Suppression of Chemically Induced Dynamic Nuclear Polarization Enhancements by Nuclei with Large Hyperfine Coupling Constants

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The CIDNP enhancement induced in a weakly coupled magnetic nucleus, N_w, can be suppressed in the presence of a strongly coupled nucleus, N_s. This effect was observed at high fields (58.3 kG) for both biradicals and radical pairs, irrespective of whether the two magnetic nuclei belong to the same radical or to different radicals. The observed effects can be rationalized on the basis of the exact radical-pair theory. This is the first report of such phenomena.

Introduction

Since the discovery of nuclear polarization phenomena in the benzoyl peroxide induced polymerization of styrene over 20 years ago,[1] chemically induced dynamic nuclear polarization (CIDNP) has been intensively studied[2] and proved to be a very useful tool for organic mechanistic studies.[3] Most CIDNP results reported in the literature can be described in terms of the radical-pair theory,[4] which explains the polarization as a result of singlet–triplet mixing in radical or radical ion pairs. This theory allows the simulation of CIDNP intensity ratios from reaction and relaxation rates and characteristic parameters of the radical pair, the individual radicals, and the products. A simple sign rule, proposed by Kaptein,[5] is widely used to predict the CIDNP pattern, if these parameters are known or can be assigned. Alternatively, an observed polarization pattern can be used to determine one unknown parameter, if the others are known.

However, we[6a,b] and others[6c,d] have reported that the polarization patterns of nuclei with small hyperfine constants (hfc) will be strongly affected by the presence of nearby nuclei with larger hfcs. These effects were evaluated as a function of experimental variables such as the following: the external magnetic field, H_0; the g-factor difference, Δg, between the radicals; and the ratio, a_1/a_2, of their hfcs. The effect of the external magnetic field on the polarization patterns of systems with two or more magnetic nuclei was studied by carrying out the experiments in two different spectrometers operating at different magnetic fields. The g-factor difference was varied by chemically modifying one of the radicals. However, it proved difficult to vary the hfc in a predictable manner; this factor was evaluated in strictly empirical fashion.

In this publication, we report that the CIDNP enhancement factor induced in a nucleus, N_w, with a weak hfc can be suppressed in the presence of another nucleus, N_s, with a substantially stronger hfc. This effect can be observed irrespective of whether the two magnetic nuclei belong to the same radical or to different radicals. Examples are presented both for a biradical (generated by photocleavage of 2-phenylcyclododecanone) and several radical-pair systems (generated by intermolecular photoreactions of benzaldehyde). The phenomena can be explained by the exact radical-pair theory in terms of the efficiency of spin-sorting processes required for the observation of high-field CIDNP due to T_0–S mixing. To the best of our knowledge, this is the first report concerning such phenomena.

Experimental Section

The CIDNP experiments were performed on a Bruker AF 250-MHz FT NMR spectrometer. The CIDNP probe was equipped with a glass rod with mirrors at both ends, which allows a collimated light beam to be directed into the NMR probe. For the irradiation of 2-phenylcyclododecanone (1), the light of a Hanovia 1000-W high-pressure mercury lamp, filtered through

an aqueous $CoSO_4$ solution, was employed. In the case of benzaldehyde CIDNP, an ILC Technologies 300-W high-pressure xenon lamp fitted with a water filter served as the light source.

The NMR solvents, cyclohexane-d_{12} (99% D, Aldrich), chloroform-d (99% D, Aldrich), and tetrachloromethane (Aldrich, Gold Label) were used without further purification. The ^{13}C-labeled benzaldehyde (90% [13]C=O) was purchased from MSD Isotopes Division.

The cyclic ketone 1 was synthesized according to literature procedures.[7] Doubly ^{13}C labeled ketone, 1-[13]C_2, was synthesized
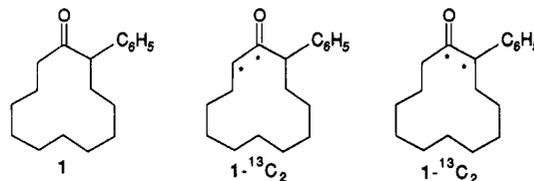
from ^{13}C-labeled cyclododecanone (99% [13]C=O, 49.5% [13]C in each of the α-positions C-2 and C-12).[8] This ketone, in turn, was obtained by intramolecular acyloin condensation of dodecanedioic acid-([13]$COOH)_2$ and subsequent reduction. In the resulting ketone either C-2 *or* C-12 is labeled, but not C-2 *and* C-12.

Results

The photochemistry of 2-phenylcyclododecanone (1) has been studied previously, and the photoproducts are well characterized.[7] Photoexcitation of 1, followed by rapid intersystem crossing (isc) and α-cleavage gives rise to a triplet 1-acyl-12-benzyl biradical, BR. After intersystem crossing the singlet biradical undergoes

(1) Bargon, J.; Fischer, H.; Johnson, U. *Z. Naturforsch., A* **1967**, *22*, 1551.
(2) (a) *Chemically Induced Magnetic Polarization*; Muus, L. T., Atkins, P. W., McLauchlan, K. A., Pederson, J. B., Eds.; Reidel: Dordrecht, 1977. (b) Kaptein, R. *Adv. Free Radical Chem.* **1975**, *5*, 319–380. (c) Buchachenko, A. L. *Chemical Polarization of Electrons and Nuclei*; Nauka: Moscow, 1974. (d) Lepley, A. R.; Closs, G. L. *Chemically Induced Magnetic Polarization*; Wiley: New York, 1973. (e) Lawler, R. G. *Prog. Nucl. Magn. Reson.* **1973**, *9*, 145–211.
(3) (a) Roth, H. D. *Acc. Chem. Res.* **1987**, *20*, 343–350. (b) Roth, H. D. *Mol. Photochem.* **1972**, *5*, 91–126. (c) Roth, H. D. In *Chemically Induced Magnetic Polarization*; Muus, L. T., Atkins, P. W., McLauchlan, K. A.; Pederson, J. B., Eds.; Reidel: Dordrecht, 1977; pp 39–119.
(4) (a) Closs, G. L.; Trifunac, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 2183. (b) Kaptein, R.; Oosterhoff, J. L. *Chem. Phys. Lett.* **1969**, *4*, 195, 214.
(5) Kaptein, R. *J. Chem. Soc., Chem. Commun.* **1971**, 732–733.
(6) (a) Roth, H. D.; Hutton, R. S.; Hwang, K. C.; Turro, N. J.; Welsh, K. M. *J. Phys. Chem.* **1989**, *93*, 5697–5701. (b) Hutton, R. S.; Roth, H. D.; Bertz, S. H. *J. Am. Chem. Soc.* **1983**, *105*, 6371–6377. (c) Salikhov, K. M. *Chem. Phys.* **1981**, *64*, 371–379. (d) Hore, P. J.; Stob, S.; Kemmink, J.; Kaptein, R. *Chem. Phys. Lett.* **1983**, *98*, 409.
(7) Lei, X.; Doubleday, C., Jr.; Turro, N. J. *Tetrahedron Lett.* **1986**, *27*, 4671–4675.
(8) Rao, V. P.; Wang, J. F.; Turro, N. J.; Doubleday, C., Jr. *J. Labelled Compd. Radiopharm.* **1989**, *28*, 193–201.

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recombination, either regenerating the starting material **1** or a ring-extended para product, **2**, as major products. The alkylidenecyclohexadiene moiety of the latter undergoes a H shift to form **3**. This reaction does not give rise to steady-state CIDNP:
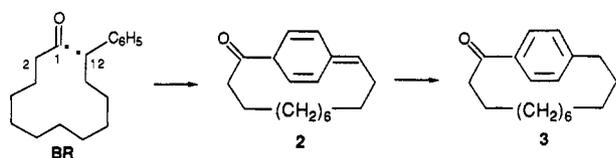
effects due to T_0–S mixing cannot be observed due to a lack of a spin-sorting process and effects due to T_-–S mixing are negligible at the high field (58.3 kG) of the spectrometer employed. Such effects fall off rapidly with increasing magnetic field beyond the optimum field for a 1,12-biradical (<0.1 kG).[9]

However, in the presence of radical scavengers, such as O_2 or CCl_4, dramatic nuclear polarization effects are observed.[10] The effect of molecular oxygen can be rationalized via the selective reaction of those biradicals, which have longer lifetimes because of retarded intersystem crossing. When CCl_4 is used as solvent, a chemical scavenging reaction introduces a spin-sorting process. Here, the acyl radical center of the biradical abstracts a chlorine atom from the solvent to form radical pair (A), consisting of a trichloromethyl and an extended benzyl radical; subsequent coupling leads to product **4**. The structure of **4** is assigned on
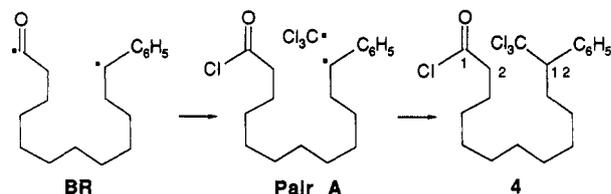
the basis of the ^{13}C NMR spectrum of the reaction mixture obtained from **1**-$^{13}C_2$. An apparent triplet at 172.3 ppm is explained as a doublet plus a singlet, representing ^{13}C=O groups (C-1) next to $^{13}CH_2$ and $^{12}CH_2$, respectively. A doublet at 47.5 ppm is identified as C-2 because of the coupling constant it shares with C-1 ($^1J_{C,C=O}$ = 53 Hz). This assignment is further supported by the observation that the peak at 172.3 ppm remained unchanged as a singlet for the product obtained when **1** was photolyzed in $^{13}CCl_4$ (99% ^{13}C).

The ^1H CIDNP spectrum observed upon photolysis of **1** in CCl_4 shows the benzylic methine signal (3.0 ppm) of **4** in weakly enhanced absorption as a triplet due to coupling with the protons at C-11. When **1** was photolyzed in $^{13}CCl_4$ (99% ^{13}C), the ^1H NMR spectrum of products shows two triplets at 3.0 ppm with a separation of 3.8 Hz, characteristic for a $^2J_{CH}$ coupling. This observation further supports the structure of **4**.

All CIDNP effects observed in this reaction can be ascribed to T_0–S mixing in the 1,12-biradical, BR. The effective-spin-sorting mechanism is based on the competition between the electron-spin-dependent recombination reaction and the electron-spin-independent scavenging reaction. No CIDNP effects originating in pair A were observed. As illustrated in Figure 1, pronounced differences are observed between the ^{13}C-labeled samples and those with ^{13}C at natural abundance. The unlabeled sample (45 mM solution; Figure 1, bottom) gives rise to two emission signals, representing the carbonyl carbons of the starting material (**1**; 210 ppm) and the ring-extended ketone (**2**; 206 ppm), and two absorption signals, representing C-1 and C-2 of the scavenging product **4**. During the photolysis of the ^{13}C-labeled sample (5 mM solution; Figure 1, top) the three carbonyl signals remain, with characteristic changes caused by the interaction of adjacent ^{13}C nuclei. In dramatic contrast, the α-carbon of this

(9) Zimmt, M. B.; Doubleday, C., Jr.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 6726–6727.

(10) (a) Turro, N. J.; Hwang, K. C.; Rao, V. P.; Doubleday, C., Jr., to be published. (b) Hwang, K. C.; Lei, X. G.; Turro, N. J.; Doubleday, C., Jr.; to be published.
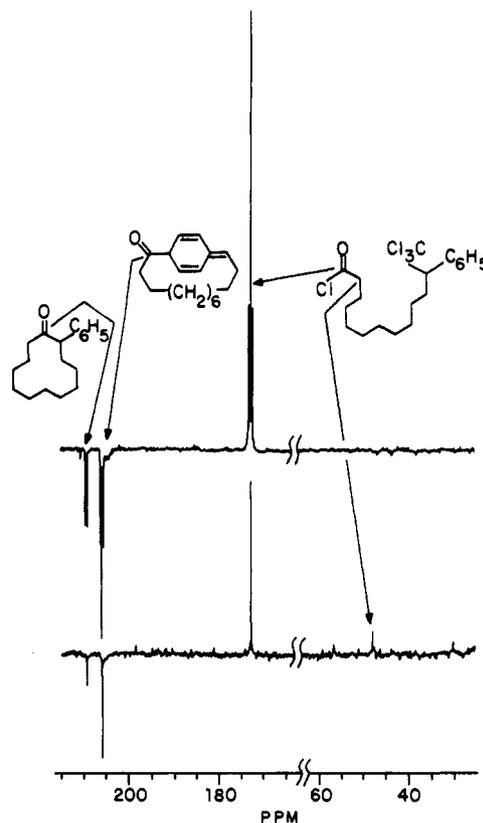
Figure 1. The 62.9-MHz CIDNP spectra observed during UV irradiation of 2-phenylcyclododecanone (**1**) in CCl_4; benzene-d_6 in a capillary tube was used to lock the NMR frequency. Top: 5mM doubly ^{13}C labeled **1** with the following acquisition parameters: rf pulse angle 90°, delay time 0.5 s, and 48 scans. Bottom: 45 mM **1**, at natural abundance with rf pulse angle 90°, delay time 0.5 s, and 760 scans. Only the solvent peak can be observed in the dark spectra recorded before or after irradiation in either the labeled or natural abundance samples.

SCHEME I
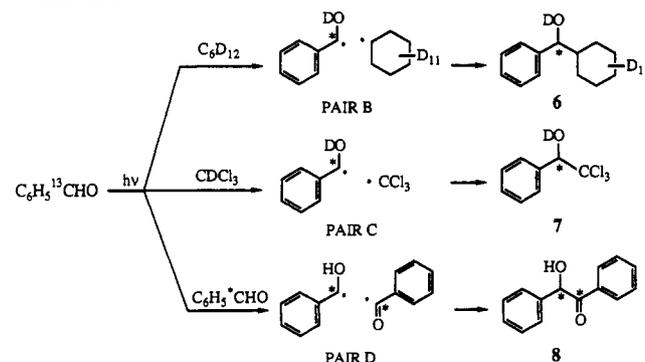
product showed no detectable polarization.

When **1**-$^{13}C_2$ is photolyzed instead of **1**, the signal of the starting material appears as a doublet due to the coupling to one or the other of its two α-carbons (C-2 and C-12; $^1J_{1,2} \cong {}^1J_{1,12}$). The emission of the ring-extended product is replaced by a doublet flanking a singlet; these are assigned to product molecules in which the second ^{13}C label lies across the six-membered ring (negligible coupling) or in the α-position ($^1J_{C,C=O}$ = 41 Hz). A similar three-line feature was observed for the carbonyl signal of the scavenging product **4**. The polarization intensity ratio of the carbonyl signals of products **1**, **2**, and **4** is the same, approximately 1:3:5, for labeled and unlabeled samples. Since the polarization intensity of the scavenging product (**4**) outweighs the sum of the intramolecular products (**1** and **2**), **4** must have a slightly longer spin–lattice relaxation time (T_1) than **1** and **2**. However, the CIDNP enhancement of the 2-carbon of **1**-$^{13}C_2$ must be suppressed by a factor of at least 10 (Figure 1, top vs bottom, 47.5 ppm). A decrease of this magnitude can hardly be caused by a subtle

(A)

(B)

(C)

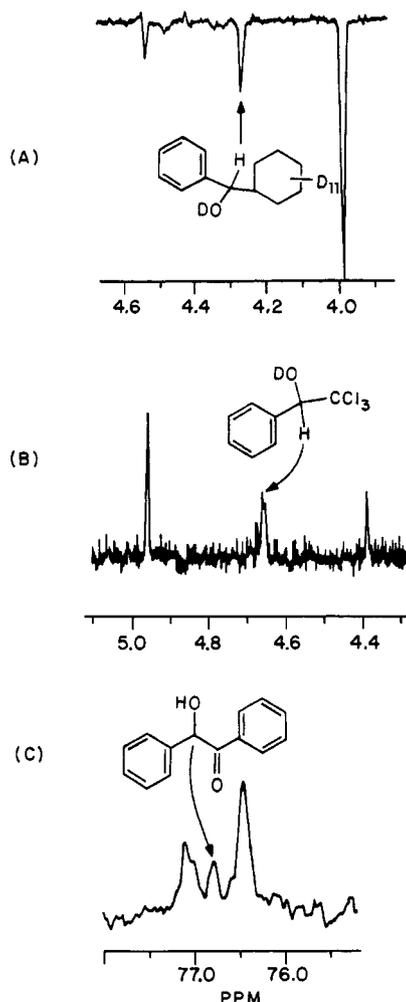**Figure 2.** CIDNP spectra of (A) the benzylic proton of phenylcyclohexylmethanol generated from the photolysis of benzaldehyde (90% ^{13}C=O) in cyclohexane-d_{12} (250 MHz), (B) the benzylic proton of 1-phenyl-2,2,2-trichloroethanol generated from photolysis of benzaldehyde (90% ^{13}C=O) in chloroform-d (250 MHz), and (C) the hydroxybenzyl carbon of benzoin generated from the photolysis of benzaldehyde (90% ^{13}C=O) in cyclohexane-d_{12} (62.9 MHz). In each spectrum, the doublets (higher and lower field peaks) are due to coupling to a ^{13}C nucleus in the benzyl (spectra A, and B) or the benzoyl moiety (spectrum C), respectively.

change in the relaxation time; clearly, the expected CIDNP effect for the α-carbon must be suppressed as a result of a hitherto unappreciated effect.

Additional instances in which the CIDNP enhancement of a nucleus with small hfc is suppressed in the presence of a nearby nucleus with a larger hfc were observed in several radical-pair reactions, during irradiation of benzaldehyde (90% ^{13}C=O) in cyclohexane-d_{12} and chloroform-d.[6a,b] Photoexcited benzaldehyde can abstract a deuterium from either solvent or a hydrogen from ground-state benzaldehyde to form radical pairs (pairs B, C, and D; Scheme I; * = ^{13}C), initially of triplet multiplicity. Intersystem crossing followed by recombination of the respective radical pairs results in the formation of products **6–8**.

The ^{1}H or ^{13}C CIDNP effects induced in the photoreactions of ^{13}C-labeled benzaldehyde (90% ^{13}C=O) are shown in Figure 2A, B, and C, respectively, with assignments as shown. The central peaks in spectra A and B represent the benzylic H of products **6** and **7**, respectively, with ^{12}C in the benzylic position (10%); the doublets comprised of the higher and lower field peaks are due to the coupling, $^1J_{CH}$, between the benzylic H and ^{13}C nuclei. The ratio of polarization intensities for **6** and **7** with ^{13}C in the benzylic position (the doublet) to those of **6** and **7** with ^{12}C at the benzylic carbon (the central peak) is expected to be 9:1, as confirmed by measurement of the dark spectrum, since the starting benzaldehyde is 90% ^{13}C=O labeled. However, the observed polarization in-
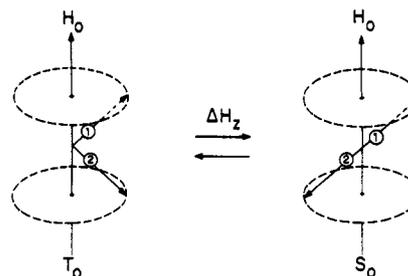

Figure 3. Spin vector model for a singlet (S) and triplet (T_0) radical pair or biradical.

tensity ratio is 5:1 for **6** and 3.3:1 for **7**.

The central peak in Figure 2C is due to the benzylic carbon (^{13}C–OH) of benzoin adjacent to ^{12}C=O, whereas the doublet is due to ^{13}C–OH adjacent to ^{13}C=O. Again, the ratio of the doublet to singlet polarization intensities is expected to be 9:1 because of the ratio of ^{13}C=O to ^{12}C=O in the benzaldehyde sample used, but the observed ratio falls short of that value, 5.6:1. These examples again show clearly that the CIDNP enhancement of nuclei with small hfc an be suppressed in the presence of a nearby nucleus with a larger hfc. In the example shown in Figure 2C the two magnetic nuclei are coupled to the electron spins of different radicals, whereas in the other examples (Figures 1 and 2A,B) the two magnetic nuclei are coupled to the same electron spin.

In summary, we have observed three different cases in which the polarization of weakly coupled nuclei is suppressed upon the introduction of more strongly coupled nuclei: a biradical with one or two ^{13}C nuclei (Figure 1); radical pairs in which a ^{1}H nucleus is attached to either a ^{13}C or a ^{12}C nucleus (Figure 2A,B); and a radical pair in which a ^{13}C-labeled radical interacts with a second radical with either ^{12}C or ^{13}C in a position of high electron spin density (Figure 2C).

Discussion

The selective suppression of CIDNP enhancements can be understood as a consequence of the various processes and reactions occurring in a radical pair or biradical in competition with one another. For the primary biradical, BR, discussed here we consider the following: (a) its intersystem crossing (k_{isc}) and chain dynamics; (b) its recombination to regenerate the starting ketone, **1**, or the primary ring-extended ketone, **2**; and (c) its reaction with the scavenger to form pair A. Previous studies have shown that the decarbonylation of BR to generate a 1,11-biradical is not competitive and that the chain dynamics are faster than isc, at least at room temperature and in nonviscous media. Among these reactions, the formation of **1** and **2** are electron spin dependent: only singlet pairs can couple to form the ground-state products. The chlorine abstraction and decarbonylation reactions, on the other hand, are electron spin independent. Accordingly, the spin-sorting mechanism in this system is based on the rates of coupling ($\rightarrow$**1**, **2**; $k_{1,2}$) on the one hand and chlorine abstraction ($\rightarrow$pair A; k_{sc}), on the other, relative to the rate of intersystem crossing (k_{isc}).

In the high-field radical-pair mechanism of CIDNP, the intersystem-crossing rate of a biradical or radical pair (T_0–S mixing) is nuclear spin dependent; it is determined by the difference in the precession frequencies between the two electron spins around the external magnetic field axis. The configuration of the two electron spin vectors for the T_0 triplet sublevel and the singlet state are shown in Figure 3; their precession frequencies around the external magnetic field axis can be expressed by eq 1. Their

$$\omega_{s1} = \beta h^{-1}[g_1 H_0 + \Sigma a_1 m_1]$$
$$\omega_{s2} = \beta h^{-1}[g_2 H_0 + \Sigma a_2 m_2]$$
(1)

$$\Delta\omega = (\omega_{s1} - \omega_{s2}) = \beta h^{-1}[(g_1 - g_2)H_0 + (\Sigma a_1 m_1 - \Sigma a_2 m_2)]$$
(2)

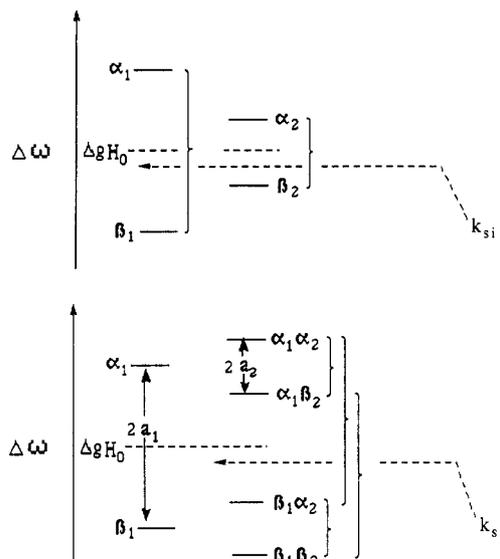frequency difference is determined by the electron g factor dif-

Figure 4. Top: schematic representation of the effect of a magnetic nucleus, either N_1 or N_2, on the electron precession frequencies of a radical pair (A); an electron-spin-independent reaction (k_{si}) in an appropriate frequency range, $\Delta\omega_{\alpha_n}$ to $\Delta\omega_{\beta_n}$, will allow efficient spin sorting of both N_1 and N_2. Bottom: if both nuclei, N_1 and N_2, interact simultaneously with the electron spin, the spin-independent reaction cannot efficiently sort both types of nuclei.

ference (Δg), the external magnetic field strength (H_0), and the hyperfine coupling constants of nearby magnetic nuclei, as expressed by eq 2. In the absence of magnetic nuclei, the inter-system–crossing rate is determined solely by the $\Delta g H_0$ term.

At natural abundance, only 1.1% of all carbons are labeled with ^{13}C; the probability of having two ^{13}C nuclei in adjacent positions is negligible. Therefore, in any of the biradicals derived from **1** only one ^{13}C nucleus, either in the carbonyl or in the 2-position, affects the precession frequency of the electron spin. The effect on the intersystem-crossing rate ($\Delta\omega$) is represented schematically in Figure 4, top. The contributions of α and β spins to $\Delta\omega$ are appreciably different, allowing appreciably different intersystem-crossing rates (k_α vs k_β) for large or small hyperfine constants. This may lead to spin sorting for either nucleus, if one key reaction rate falls into the appropriate "kinetic window" between the intersystem-crossing rates, k_α and k_β. For the biradical BR, generated from a triplet precursor, effective spin sorting is possible, if the scavening rate falls between k_α and k_β, i.e., if $k_{1,2} \gg k_\alpha > k_{sc} \geq k_\beta$. Accordingly, α_1 or α_2 spins can be separated readily from β_1 or β_2 spins, resulting in appreciable accumulation of α spins (accelerated isc) in the combination products and of β spins (retarded isc) in the escape products.

In the doubly ^{13}C labeled biradicals, BR-$^{13}C_2$, two (^{13}C) magnetic nuclei, one in the carbonyl function and the other at either C-2 or C-12, simultaneously operate on the electron spins of the radical centers. The hfc of the carbonyl carbon is ~ 125 G,[11] whereas the α-carbon (C-2; ~ 50 G) and the benzylic carbon (C-12; ~ 25 G) are less strongly coupled. The effect of two nuclear spins on the intersystem-crossing rate of the biradical is represented schematically in Figure 4, bottom.

Two magnetic nuclei will cause four different incremental contributions to the intrinsic rate, $k_0 = \beta h^{-1}(\Delta g H_0)$. For example, if $k_0 \gg \Sigma a$ and $a_1, a_2 > 0$, the relative rates of isc will be in the order $k_{\alpha_1\alpha_2} > k_{\alpha_1\beta_2} > k_0 > k_{\beta_1\alpha_2} > k_{\beta_1\beta_2}$. This rate differentiation leaves the kinetic window for the sorting of N_s in the same general range but splits the window for the sorting of N_w into two separate ranges, requiring faster or slower scavenging rates for an appreciable spin sorting. The effect on the CIDNP enhancements of the two nuclei, N_s and N_w, depends on the magnitude of k_{sc} relative to the intrinsic intersystem-crossing rate, k_0. If $k_{sc} \approx k_0$, the polarization of N_s will not be substantially affected, whereas the polarization of N_w will be essentially eliminated.

The combination products will be enriched in α_1 spins (N_s enhanced absorption) and the escape products will be enriched

in β_1 spins (N_s emission). However, for the weakly coupled nucleus, N_w both combination and escape products contain α_2 as well as β_2 spins, resulting in an inhibition of CIDNP effects. In essence, the CIDNP enhancement of a nucleus with smaller hfc can be suppressed because of the interaction with a nucleus with larger hfc.

The predictions based on these simple qualitative arguments are born out by quantitative considerations. In the case of the 1-acyl-12-benzyl biradical, BR, the intrinsic rate k_0 has been assigned a value, $k_0 \sim 10^7$ s^{-1}, based on the following considerations. The acyl and benzyl radical centers are assigned electron g factors of 2.0008 and 2.0025, respectively, in analogy to appropriate mono radicals.[11] In the absence of magnetic nuclei, $\Delta\omega \sim |\Delta g| H_0$; at 58.3 kG $\Delta\omega \sim 99$ G ($|2.0008 - 2.0025| \times 58,300$). For the 1-acyl-12-benzyl biradical system discussed here, the rate of intersystem crossing has been measured by laser spectroscopy[12] (k_{isc} 1.5 $\times$ 10^7 s^{-1} at "zero" field). Since an external magnetic field had a moderate effect on this rate, it was concluded that the contribution of ^1H hyperfine coupling to k_{isc} was moderate; hence, $k_0 \sim 10^7$ s^{-1}.[12] In the presence of a ^{13}C in the carbonyl position ($a_{C=O} \sim 125$ G), the isc rate can be either $2.26k_0$ ($|99 + 125|/99$) or $0.26k_0$ ($|99 - 125|/99$). With a ^{13}C at C-2 ($a_{2-C} \sim 50$ G), the isc rate can be either $1.50k_0$ ($|99 + 50|/99$) or $0.50k_0$ ($|99 - 50|/99$). Given a scavenging rate near k_0, a spin-sorting process can effeciently separate the α and β spins of a magnetic nucleus at either C-1 or C-2.

When two ^{13}C nuclei (C-1 and C-2) are coupled to the same electron spin (Figure 4, bottom), the biradicals can have four different isc rates: $2.77k_0$ ($|99 + 125 + 50|/99$), $1.76k_0$ ($|99 + 125 - 50|/99$), $0.24k_0$ ($|99 - 125 + 50|/99$), and $0.77k_0$ ($|99 - 125 - 50|/99$). The efficiencies of separation of α and β spins in each set of doubles are different, depending on the kinetic window (the ratio of isc rates of different sets of spins) available for the spin-sorting process. The given process can separate the α and β spins of the $^{13}C=O$ efficiently, since its α spins are sorted into the singlet biradical with rates of $0.24k_0$ and $0.77k_0$, sufficiently slower than its β spins, $2.77k_0$ and $1.76k_0$. In contrast, the α and β spins of the ^{13}C at C-2 are sorted into the singlet biradical with rates of $1.76k_0$ and $0.77k_0$, and $2.77k_0$ and 0.24 k_0, respectively, and thus cannot be separated efficiently by the given spin-sorting process.

When two magnetic nuclei are coupled independently to the two different electron spins of a radical pair, the overall effect on the intersystem crossing of the pair is the same as for the case where the two nuclei are coupled to the same radical center. The α and β spins of the more strongly coupled nucleus can be separated with relative efficiency, whereas the corresponding separation of α and β spins will become less efficient for the nucleus with smaller hfc.

The experimentally observed signal intensities (Figures 1 and 2) provide for an interesting comparison of CIDNP enhancements induced in radical pairs differing solely in the presence or absence of a single ^{13}C nucleus. This comparison should eliminate any distortions arising from differences in the nuclear spin–lattice relaxation times of the two products. According to the radical-pair theory[2] the intensities of CIDNP signals are determined by the differences in the corresponding electron precession frequencies (eq 3).

$$I_{N_n} = \pm [\omega_{N_+}{}^{1/2} - \omega_{N_-}{}^{1/2}] \qquad (3)$$

The calculated intensity ratios and the experimentally observed ones are compared in Table I. The comparison reveals satisfactory agreement, with the notable exception of the intensity ratio observed for product **7**. This product logically arises from pair C, and the latter might be formed via deuterium abstraction by photoexcited benzaldehyde from chloroform-d. However, the

(11) (a) Paul, H.; Fischer, H. *Helv. Chim. Acta* **1973**, *56*, 1575–1594. (b) Carrington, A.; Smith, I. C. P. *Mol. Phys.* **1965**, *9*, 138. (c) Cf. Turro, N. J. *Pure Appl. Chem.* **1981**, *53*, 259.
(12) Zimmt, M. B.; Doubleday, C., Jr.; Gould, I. R.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 6724–6726.
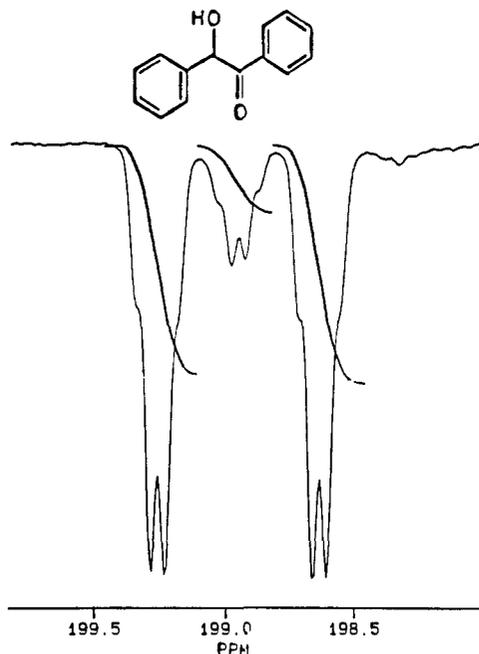
Figure 5. ^{13}C CIDNP spectra (62.9 MHz) of the carbonyl signal of benzoin generated by photolysis of benzaldehyde (90% ^{13}C=O) in cyclohexane-d_{12}. The quartets at higher and lower fields are due to ^{13}C nuclei adjacent to a $^{13}CHOH$ group.

TABLE I

pro-duct	observed nucleus		interacting nucleus		$\Delta g H_0$, G at 58.3 kG	CIDNP ratio	
	identity	hfc, G	identity	hfc, G		obsd	calcd
6	^1H	−16.3	$^{13}C(OH)$	23	29.2	5.1	5.5
7	^1H	−16.3	$^{13}C(OH)$	23	−350	3.3	9.0
8	$^{13}C(OH)$	23	^{13}C(=O)	130	134	5.6	5.8
4	^{13}C(=O)	130	^{13}C(benzyl)	23			
			$^{13}C(H_2)$	50	105	1.5	
	$^{13}C(H_2)$	50	^{13}C(=O)	130	105	<0.1	~0.5

rather large Δg term for pair C does not provide any differentiation between the ^{12}C=O and ^{13}C=O products, certainly not of the magnitude suggested by the experiment (Figure 2). The relatively poor signal-to-noise ratio in this experiment does not entirely explain the observed differences. Therefore, an alternative mechanism is contemplated, in which pair C is formed, at least in part, by pair substitution.[13] If pair C is formed, in part, by

reaction of pair D with the solvent chloroform, some of the enhancement differences inherent in pair D may be transferred to pair C.
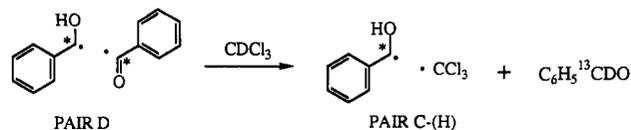
The dramatic CIDNP suppression observed for the scavenging product of doubly labeled BR occurs, because the rate constants, k_{sc} and k_0, apparently are closely matched in this system. In cases where the match of k_{sc} and k_0 is less close or outright poor, the resulting suppression of N_w polarization will be less pronounced, as illustrated by the various effects in Figure 2. In fact, the possibility exists that the polarization of the more strongly coupled nucleus is reduced due to interaction with the more weakly coupled nucleus. This type of effect is observed for the (^1H nondecoupled) ^{13}C=O signals of benzoin formed by irradiation of benzaldehyde-^{13}C=O (Figure 5).

Each of the signals appears as a quartet, due to coupling to one ^1H nucleus on the α-carbon ($^2J_{C,H}$) and two ^1H nuclei in the ortho positions ($^3J_{C,H}$). The observed pattern suggests that the corresponding coupling constants are nearly identical. The central quartet is due to ^{13}C=O adjacent to a ^{12}C nucleus, whereas the outer quartets represent ^{13}C=O groups next to a $^{13}CHOH$ moiety. The intensity ratio of outer to central signals was 6.8:1, whereas the relative abundance of the reactant ^{13}C=O benzaldehyde was 8.8:1, clearly showing a reduction of ^{13}C=O enhancement for nuclei next to a $^{13}CHOH$ group.

Conclusion

Regardless of whether the two magnetic nuclei belong to the same radical or to different radicals, the CIDNP enhancement of a nucleus with small hfc constant can be suppressed if another nucleus with a larger hfc is present. Such effects have been illustrated for both biradical and radical-pair systems at high fields, where the radical-pair mechanism (T_0–S mixing) is operative. The phenomena can be explained by the exact radical-pair theory in terms of the competition between the intersystem-crossing rate and the spin-sorting process.

(13) Cooper, R. A.; Lawler, R. G.; Ward, H. R. *J. Am. Chem. Soc.* **1972**, *94*, 552–556.