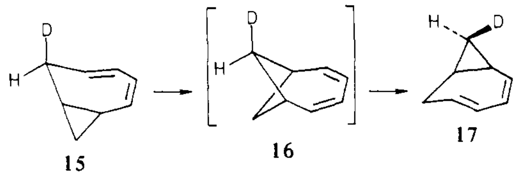
produce inversion of configuration. Alternatively, the transformation of **1** to **2** might proceed by a concerted pathway with subjacent orbital interactions[18] contributing to the observed preference for inversion.

A result already in the literature may bear on this question. Grimme and Doering have observed the interconversion of bicyclo[5.1.0]octa-2,4-dienes **15** and **17**.[19] Although they proposed a concerted sigmatropic reaction to account for this transformation, we have noted[7] that the intermediacy of bicyclo[4.1.1]octa-2,4-diene **16** is at least a possibility.



If **16** is, in fact, an intermediate, Grimme and Doering's result would indicate that the [1,5] sigmatropic shift of **16** to **17**, like that of **1** to **2**, proceeds with inversion of configuration. However, unlike the case in **1** or in the norcaradienes that have been studied,[17] the migrating carbon in **16** is unsubstituted. Therefore, if the rearrangement of **15** to **17** is shown to involve **16**, slow rotation at a tertiary carbon in a putative diradical intermediate cannot be invoked to explain the stereochemical outcome of this reaction.[20]

Acknowledgments. We thank the National Science Foundation for support of this research and George Renzoni for FT-NMR and mass spectra.

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[17] The migrating carbon has been tertiary in each of the norcaradienes that has been used to study the stereochemistry of the ring-walk.[1,4-6]

[18] Berson, J. A.; Salem, L. *J. Am. Chem. Soc.* **1972**, *94*, 8917. Borden, W. T.; Salem, L. *Ibid.* **1973**, *95*, 932.

[19] Grimme, W.; Doering, W. von E. *Chem. Ber.* **1973**, *106*, 1965.

[20] **Note Added in Proof**: Evidence supporting the mechanism proposed by Grimme and Doering for the rearrangement of **15** to **17** has recently been published by Kirmse, W.; Kuhr, R.; Murawski, H.-R.; Scheidt, F.; Ullrich, V. *Chem. Ber.* **1980**, *113*, 1272.

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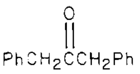
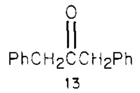
Magnetic Field and Magnetic Isotope Effects on Cage Reactions in Micellar Solutions

Sir:

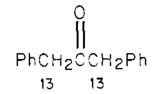
A fundamental premise of the theory of CIDNP is the postulate that the chemical reactivity of radical pairs in solution may be influenced by nuclear spins, because intersystem crossing in radical pairs may occur predominately by electron–nuclear hyperfine interactions.[1] Several chemically significant corollaries follow[2] from the radical-pair model of CIDNP: (1) observed kinetic isotope effects may arise from differences in nuclear magnetic moments rather than from differences in nuclear masses, e.g., isotope effects on the competition between cage reactions and cage escape (the cage effect) may be due to nuclear spin isotope effects;[3] (2) products of reactions of radical pairs may be enriched in (or impoverished in) magnetic isotopes, e.g., ^{13}C may be enriched in cage products of triplet radical pairs;[4] (3) the cage effect and isotope enrichment will be magnetic field dependent.[5] It has been proposed that the following is an important criterion for distinguishing between nuclear spin isotope effects and mass isotope effects:[6] *the yields of products from a radical pair containing a magnetic nucleus should be magnetic field dependent with an extremum near the field corresponding to the hyperfine coupling between the nucleus and the unpaired electron in the radical.* We report here an investigation of the cage effect and ^{13}C isotope enrichment in the photolysis of dibenzyl ketone (DBK) and of isotopically labeled ketones in aqueous solutions containing hexadecyltrimethylammonium chloride (HDTCl) which meets this criterion and clearly establishes the operation of kinetic nuclear spin isotope effects.


$PhCH_2\overset{O}{\overset{\|}{C}}CH_2Ph$

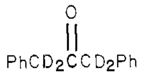
DBK
(natural abundance)


$PhCH_2\underset{13}{\overset{O}{\overset{\|}{C}}}CH_2Ph$

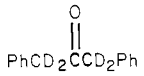
DBK-*1*-^{13}C
(90% ^{13}C, carbonyl)


$Ph\underset{13}{C}H_2\overset{O}{\overset{\|}{C}}\underset{13}{C}H_2Ph$

DBK-α,α′-$^{13}C_2$
(90% ^{13}C, methylene)


$PhCD_2\overset{O}{\overset{\|}{C}}CD_2Ph$

DBK-α,α,α′,α′-d_4
(>90% D, methylene)


$PhCD_2\overset{O}{\overset{\|}{C}}CD_2Ph$

DBK-^{13}C,α,α,α′,α′-d_4
(90% ^{13}C, carbonyl, >90% D methylene)

The salient features of our results are the following: (1) the efficiency of ^{13}C enrichment (Figure 1) and the magnitude of the cage effect (Figure 2) are strongly magnetic field dependent in the range 0–500 G; (2) the behavior of enrichment efficiency as a function of magnetic field strength is qualitatively different for $PhCH_2COCH_2Ph$ and for $PhCD_2COCD_2Ph$; (3) the extent of cage reaction for $Ph^{13}CH_2CO^{13}CH_2Ph$ is dramatically higher than that for $PhCH_2COCH_2Ph$.

The photolysis of DBK in micellar (HDTCl) solution has been shown[7] to result in the ^{13}C enrichment of recovered DBK. The mechanism of the enrichment (Scheme I) was proposed to be a nuclear spin isotope effect on the competition between decarbonylation and intersystem crossing of the triplet radical pair ^3D-$(PhCH_2\dot{C}O\ \dot{C}H_2Ph)$.

We have measured the efficiency of ^{13}C enrichment of recovered DBK in terms of Bernstein's parameter,[8] α. This parameter was evaluated by mass spectrometric analysis of the ^{13}C content of DBK recovered from partially photolyzed solutions (α^{MS})[7] and by determination of the ratio of quantum yield of reaction of DBK-*1*-^{13}C to that of DBK (α^{Φ}).[9a,10] For quantum yield measurements, the photolysis lamp was situated approximately 1 m away from the sample which in turn was centered between the pole faces of an electromagnet. The magnetic field strength in the vicinity of the lamp housing was measured to be about 10 G when the magnet was operated at 0 G. The additional magnetic field strength near the lamp housing was less than 0.5 G when the magnet was operated in the range 0–500 G, and less than 1 G when the magnet was operated at 5 KG.

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[1] Kaptein, R. *Adv. Free-Radical Chem.* **1975**, *5*, 381. Closs, G. L. *Proc. Int. Congr., Pure Appl. Chem. 23rd ed.* **1971**, *4*, 19. Ward, H. R. *Acc. Chem. Res.* **1972**, *5*, 18. Lawler, R. G. *Ibid.* **1972**, *5*, 25. Buchachenko, A. L.; Zhiromirov, F. M. *Russ. Chem. Rev.* **1971**, *40*, 801.

[2] Lawler, R. G.; Evans, G. T. *Ind. Chim. Belge* **1971**, *36*, 1087.

[3] Buchachenko, A. L. *Russ. Chem. Rev.* **1976**, *45*, 761.

[4] Buchachenko, A. L. *Russ. J. Phys. Chem.* **1977**, *51*, 2461.

[5] Sagdeev, R. Z.; Salikhov, K. M.; Molin, Y. M. *Russ. Chem. Rev.* **1977**, *46*, 297.

[6] Lawler, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 430.

[7] Turro, N. J.; Kraeutler, B. *J. Am. Chem. Soc.* **1978**, *100*, 7432.

[8] Bernstein, R. B. *J. Phys. Chem.* **1952**, *56*, 893; *Science* **1957**, *126*, 119.

[9] (a) Turro, N. J.; Kraeutler, B.; Anderson, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 7435. (b) For a derivation of the relationship of α to photochemical quantum yields, see: Kraeutler, B. J.; Turro, N. J. *Chem. Phys. Lett.* **1980**, *70* 266.

[10] Typically, the measurement of α^{Φ} was made as follows: an aqueous solution containing 0.005 M ketone and 0.05 M HDTCl was photolyzed to 10% conversion (1000-W high-pressure Hg lamp, Pyrex filter). Analyses were performed on a Varian 3700 gas chromatograph (6 ft 3% OV-17 column, column temperature = 185 °C) employing a Varian CDS 111 minigrator. Typically, α^{MS} was determined by photolysis of solutions as described for determination of α^{Φ}. Conversions were generally between 40 and 90% and analyses were made by GC-MS (Finnigan 3200, 10%, SE-30 column).

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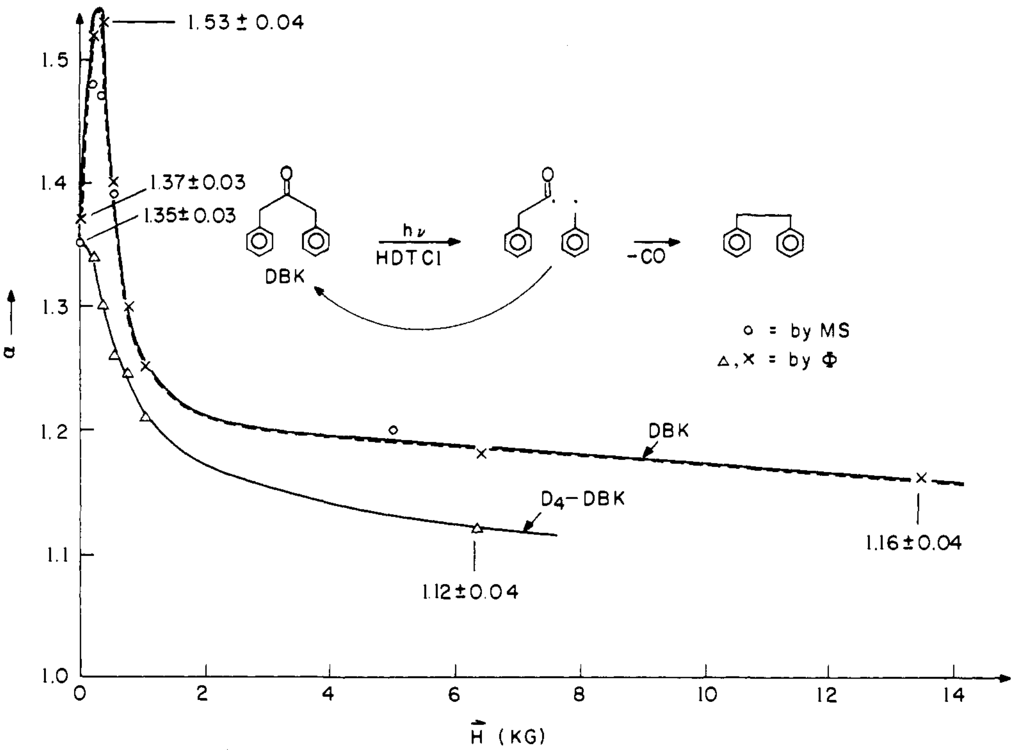

Figure 1. ^{13}C enrichment parameter at a given magnetic field H.

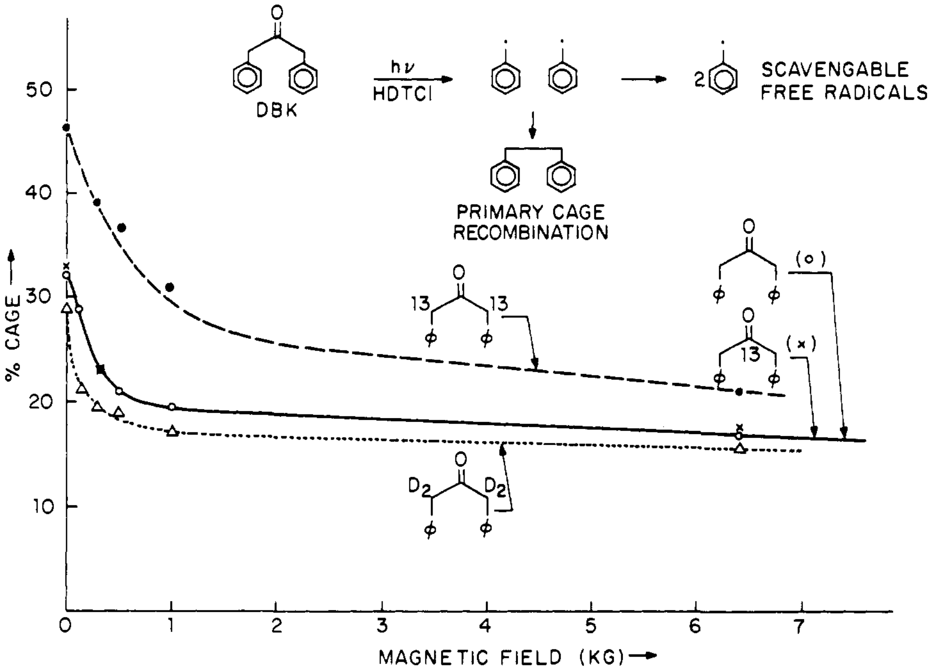

Figure 2. Cage effect for the formation of DPE as a function of magnetic field for DBK and several labeled DBK's.

The effect of deuteration was investigated by measuring $\alpha_D{}^{\Phi}$[11] in photolysis of bis(benzyl-α,α-d_2) ketone and bis(benzyl-α,α-d_2) ketone-^{13}C. Plots of α as a function of magnetic field strength are shown in Figure 1. The first point to be noted is that the values of α^{MS} and α^{Φ} for DBK are experimentally identical, thereby confirming the validity of the theory of quantum yield measurements[9b] as a reliable measure of the efficiency of ^{13}C enrichment. The next point to be noted is the occurrence of a *maximum* value of α for fields ~150–300 G for DBK. Finally, deuteration is found not to significantly alter the value of α at 0.5 G (earth's field); however, the field dependence of α for DBK-d_4 is qualitatively different from that for DBK (no maximum in the value of α).

We have determined the "cage effect" for formation of diphenylethane (DPE) in the photolysis of DBK and several isotopically labeled ketones.[12] Measurement of the efficiency of

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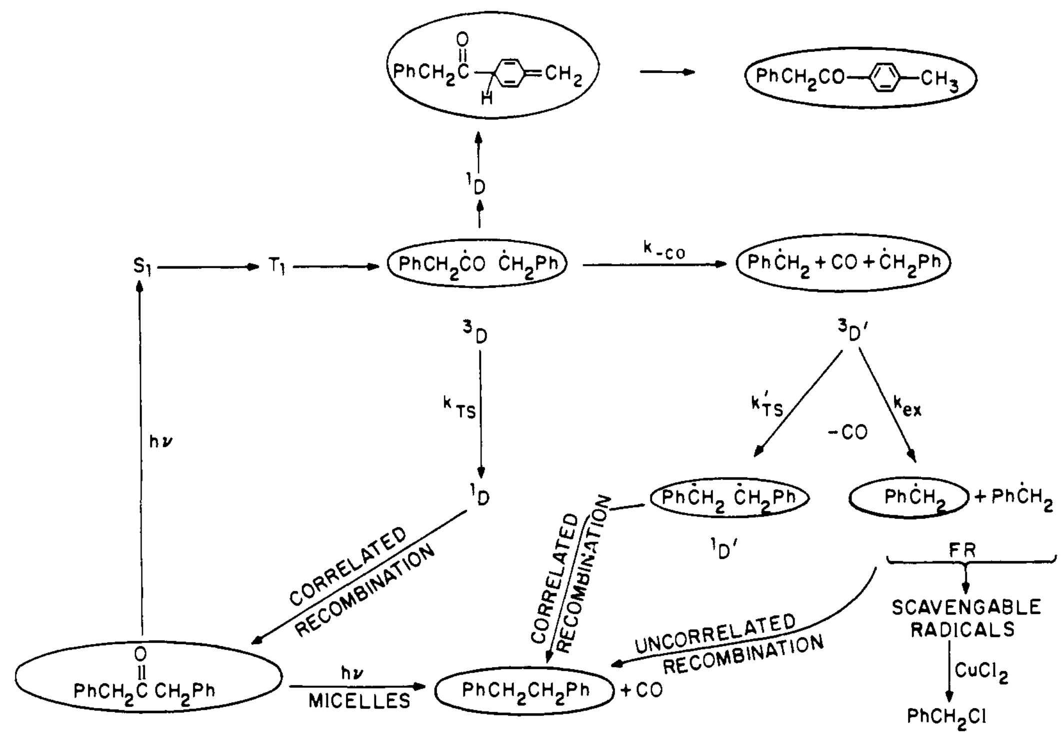
[11] We were incapable of measuring $\alpha_D{}^{MS}$ because of severe isotopic exchange (H for D) during the GC–MS analysis.

[12] The cage effect for $^3D'$ is defined (in terms of Scheme I) as the ratio of the rate of intersystem crossing of $^3D'$ to $^1D'$ to the sum of the rates of all processes that destory $^3D'$. The cage effect for $^3D'$ radical pairs was measured employing solutions containing 0.001 M ketone, 0.05 M HDTCl, and 0 M or 0.005 M $CuCl_2$. Photolyses and analyses were described in ref 10. Conversions were typically ~30%.

Scheme I



formation of DPE in the presence and absence of Cu^{2+} yields the cage effect for $^3D'$ radical pairs. Intersystem crossing ($^3D' \rightarrow {}^1D'$) presumably precedes efficient coupling to form DPE (Scheme I). The cage effect for the various ketones investigated was measured as a function of magnetic field strength (Figure 2). The "cage effect" was also measured in an alternate manner that did not require a scavenger in order to determine whether aqueous $CuCl_2$ traps all the benzyl radicals which escape from micelles or whether the micellar system is significantly perturbed by the addition of scavenger. A 0.05 M HDTCl solution containing 0.001 M 4-$CH_3C_6H_4CH_2COCH_2C_6H_5$ (A–CO–B) was photolyzed at 0.5 G. The ratio of yields of BB:AB:AA was found to be 1.0:6.52:1.04, from which a cage effect of 52 ± 3% can be computed. In the presence of 0.007 M $CuCl_2$ a solution of 0.05 M HDTCl containing 0.001 M ACOB, a cage effect of 48 ± 4% was computed from the amount of unscavengable coupling product, AB. No AA or BB were detected in the latter experiment. Several salient points are apparent. Only a small difference is noted for DBK and either DBK-*1*-^{13}C or DBK-d_4. However, it is expected from Scheme I that if triplet $Ph^{13}{\cdot}CH_2$ pairs undergo more rapid intersystem crossing than triplet $Ph^{12}{\cdot}CH_2$ pairs this will lead to a higher yield of cage product resulting from recombination of the $Ph^{13}CH_2$ radical pairs as is found experimentally: DBK, cage effect = 32 ± 2%; DBK-α,α'-$^{13}C_2$, cage effect = 46 ± 3%. For each ketone studied, a major decrease in the cage effect occurs only for field strengths less than 1000 G.

In conclusion, the results shown in Figures 1 and 2 provide substantial evidence that nuclear spin isotope effects are significant in the photochemistry of DBK in micellar solution. Fitting the details of the curves to a quantitative theory may provide important information relevant to parameters involved in CIDNP and in micellar structure and dynamics.

Acknowledgments. The authors thank the National Science Foundation and the Department of Energy for their generous support of this research. We also thank Professor R. Lawler for a preprint of his thoughtful paper on criteria for establishing nuclear spin isotope effects.

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[13] Since we now have discovered that α is extremely sensitive to magnetic field strength for fields in the range of 100–300 G, we have reexamined previously reported data.[7] We find that the reported values of α for "control experiments" that were run on samples within the gap of a magnet nominally at 0 G are consistently highr (α ~1.47) than the values of α (~1.35) found for "control experiments" that were run on samples on a bench. It appears likely that a residual field on the order of 100–200 G persisted in the "control experiments" run in the magnet. Also, a better correlation exists between α and quantum yields for disappearance of DBK than for the appearance of DPE. This is because it is now known that an isomer of DBK is also formed[14] in low yield so that the quantum yield for disappearance of DBK does not exactly equal the quantum yield for appearance of DPE. The value of 1.41 reported earlier[9] was based on the quantum yield for formation of DPE. We consider the quantum data reported here, since they are based on DBK disappearance, provide the most accurate values of α (1.35 ± 0.03).

[14] Kraeutler, B.; Turro, N. J. *Chem. Phys. Lett.* **1980**, *70*, 270.

α-Fluorination of Carbonyl Compounds with CF_3OF

Sir:

We have found a convenient, two-step method for the introduction of fluorine adjacent to the carbonyl group of ketones, aldehydes, esters, and amides. This is accomplished by first converting the carbonyl compounds to their trimethylsilyl enol ethers and then treating these resultant ethers with trifluoromethyl hypofluorite (CF_3OF) at −70 °C in an inert solvent to give directly the corresponding α-fluorocarbonyl compound.

Previous investigators[1] have found that enol acetates could be treated with CF_3OF to give mixtures of α,β-difluoroalkyl acetates and α-trifluoromethoxy-β-fluoroalkyl acetates, both of which could be hydrolyzed to α-fluoro ketones. Vinyl ethers and enamines can also be converted to α-fluoro ketones by similar chemistry.[1] These procedures work well for the preparation of α-fluoro ketones, but they appear to lack generality and have not been applied to the syntheses of other α-fluorocarbonyl compounds such as aldehydes, esters, and amides. These procedures also have a further

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[1] Barton, D. H. R.; Godinho, L. S.; Hesse, R. H.; Pechet, M. M. *Chem. Commun.* **1968**, 804–806. Hesse, R. H. *Isr. J. Chem.* **1978**, *17*, 60–70 and references cited therein.