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Chemically Induced Dynamic Nuclear Polarization from the Selective Recombination of Radical Pairs in Micelles

Sir:

Chemically induced nuclear polarization (CIDNP) effects in homogeneous solutions are generally interpreted on the basis of spin selection in competing radical-pair reactions, e.g., recombination, an electron spin dependent reaction, and diffusional separation, an electron spin independent reaction.[1,2] A radical pair that is generated in a micelle is in a qualitatively different situation: the micelle limits the diffusional migration and thereby prevents complete separation of the pair. It is of interest to compare CIDNP effects generated in homogeneous solutions with those observed in micelle-forming detergent solutions, in order to evaluate the impact of the restricted dimensionality imposed by the micelle.

In homogeneous solution, the photolysis of 1,3-diphenylacetone leads to photodecarbonylation[3] accompanied by strong CIDNP effects for the starting material and for the decarbonylation product, 1,2-diphenylethane.[4] The photolysis of asymmetrical diarylacetones, e.g., 1-(*p*-tolyl)-3-phenylacetone (**1**), results in the formation of three coupling products in exactly the ratio (1:2:1) expected for the statistical coupling of the free radicals, benzyl and *p*-methylbenzyl.[5] During this photolysis the methylene protons of the starting material (3.36, 3.39 ppm) appear in emission and its methyl group (2.24 ppm) appears in enhanced absorption (Figure 1).

These effects can be ascribed to the radical pairs, A and B. An analysis of the signal directions in terms of the formalism suggested by Kaptein[6] indicates that these pairs are generated from a triplet precursor ($\mu > 0$) since the benzyl radical has

Figure 1. ¹H NMR spectrum (90 MHz) of *p*-methylbenzyl benzyl ketone in the dark (bottom) and during UV irradiation (center). The top trace represents the difference between the dark spectrum and that observed during irradiation.


Figure 2. ¹H NMR spectrum (90 MHz) of *p*-methylbenzyl benzyl ketone in an aqueous solution containing hexadecyltrimethylammonium chloride in the dark (bottom) and during UV irradiation (top).

a negative hyperfine coupling constant ($a < 0$) and a larger g factor (2.0025)[7] than the acyl radical (2.0007;[8] $\Delta g > 0$). At the same time, three polarized bibenzyls (**2a–c**) are observed; their polarization is complementary to that of the ketone, enhanced absorption for the methylene protons (2.77, 2.80, 2.84 ppm) and emission for the methyl signal (2.33 ppm), indicating that these products are formed via a free-radical mechanism ($\epsilon < 0$) but from the same precursor pairs. The signal intensity of the bibenzyls is substantially lower than that of the ketone. This is in part due to the slightly shorter spin-lattice relaxation times of **2a–c** (1.5 ± 0.1 s compared with 2.1 ± 0.2 s for **1**) but mainly to the fact that the free benzyl radicals suffer relaxation

before they recombine.

When the same reaction is carried out in an aqueous solution containing hexadecyltrimethylammonium chloride (HDTCl) a similar polarization pattern is observed (Figure 2). However, in this case only a single benzylic methylene peak, that of 1-(p-tolyl)-2-phenylethane (**2b**), is observed, even though the chemical shifts of the three bibenzyls in aqueous HDTCl are sufficiently different to allow **2a** and **2c** to be detected separately if they were formed in any significant amount. These results confirm the selectivity of bibenzyl formation from an unsymmetrical ketone in a micellar environment.[5]

The observation of nuclear spin polarization as a result of a radical-pair reaction in micellar solution implies a spin sorting mechanism different from the one operating in homogeneous solutions. Most commonly, spin sorting occurs as

a) X, Y = H
b) X = H, Y = CH₃
c) X, Y = CH₃
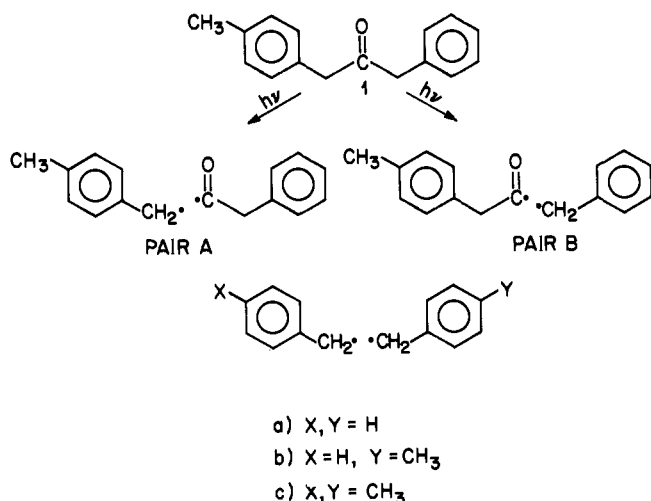
a result of a hyperfine dependent intersystem crossing and a subsequent competition between an electron spin dependent radical-pair reaction (recombination) and an electron spin independent reaction (separation by diffusion). In the photolysis of dibenzyl ketone, for example, the nuclear spin states which allow fast intersystem crossing will be overrepresented in the recombination product, the ketone, whereas those causing slower intersystem crossing will be overrepresented in the escape products, the bibenzyls.

In the micellar environment separation is precluded and coupling is the only available alternative. In this situation the decarbonylation reaction provides for spin selection: the nuclear spin states which allow fast intersystem crossing will predominate in the regenerated starting material whereas those causing slower intersystem crossing will accumulate in the decarbonylated product. In order to allow efficient spin selection, the decarbonylation must occur at a rate comparable with that of the hyperfine induced intersystem crossing. It is noteworthy that the ratio of bibenzyl to ketone polarization is higher in the micelle than in homogeneous solution and is close to the ratio expected on the basis of the spin lattice relaxation times of **1** and **2b**, 2.1 and 1.5 s, respectively. Apparently, the lifetime of the secondary pair is not long enough to allow any significant relaxation of the nuclear spin polarization before coupling.

The CIDNP spectra observed in either cyclohexane or aqueous HDTCl reveal an additional mechanistic detail which would be difficult to determine by classical photochemical techniques. Both spectra show different intensities for the two methylene groups of the regenerated ketone; in both solutions the signal of the p-tolylmethylene group is ~1.5 times as large as that of the benzyl group. Since the spin lattice relaxation times of these protons are identical within experimental error (2.1 ± 0.2 s), we interpret the different signal intensities as

evidence for a preferential cleavage of the p-methylbenzyl bond (to form pair A).

A more detailed analysis of the benzylic polarization reveals that the preference for the formation of pair A may be slightly higher than the 3:2 ratio of the two benzylic signals. This is due to the fact that each pair generates polarization in both benzylic methylene groups. In addition to the main polarization induced in the α protons of the benzyl radicals ($a = -16.3$ G;[7] $\Delta g > 0$), a smaller effect of the same direction is induced in the β protons of the acyl radicals ($a \sim 1$ G;[8d] $\Delta g < 0$). However, the ^{1}H hyperfine coupling in the β position of acyl radicals is small so that the contribution of these nuclei to the overall polarization must be minor.

The results reported here reveal several details of the photoreactions of dibenzyl ketones and allow an insight into the behavior of radical pairs in the restrictive environment of the micelle. Other aspects of this interesting system, including the fate of a chiral center and of specifically ^{13}C-labeled ketones are under investigation.

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Oxidations and Oxygen Transfers Effected by a Flavin N(5)-Oxide. A Model for Flavin-Dependent Monooxygenases

Sir:

The flavin-dependent monooxygenases bind and activate molecular oxygen, ultimately transferring one oxygen atom to substrate and releasing the second as water.[1] Among the reactions catalyzed by the flavin monooxygenases are the hydroxylation of p-hydroxybenzoate,[2] the oxidative decarboxylation of salicylate,[3] and a variety of amine oxidations mediated by the mixed-function amine oxidase system.[4] Although flavin monooxygenations have been the object of extensive investigation, the structure of the flavin oxygenating species remains unknown. Recent work strongly implicates the 4a-hydroperoxyflavin as an initial intermediate in the enzymic oxidations; this intermediate and derived species have been offered to explain the reactivity of the flavin, oxygen-transferring systems.[5] Herein we present a study of nonenzymic oxidations and oxygenations effected by flavin N(5)-oxides