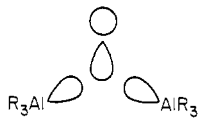
the R–Al···H angle optimizes to nearly the same value for both R = H and R = CH_3.

We have calculated the energy required to produce small deformations from linearity around the Al···H···Al bond by using our best structure and inducing angles of 5° and 10°, without performing any further geometry optimization. The energy required for these excursions was 0.04 and 0.14 kcal/mol, respectively.

For purposes of comparison, we have studied the $[H_3AlCl\text{-}AlH_3]^-$ analogue of the $[Cl_3AlClAlCl_3]^-$ ion, which is known to have a nonlinear Al–Cl–Al bond. We have performed the 3-21G optimization of the structure of $[H_3AlClAlH_3]^-$. The results are shown in Table II along with experimental data obtained for $[Cl_3AlClAlCl_3]^-$ ion. We ascribe the nonlinearity of the central three-center bond to an increased stabilization that occurs for a molecular orbital of a_1 symmetry (C_{2v}) upon bending (see **3**).



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The orbital energy of the MO shown in **3** is found to decrease as the bend increases (a change of −0.6 kcal/mol occurs in going from a 180° to a 140° angle). Gimarc[6] and, earlier, Walsh[7] have studied such deformations. Clearly, the participation of the occupied p orbitals is important in producing a nonlinear structure.

Acknowledgment. We wish to acknowledge Professor Atwood for kindly providing us with a copy of his paper prior to publication.

Registry No. $H_3AlHAlH_3^-$, 65856-39-5; $(CH_3)_3AlHAl(CH_3)_3^-$, 81523-03-7.

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(6) Gimarc, B. M. *Acc. Chem. Res.*, **1974**, *7*, 384.

(7) Walsh, A. D., *J. Chem. Soc.* **1953**, 2260, and papers immediately following.

CIDNP and Triplet-State Reactivity of Biradicals

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Abstract: From an analysis of magnetic-field-dependent (mfd) CIDNP effects obtained during cycloalkanone photolysis, it is concluded that the self-reactions of the intermediate biradicals occur not only from the singlet state but also from the triplet state. Triplet-state reactivity is presumably mediated by spin–orbit coupling, allowing transitions to occur directly from the triplet-biradical manifold to singlet product states. As the product selectivity of the triplet-state reactions in general will be different from that of the singlet reactions, this provides a new spin-sorting pathway, allowing T_0–S type CIDNP effects to be generated in biradical products. These effects have indeed been observed for 1,4, 1,5, and 1,6 biradicals. A previously developed theory for biradical CIDNP based on the stochastic Liouville equation is extended to include product formation from triplet-state biradicals. The theory can satisfactorily account for ^1H mfd CIDNP curves obtained for cyclohexanone (**1**) and bicyclo[3.2.1]octan-2-one (**2**). Furthermore, simulations of ^{13}C mfd curves recently obtained by Doubleday for 2-phenylcycloalkanones yielded both triplet- and singlet-state-reactivity parameters for the intermediate acyl–alkyl biradicals. It can be concluded that the direct reaction from the triplet state for these biradicals leads predominantly to ketene product; cyclization to the parent ketone is also relatively favorable whereas formation of alkenal is negligible. These reactivities are quite different from those of singlet-state biradicals. The effects of spin–orbit coupling in acyl–alkyl biradicals are qualitatively discussed, and an attempt is made to rationalize the observed trends by considering biradical conformations in which this interaction is maximized.

Introduction

Biradicals constitute an important class of reaction intermediates, but because of their short lifetimes, remain an elusive species. Only recently has a true biradical intermediate (the one that occurs in the Norrish type II photoreaction of valerophenone) been directly observed in a flash photolysis experiment.[2] A somewhat less direct but often more simple way of detecting biradicals is provided by the chemically induced dynamic nuclear polarization (CIDNP) method. Here, the nuclear-spin polarization patterns observed in reaction products and the magnetic-field dependence thereof give information on the intermediacy of biradicals and on their dynamic behavior and magnetic parameters (hyperfine couplings, exchange interaction, etc.).[3–6]

Most high-field CIDNP spectra of biradicals generated from triplet-state precursors show exclusively emission effects[3–6] as opposed to the mixtures of emission and enhanced absorption that are characteristic for radical-pair CIDNP.[7] The fact that nuclear-spin polarization is observed in a biradical product indicates that electron–nuclear hyperfine coupling contributes significantly to the intersystem crossing in the biradical. The emission effect is easily explained by noting that in the presence of an exchange interaction between the "unpaired" electrons, hyperfine induced triplet–singlet (T → S) transitions from *one* of the three triplet states (the T_- state) favored. Provided the biradical has a singlet ground state, this leads to overpopulation of the higher nuclear-spin levels in the products. This effect was first reported by Closs[8] and has subsequently been observed for many biradicals with relatively long flexible chains.[3–6] We have recently developed a quantitative theory based on the stochastic Liouville equation to account for this effect and its magnetic-field dependence.[5] In the early seventies, however, anomalies had already been observed in several laboratories, especially for the short-chain biradicals.[9]

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(1) Department of Physical Chemistry, Free Univeristy, DeBoelelaan, Amsterdam, The Netherlands.

(2) R. D. Small and J. C. Scaiano, *Chem. Phys. Lett.*, **50**, 431 (1977).

(3) (a) G. L. Closs and C. E. Doubleday, *J. Am. Chem. Soc.*, **94**, 9248 (1972); (b) *ibid.*, **95**, 2735 (1973); (c) C. E. Doubleday, *Chem. Phys. Lett.*, **64**, 67 (1979); (d) *ibid.*, **77**, 131 (1981); (e) *ibid.*, **79**, 375 (1981).

(4) R. Kaptein, R. Freeman, and H. D. W. Hill, *Chem. Phys. Lett.*, **26**, 104 (1974).

(5) F. J. J. de Kanter, J. A. den Hollander, A. H. Huizer, and R. Kaptein, *Mol. Phys.*, **34**, 857 (1977).

(6) G. L. Closs, in "Chemically Induced Magnetic Polarization", L. T. Muus, P. W. Atkins, K. A. McLauchlan, and J. B. Pedersen, Eds., D. Reidel, Dordrecht, 1979, p 225.

(7) For reviews, see (a) G. L. Closs, *Adv. Magn. Reson.*, **7**, 157 (1974); (b) R. Kaptein, *Adv. Free-Radical Chem.*, **5**, 319 (1975); (c) L. T. Muus, P. W. Atkins, K. A. McLauchlan, and J. B. Pedersen, Ed., "Chemically Induced Magnetic Polarization", D. Reidel, Dordrecht, 1977.

(8) G. L. Closs, *J. Am. Chem. Soc.*, **93**, 1546 (1971).

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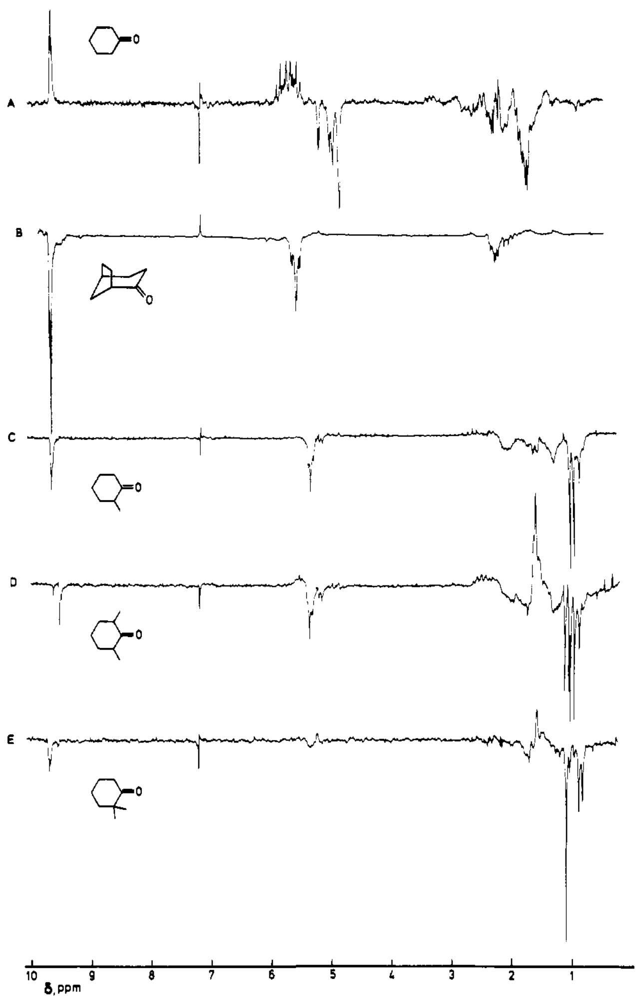
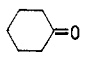


Figure 1. Light *minus* dark 100-MHz ^1H photo-CIDNP difference spectra of the ketones **1**, **2**, **5a**, **5b**, and **5c**, 0.1 M solutions in $CDCl_3$. The spectra were obtained with a 30° flip angle rf pulse; for other experimental details see the Experimental Section.

For instance, products from biradicals with five and six C atoms showed absorption effects that remained ill understood for many years. The basic problem was that while these observations seemed to follow a T_0–S-type polarization mechanism, it was not clear, first, how $T_0 \rightarrow S$ transitions could compete with $T_- \rightarrow S$ transitions in a situation of relatively strong exchange and, second, what the "escape route" competing with the self-reaction would be. Such a pathway competing with geminate-pair recombination is always required in the spin-sorting $T_0 \rightarrow S$ mechanism. In radical-pair CIDNP, this escape route is usually provided by diffusion from the cage or by spin-independent reaction (e.g., radical scavenging).[10]

It is the purpose of this paper to show that with an appropriate extension of the stochastic biradical theory,[5] many of these observations can be explained. In particular, we shall address ourselves to the following hitherto puzzling phenomena:

(1) UV irradiation of cyclohexanone **1** in the NMR probe gives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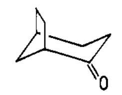
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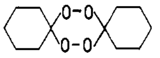
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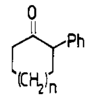
rise to $T_0 \rightarrow S$ type polarization for the alkenal product (e.g., enhanced absorption for the aldehyde proton).[6,9] This has also been observed[9] for a variety of methyl-substituted cyclohexanones and cyclopentanones (cf. also Figure 1). In contrast, the bridged cyclohexanone **2** follows the $T_- \rightarrow S$ mechanism (emission only).[6]

(2) The field dependence of the CIDNP effect for ketones **1** and **2** shows contrasting behavior in the high-field region, whereas at low field emission it is observed for the aldehyde proton in both cases (see below).[14]

(3) In the thermal decomposition of cyclohexanone diperoxide (**3**), decene, a product of the decamethylene biradical, shows $S \rightarrow T_0$ multiplet effects.[15] In the early development of the theory, this observation served to support the radical-pair character of the CIDNP mechanism.[16] The problem here, however, is that the reaction of the biradical with the inert solvent used (*m*-dibromobenzene) is probably too slow by several orders of magnitude to compete with the self-reactions of the singlet biradical, so this reaction is not likely to serve as an escape route as was previously supposed.[15]

(4) Recently, Doubleday[3c] reported a series of field-dependent ^{13}C CIDNP measurements for α-phenyl-substituted cyclic alkanones **4**. He observed a different behavior of the polarization


4a n = 1
4b n = 2
4c n = 3

effects for the aldehyde and ketone vs. ketene products in very high magnetic fields.

(5) We have recently reported the first observation of CIDNP from a 1,4 biradical occurring in the Norrish type II photoreactions of valerophenone.[17] Here, $T_0 \rightarrow S$ polarization was observed in products of the 1,4 biradical, i.e., in valerophenone itself, in the elimination-product propene, and in the *cis*- and *trans*-cyclobutanols from biradical cyclization.

To account for these observations, we shall explore a recent remark by Closs,[6] who, in an attempt to rationalize the cyclohexanone results, suggested that an explanation may be based on *spin–orbit coupling accompanied with product selectivity* providing an alternative pathway for intersystem crossing in biradicals.[18] In this view, transitions are possible from the triplet to the singlet manifold of the biradical, which, because of the presumed selectivity, must *directly* lead to a reaction product. This amounts to a certain reactivity of the *triplet-state* biradical. We have incorporated this triplet reactivity in the stochastic biradical theory, and we shall show that with this extension, the experimental results

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[9] These effects were observed in the laboratories of H. Fischer, G. L. Closs, and A. M. Trozzolo (personal communications to R.K.) and by the authors in 1970 at the University of Leiden.

[10] The terminology "recombination" and "escape" polarization, although commonly used in the CIDNP literature, lacks generality. In a recent paper Roth and Manion Schilling[11] discuss three spin-sorting mechanisms operative in radical pairs: (i) the most common one involving recombination from a singlet-state pair vs. cage escape by diffusion, (ii) formation of singlet-state products vs. triplet-excited-state products,[11] and (iii) a mechanism based on fast vs. slow intersystem crossing in radical pairs.[12] In this paper we shall identify a fourth spin-sorting mechanism, i.e., formation of *singlet-state* products from *singlet*- vs. *triplet*-state radical pair (or biradical). Thus, a more general way to refer to these spin-sorting processes would be in terms of *singlet and triplet exit channels* of a radical pair (or biradical) instead of recombination and escape. Accordingly, the ϵ parameter of the qualitative CIDNP rules[13] could be reinterpreted as $\epsilon = +$ (singlet exit) and $\epsilon = -$ (triplet exit). Note that this leads to a more symmetrical relation between the μ and ϵ parameters, defining the electronic spin state of entry into and exit from the radical pair, respectively.

[11] H. D. Roth and M. L. Manion Schilling, *J. Am. Chem. Soc.*, **102**, 4303 (1980).

[12] R. S. Hutton, H. D. Roth, B. Kraeutler, W. R. Cherry, and N. J. Turro, *J. Am. Chem. Soc.*, **101**, 2227 (1979).

[13] R. Kaptein, *J. Chem. Soc., Chem. Commun.*, 732 (1971).

[14] Field-dependent CIDNP curves for ketones **1** and **2** have also been obtained by G. L. Closs, personal communication.

[15] R. Kaptein, M. Fräter-Schröder, and L. J. Oosterhoff, *Chem. Phys. Lett.*, **12**, 16 (1972).

[16] R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **4**, 214 (1969).

[17] R. Kaptein, F. J. J. de Kanter, and G. H. Rist, *J. Chem. Soc., Chem. Commun.*, 499 (1981).

[18] A referee pointed out that the basic idea of opening a $T_0 \rightarrow S$ escape route in biradicals by a product-selective SOC mechanism has been described already in the doctoral thesis of C. E. Doubleday (Chicago, 1973), of which the authors were unaware. Therefore, Doubleday deserves credit for first realizing the importance of this mechanism for biradical CIDNP.

listed above can be well accounted for.

Some key experiments on cyclic ketones will be presented. Magnetic-field-dependent CIDNP curves for ketones **1** and **2** and those obtained by Doubleday[3c] are calculated on the basis of the theory discussed in the theoretical section. These computer simulations yield information on the rates of spin–orbit coupling (SOC) induced reactions of triplet biradicals. The general conditions under which these SOC-induced reactions are likely to occur for acyl–alkyl and alkyl–alkyl biradicals will be discussed, and we shall attempt to give an explanation for the observed product selectivities.

To account for his observations, Doubleday[3c] proposed a kinetic scheme, which has important features in common with the theory we present here, including SOC-induced intersystem crossing. However, apart from the oversimplification of limiting the biradical to two conformations, there are some conceptual differences with our model that we shall also discuss.

Theory of Biradical CIDNP

The theory of CIDNP from flexible-chain biradicals can be formulated in terms of a density matrix equation of motion describing the dynamics of both the electron–nuclear spin system and the nuclear framework.[5] The chain motion is treated in an idealized way: biradical conformations are not explicitly taken into account but are represented by a set of end-to-end distances, between which jumps are made in a diffusion-like fashion. Previously, we considered only product formation from the singlet-state biradical.[5] The theory will now be extended to include product formation from the triplet state mediated by SOC-induced intersystem crossing.

We consider a biradical containing one nuclear spin with $I = {}^1/_2$. Nuclear-spin polarization is calculated by solving the stochastic Liouville equation for a biradical formed at $t = 0$ (eq 1).

$$\mathrm{d}\rho(t)/\mathrm{d}t = (-i\mathcal{H}^{\times} + \mathbf{R} + \mathbf{W} + \mathbf{K})\rho(t) \qquad (1)$$

The elements of the density matrix $\rho(t)$ correspond to the electronic (S, T_+, T_0, T_-) and nuclear spin-states of the biradical and its reaction products and to a number of end-to-end distances r between the radical sites a and b. $\mathcal{H}^{\times}$ is the Liouville superoperator associated with the spin Hamiltonian $\mathcal{H}$ (in rad s^{-1}):

$$\mathcal{H}^{\times}\rho(t) = \mathcal{H}\rho(t) - \rho(t)\mathcal{H} \qquad (2)$$

$$\mathcal{H} = \beta\hbar^{-1}B_0(g_aS_{az} + g_bS_{bz}) + AIS_a - J(r)(1/2 + 2S_aS_b) \qquad (3)$$

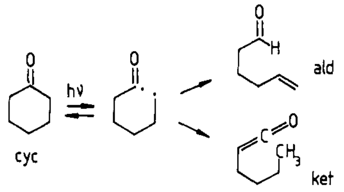
Here, B_0 is the external magnetic field, while the magnetic properties of the biradical are defined by the g factors g_a and g_b and the hyperfine coupling constant A. The r dependence of the spin Hamiltonian enters through the exchange interaction (or singlet–triplet splitting), which is taken to be exponentially dependent on the end-to-end distance r:

$$J(r) = J_0 \exp(-\alpha r) \qquad (4)$$

The equation of motion (1) further takes into account spin relaxation via the Redfield relaxation superoperator (or matrix) **R**, while the motion of the biradical is described by **W**; the matrix **K**, finally, describes the chemical reactions and needs to be modified for the present purpose.

We have explored two motional models:[5] the rotational-isomeric-state model (RIS) and the restricted-diffusion (RD) model. The RIS model cannot easily be used for intermediate size biradicals, because the problem dimensions become too large. Therefore, we restrict the discussion to the RD model, which starts with a calculation of the end-to-end-distance distribution by a Monte Carlo method. This distribution is then divided into a number of segments (say 20) of equal probability (area), each with a corresponding distance r. The **W** matrix then contains the rate constants for diffusion-like jumps between these "conformations" (segments with certain r values), chosen in such a way that on the average taken over a long time (in the absence of chemical reactions), the Monte Carlo distribution would be reproduced. $\mathcal{H}^{\times}$ and **R** induce transitions between density matrix elements with the same r value, whereas **W** induces transitions between elements with the same spin-state labels.

Scheme I



The **K** matrix describes both the self-reactions and possible scavenging reactions of the biradical.[5] Self-reactions are assumed to occur only from the conformation with the smallest end-to-end distance $r = r_d$. We shall now allow several products to be formed, not only from the S state but also from the T states of the biradical, with first-order rate constants $k_{S,n}$ and $k_{T,n}$, where n labels the various products. Rate constants for reactions from the three T states, T_+, T_0, and T_-, are assumed to be equal; these reactions are presumably SOC induced. Product specificity arises because $k_{S,n}$ and $k_{T,n}$ may take different values for different products. These rate constants are not known a priori, but will be obtained by fitting calculated to experimental field-dependent CIDNP curves (see below). It should be emphasized that in the present treatment, $k_{S,n}$ and $k_{T,n}$ are *not* the total rate constants for product formation from S- and T-state biradicals, but rather from biradicals with $r = r_d$. Since the value of r_d will depend on the number of segments chosen and is therefore somewhat arbitrary, we feel that only relative magnitudes of the k's are physically meaningful.

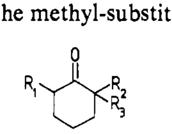
It may be clear that the two intersystem-crossing mechanisms, SOC and hyperfine coupling (HFC), are treated differently. The HFC mechanism arises through the action of $\mathcal{H}^{\times}$; it is independent of the biradical conformation, and its efficiency is only modulated by the exchange interaction. By contrast, the SOC mechanism acts only in the direct conversion of the T-state biradical into product at the short distance $r = r_d$. This is reasonable, since due to the two-center nature of the coupling matrix element, the SOC mechanism is not very efficient as an intersystem-crossing mechanism for a radical pair as soon as the distance is larger than a few angstroms.[19] However, at short distances it may become quite important, as we shall see.

It should be noted further that the equation of motion (1) is still perfectly general. The present model has been developed specifically for intermediate size and large flexible biradicals and is defined by the exponential dependence of the exchange J on r (eq 4) and the motional model contained in **W**. However, it is conceivable that for small biradicals, a limited number of *specific* conformations could be enumerated. If it would be possible to evaluate the exchange interaction for these conformations (possibly including orbital orientation effects) and jump rates between them, the present theory could be easily adjusted to this situation, and the mathematical formalism would remain the same.

For a more elaborate discussion of the various matrix elements and for the procedure for the solution of eq 1, consult ref 5.

Results

High-Field CIDNP of Cyclohexanones. We have measured the 100-MHz ^1H photo-CIDNP spectra of $CDCl_3$ solutions of the ketones **1** and **2** and of the methyl-substituted cyclohexanones **5**.



5a, $R_1 = CH_3$; $R_2 = R_3 = H$
5b, $R_1 = R_2 = CH_3$; $R_3 = H$
5c, $R_1 = H$; $R_2 = R_3 = CH_3$

The Norrish type I photocleavage of the triplet excited ketones yields 1,6-acyl–alkyl biradicals, which give rise to three types of products, as shown in Scheme I for cyclohexanone.[20]

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[19] R. Kaptein, *J. Am. Chem. Soc.*, **94**, 6251 (1972).

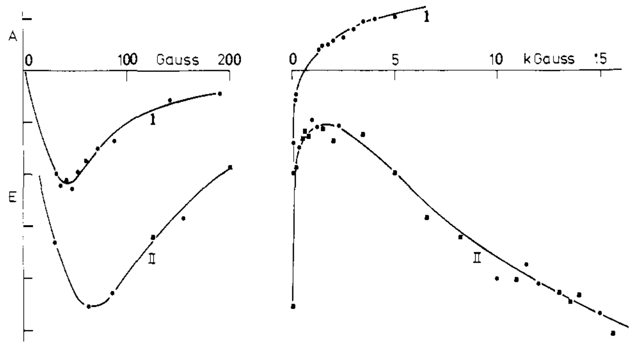

Figure 2. Magnetic-field-dependent ^{1}H CIDNP curves for the aldehydes for photolysis of ketones **1** and **2**. Curve I, cyclohexanone (**1**); curve II, bicyclic ketone (**2**). The left-hand side is an expansion of the low-field part of the curves at the right-hand side of the figure. The lines drawn represent smooth curves through the experimental points. (A) Enhanced absorption; (E) emission.

Cyclization of the biradical leads to the parent ketone, whereas disproportionation gives rise to alkenal and ketene product (ketene is usually trapped by traces of H_2O as the carboxylic acid). For later reference these products are indicated by cyc, ald, and ket, respectively.

Figure 1 shows photo-CIDNP different spectra for the ketones **1**, **2**, and **5**. Comparison of Figure 1, A and B, reveals a striking difference in behavior of ketones **1** and **2**. As has also been observed by Closs,[6] the alkenal from **1** (Figure 1A) shows enhanced absorption (A) for the aldehyde proton (9.8 ppm) and methine protons (5.7 ppm) and emission (E) for the vinylic CH_2 protons at 5.0 ppm. In contrast, the spectrum of Figure 1B for the bicyclic ketone **2** is totally emissive. The CIDNP effects of the alkenal in Figure 1A are reminiscent of radical-pair CIDNP and follow the T_0–S CIDNP rules[13] for a recombination product. The opposite ("escape") polarizations are observed for cyclohexanone: E for the β protons (1.8 ppm) and A for the α protons (2.3 ppm), although for the latter, this is not so clear because of overlap with other lines. For the alkenal from ketone **2**, emissions are found in Figure 1B, irrespective of the sign of the HFC constants in the biradical, as is expected for $T_- \rightarrow S$ polarization from a singlet ground-state biradical formed in the triplet state.

This pattern is also observed for the methyl-substituted cyclohexanones **5** in Figure 1C–E. **5a** shows emission for all three products: alkenal at 9.8 ppm and 5.4 ppm, ketene methyl group at 0.9 ppm, and the ketone methyl doublet at 1.03 ppm. Ketone **5b** was irradiated as the cis–trans mixture, and the reactants show two methyl doublets in emission at 1.09 and 1.00 ppm (Figure 1D). Both alkenal (9.6 and 5.4 ppm) and ketene (0.85 ppm) also show emission. It should be noted that the methyl group emissions could result from the $T_- \rightarrow S$ mechanisms or could be $T_0 \rightarrow S$ escape polarization. Since the spectrum of Figure 1D contains several absorption components, e.g., for the α protons at 2.7 ppm and at 1.6 ppm (unassigned), it is likely that it represents a combination of both types of polarization.

Finally, photolysis of **5c** also yields predominantly emission for alkenal, ketene (methyl doublet at 0.85 ppm), and ketone (methyl singlet at 1.10 ppm), with some absorption components around 1.6 ppm. Since **5c** contained a few percent of the isomer **5b** as an impurity, it cannot be excluded that the absorption at 1.6 ppm is due to the latter compound.

Summarizing the CIDNP results for the cyclohexanones, it is clear that **1** and **2** are extremes in showing pure $T_0 \rightarrow S$ and $T_- \rightarrow S$ polarization, respectively. Methyl substitution changes the balance for the low-field aldehyde line to emission ($T_- \rightarrow S$). The polarizations of Figure 1C–E are due to the $T_- \rightarrow S$ mechanism with admixtures of $T_0 \rightarrow S$ effects (most pronounced in Figure 1D). By analogy with radical-pair CIDNP, the $T_0 \rightarrow S$ component for the alkenals shows recombination-type polarization (singlet exit channel),[10] while the cyclic ketones and ketenes give rise to escape polarization (triplet exit channel).[10]

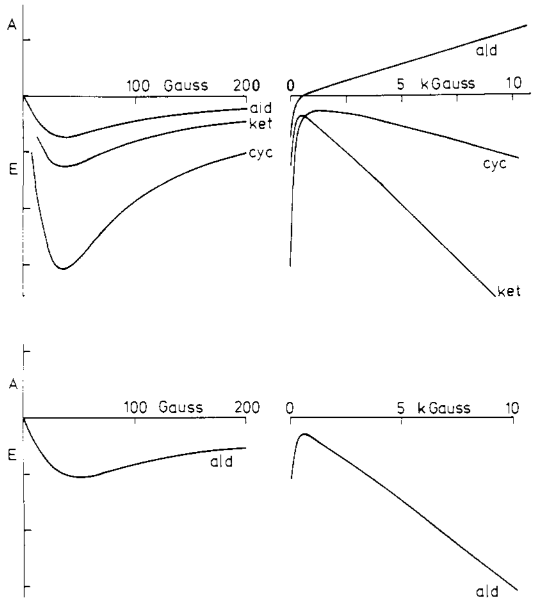

Figure 3. Calculated magnetic-field-dependent ^{1}H CIDNP curves for products of a one-proton C_6 acyl–alkyl biradical. Lower: only the alkenal product is formed from a singlet-state biradical. Upper: three products (alkenal, ketene, and cyclic ketone) are formed with rate constants given in Table I. The curves at the left-hand side are low-field expansions of the full curves at the right. (A) Enhanced absorption; (E) emission. For other parameters used in the calculations, see the text.

Magnetic-Field-Dependent CIDNP of Ketones 1 and 2. The magnetic-field dependence (mfd) of the aldehyde ^{1}H CIDNP signal was measured for cyclohexanone **1** and the bicyclic ketone **2** by the manual transfer method.[14] As shown in Figure 2, in the low-field region the mfd curves for both ketones are qualitatively similar. They show emission maxima of 40 G for **1** and 70 G for **2**. However, at higher fields the curve for **1** changes sign to absorption at ca. 800 G, whereas for **2** the effect remains negative; the magnitude of the emission for **2** goes through a minimum and increases again.

Calculations of Field-Dependent CIDNP. We set ourselves the task of simulating the mfd curves of biradical CIDNP that are presently available. Previously, ^{1}H data for the C_7–C_{11} cyclic ketones[5] and ^{13}C data for the C_8–C_{12} ketones[21] could be satisfactorily accounted for. Now we shall focus on the C_6 biradicals from ketones **1** and **2** (Figure 2) and the ^{13}C mfd curves for ketones **4a–c**, recently published by Doubleday.[3c] His data are particularly interesting because he obtained mfd curves for three reaction products over a wide range of magnetic fields (0–85 kG).

Our simulations are based on the theory outlined in the theoretical section, using as much as possible parameters that had been optimized previously.[5,21] Thus, the parameters used for the exchange interaction, spin relaxation, and biradical dynamics were the same as before.[5,21] Only for the phenyl-substituted biradicals derived from **4**, which contain a more delocalized radical center, did it prove to be necessary to adjust the exchange parameters. The new element is the triplet reactivity, for which the rate constants were obtained by fitting the calculated curves to the experimental ones.

In Figure 3, mfd curves are presented, calculated for a C_6 acyl–alkyl biradical containing one proton with $A = +25$ G (β proton) on the alkyl site. This proton would correspond to the aldehyde proton in an alkenal product. For the lower part of Figure 3, only one product was allowed to be formed from the S state of the biradical, as was previously done for the larger biradicals.[5] The curve is seen to correspond with the experimental mfd curve of the bicyclic ketone **2** (Figure 2). The general form

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(20) N. J. Turro, "Modern Molecular Photochemistry" Benjamin, Menlo Park, CA, 1978, p 533.

(21) F. J. J. de Kanter, R. Z. Sagdeev, and R. Kaptein, *Chem. Phys. Lett.*, **58**, 334 (1978).

Table I. Reaction Rate Constant (s^{-1}) for Product Formation from Singlet- and Triplet-State Biradicals[a]

	biradical		
	C_6	C_7	C_8
$k_{S,ald}$	8.10^{11}	5.10^{10}	9.10^{9}
$k_{S,cyc}$	2.10^{12}	2.10^{11}	2.10^{11}
$k_{S,ket}$	1.10^{9}	3.10^{9}	1.10^{10}
$k_{T,ald}$	0.0	0.0	0.0
$k_{T,cyc}$	2.10^{8}	5.10^{6}	5.10^{6}
$k_{T,ket}$	1.10^{9}	5.10^{7}	6.10^{7}

[a] Rate constants are for formation of alkenal (ald), cyclic ketone (cyc), and ketene (ket) from alkyl–acyl biradicals in configurations with $r = r_d$ (see text). They are used in the calculations of magnetic-field-dependent CIDNP as shown in Figures 3–6.

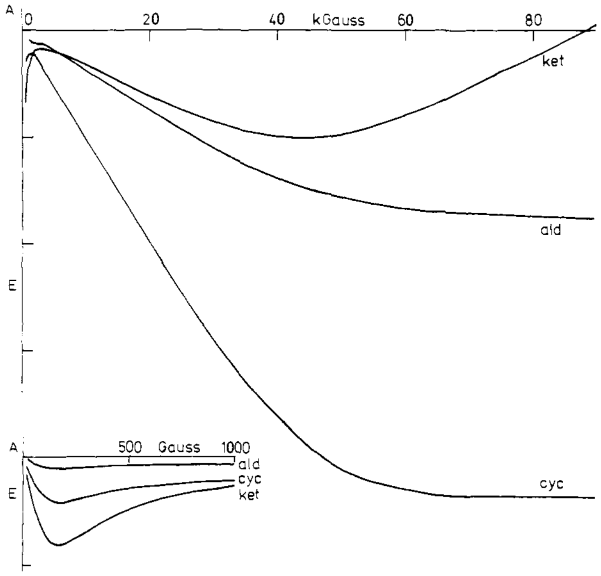

Figure 4. Calculated magnetic-field-dependent ^{13}C CIDNP curves for a one-nucleus C_6 biradical. Three products (ketene, alkenal, and cyclic ketone) are formed with rate constants given in Table I. The insert shows an expansion of the low-field part of the curves.

of the emission curve is nicely reproduced, although experimentally the first maximum is slightly larger and shifted to larger fields (70 vs. 50 G). This may be due to the fact that in reality more hyperfine-coupled nuclei are present than the one taken into account. The upper part of Figure 3 shows mfd curves calculated for three products formed from both S and T states of the C_6 biradical. The rate constants used in the calculation are given in Table I. The alkenal is assumed to be formed from the S state only. Cyclic ketone and ketene are formed from both S and T states. At low fields, all three curves are emissive, due to $T_- \rightarrow S$ mixing, with a maximum at 40 G. At higher fields, the $T_0 \rightarrow S$ mechanism becomes operative. This changes the sign of the polarization of the aldehyde proton (Δg effect), while the cyclic ketone and ketene products remain in emission. For the aldehyde proton (the only one for which mfd curves were obtained), this corresponds to the behavior of cyclohexanone **1** as seen in Figure 2. The emission maximum and the zero crossing point at 800 G are almost exactly reproduced. In fact, the proton data do not allow the determination of separate rate constants for ketene and cyclic ketone formation and could have been fitted with a single T-state product (apart from the S-state alkenal product). The rate constants given in Table I made it possible to simultaneously fit the ^{13}C mfd curves (see below).

Thus, it is clear from Figure 3 that inclusion of triplet-biradical reactivity has a profound effect on the mfd curves. It allows the $T_0 \rightarrow S$ spin-sorting process to manifest itself, which, for instance, can also be clearly seen in the high-field spectrum of cyclohexanone (Figure 1A).

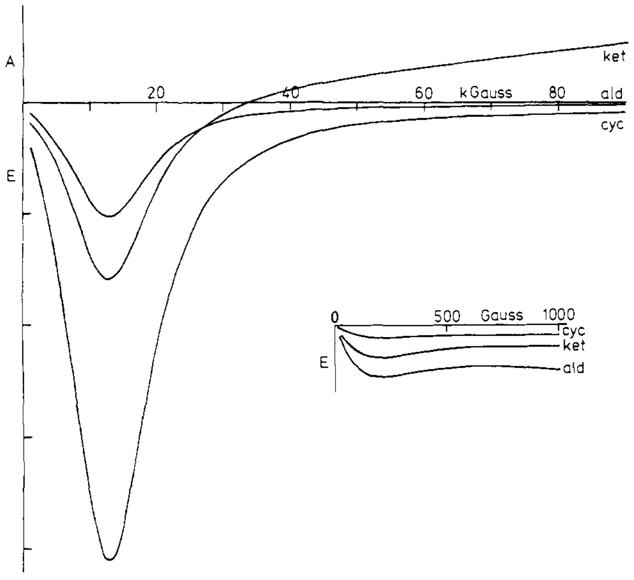

Figure 5. Calculated magnetic-field-dependent ^{13}C CIDNP curves for a C_7 biradical. Three products are formed as in Figure 4. For rate constants, see Table I. The insert shows an expansion of the low-field part of the curves.

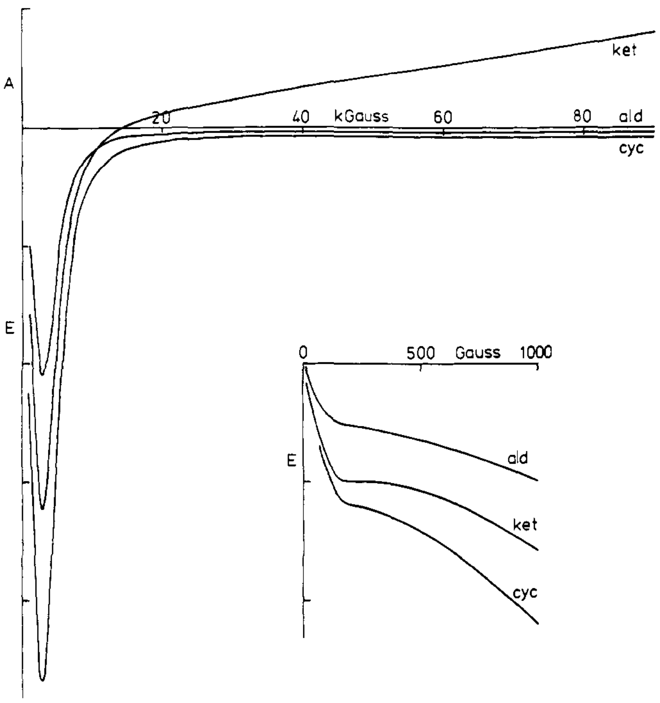

Figure 6. Calculated magnetic-field-dependent ^{13}C CIDNP curves for a C_8 biradical. Three products are formed as in Figure 4. For rate constants, see Table I. The insert shows an expansion of the low-field part of the curves.

Figures 4, 5, and 6 show ^{13}C mfd curves for the products from the C_6, C_7, and C_8 biradicals derived from ketones **4**. The curves were calculated for a carbonyl ^{13}C, with $A = +150$ G (at the acyl site in the biradicals). The exchange parameters $\alpha = 2.709$ Å^{-1} and $J_0 = -0.446 \times 10^{19}$ rad s^{-1} matched the experimentally observed[3c] emission maxima better than the values used before ($\alpha = 2.136$ Å^{-1}, $J_0 = -0.167 \times 10^{18}$ rad s^{-1}). However, the same values were used for the C_6, C_7, and C_8 biradicals. This procedure seems justified in view of the different character of the phenyl-conjugated alkyl radical site. The singlet and triplet self-reaction rate constants were adjusted to obtain the best agreement with the experimental curves.[3c] These parameters are summarized in Table I. One may wonder why now the ketene changes sign, whereas in Figures 2 and 3 this was observed for the aldehyde. This is, however, a consequence of the fact that the polarized ^{13}C nucleus is now at the acyl site of the biradical ($\Delta g < 0$) whereas the proton is located at the alkyl radical site ($\Delta g > 0$). It is in agreement with the $T_0 \rightarrow S$ polarization rules.[13] Comparison with Doubleday's[3c] experimental mfd curves shows that the fit is remarkable. Almost all details such as the zero crossings for the ketenes, the crossings of the curves among themselves, and also the low-field behavior are correctly calculated. The ketene sign reversals for the C_7 (Figure 5) and C_8 (Figure 6) biradicals occur at the correct fields (34 and 15 kG, respectively). For the C_6 biradical, the crossing is somewhat too high: it is calculated at 88 kG, whereas experimentally it is ill defined due to weak signal to noise but would seem to occur between 40 and 50 kG.[3c] As might be expected, the zero crossing points are quite sensitive to the ratios of triplet- vs. singlet-state rate constants, because these determine the amount of $T_0 \rightarrow S$ polarizaiton observed. Table I shows that in all cases, the singlet and triplet reactivities are quite different. For instance, from triplet-state biradicals, ketenes are formed preferentially, whereas in the singlet-state cyclization to the parent, ketones have a higher probability. Apparently no or little alkenal is formed from the triplet state, although the value of $k_{T,ald}$ could be as high as 10^6 s^{-1} without affecting the results significantly.

Discussion

From Figure 1 it is clear that the ^1H photo-CIDNP spectrum of cyclohexanone is dominated by $T_0 \rightarrow S$ polarization, whereas those of α-substituted cyclohexanones predominantly show $T_- \rightarrow S$ effects. This difference in behavior is also reflected in the mfd curves of Figure 2 and, as noted in the Introduction, has been a long-standing puzzle. It is now clear from the simulations of Figure 3 that we can satisfactorily account for these results by introducing selective product formation from triplet-state biradicals. This allows the spin-sorting $T_0 \rightarrow S$ mixing mechanism to contribute and at high fields even dominate over the $T_- \rightarrow S$ mechanism. We have previously shown for C_8–C_{12} biradicals that the $T_0 \rightarrow S$ mechanism can manifest itself when the escape route is provided by a fast scavenging reaction.[22]

In principle, the present results could also be explained by the formation of products in the *triplet excited state* and subsequent radiationless transitions to the ground state as has been observed in the case of electron-transfer reactions.[11] However, in view of the high triplet-state energies involved (e.g., 78 kcal mol^{-1} for cyclohexanone),[23] this is very unlikely. Apparently, the exceptional position of the biradical from cyclohexanone lies in the availability of SOC-induced reaction pathways not available to the bridged biradical from **2** and to a lesser extent to those from **4**. We shall come back to this point later.

When field-dependent CIDNP data are available for various reaction products, computer simulations of the mfd curves yield values for the rate constants for singlet- and triplet-state self-reactions. The good agreement between the calculated curves shown in Figures 4, 5, and 6 and the ^{13}C measurements of Doubleday[3c] shows that the stochastic biradical theory modified as described in the theoretical section is adequate for a quantitative description of mfd CIDNP of biradicals. Thus, the exponnential exchange model (eq 4) appears to work reasonably well, even for 1,6 biradicals, although the exchange parameters probably have to be readjusted for each set of homologous biradicals. Also, the approximations involved in the restricted-diffusion model[5] seem to be appropriate for a description of biradical dynamics. The rate constants given in Table I should be treated with some caution. First, the experimental ^{13}C mfd curves were not corrected for differences in nuclear-spin relaxation times (T_1) of the products. Second, it is not excluded that secondary photoreactions of the products may have affected the curves to some extent (cf. ref 17). However, we feel that although the magnitudes of the rate constants may be subject to some error, the observed reactivity trends should still be valid. Thus, in all cases we found that the rate of product formation from the *triplet* biradical decreased in the order ketene > cycloalkanone > alkenal, whereas for the *singlet* biradical, quite different reactivities were found, which varied somewhat with biradical size (see Table I).

Some other features of the mfd curves deserve comment. The A effect in the high-field region, which is due to $T_0 \rightarrow S$ mixing, increases linearly with magnetic field. This is quite different from radical-pair polarization, where the mfd curves show a maximum at the field $B_0 = \hbar A/2(\Delta g)\beta$, which would be at 14 kG for the proton coupling of 25 G and 83 kG for the ^{13}C coupling (A = 150 G). This difference is related to the different motional properties of the species (restricted diffusion vs. free three-dimensional diffusion). Provided a spin-sorting process can occur, the $T_0 \rightarrow S$ effect wins out at the higher fields. This is due to canceling effects of T_+–S and T_-–S mixing at high fields, where $B_0 \gg 2\hbar\langle J\rangle/g\beta$, i.e., where the Zeeman splitting is much larger than the average singlet–triplet splitting $2\langle J\rangle$. The larger biradicals (Figures 4 and 5), especially, still show pronounced emission maxima, due to T_-–S mixing, approximately at fields in which Zeeman and exchange energies match.

One may wonder if inclusion of triplet reactivity might modify the mfd curves for C_7–C_{11} biradicals that we have previously calculated.[5] We repeated these calculations with the rate constants of Table I. The result was that the aldehyde polarizations for C_7–C_{11} biradicals were hardly affected in the field range up to 20 kG for which experimental data are available. Apparently, for the larger biradicals the $T_- \rightarrow S$ effect is dominant in this range of magnetic fields, and the $T_0 \rightarrow S$ effect is expressed only at much higher fields.

We should like to comment on the kinetic model proposed by Doubleday[3c] to account for his ^{13}C data. This model also includes a SOC-induced intersystem-crossing pathway to allow for a spin-sorting process. The density matrix equation is solved for a kinetic scheme in which the biradical can adopt two conformations differing in SOC-induced $T \rightarrow S$ interconversion rates and J. There are two main differences between his theory and the one presented here. First, considering only two biradical conformations (with ad hoc values of J) seems an unnecessary restriction. We have shown[5] that the restricted-diffusion model combined with a single-functional form of J for a series of homologous biradicals gives a good description of the mfd behavior. A second and more fundamental conceptual difference regards the treatment of SOC. In Doubleday's model, relaxation, product formation, SOC-induced intersystem crossing, and interconversion between conformations are all treated as first-order rate processes; the SOC mechanism causes transitions between triplet and singlet states of the biradical in a certain conformation. In our view, however, the necessary product selectivity indicates that the SOC-induced transitions are intimately connected with the product-forming reaction step. In other words, we believe that SOC couples *triplet biradical states* with *singlet product states.* In this respect, it is quite different from the HFC mechanism, which couples singlet and triplet states of the biradical.

It may be useful to summarize the various intersystem-crossing pathways available to a biradical and their kinetic treatment in the present theory:

Electron–nuclear hyperfine coupling and *g* factor differences (often lumped together as the HFC mechanism) are described by the Liouville operator $\mathcal{H}^{\times}$ and cause a coherent quantum-mechanical mixing of T and S states, which, for a fixed conformation with constant J, would be oscillatory in nature.

Electron-spin relaxation is described by the Redfield relaxation matrix **R**. Transitions between spin states are treated as first-order rate processes. Only electron relaxation, which is uncorrelated at the two radical sites (e.g., by random external fields), induces $T \rightarrow S$ transitions. Electron-dipolar relaxation only couples states within the triplet manifold.

Spin–orbit coupling (SOC) occurs only at certain triplet–singlet surface crossings. It leads to self-reactions from the triplet state described by the reactivity matrix **K**, which couples triplet biradical configurations with $r = r_d$ to singlet product states.

We shall now come back to the observed triplet reactivities as summarized in Table I and try to identify biradical conformations and reaction modes that are conducive to enhanced spin–orbit coupling.

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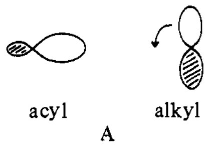
[22] F. J. J. de Kanter and R. Kaptein, *Chem. Phys. Lett.*, **58**, 340 (1978).
[23] Reference 20, p 290.

SOC-Induced Triplet Reactivity of Biradicals

It should be noted that differences in singlet and triplet reactivity as we observed here for acyl–alkyl biradicals are by no means unique. There are several reports in the literature of different product ratios found for a biradical depending on whether it is generated in the singlet or the triplet state. This was found, for instance, in Bartlett and Porter's[24] classic study of the direct and triplet-sensitized photolysis of tetramethylenediazenes, in studies by Overberger and Stoddard[25] on similar systems, and in the Norrish type II photoreactions of ketones with γ hydrogens.[26] Often these differences between S- and T-state biradicals can be partially explained by the very short lifetimes of S-state biradicals not allowing stereochemical isomerizations by bond rotations. However, real differences in reactivity have also been observed, for instance, in different disproportionation vs. ring closure ratios.[24-27] A unique feature of CIDNP in this respect is that information on S- and T-state reactivity is revealed for biradicals that are only formed in the triplet state!

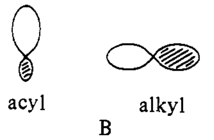
The problem of SOC-induced spin inversions in biradicals has been extensively discussed, for instance, by Salem and Rowland[27] and more recently by Shaik and Epiotis.[28] Without going into much detail, the conclusions by these authors can be summarized as follows. The rate of such a process will be proportional to the SOC matrix element coupling S and T states and is inversely proportional to the energy gap between these states. Since the SOC matrix elements for organic biradicals will be at most a few cm^{-1}, this means in practice that transitions will occur only at crossings (or touchings) of S and T surfaces. A further requirement for efficient intersystem crossing comes from the nature of the SOC matrix element, which is only nonzero for a simultaneous change in spin and orbital angular momentum. For the present purpose, this implies that S and T states are coupled efficiently when a rotation of p orbitals is involved.

In the case of our acyl–alkyl biradicals, an odd-electron orbital orientation favoring SOC-mediated cyclization from the triplet state would be the following:



A

A biradical conformation with this orbital orientation would also satisfy the energetic requirement. As shown schematically in Figure 7, the perpendicular orientation A would be expected to have a triplet-state energy below that of the singlet state, quite analogous to twisted ethylene.[27] Thus, upon rotation away from the 90° position, a T → S crossing region would be passed where SOC-induced spin inversion could take place. Note that at the acyl radical site, the odd electron is in a σ orbital having s character, so that in the alternative perpendicular orientation B, overlap would be appreciable, and the energy of the T state would probably be too high for a crossing with the singlet surface.



B

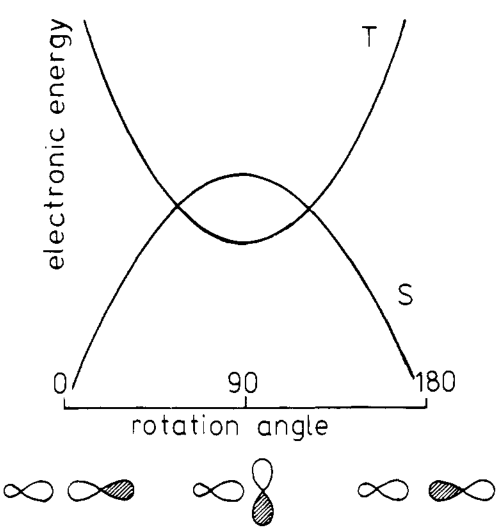


Figure 7. Schematic representation of the dependence of singlet (S) and triplet (T) state energies upon orbital orientation for an acyl–alkyl biradical.

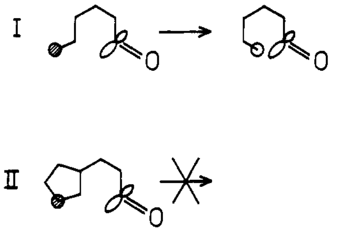


Figure 8. Conformations of acyl–alkyl biradicals derived from cyclohexanone (I) and bicyclooctanone (II). For biradical I, the conformation with orbital orientation A, favorable for SOC-induced triplet-state cyclization, can be thought to occur via rotation about the C_4–C_5 bond. For biradical II, the ethylene bridge precludes this rotation, and orientation A cannot be attained.

A *perpendicular* approach of orbitals as in A satisfies both the energy and p-orbital rotation requirements of the SOC mechanism and is therefore favorable for a cyclization reaction from the triplet state. This should be contrasted with the *parallel* approach C, which is likely to be favorable for the singlet-state cyclization. We believe that the difference in CIDNP behavior of ketones **1** and **2** can be explained on this basis. Whereas the biradical derived from cyclohexanone **1** can easily adopt a conformation with the perpendicular orbital orientation A, this is impossible for the biradical from **2**! Figure 8 shows this difference schematically. Model-building studies confirm unambiguously that the ethylene bridge precludes any conformations such as A at short separation of the radical sites and therefore the triplet cyclization reaction. Also, disproportionation to form the ketene product will be severely hindered by the presence of the bridge, although for this reaction it is more difficult to pinpoint exactly the conformation that would be utilized by the triplet biradical. Thus, the biradical from **2** having no triplet reaction path (and therefore no spin-sorting route) available gives rise to T_- → S CIDNP effects only. It can now be understood that methyl substitution at the α position as in the ketones **5** also hinders the triplet-cyclization and ketene-forming reactions, although possibly not to the same extent as in the bridged biradical.

C

It is not so easy to explain the observed triplet reactivity trend (ketene > cyclic ketone > alkenal; see Table I), because the conformations from which the triplet disproportionations take place are not known. In general, one might expect a somewhat larger separation of the radical centers in the transition state for disproportionation than for cyclization, with a concomitant decrease in SOC efficiency. This might be the reason for our finding that

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[24] P. D. Bartlett and N. A Porter, *J. Am. Chem. Soc.*, **90**, 5317 (1968).

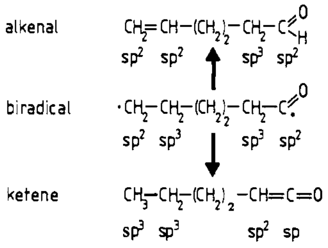
[25] C. G. Overberger and J. W. Stoddard, *J. Am. Chem. Soc.*, **92**, 4922 (1970).

[26] P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971).

[27] (a) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972); (b) L. Salem, *Pure Appl. Chem.*, **33**, 317 (1973).

[28] (a) S. S. Shaik, *J. Am. Chem. Soc.*, **101**, 3184 (1979); (b) S. S. Shaik and N. D. Epiotis, *ibid.*, **102**, 122 (1980); (c) N. D. Epiotis, in "Theory of Organic Reactions", Springer, Berlin, 1978, p 226.

Scheme II



$k_{T,cyc} >> k_{T,ald}$. The surprisingly large rate constant for ketene formation ($k_{T,ket}$) does not seem to agree with this expectation. However, we suggest that another factor may compensate in this case, i.e., the much larger extent of rehybridization occurring in the ketene-forming reaction than in the disproportionation to alkenal. As shown in Scheme II the biradical → ketene reaction involves three changes in C-atom hybridization, whereas that to alkenal involves only one. Probably even more important is the fact that for the carbon atoms that carry the unpaired electrons, there is no change in going to alkenal, while both carbons change their hybridization state in the reaction to ketene. Pyramidalization of trigonal centers and the reverse process involve partial rotation of p orbitals and thereby enhance the SOC matrix element.[28] Although it is not clear at this point whether this effect can fully account for rate enhancements by several orders of magnitude, it could well contribute.

The early CIDNP results on the decamethylene biradical from **3** can now also be better understood.[15] In this case the biradical is symmetric, so there is only one disproportionation product, decene-1, showing a pure EA multiplet effect (recombination or singlet exit channel). By analogy with the acyl–alkyl biradicals, it is likely that here also a S → T_0 spin-sorting route is opened by partial cyclization from the triplet-state biradical, while disproportionation would only proceed from the singlet state. One might expect to find the opposite polarization (AE multiplet) in the cyclization product cyclodecane, but since this gives rise to a single NMR line, a multiplet effect is by definition unobservable for this product.

The recent CIDNP observations in the Norrish type II reaction of valerophenone[17] can be rationalized along similar lines. The situation for the 1,4 biradical is somewhat different in that the escape route or triplet exit channel is now mainly provided by the back reaction to valerophenone ("disproportionation"), whereas the cyclization and fragmentation products show polarizations indicating singlet-state reactivity. A more detailed analysis of this system must await the result of a magnetic-field-dependent CIDNP study.

It should be noted that CIDNP from 1,4 or 1,3 biradicals[29] is probably not generally observable. In these species the SOC mechanism may often be too strong, while for CIDNP observation, the HFC mechanism should at least contribute to the intersystem crossing. The requirements for this are that the biradical lives long enough (1–10 ns) and moreover spends an appreciable fraction of its lifetime in conformations in which the exchange interaction is either comparable to the Zeeman energy ($T_+ \rightarrow S$ or $T_- \rightarrow S$ mixing) or of the order of (or smaller than) the hyperfine interactions. In addition, for the $T_0 \rightarrow S$ mechanism, spin-sorting reaction pathways are required.

Summary and Conclusions

CIDNP spectra of reactions involving biradical intermediates sometimes show effects due to $T_0 \rightarrow S$ mixing. In particular, this has been observed for biradicals that occur in the photolysis of cycloalkanones[3c,6] and valerophenone.[17] These effects can be understood by assuming that spin sorting occurs by product-selective reactions from both singlet- and triplet-state biradicals. A stochastic theory of biradical CIDNP modified to include triplet-state reactivity can quantitatively account for magnetic-field-dependent CIDNP data. Computer simulations of mfd curves yield rate constants for the self-reactions of singlet and triplet biradicals. Reactions from the triplet state are presumably mediated by spin–orbit coupling. An attempt was made to rationalize the observed reactivity trends by analyzing the factors that maximize this interaction, especially in the case of acyl–alkyl biradicals.

Finally, it is worth noting that if triplet-state reactions are important for biradicals, there is no reason why they would not play a role in reactions of radical pairs. CIDNP detection would be more difficult in that case, because $T_0 \rightarrow S$ polarization already arises from another spin-sorting route, i.e., recombination vs. cage escape. The photo-Claisen rearrangement of an aryl allyl ether[30] may be one example of a direct conversion of a triplet radical pair into product. It seems worthwhile to look for more.

Experimental Section

Cyclohexanone (**1**), bicyclo[3.2.1]octan-2-one (**2**), 2-methylcyclohexanone (**5a**), 2,6-dimethylcyclohexanone (**5b**) and 2,2-dimethylcyclohexanone (**5c**) were purchased from Aldrich and distilled before use. For the high-field CIDNP studies, a difference method was used: 0.1 M solutions in $CDCl_3$ were irradiated with the light of a Philips SP 1000-W lamp inside the probe of a Varian XL-100 spectrometer for 15 s. A "light" free-induction decay (FID) was collected and after a 40-s delay, a "dark" FID was subtracted from the light FID; light minus dark FIDs were accumulated 10 times. After Fourier transformation, the CIDNP difference spectrum was obtained. For the magnetic-field-dependent studies, 0.2 M solutions in CH_2Cl_2 were irradiated in an auxiliary magnet with the light of an Osram HBO 1000-W high-pressure mercury lamp for 50 s. After manual transfer of the sample to the probe of an A-60 spectrometer (transfer time 2.5 s), the aldehyde proton signal was recorded.

Acknowledgment. We are indebted to Dr. G. L. Closs, C. Doubleday, H. Fischer, and A. M. Trozzolo for communicating results prior to publication. We especially thank Dr. G. L. Closs for a fruitful exchange of ideas from which this work has greatly benefited.

Registry No. 1, 108-94-1; **1** biradical, 82352-62-3; **2**, 5019-82-9; **2** biradical, 82352-63-4; **4a**, 1444-65-1; **4a** biradical, 82352-64-5; **4b**, 14996-78-2; **4b** biradical, 82352-65-6; **4c**, 14996-79-3; **4c** biradical, 82352-66-7; **5a**, 583-60-8; **5a** biradical, 82352-67-8; *cis*-**5b**, 766-42-7; *trans*-**5b**, 766-43-8; **5b** biradical, 82352-68-9; **5c**, 1193-47-1; **5c** biradical, 82352-69-0.

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(29) S. L. Buchwalter and G. L. Closs, *J. Am. Chem. Soc.*, **97**, 3857 (1975).

(30) W. Adam, H. Fischer, H. J. Hansen, H. Heimgartner, H. Schmid, and H. R. Waespe, *Angew. Chem.*, **85**, 669 (1973).