanol and dried subsequently under 10^{-2} torr pressure at room temperature.

Analyses. Analyses were performed by VPC with a 15% SE-30/Chromasorb W column (column temperature 180–200 °C) on a Varian Aerograph 3700 equipped with a Spectra Physics digital integrator (molar response ratios were generally determined, and computed areas were corrected for differences in response factors). For preparative VPC (Figure 3) the same column material and conditions were employed. For GC/MS, a Finnigan 3300 with data system 6000 was used (OV-1 column, programmed temperature 150–200 °C, chemical ionization with methane). Overall separation factors *S* were obtained by simulation of the mass spectrometric isotopic pattern of the molecular ion by superposition of appropriate fractions of signals due to DBK-*1*-^{12}*C* and DBK-*1*-^{13}*C*, taking into account the natural abundance distribution of carbons other than those at C-1 and of the hydrogens in the molecule. A calibration of this method was obtained by preparing mixtures of natural abundance DBK and DBK-*1*-^{13}*C* (90.9%) and comparing the enrichments determined by mass spectrometric data with the compositions based on the known compositions of the mixtures. The agreement betweent the two methods was excellent over the full concentration range studied in this work. Samples were injected as solutions in cyclohexane. NMR spectra were recorded on Varian HA-100, Brucker WP-80, and JEOL PFT 100 instruments at room temperature.

Standard Preparative Photolysis Experiments. For experiments in the absence of an external magnetic field, appropriate amounts of purified unlabeled DBK and ^{13}C-labeled DBK (^{13}C-DBK) were dissolved in aqueous detergent solution (usually 0.05 M) by being shaken overnight in a tightly stoppered flask (at room temperature and under protection from light). A sample of the resulting clear colorless solution was used as a standard for the enrichment experiments. The products were worked up as follows. The detergent solution was diluted with an equivalent amount of saturated aqueous sodium sulfate solution and extracted with an equivalent amount of CH_2Cl_2 or diethyl ether. The solvent was then evaporated (Büchi evaporator, room temperature, reduced light) and then stored under nitrogen at 0 °C in the dark as a frozen solution. Samples of the starting detergent solution were placed into a quartz reaction vessel and deoxygenated by bubbling with nitrogen (for ca. 30 min before and during the experiment for solution agitation). The agitated detergent solution was irradiated with a water-cooled, medium-pressure, Hanovia Hg lamp immersed in a quartz vessel, and samples of specific solution volumes were removed at appropriate time intervals. The organic materials were recovered by extraction with CH_2Cl_2 (as described above for the standard) and analyzed by VPC, GC/MS, and, when desired, by ^{1}H and/or ^{13}C NMR spectroscopy (to determine the extent converstion, ^{13}C enrichment, and identity of the products).

Preparative VPC (15% SE-30/Chromosorb W, 180 °C) was employed to purify samples before subjecting them to quantitative ^{13}C analysis by ^{13}C NMR. The major effect of this purification was to remove the decarbonylation product DPE from the reaction mixture. The ^{1}H NMR spectrum shown in Figure 3 was obtained from a sample purified as described above.

Experiments at Zero Applied Laboratory Magnetic Fields. Experiments were conducted at (nominal) zero external magnetic field by photolyzing samples within the gap of an Alpha Model 4500, 4-in., adjustable-gap electromagnet. For the preparative photolyses, samples of aqueous, deoxygenated detergent solutions of DBK mixtures of known degree of ^{13}C labeling were placed into a quartz tube (vide supra) and positioned in the center of the gap of the electromagnet. A (nominal) zero magnetic field was produced by applying a small current to compensate for any residual fields within the gap. The magnitude of the magnetic field at the sample under these conditions was measured to be less than 0 ± 0.5 G. Experiments at variable magnetic fields are discussed in the next paper in this series.

Data Treatment. The ^{13}C content (as determined mass spectroscopically and in several cases by the ^{1}H NMR satellite method) of the recovered ketones as well as the conversion of the photolyses (determined by calibrated and standardized VPC) were determined, and the single stage enrichment factors α were calculated by using Bernstein's formula[9] (eq 6). For experiments where strongly ^{13}C-enriched DBK was used as starting material, eq 6 becomes less accurate and yields α values which are high by typically 5% (this method was used in some earlier reports).[5b,7a] The single-stage enrichment factor α' for PMAP was determined directly by comparing the ^{13}C content of starting DBK and that of PMAP, extrapolated to zero conversion.

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