

Utilization of Radical Scavenging To Develop Nuclear Spin Polarization and Magnetic Isotope Separation in Long Flexible Biradicals†

Nicholas J. Turro,* Kuo Chu Hwang, V. Pushkara Rao, and Charles Doubleday, Jr.*

Department of Chemistry, Columbia University, New York, New York 10027 (Received: April 16, 1990; In Final Form: June 12, 1990)

Irradiation of argon-purged acetonitrile solutions of 2-phenylcyclododecanone (**1**) in the probe of a 250-MHz NMR spectrometer does not produce significant ^1H or ^{13}C chemically induced dynamic nuclear polarization (CIDNP). However, irradiation of **1** in oxygen-purged acetonitrile, argon-purged acetonitrile containing small amounts of bromotrichloromethane, or argon-purged carbon tetrachloride solutions, in the probe of a 250-MHz NMR spectrometer, produces intense ^1H and ^{13}C CIDNP. Irradiation of argon-purged acetonitrile solutions of **1** in the earth's field does not lead to measurable ^{13}C enrichment of the recovered starting material or in the products of photolysis. However, irradiation of **1** in carbon tetrachloride or in acetonitrile solutions purged with oxygen or containing small amounts of bromotrichloromethane results in significant enrichment of an isomeric product, **2**. The development of CIDNP and of isotopic enrichment is proposed to result from a common feature of the systems containing oxygen, carbon tetrachloride, or bromotrichloromethane: the opening of a competitive chemical scavenging pathway (oxygen, carbon tetrachloride, or bromotrichloromethane as scavengers) for the triplet biradical (^3BR) produced by homolytic cleavage of electronically excited **1**. This competitive pathway, when its rate is within an appropriate "kinetic window", provides a mechanism for effective sorting of nuclear spins to develop CIDNP and the effective sorting of nuclear isotopes to develop isotopic separation.

Introduction

The past two decades have seen the evolution of a field that is concerned with magnetic effects on chemical reactivity, *magnetokinetics*,¹ from a poorly understood, skeptically viewed science to a thriving discipline that is supported by a readily understood and well-defined theoretical and experimental base. Among the important contributions that have led to the current status of the field, one must include the discovery and development of the following phenomena: (1) chemically induced dynamic nuclear polarization (CIDNP),² (2) magnetic isotope effects (MIE),³ and (3) magnetic field dependences on chemical reactivity (MFD).⁴ These three phenomena possess a common physical basis and share a theoretical paradigm associated with the dynamics of radical pairs and its obvious extension to the dynamics of flexible biradicals. We are concerned in this report with the CIDNP and the MIE of the *flexible, long-chain* biradical produced by the photolysis of 2-phenylcyclododecanone. The MFD of the lifetime of this biradical has been reported.⁵

CIDNP of Long Flexible Biradicals. Triplet biradical CIDNP differs from triplet radical pair CIDNP in several important aspects.⁵⁻⁷ Furthermore, a critical structural difference exists between *flexible* triplet biradicals and triplet radical pairs: the presence of a mobile constitutional (bonded) connection between the radical termini in the biradical that is absent in the radical pair. This flexible connection prevents an unlimited separation of the radical termini of the triplet biradical, which in turn prevents the reduction of the value of the exchange integral to a vanishingly small quantity, as is the case for the radical pair. Experimentally, the products formed (in the absence of efficient scavengers) from biradicals result from combination or disproportionation reactions of the radical termini (so-called geminate "cage products"); thus, the only significant reaction pathways for triplet biradicals correspond to the *geminate reactions* of radical pairs. In contrast, the major portion of products formed (in the absence of efficient radical scavengers) from triplet radical pairs result from coupling or disproportionation reactions of *free radicals* encountering as pairs (so-called "escape products").⁶ The impossibility of "infinite" separation of radical termini for short (number of carbons in cyclic ring, $n \leq 5$) and medium ($6 \leq n \leq 9$) triplet biradicals results in a nonzero average value of the exchange interaction (J) and tends to "quench" the T_0 -S CIDNP mechanism (most commonly associated with radical pairs) by causing the T_0 and S states to be "off resonance" by an amount of energy equal to the sin-

gle-triplet energy gap ($2J$ is usually defined as the singlet-triplet splitting, ΔE_{ST}). For long ($n \geq 10$) flexible biradicals, the T_0 and S states are nearly degenerate (i.e., exchange interaction J is very small or negligible). Therefore development of biradical CIDNP essentially follows a T_0 -S mechanism. However, the development of T_0 -S CIDNP requires a competition between a nuclear spin selective intersystem crossing leading to "cage" products and nuclear spin independent "escape" products. This different set of products, one set from cage reaction and the second set from escape, is generally not available to typical flexible organic biradicals, which generally lead to one set of products, i.e., geminate cage products. Thus, both the exchange interaction and the lack of an escape pathway serve to "quench" T_0 -S CIDNP of long-chain, flexible biradicals.

The nonzero J associated with a biradical introduces a second potential mechanism for CIDNP involving T_{\pm} -S CIDNP that may become effective if the energies of the T_{\pm} (or the T_{\pm}) level can be brought into resonance with the S level by the application of

(1) Steiner, U. E.; Ulrich, T. *Chem. Rev.* **1989**, *89*, 51.

(2) For reviews of the theory of CIDNP see: (a) Lepley, A. R.; Closs, G. L. *Chemically Induced Magnetic Polarization*; Wiley: London, 1978. (b) Lawler, R. G. *Acc. Chem. Res.* **1972**, *5*, 25. (c) Salikhov, K. M.; Buchachenko, A. L.; Molin, Y. N.; Sagdeev, R. Z. *Spin Polarization and Magnetic Effects in Radical Reactions*; Elsevier: Amsterdam, 1982.

(3) For reviews of the magnetic isotope effects see: (a) Buchachenko, A. L. *Prog. React. Kinet.* **1984**, *13*, 163. (b) Buchachenko, A. L.; Tarasov, V. F.; Malisev, V. I. *Russ. J. Phys. Chem.* **1981**, *55*.

(4) (a) Weller, A. *Z. Phys. Chem. (Frankfurt/Main)* **1982**, *130*, 129. (b) Weller, A.; Nolting, F.; Staerk, H. *Chem. Phys. Lett.* **1983**, *96*, 24. Weller, A.; Staerk, H.; Treiche, R. *J. Chem. Soc., Faraday Discuss.* **1984**, *78*, 271, 332. (d) Weller, A. In *Supramolecular Photochemistry*; Balzani, V., Ed.; Reidel: Dordrecht, The Netherlands, 1987; p 343. (e) Weller, A.; Staerk, H.; Schomburg, H. *Acta Phys. Pol.* **1987**, *A71*, 707.

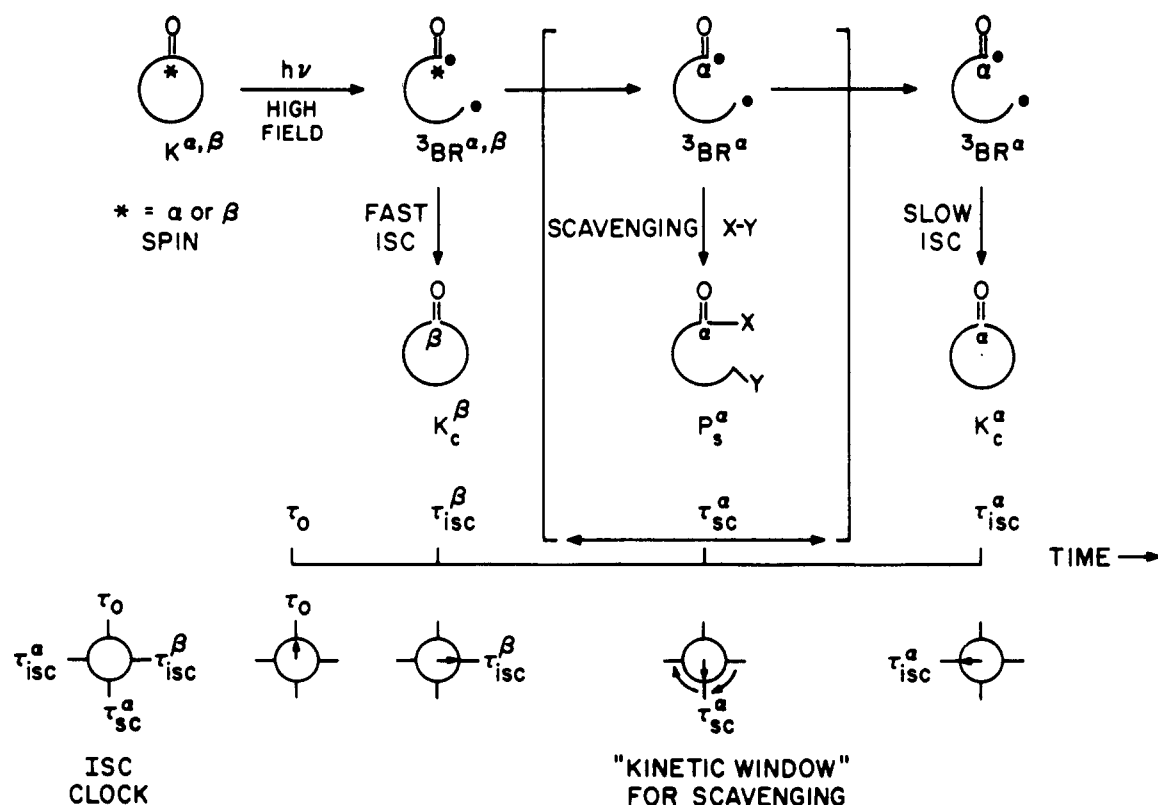
(5) For biradical lifetime measurements see: (a) Doubleday, C., Jr.; Turro, N. J.; Wang, J. F. *Acc. Chem. Res.* **1989**, *22*, 199. (b) Wang, J. F.; Walsh, K. M.; Waterman, K. C.; Fehner, P.; Doubleday, C., Jr.; Turro, N. J. *J. Phys. Chem.* **1988**, *92*, 3730. (c) Wang, J. F.; Doubleday, C., Jr.; Turro, N. J. *Ibid.* **1989**, *93*, 4780. (d) Wang, J. F.; Doubleday, C., Jr.; Turro, N. J. *J. Am. Chem. Soc.* **1989**, *111*, 3962. (e) Zimmt, M. B.; Doubleday, C., Jr.; Turro, N. J. *Ibid.* **1985**, *107*, 6724, 6726. (f) Zimmt, M. B.; Doubleday, C., Jr.; Turro, N. J. *Ibid.* **1986**, *108*, 3618.

(6) Turro, N. J. *Modern Molecular Photochemistry*, The Benjamin/Cummings Publishing Co.: Menlo Park, CA, 1978.

(7) For field dependence of CIDNP see: (a) De Kanter, F. J. J.; Sagdeev, R. Z.; Kaptein, R. *Chem. Phys. Lett.* **1978**, *58*, 334. (b) De Kanter, F. J. J.; Den Hollander, J. A.; Hulzer, A. H.; Katpein, R. *Mol. Phys.* **1977**, *34*, 857. (c) Katpein, R.; Van Leeuwen, P. W. N. M.; Huis, R. *Ibid.* **1976**, *41*, 264. (d) Closs, G. L.; Doubleday, C., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 2735. (e) Doubleday, C. *Chem. Phys. Lett.* **1979**, *64*, 67; **1981**, *79*, 375; **1981**, *77*, 131.

† Dedicated to Professor Albert Weller on the occasion of his 65th birthday.

SCHEME I



an external field (i.e., when the values of the Zeeman energy and $2J$, the singlet-triplet gap, are closely matched).⁷ However, at the high field of a superconducting NMR spectrometer, T_{\pm} -S CIDNP is also quenched for long, flexible biradicals because the magnetic field strength causes the T_{\pm} levels to be far off resonance with S. Thus, the lack of an escape process to develop T_0 -S CIDNP and the strong field quenching of T_{\pm} -S CIDNP make the observation of biradical CIDNP, by any conventional mechanism, somewhat problematical in a conventional high-field NMR spectrometer. This generalization is particularly true for long ($n \geq 10$) flexible biradicals (biradicals connected by, say, nine or more methylene groups), which display maximum CIDNP intensity at fields less than 1 kG (small values of $\langle 2J \rangle$). For example, the field strength of a 250-MHz NMR spectrometer is 58.3 kG, whereas the maximum T_{\pm} -S CIDNP intensity for a biradical separated by 10–12 methylene groups will show a CIDNP maximum at ca. 100 G.⁷ Thus, at the high field of a superconducting magnet CIDNP from both the T_{-} and the T_{+} states is quenched because the Zeeman effect is huge compared to $\langle 2J \rangle$ and drives the states far off resonance from S.

Use of Scavenging To Develop CIDNP in Long, Flexible Biradicals. Several examples of the use of radical scavengers to induce and tune spin sorting in order to develop T_0 -S biradical CIDNP have been reported in the literature.¹⁰ From the simulation of the magnetic field dependence of the CIDNP, the rate constants of the scavenging process have been evaluated.¹⁰ As discussed above, a nuclear spin independent escape pathway capable of producing products that are different from the products of cage reaction of the biradical is required. The escape pathway may involve an intrinsic nuclear spin independent physical re-

laxation (e.g., induced by spin-orbit coupling^{7e} or spin-lattice relaxation) or an extrinsic physical relaxation (e.g., induced by an external paramagnetic species). The most efficient escape pathway for producing biradical T_0 -S CIDNP, however, is often¹⁰ a chemical reaction of one of the radical termini with an added scavenger. In contrast to physical relaxation, chemical scavenging produces a unique set of products that prevents cancellation of nuclear polarization within the same set of products. Furthermore, the scavenging rate may be "tuned" by systematic variation of the scavenging rate constant and/or the concentration of scavenger. The rate constants for many reactions of organic radicals with a wide range of scavengers are compiled in the literature⁸ so that the expected rate of reaction of each end of a biradical (assuming that the inherent reactivity, or rate constant, of each radical center with scavengers is essentially the same in the biradical and in the most closely analogous monoradical)⁹ may be readily estimated and may be smoothly tuned by varying the scavenger concentration.

With these considerations we refer to Scheme I, which displays a simplified representation of how radical scavenging can serve as a basis for spin sorting in biradicals. Photolysis of a cyclic ketone, $K^{\alpha,\beta}$, produces (after the usual absorption of a photon to produce a n,π^* singlet, followed by molecular intersystem crossing to a triplet and α cleavage) a triplet biradical $^3BR^{\alpha,\beta}$. The superscript labels α and β refer to the nuclear spin population at (for example) ^{13}C at the carbonyl carbon of the starting material, biradical intermediates, or products. If the reaction is run in a strong magnetic field, the system starts with a Boltzmann distribution of nuclear spins, i.e., with a slight excess of α spins over β spins. The symbol α,β refers to the Boltzmann population of nuclear spins, and the spin system is said to be *unpolarized*. The symbol α alone or β alone as a superscript refers to a *polarized* system (excess α or excess β spins, respectively).

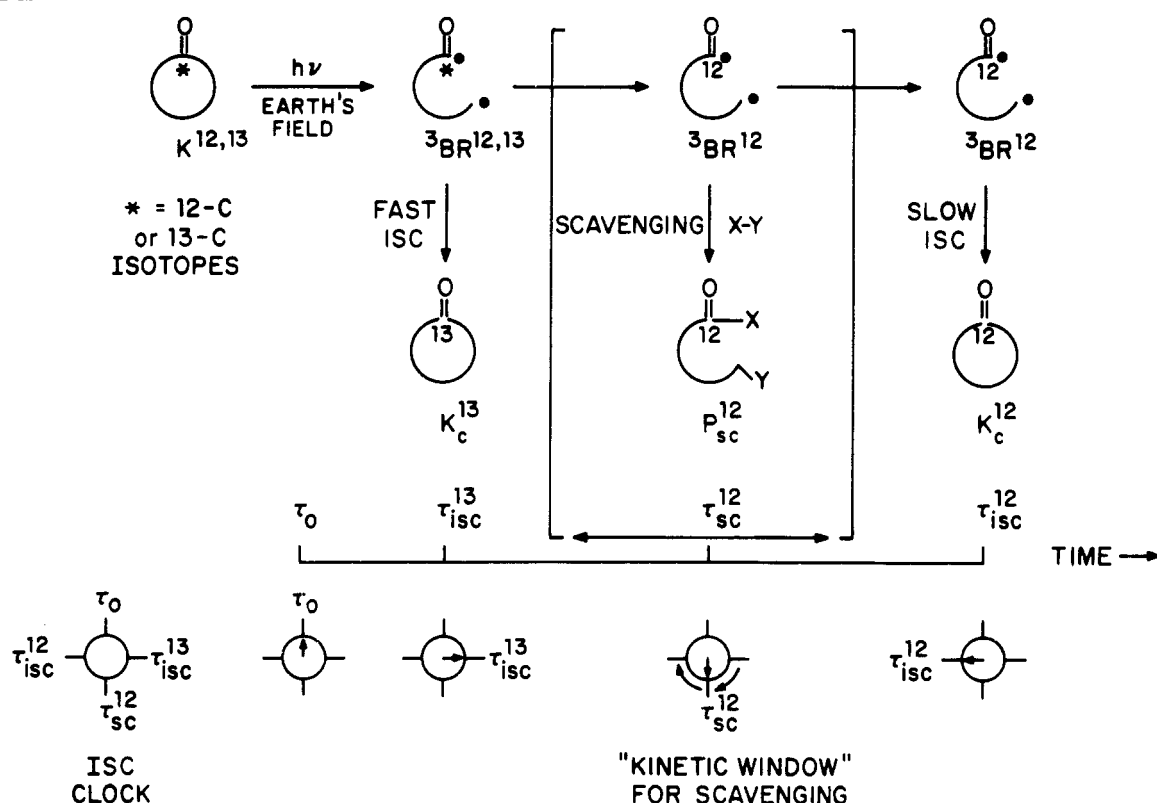
From Scheme I we can follow the sorting strategy. The initially formed biradical $^3BR^{\alpha,\beta}$ is assumed (for the sake of argument and because this situation is commonly observed)³ to undergo a faster intersystem crossing for ^{13}C β spins than for ^{13}C α spins. This is the actual situation for the carbonyl carbon of acyl alkyl biradicals produced by photolysis of cyclic ketones.^{7e} Let τ_{isc}^{β} , τ_{sc}^{β} , and τ_{sc}^{α} be the average time constants associated with a faster intersystem crossing of the biradicals containing ^{13}C in the β spin

(8) (a) Johnston, L. J.; Scaiano, J. C. *Chem. Rev.* **1989**, *89*, 521. (b) *Numerical Data and Functional Relationship in Science and Technology: Carbon-Centered Radicals II*; Hellwege, K. H., Madelung, O., Eds.; Landolt-Bornstein: New York, 1984; Vols. a, b.

(9) (a) Kuwae, Y.; Kamachi, M.; Hayaske, K.; Viche, H. G. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2325. (b) Kuwae, Y.; Kamachi, M. *Ibid.* **1989**, *62*, 2474. (c) Encinas, M. V.; Wagner, P. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 1357. (d) Scaiano, J. C.; Abain, E. B.; Stewart, L. C. *Ibid.* **1982**, *104*, 5673.

(10) (a) De Kanter, F. J. J.; Sagdeev, R. Z.; Kaptein, R. *Chem. Phys. Lett.* **1978**, *58*, 340. (b) Bondarenko, M. A.; Pichuzhkin, V. I.; Knyazev, D. A. *Zh. Fiz. Khim.* **1987**, *61*, 1306.

SCHEME II



state ($^3\text{BR}^\beta$), with a slower intersystem crossing of biradicals containing ^{13}C in the α spin state ($^3\text{BR}^\alpha$), with scavenging of the shorter lived biradicals containing ^{13}C in the β spin state, and with scavenging of the longer lived biradicals containing ^{13}C in the α spin state, respectively. It is important to note that the scavenging rate constant is *not* spin selective. The efficiency of sorting α spins from β spins will be a function of the size of the inherent "kinetic window for sorting", which is equal to the difference between τ_{isc}^β and τ_{isc}^α , and the ability to "tune" the time constant for scavenging to a value within this window. The latter is not a serious constraint since both the rate constant of the scavenging reactions and the concentration of the scavenger may be varied over a wide range.

In an idealized situation in the presence of a tunable scavenger, the biradicals $^3\text{BR}^\beta$ intersystem cross to the singlet biradicals $^1\text{BR}^\beta$ (not shown in Scheme I because the chemical dynamics of product formation from singlet biradicals is generally not rate determining) faster than do the biradicals $^3\text{BR}^\alpha$. In the absence of scavenging, both the faster intersystem crossing $^3\text{BR}^\beta$ and the slower intersystem crossing $^3\text{BR}^\alpha$ eventually form singlet biradicals that collapse to products K_c^β and K_c^α , respectively, and the products do not show any CIDNP, i.e., the Boltzmann population of nuclear spins is simply carried from the starting ketone through the biradical and into the products.

Suppose, however, that the short-lived (τ_{isc}^β) $^3\text{BR}^\beta$ biradicals collapse to the combination products K_c^β but that the longer lived (τ_{isc}^α) $^3\text{BR}^\alpha$ biradicals are scavenged to form the products $\text{P}_{\text{sc}}^\alpha$ faster than they undergo intersystem crossing. The net result is sorting of the nuclear spins into two sets of products: the β nuclear spins flow into the cage combination products K_c^β and the α nuclear spins flow into the scavenged products $\text{P}_{\text{sc}}^\alpha$. As a result, the combination and scavenging products will show (within the relaxation time of the nuclear spin in K) a deviation from the Boltzmann distribution and will be polarized. In a CIDNP experiment the products K_c^β will show a strong CIDNP emission (excess β spins), and the products $\text{P}_{\text{sc}}^\alpha$ will show a strong CIDNP absorption (excess α spins).

Use of Scavenging To Develop MIE for Long, Flexible Biradicals. The simple physical theory discussed above to explain nuclear spin sorting (i.e., separation of α nuclear spins from β nuclear spins) CIDNP can be employed, with a minor modification (Scheme II), to explain the sorting of magnetic isotopes from

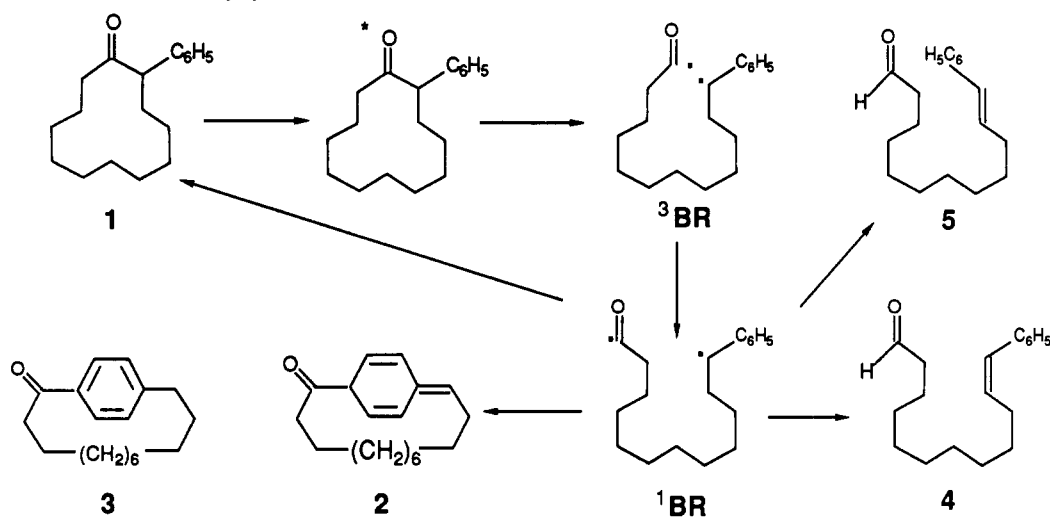
nonmagnetic isotopes. This is done in Scheme II by replacing β spins with ^{13}C isotopes and α spins with spinless ^{12}C isotopes.³ In the case of isotope separation (which, in contrast to CIDNP, is performed at low magnetic fields), the biradicals ($^3\text{BR}^{13}$) containing ^{13}C , a magnetic nucleus, at the carbonyl carbon, undergo faster intersystem crossing (with the time constant τ_{isc}^{13}); the biradicals ($^3\text{BR}^{12}$) containing ^{12}C , a nucleus without spin and therefore without magnetic properties, at the carbonyl carbon, undergo slower intersystem crossing (with the time constant τ_{isc}^{12}). As was the case for the development of triplet biradical CIDNP by sorting of nuclear spins, application of scavenging reactions with a rate in the "kinetic window" for isotope separation will allow the separation of magnetic isotopes. Although the concept of using a scavenger to affect CIDNP has been reported^{10a} and an attempt to employ scavenging to develop the efficiency of the magnetic isotope effect has been reported,^{10b} the use of radical scavengers to develop both CIDNP and magnetic isotope separation¹² for the same biradical system has not been reported. We demonstrate that radical scavenging may be employed to develop both CIDNP and magnetic isotope separation in a long flexible biradical.

The Paradigm for Photolysis of Large-Ring α -Phenylcyclohexanones. The photochemistry^{11a} of large ring α -phenylcyclohexanones provides a convenient and efficient method for the production of long-chain, flexible biradicals and results in the products shown in Scheme III. We have conducted an extensive study of these reactive intermediates by direct time-resolved laser spectrometric measurements of the biradical lifetimes and by the magnetic field dependence of lifetimes of the triplet biradicals produced by α -cleavage.⁷ As complementary studies we searched for ^{13}C CIDNP (at 250 MHz) and for ^{13}C enrichment (at zero field, via a magnetic isotope effect) in the recovered starting material and in the products 2 and 3 of photolysis of α -phenylcyclohexanone (1). Neither attempt was successful, but the negative results are easily understood on the basis of radical pair theory of magnetic effects as discussed above in Schemes I and

(11) (a) Lei, X. G.; Doubleday, C. Jr.; Turro, N. J. *Tetrahedron Lett.* **1986**, 27, 4671, 4675. (b) Rao, P. V.; Wang, J. F.; Turro, N. J.; Doubleday, C., Jr. *J. Labelled Comp. Radiopharm.* **1990**, 28, 193.

(12) (a) Turro, N. J.; Doubleday, C., Jr.; Hwang, K. C.; Cheng, C. C.; Fehlner, J. R. *Tetrahedron Lett.* **1987**, 28, 2929. (b) Klimentko, B. B.; Tarasov, V. F.; Buchachenko, A. L. *Bull. Acad. Sci. USSR* **1984**, 33, 1072.

SCHEME III: Photoreaction of 2-Phenylcyclo-dodecanone



II, since an efficient pathway for the formation of escape products is absent in this system.¹¹

Since radical scavenging of biradicals would create and allow systematic tuning of the rate of the escape processes available to biradicals,¹⁰ this method of developing T_0 -S CIDNP and ^{13}C separation was selected. It was decided to first investigate the influence of the type of quencher, i.e., physical (paramagnetic spin relaxation) or chemical (radical reaction), on the development of T_0 -S CIDNP and then to employ the resulting information to suggest conditions to develop ^{13}C separation. Of course, the absolute position in time and the width of the "kinetic window" of the scavenging rate will in general be different for the nuclear spin and nuclear isotope sorting processes. However, with the results of T_0 -S CIDNP in hand, it seemed likely that specific experimental strategies to induce ^{13}C enrichment of α -phenylcyclo-dodecanone would be apparent.

Experimental Section

Materials. The synthesis of α -phenylcyclo-dodecanone (1) is reported in the literature.¹¹ Doubly labeled α -phenylcyclo-dodecanone ($1\text{-}^{13}\text{C}_2$, 99% at C-1 and 49.5% at both C-2 and C-12) was obtained by applying the literature procedure for synthesis of α -phenylcyclo-dodecanone, starting from a labeled sample of cyclo-dodecanone (99% at C-1 and 49.5% at C-2 and C-12), which was in turn prepared by intramolecular acyloin condensation of dodecanedioic acid (99% ^{13}C at the acid carbon) and reduction.¹¹

CIDNP Measurements. The CIDNP experiments were performed on a Bruker AF 250-MHz FT NMR equipped with a CIDNP probe possessing a glass rod with mirrors at both ends, allowing a collimated light beam to be directed into the probe. The exciting light was provided by a Hanovia 1000-W high-pressure mercury lamp, filtered through an aqueous CoSO_4 solution. A 90° rf pulse angle with acquisition delay time of 0 s for ^1H CIDNP and of 0.5 s was employed to obtain the ^{13}C CIDNP spectra. The proper number of scans was chosen to obtain good S/N ratio. The acquisition condition was set as above, unless otherwise mentioned.

Procedure for Measurement of ^{13}C Separation. To enhance the accuracy of the ^{13}C measurements, an enriched sample of 2-phenylcyclo-dodecanone ($1\text{-}^{13}\text{C}_2$ described above) was photolyzed. In a typical experiment, 1.7 mg of $1\text{-}^{13}\text{C}_2$ (in the enrichment $\sim 5.6\%$ $^{13}\text{C}=\text{O}$ was employed) in 1 mL of acetonitrile containing 10% v/v methanol was purged with argon for approximately 10 min. The solution was then photolyzed by a medium-pressure Hg lamp filtered with a $\text{K}_2\text{Cr}_2\text{O}_7$ aqueous solution. The photolysis time was adjusted to achieve substantial (60–90%) conversion. After photolysis, the photosate was passed through a small silica gel column to convert the unstable primary product 2 to the stable cyclophane 3. The ^{13}C content of residual 1 and of 3 was determined by mass spectrometric analysis employing the GC/MS technique described earlier,^{12a} with a Hewlett-Packard Model 5988

A GC/MS. The isotopic content of 1 and 3 was determined by measuring the $(M+2)/M$ ratio, which is directly related to the ^{13}C content of 1 and 3. Natural abundance 2-phenylcyclo-dodecanone and unphotolyzed starting $1\text{-}^{13}\text{C}_2$ were employed for calibration and controls.

In the oxygen-scavenging experiments, the photolyzed solutions were comparable to those described above, except that oxygen rather than argon was used for bubbling the solution during photolysis. In the carbon tetrachloride scavenging experiments, the concentrations of $1\text{-}^{13}\text{C}_2$ were comparable to those described above, carbon tetrachloride was employed as solvent, and the solutions were argon purged. In the bromotrichloromethane experiments acetonitrile solutions containing $1\text{-}^{13}\text{C}_2$ and millimolar amounts of CBrCl_3 and 10% v/v methanol were purged by argon for 10 min before irradiation. The presence of 10% methanol has two advantages: (1) methanol rapidly converts the scavenged product, an acid bromide, to a stable ester,¹³ and also generates HBr; (2) the HBr generated from step 1 catalyzes the H shift of unstable 2 to stable cyclophane 3.

Results

Photochemistry of 2-Phenylcyclo-dodecanone. The room-temperature photolysis of 1 in argon-purged homogeneous solutions (e.g., acetonitrile or hexane) has been shown¹¹ to result in formation of a triplet 1,12-acyl benzyl biradical, ^3BR , whose lifetime is determined by the rate of intersystem crossing. The lifetime⁵ of ^3BR is 66 ns in methanol in the earth's field (0.5 G) and 83 ns in a field of 2 kG, corresponding to intersystem crossing rates of 1.5×10^7 and $1.2 \times 10^7 \text{ s}^{-1}$, respectively. Intersystem crossing to the singlet biradical, ^1BR , leads to two cyclization products (the "pre-cyclophane", 2, and the cyclophane, 3; see scheme III) as the major products. The enal disproportionation products 4 and 5 are formed as minor products and will not be considered further in this report.¹¹ The photolysis of 1 in acetonitrile at -40°C leads to 2 as the exclusive product (determined by NMR analysis). 2 is stable in acetonitrile for several hours at room temperature and reverts thermally to 1.

^{13}C CIDNP of 2-Phenylcyclo-dodecanone. The photoinduced ^{13}C CIDNP of 2-phenylcyclo-dodecanone at 250 MHz (58.3 kG) was investigated in acetonitrile and carbon tetrachloride solvents for natural-abundance 1 and for samples of $1\text{-}^{13}\text{C}_2$ that was doubly ^{13}C labeled at the carbonyl (99% at the 1 position) and the α -methylene (49.5% at the 12 position) and the methine (49.5% at the 2 position) carbon atoms but did not possess a ^{13}C label simultaneously at the 2 and 12 positions.

(13) In the presence of 10% v/v methanol, the enhanced absorption at 171.1 ppm of acid bromide decreased dramatically. Another peak at 175.1 ppm with 5 times the intensity as that of 171.1 ppm grows up, which is assigned to be of the corresponding ester. Therefore the esterification rate of the acid bromide must be within the acquisition time scale, that is, a few seconds.

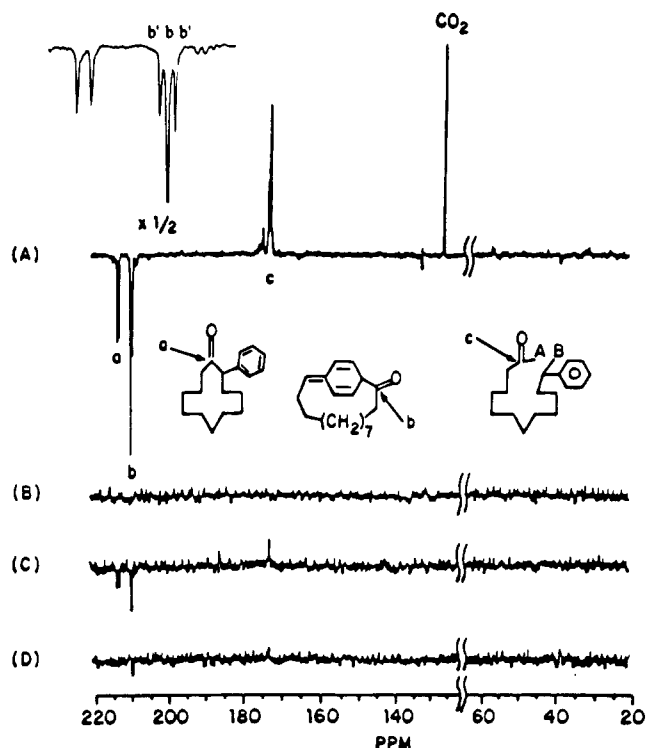
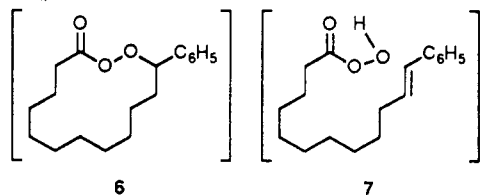


Figure 1. ^{13}C CIDNP of 5 mM 2-phenylcyclohexanone (doubly ^{13}C labeled) in acetonitrile in a Bruker 62.9-MHz FT NMR with solution bubbled (A) by molecular oxygen, (B) by argon, (C) by argon in the presence of 0.02 mM TEMPO, and (D) by argon in the presence of 0.02 mM Gd^{3+} . The scale of spectra (A) is only half of those in B–D. The acquisition parameters used are 90° rf pulse, 0.5-s delay time, acquisition time of 0.26 s, and 128 scans.

For natural-abundance **1**, at best only a very weak CIDNP signal could be observed for samples purged with argon gas, and only a very weak CIDNP signal was observed with oxygen purging. The search for CIDNP was more successful when $1\text{-}^{13}\text{C}_2$ was irradiated in acetonitrile as shown in Figure 1. Under comparable conditions of irradiation and data accumulation, samples purged with argon gas displayed only a very weak CIDNP signal (Figure 1B), whereas samples purged with oxygen gas displayed intense CIDNP signals (Figure 1A).

The interpretation of the CIDNP spectrum is as follows: The doublet (212.9/212.3 ppm, E/E, $J = 37.7$ Hz) is assigned to the carbonyl carbon of $1\text{-}^{13}\text{C}_2$. The apparent triplet (209.3/209.0/208.7 ppm, E/E/E) is assigned to the overlap of a true doublet (satellite peaks) and a singlet (central peak) of the carbonyl carbon of the precyclophane $2\text{-}^{13}\text{C}_2$. The singlet arises from molecules of $2\text{-}^{13}\text{C}_2$, which possess ^{12}C at the 12 position and therefore do not exhibit coupling from the excess ^{13}C label at the carbonyl position. The doublet ($J = 40.9$ Hz) arises from molecules of $2\text{-}^{13}\text{C}_2$, which possess the ^{13}C label at the 2 position of $2\text{-}^{13}\text{C}_2$. A series of enhanced absorption multiplets occur in the region of ca. 175 ppm. These enhanced absorption resonances are assigned to oxidized carbon atoms of products that arise from reaction of the termini of biradical $^3\text{BR}\text{-}^{13}\text{C}_2$ with molecular oxygen. These products are expected to be peractones such as **6** or peracids such as **7** (and their decomposition products). The strong absorption



at 125.7 ppm is due to CO_2 , which presumably derived from decomposition of the putative peracid or peractone products resulting from reactions of molecular oxygen with $^3\text{BR}\text{-}^{13}\text{C}_2$. The observation that the integral of the areas of emissive resonances

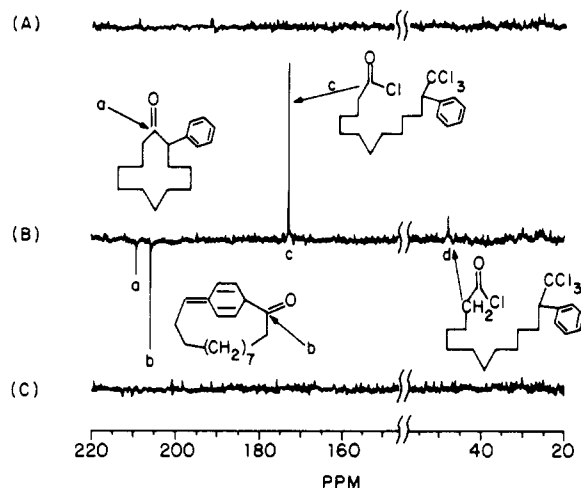
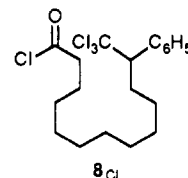


Figure 2. ^{13}C CIDNP of 45 mM 2-phenylcyclohexanone in neat CCl_4 with benzene- d_6 as external lock in a Bruker 62.9-MHz FT NMR. The solution was bubbled with argon for 15 min before irradiation. Spectrum A is before irradiation, B during irradiation, and C after irradiation. The acquisition conditions used are 90° rf pulse, 0.5-s acquisition delay, acquisition time of 0.26 s, and 760 scans.

for the carbonyl carbons for $1\text{-}^{13}\text{C}_2$ and for $2\text{-}^{13}\text{C}_2$ are comparable to the integral of the areas of the absorptive resonances of the oxidized carbons is consistent with a spin-sorting $T_0\text{-S}$ mechanism for development of the CIDNP and for oxygen serving as a spin-sorting scavenger.

Since the impressive effect of oxygen on the development of CIDNP might be due to a combination of reactive scavenging and relaxation effects, we tested two other paramagnetic species, Gd^{3+} , and the stable nitroxide radical, Tempo, as scavengers that might elicit $T_0\text{-S}$ CIDNP. However, very weak CIDNP, similar in form to that observed with oxygen purging, was observed with 0.02 mM Tempo (Figure 1C) and with Gd^{3+} at 0.02 mM no CIDNP was observed (Figure 1D). Increasing the concentration of Tempo led to the loss of the weak polarization observed at 0.02 mM. Purging samples containing Gd^{3+} or Tempo with oxygen resulted in the observation of CIDNP of intensity comparable to that shown in Figure 1A. These results argue against a paramagnetic relaxation mechanism for the development of CIDNP in the case of molecular oxygen.

In contrast to the results in acetonitrile, irradiation of samples of natural-abundance **1** in argon-purged CCl_4 shows a strong CIDNP (Figure 2). The emissive singlet at 209.2 ppm is assigned to the carbonyl carbon of **1**, and the emissive singlet at 205.8 ppm is assigned to the carbonyl carbon of **2**. The strong enhanced absorption at 172.7 ppm is assigned to the carbonyl of a product from CCl_4 scavenging of the biradical BR, i.e., the acid chloride **8_{Cl}**. The enhanced absorption at 47.7 ppm is assigned to the 2-methylene carbon of the same acid chloride.



These assignments are supported by the CIDNP of irradiated $1\text{-}^{13}\text{C}_2$ (99% $^{13}\text{C}=\text{O}$) in CCl_4 . Because the ^{13}C content of $1\text{-}^{13}\text{C}_2$ is very high, carbon-carbon couplings allow a more confident basis for assignments. The enhanced singlet absorption at 172.7 ppm that appears in the irradiation of **1** becomes an apparent triplet (172.8/172.3/171.9 ppm, A/A/A) for $1\text{-}^{13}\text{C}_2$, and the enhanced singlet absorption at 47.7 ppm that appears in the irradiation of **1** becomes a doublet¹⁴ (47.9/47.1 ppm, A/A, $J = 53.4$ Hz) for

(14) This doublet was observed only when a 0-s acquisition delay time was used. If 0.5 s of acquisition delay time was used, this doublet was not observed. These results are to be published elsewhere.

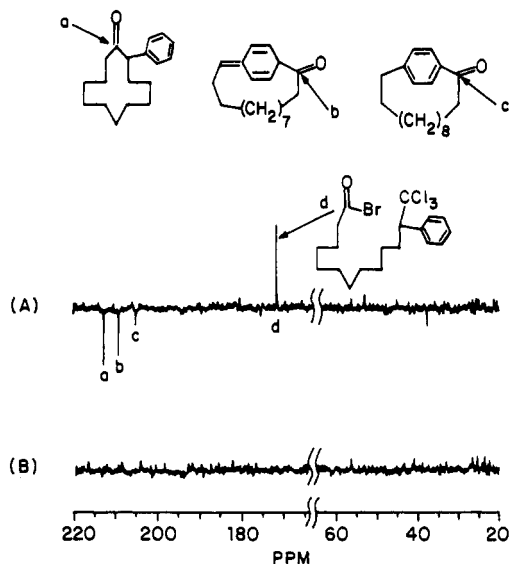


Figure 3. ^{13}C CIDNP of 45 mM 2-phenylcyclododecanone (natural abundance) in acetonitrile in the presence of 20 mM CBrCl_3 solution purged with argon. Spectra A during irradiation and B before irradiation have common acquisition conditions of 90° rf pulse, 0.5-s acquisition delay, acquisition time of 0.26 s, and 760 scans.

$1\text{-}^{13}\text{C}_2$. The apparent triplet is in fact a doublet ($J = 53.4$ Hz) due to coupling of the carbonyl carbon of 8_{Cl} with the enriched ^{13}C at the 2 position, and a central peak assigned to molecules of 8_{Cl} which possess mainly ^{12}C at the 2 position. Further support for the assignment comes from the observation that enhanced absorption is observed at 47.7 ppm when natural-abundance 2-phenylcyclanones (of ring size 9, 10, 11, and 15) is irradiated in CCl_4 solvent.¹⁵

Although CIDNP was not observed for ^{13}C at the 12 position of **8** (which is expected to occur near 65 ppm from model compounds) the regiochemistry of the addition of CCl_4 to ^3BR was established by analysis of the ^{13}C NMR of the products of photolysis of **1** photolyzed in neat $^{13}\text{CCl}_4$ (99% ^{13}C). The carbonyl peak at 172.8 ppm remained as a singlet, indicating that Cl and not $^{13}\text{CCl}_3$ had added to the acyl radical. The signal for the $^{13}\text{CCl}_3$ that coupled to the 12 position of the biradical was found at 104.3 ppm. The ^1H NMR of the product mixture (vide infra) provides further support for the assignment (see results below).

The effect of another efficient radical scavenger, CBrCl_3 to the generation of CIDNP is also tested by performing ^{13}C CIDNP of 45 mM **1** in argon-purged acetonitrile in the presence of 20 mM CBrCl_3 . As expected, intense nuclear polarization is observed as shown in Figure 3. The emission signals at 212.5, 208.9, and 205 ppm are the carbonyl carbons of **1**, **2**, and **3**, respectively. The enhanced absorption at 171.1 ppm is assigned to the carbonyl carbon of the scavenged product, an acid bromide whose structure is the analogue of the acid chloride, 8_{Cl} .¹³

^1H CIDNP of 2-Phenylcyclododecanone. As was the case for the ^{13}C CIDNP of **1**, the ^1H CIDNP of **1** in acetonitrile is extremely weak for argon-purged solutions but is significant for oxygen-purged solutions (Figure 4, middle). For clarity, sections of the ^1H CIDNP spectrum below 7.0 ppm and above 3.0 ppm, which are too congested for analysis, are not shown.

Two of the products expected to show oxygen-enhanced CIDNP are the "cage" products **1** and **2**. The only ^1H resonance of **1** in the region 3.0–7.0 ppm is due to the methine proton at C-2 (doublet/doublet, at ~ 4.1 ppm, $J = 2.7, 12.2$ Hz). Comparison of Figure 4, top and middle spectra (oxygen present, spectrum obtained from "before" and "during" irradiation), suggests that this proton appears as an emission (reduction of the relative absorption of the doublet/doublet at ~ 4.1 ppm during irradiation). This conclusion is justified by the observation that for ~ 48 s of irradiation, which is of the order of the acquisition time, less than

TABLE I: ^{13}C -Enrichment Studies of 2-Phenylcyclododecanone (**1**)^a in the Presence and Absence of Radical Scavengers at 20 °C and in the Earth's Field (0.5 G)

solvt	gas ^b	conversion, %	$\beta, \%$	
			1	3 ^d
C_6H_{12}	argon	75	1	7
		70	0	3
		oxygen ^e	81	20
CH_3CN	argon	91	17	67
		64	5	3
		oxygen ^e	60	0
CCl_4	argon	64	12	26
		68	11	30
		95	-70	95
		93	-24	102

^aThe starting **1** is doubly ^{13}C labeled (5.6% ^{13}C) at the carbonyl as well as either the C-2 or C-12 positions. ^bThe solution was purged by the gas listed 15 min before photolysis. ^cThe enrichment parameter, β , is defined to be the observed $^{13}\text{C}\%$ of product minus the $^{13}\text{C}\%$ of starting ketone, and then divided by the $^{13}\text{C}\%$ of starting ketone. ^d**3** is the ring extended cyclophane isomer; see Scheme III. ^eThe solution was bubbled by molecular oxygen during photolysis.

TABLE II: ^{13}C -Enrichment Studies of 2-Phenylcyclododecanone (**1**)^a in Acetonitrile (Containing 10% v/v Methanol)^b as a Function of Bromotrichloromethane Concentration at 20 °C

$[\text{CBrCl}_3], \text{mM}$	H, G	conversion, %	$\beta, \%$	
			1	3 ^d
5	0.5	55	7	9
		65	10	12
10	0.5	83	27	36
		52	19	34
20	0.5	91	9	67
		98	18	81
20	2.1×10^3	79	14	61
		82	20	66
		93	22	56
30	0.5	92	20	83
		82	23	93

^aThe starting **1** is doubly ^{13}C labeled (5.6% ^{13}C) at the carbonyl as well as either the C-2 or C-12 positions. ^bThe presence of methanol can quickly convert the quenched acid bromide to become a more stable product, ester. ^cThe enrichment parameter, β , is defined to be the observed $^{13}\text{C}\%$ of product minus the $^{13}\text{C}\%$ of starting ketone, and then divided by the $^{13}\text{C}\%$ of starting ketone. ^d**3** is the ring extended cyclophane isomer; see Scheme III.

5% conversion occurs. More obvious CIDNP occurs in a number of the protons of the precyclophane **2** (Figure 4, middle). The olefinic protons b, c, and c' and the aliphatic proton e all show emission, whereas the olefinic protons d and d' show enhanced absorption. The enhanced absorption at 5.0 ppm (doublet/doublet, $J = 5.6, 7.8$ Hz) is at a position expected for a proton attached to a saturated carbon, which is in turn attached to an oxygen atom. This resonance can be correlated with the resonances at ca. 175 ppm in the ^{13}C CIDNP of **1** and is assigned to the oxygenated 12 position of a peroxy lactone, peracid, or decomposition product. This proton is the absorptive complement of the emissive methine proton of **1** and the olefinic proton b of **2**.

The CIDNP spectrum of **1** (argon purged) in CCl_4 obtained during irradiation is shown in figure 4, bottom. The general features are similar to those observed for irradiation of **1** in the presence of oxygen (Figure 4, middle), i.e., enhanced emission due to protons b, c, c', and e of **2** and absorption due to protons d and d' of **2**. However, and importantly, the triplet at 5.0 ppm, assigned to the decomposition product of **6** and **7**, is missing in the CCl_4 experiment, and an enhanced absorption, absent in Figure 4, middle spectrum, appears at 3.0 ppm (triplet, $J = 7.2$ Hz). This resonance is assigned to the methine proton at the 12 position of 8_{Cl} . This assignment is strongly supported by the observation that for photolysis of **1** in neat $^{13}\text{CCl}_4$ (99% ^{13}C) the triplet at 3.0 ppm is transformed into a doublet of triplets with a separation of 3.8 Hz, which is expected as a result of ^{13}C coupling with the enriched

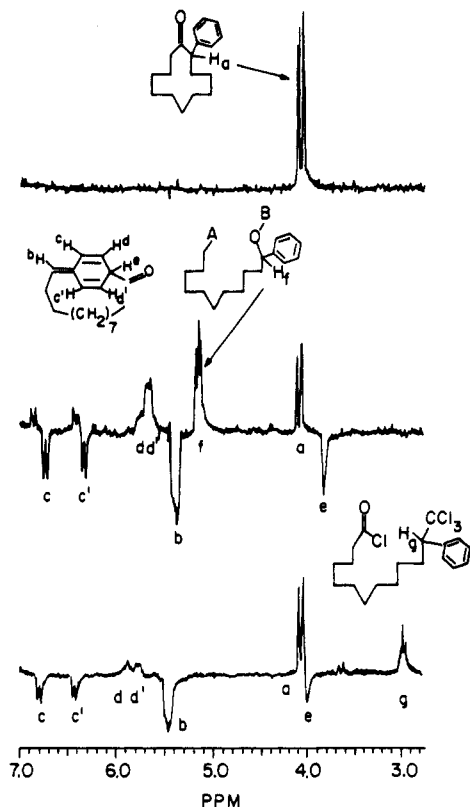


Figure 4. ^1H CIDNP of 45 mM 2-phenylcyclohexanone in acetonitrile in a Bruker 250-MHz FT NMR with (top) before irradiation spectra, (middle) during irradiation spectra, solution bubbled with molecular oxygen, and (bottom) during irradiation spectra of 45 mM 2-phenylcyclohexanone in neat CCl_4 with solution bubbled with argon. The acquisition parameters are 90° pulse angle, acquisition delay time of 0 s, acquisition time of 2.7 s, and 16 scans in top and middle spectra and 64 scans in bottom spectra.

^{13}C group that has added to the 12 position of biradical ^3BR .

^{13}C Enrichment by Photolysis of 2-Phenylcyclohexanone in the Presence of Scavengers. Tables I and II summarize the results of measurement of the ^{13}C content of the recovered 2-phenylcyclohexanone $1\text{-}^{13}\text{C}_2$ and the cyclophane **3** after photolysis of **1** to various conversions. The reproducibility of β , the measured ^{13}C enrichment (expressed on a single-atom basis), is better than $\pm 5\%$ from sample to sample. However, the actual enrichment is expected to depend on conversion if the regenerated starting ketone is enriched during the photolysis. In addition, the pre-cyclophane **2**, which may be enriched during the course of reaction, may revert partially during photolysis (thermally or photochemically) to the starting ketone. To the extent that this occurs, the enrichment of recovered $1\text{-}^{13}\text{C}_2$ is not a true indication of the inherent efficiency of enrichment of **1** from the intermediate BR . As a result of these considerations, the results in Tables I and II are taken as qualitative since the extent of enrichment is expected to depend on a number of factors, but the trends for the enrichment of **3** are clear.

The first salient results are the observations that the value of β is within the experimental error of 0% ($\pm 5\%$) for photolysis of $1\text{-}^{13}\text{C}_2$ of argon-purged acetonitrile or hexane solutions, but for comparable conversions in acetonitrile solvent the enrichment of **3** is dramatic for an oxygen-purged sample (ca. 22%) or for a solution containing 30 mM CBrCl_3 (ca. 88%). Photolysis of **1** in CCl_4 also results in very strong enrichment (ca. 98%), even with argon purging.

The second salient result is the observation that the value of β increases monotonically for photolysis of **1** in acetonitrile solutions containing increasing concentrations of CBrCl_3 (5, 10, 20, and 30 mM). The third salient result is measurable drop of β of **3** in the presence of a 2-kG field.

The results show that recovered **1** is substantially less enriched than is **3**. However, a direct comparison with the enrichment of

3 and **1** requires more research and the measurement of α , the inherent single-stage enrichment parameter.¹⁶ There appears to be a systematic connection between the β values for **3** and **1**, which, for the more precise results, have a ratio between 2 and 4 without any corrections for conversions or other factors.

Discussion

The radical pair mechanism provides a common paradigm to discuss both $T_0\text{-S}$ CIDNP and ^{13}C enrichment by the magnetic isotope effect for both radical pairs and biradicals. In both cases competing processes are needed to sort nuclear spinomers (α or β nuclear spins) or nuclear isotopomers (^{13}C or ^{12}C). In the discussion of the paradigm for the photolysis of **1** (Scheme I), for simplicity, we shall consider systems containing only one nuclear spin at the carbonyl carbon. The ideas from this idealized model can be readily extended conceptually to the more complicated case of a multispin system. We also recall that a spin-sorting process, diffusional separation that is generally available to radical pairs in nonviscous solution, is not available for biradicals.

In the case of $T_0\text{-S}$ CIDNP, by application of available EPR parameters for an acyl benzyl pair and the rules for CIDNP, for the acyl benzyl radicals, a geminate cage pathway to a product yields products enriched in β nuclear spins (triplet-to-singlet intersystem crossing is faster in radical pairs and biradicals that possess a β nuclear spin) and an escape pathway yields products enriched in α nuclear spins.¹⁷ As a result (Scheme I), the singlet biradicals, $^1\text{BR}^\beta$, formed by intersystem crossing combine to yield products, K_c^β , that for a certain period of time are produced with an excess of β spins while the remaining biradicals with α spin persist momentarily as triplets, $^3\text{BR}^\alpha$. The singlet biradicals, enriched in β spins, rapidly collapse to diamagnetic products (**1** and **2**) which will preserve the enrichment of β spins up to the nuclear relaxation lifetime of the products (a time period of seconds, which is many orders of magnitude longer than the lifetime of ^3BR , which is of the order of nanoseconds). If some "escape" process is made available to the remaining triplet biradicals containing the excess of α spins, $T_0\text{-S}$ CIDNP will be observed in a steady-state experiment conducted in a conventional NMR spectrometer. If no "escape" or spin-sorting process is available, the biradicals containing an excess of α spins will eventually intersystem cross to singlets (e.g., by uncorrelated electronic spin-lattice relaxation), and if these singlets combine to produce the same products as the biradicals containing excess β spins, cancellation of nuclear polarization occurs and no steady-state CIDNP is observed.

In a similar manner, at low field, the rate of intersystem crossing of the isotopomer triplet biradical, $^3\text{BR}^{13}$ containing a ^{13}C nucleus at the carbonyl carbon is faster than the rate of intersystem crossing of the isotopomer triplet biradical $^3\text{BR}^{12}$ containing ^{12}C at the carbonyl carbon (Scheme II). The biradicals that undergo faster intersystem crossing contain ^{13}C and therefore will rapidly form products, K_c^{13} , which are, for a certain period of time, be enriched in ^{13}C ; correspondingly, the remaining triplet biradicals are enriched in ^{12}C . If an "escape" process is available to the biradicals enriched in ^{12}C and if this escape process produces products of different structure, P_{sc}^{12} , from those produced by the ^{13}C -induced intersystem crossing, ^{13}C enrichment is observed in the cage products, K_c^{13} , resulting from the more rapid intersystem crossing and ^{13}C impoverishment in the escape products resulting from scavenging, P_{sc}^{12} .

The results demonstrate that in argon-purged acetonitrile solvent, neither CIDNP nor ^{13}C enrichment is observed for any of the products of photolysis or the regenerated starting cyclohexanone. These results are consistent with the absence of an effective escape pathway for the slower intersystem crossing spinomers ($^3\text{BR}^\alpha$) and isotopomers ($^3\text{BR}^{12}$). However, by purging the acetonitrile so-

(16) Bernstein, R. B. *J. Phys. Chem.* **1952**, *56*, 893; *Science* **1957**, *126*, 119.

(17) Electron precession rate $\omega = \beta(h/2\pi)^{-1}(gH_0 + ma)$, where $a = 130$ G, $m = -1/2$ for β nuclear spin and $+1/2$ for α nuclear spin, β (electron Bohr magneton) = 9.274×10^{-21} erg G $^{-1}$, $h = 6.626 \times 10^{-27}$ erg s, $\Delta g = 2.0025 - 2.0008 = 0.0017$, and $H_0 = 58\,300$ G.

lutions with oxygen, or by adding 20 mM quantities of CBrCl_3 , or by running the photolysis in carbon tetrachloride solvent a strong CIDNP signal was observed from **2** and significant ^{13}C enrichment was observed from **3**. The role of oxygen and carbon tetrachloride in developing CIDNP and ^{13}C enrichment is attributed to the introduction of an effective escape pathway for the slower intersystem crossing $^3\text{BR}^\alpha$ spinomers and $^3\text{BR}^{12}$ isotopomers of BR (scavenging of triplet biradicals), which serves to sort nuclear spins of the same isotope and nuclear isotopes of the same element.

We now translate the ideas of Schemes I and II into the experimental results of Figures 1–4. Type I cleavage from the cyclanone molecular triplet produces triplet biradicals, $^3\text{BR}^{\alpha,\beta}$, which possess a Boltzmann distribution of nuclear spins (i.e., only a slight excess of α spins even in a high-field NMR spectrometer). For concreteness we consider an idealized spin situation with only a single ^{13}C spin at the carbonyl carbon. As shown above, according to the theory of high-field CIDNP and from the spectroscopic constants¹⁷ for the radical centers, the β ^{13}C spins will induce a more rapid intersystem crossing than the α ^{13}C spins. As a result, singlet biradicals enriched in β ^{13}C spins will be produced and rapidly collapse to products. From Figure 1–3, excess β nuclear spin shows up in the carbonyl carbon of regenerated, cage products, i.e., in the starting ketone **1** (δ 212 in acetonitrile in the presence of oxygen and δ 209 in carbon tetrachloride) and in the precyclophane **2** (δ 208 in acetonitrile in the presence of oxygen and δ 206 in carbon tetrachloride). Resonances of the cyclophane **3** (δ 205 in acetonitrile and δ 201 in carbon tetrachloride) are not observed in CIDNP. The excess α nuclear spins associated with the carbonyl carbon must appear in products resulting from scavenging. In Figure 1 (where the A and B groups may be any of the terminating groups discussed) a series of resonances at ca. 170–175 ppm and a resonance at 125.7 ppm appear with strong enhanced absorption. The former correspond to the carbonyl carbons associated with scavenging products derived from addition of oxygen molecules to the acyl carbon atom of the biradical. The enhanced absorption bands at ca. 175 ppm appear as triplets and are assigned to a cyclic lactone or carboxylic acid or their decomposition products.

The CIDNP results together with the paradigm for generation of CIDNP and for the magnetic isotope effect predict that photolysis of **1** in CCl_4 or in acetonitrile in the presence of oxygen should result in measurable ^{13}C enrichment. The data in Table I reveal that this prediction is experimentally verified. Photolysis of argon-purged solutions of **1** in acetonitrile results in no measurable ^{13}C enrichment in recovered **1** and a slight ^{13}C enrichment in **3**. However, photolysis of **1** in argon-purged CCl_4 or in oxygen-bubbled acetonitrile result in significant enrichment in recovered **1** and in **3**.

The rate of the scavenging reactions can be estimated from the results and knowledge of the concentration of scavenger and of the rate of intersystem crossing of ^3BR , since the processes are

competitive. The measured rate of intersystem crossing⁵ of ^3BR in a strong field is ca. $2 \times 10^7 \text{ s}^{-1}$. The concentration of saturated solutions of molecular oxygen in acetonitrile¹⁸ is ca. 4 mM. From these data the scavenging rate constant of ^3BR by molecular oxygen (for 50% scavenging) is computed to be ca. $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, a value close to that expected for a diffusion-controlled reaction in acetonitrile. Most interestingly, the absolute rate constant, k_{Cl} , for the chlorine atom abstraction by an acyl radical from CCl_4 , (which although well-known in radical chemistry, to the best of our knowledge has not been reported in the literature) can be estimated from our results. From the concentration of neat CCl_4 (ca. 10 M) and the rate of intersystem crossing of ^3BR ($2 \times 10^7 \text{ s}^{-1}$), the rate constant k_{Cl} is estimated to be ca. $2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Similarly the rate constant k_{Br} is estimated to be ca. $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ by steady-state CIDNP.

The failure of Gd^{3+} and of Tempo to induce CIDNP or to enhance ^{13}C enrichment indicates the limits of potential scavengers to introduce efficient escape pathways. The results with Tempo are of particular interest since this stable free radical can both scavenge ^3BR and also induce electron spin relaxation. Both pathways are also available for molecular oxygen. However, the ratio of reaction to relaxation is evidently much greater for molecular oxygen than it is for Tempo and is the source of the greater effectiveness of the former as a spin scavenger. Indeed, data from the literature show that the rate of reaction of Tempo with radicals is generally an order of magnitude less than the value for the diffusion-controlled reaction.¹⁹

Conclusion

For argon-purged solutions of **1** in acetonitrile, neither CIDNP (at 250 MHz) nor ^{13}C enrichment (in the earth's field) is observed. However, photolysis of oxygen-purged acetonitrile or argon-purged CCl_4 solutions of **1** in a 250-MHz NMR spectrometer produces intense CIDNP, which is brought about by the introduction of scavenging pathways that allow the operation of the T_0 -S mechanism for spin sorting for the biradical ^3BR . The "geminate" or "cage" products **1** (regenerated **1**) and **2** are enriched in β nuclear spins, and the scavenging products are produced enriched in α nuclear spins. The same competition between cage and scavenging processes is successful in separating magnetic ^{13}C isotopes from nonmagnetic ^{12}C isotopes. In this case the "geminate" products **1** (regenerated **1**) and **3** (produced by hydrogen shift of the primary product **2**) are produced enriched in ^{13}C and the scavenging products are impoverished in ^{13}C .

Acknowledgment. We thank the NSF, the AFOSR, and the DOE for their generous support of this research.

(18) Murov, S. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; p 89.

(19) (a) Beckwith, A. L. J.; Bowry, V. W. *J. Org. Chem.* **1988**, *52*, 1632. (b) Chateaufort, J.; Lasztyk, J.; Ingold, K. U. *J. Org. Chem.* **1988**, *52*, 1629.