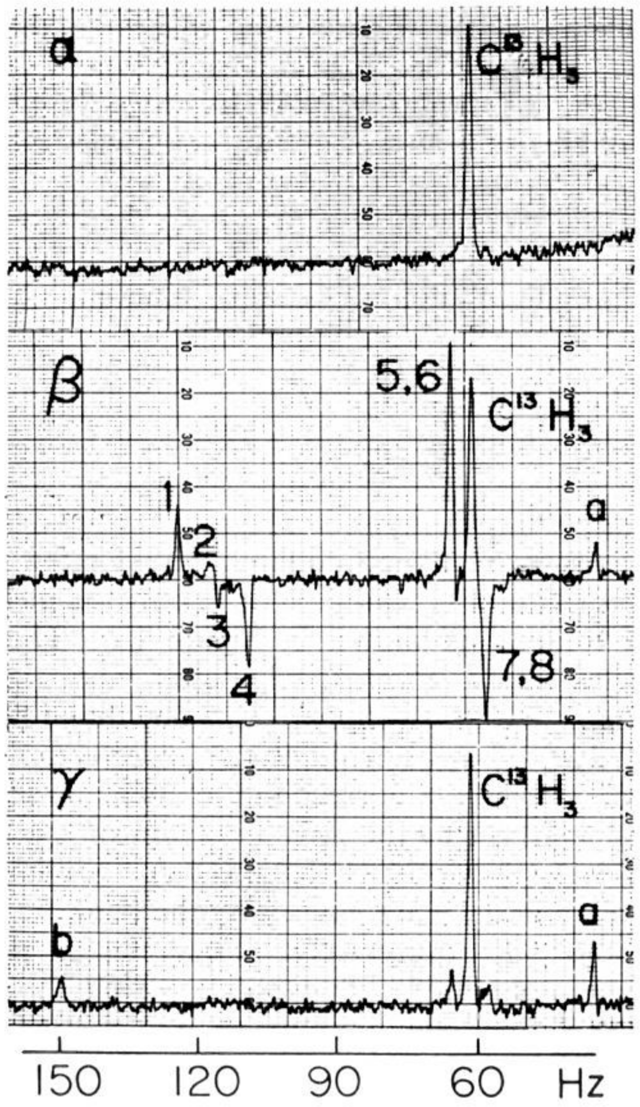
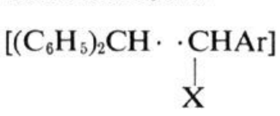


Figure 1. Nmr spectra of a solution of I (0.06 *M*) in toluene at 30°; (α) no light; (β) light admitted; (γ) after 10 min of irradiation. Chemical shifts are in hertz downfield from solvent CH_3.

Figure 2. Polarized spectrum obtained in reaction of I (0.2 *M*) in methyl phenylacetate at 140°. Chemical shifts are in hertz downfield from solvent CH_2.

Assuming positive signs for the vicinal proton spin coupling constants, analysis of the observed polarizations in compounds IVa–d in terms of relative populations of spin energy levels reveals that overpopulation is found in states with nuclear spin quantum numbers closest to zero. In the two-spin systems (IVc and IVd) these are the levels with $m_{j_z} = 0$ and the three-spin systems with $m_{j_z} = \pm {}^1/_2$. In the latter cases a small difference in population between $m_{j_z} = +{}^1/_2$ and $-{}^1/_2$ explains the low intensities of lines 2 and 3 as well as 6 and 7.[10]

The chemical mechanism of the described reactions presumably involves formation of radical pairs VII whose components may diffuse and recombine to give products IV, V, and VI. Cage recombination, giving only IV, competes with diffusion.



$$[(C_6H_5)_2CH\cdot\ \cdot\underset{\displaystyle X}{\underset{|}{C}}HAr]$$

VII

Any theory attempting to explain the observed spectra has to take into account three important facts. First, the magnitude of the observed polarizations is equal to or greater than $\gamma_e/\gamma_n = 660$ (γ_e and γ_n being the magnetogyric ratios of the electron and the proton, respectively). Second, the proton spin distribution is not describable by a spin temperature, and the over-all nuclear spin energy is not far from equilibrium (to a first approximation the integral over the spectrum is 0). Third, the polarized protons are initially not bound to the first paramagnetic species (II) in the reaction sequence. With an electron spin relaxation time for II of $<10^{-9}$ sec,[11] hydrogen abstraction occurs with the electron spin distribution of II in thermoequilibrium.[13] *As a consequence, nuclear spin polarization must occur in the product-forming steps, rather than in the formation of the paramagnetic species.* None of the previously formulated schemes is capable of accommodating these three facts.

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[10] Lines 5 and 6 as well as 7 and 8 are nearly degenerate transitions and are not resolvable. However in each degenerate pair only one line is strongly polarized, as can best be seen by comparing the relative intensities of lines 1 and 4 with the upfield doublet (5,6 and 7,8) in the polarized and unpolarized spectra of IVa.

[11] Calculated from[12]

$$1/T_1 = \frac{6\hbar^2\gamma^4}{20b^6}\left[\frac{\tau_c}{(1+\omega^2\tau^2)} + \frac{4\tau_c}{1+\omega^2\tau_c^2}\right]$$

where τ_c was taken as the tumbling frequency of II ($\tau_c = 4\pi\eta a^3/(3kT) = 1.7 \times 10^{-11}$ sec) and ω is the angular precession frequency of the electron (2.486×10^{11} Hz). The average distance of the electrons, *b*, is available from the esr spectra (*D* = 0.4 cm), and *a*, the radius of the tumbling molecule, was taken as the mean of the three molecular dimensions (3.2 Å).

[12] I. Solomon, *Phys. Rev.*, **99**, 559 (1955).

[13] From the known rates of hydrogen abstraction in excited ketones, which are less selective and consequently more reactive, the lifetime of II is estimated to be greater than 10^{-5} sec when toluene is used as a solvent. Experiments in which toluene was diluted tenfold with benzene resulting in a tenfold increase of the lifetime of II left *P* unchanged.

G. L. Closs, L. E. Closs
Department of Chemistry, The University of Chicago
Chicago, Illinois 60637

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Induced Dynamic Nuclear Spin Polarization in Photoreductions of Benzophenone by Toluene and Ethylbenzene[1]

Sir:

In the preceding communication we reported that it is possible to carry out photochemical reactions inside an nmr spectrometer and to observe nuclear spin polarizations with sufficient signal-to-noise ratios to allow detection without special signal enhancement techniques.[2] To assess the usefulness of this potentially valuable tool for mechanistic studies in photochemistry

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[1] Work supported in part by National Science Foundation Grant GP-7043X.

[2] G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **91**, 4549 (1969).

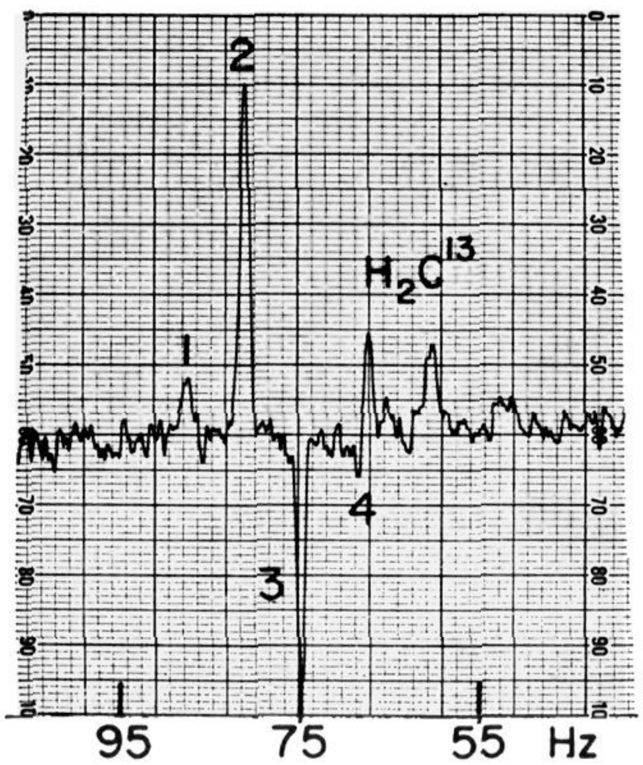
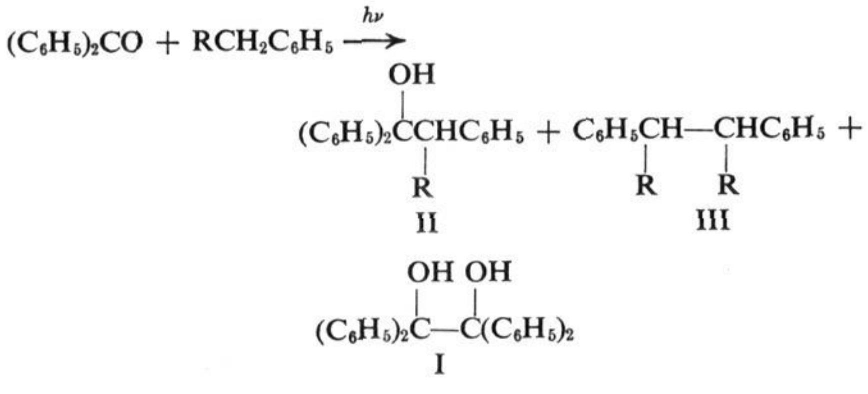


Figure 1. Nmr spectrum of a solution of benzophenone (0.05 *M*) in ethylbenzene at 30° with ultraviolet irradiation. The ^{13}C satellite of the solvent CH$_2$ group appears at the high-field part and interferes with resonance 4 of the polarized spectrum.

we have applied it to the photoreduction of benzophenone.

When benzophenone is illuminated with ultraviolet light in the presence of a hydrocarbon containing benzylic hydrogen the products are benzpinacol (I), the carbinol II, and the hydrocarbon dimer III.[3] A 0.1 *M* solution of benzophenone in toluene was irradiated inside the probe of an HR-60 nmr spectrometer with the focused and Pyrex-filtered light beam of an Osram 500-W super-high-pressure mercury arc. The spectrum showed besides the solvent resonances a single absorption line with a chemical shift of 76 Hz downfield from the toluene methyl proton absorption. This line was shown to be a true photosignal because it collapsed within a few seconds after irradiation was ceased and was regenerated after the light was readmitted. The line was identified by chemical shift measurements as the resonance caused by the methylene protons of the carbinol IIa. The steady-state concentration of polarized IIa is given by $[\mathrm{IIa}^*]_s = nk_LT_1$, where n is the yield of IIa in the photochemical reaction, k_L is the zero-order rate constant of disappearance of benzophenone, and T_1 is the spin–lattice relaxation time of the methylene protons in IIa. Independent determination of these parameters ($n = 0.4$ by glpc, $k_L = 2.3 \times 10^{-4}$ *M* sec^{-1} by ultraviolet analysis of the reaction mixture, and $T_1 = 2.2$ sec by the 180° pulse method on IIa) gave a value for $[\mathrm{IIa}^*]_s$ of 2.0×10^{-4} *M*. Comparison of the intensity of the photosignal with that of a standard solution of IIa gave a polarization, as previously defined,[2] of 250 ± 25.



$$(\mathrm{C_6H_5})_2\mathrm{CO} + \mathrm{RCH_2C_6H_5} \xrightarrow{h\nu} \underset{\mathrm{II}}{(\mathrm{C_6H_5})_2\overset{\mathrm{OH}}{\underset{\mathrm{R}}{\mathrm{C}}}\mathrm{HC_6H_5}} + \underset{\mathrm{III}}{\mathrm{C_6H_5}\underset{\mathrm{R}}{\mathrm{C}}\mathrm{H}\text{—}\underset{\mathrm{R}}{\mathrm{C}}\mathrm{HC_6H_5}} + \underset{\mathrm{I}}{(\mathrm{C_6H_5})_2\overset{\mathrm{OH}}{\mathrm{C}}\text{—}\overset{\mathrm{OH}}{\mathrm{C}}(\mathrm{C_6H_5})_2}$$

a, R = H; b, R = CH$_3$

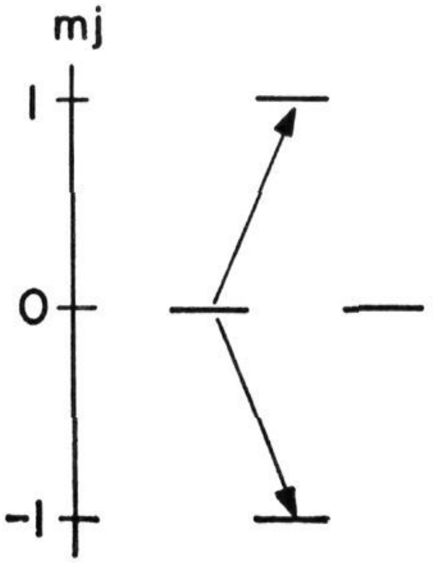


Figure 2. Transition diagram for a system with two equivalent spins (A$_2$). The levels with $m_j = 0$ are assumed to be overpopulated.

When ethylbenzene was used as a solvent the quartet of the methine proton of IIb appeared as a strong photosignal (Figure 1) with the two low-field peaks in the absorption mode while the two high-field transitions gave emission. The polarization of the two center peaks was determined by the same method as outlined above and gave $P = 1300 \pm 200$ ($n = 0.4$, $k_L = 1.7$ 10^{-4} *M* sec^{-1}, and $T_1 = 2.0$ sec). Polarizations of the methyl protons in IIb could not be determined because of solvent absorption interference.

Analysis of the polarization in terms of relative populations of the nuclear energy levels in IIa and IIb leads to diagrams as shown in Figures 2 and 3. In the case of IIa it can be seen that the net polarization observed corresponds to the difference in population of energy levels with $m_j = \pm 1$. Because of the degeneracy of the transitions it is not possible to determine the relative population of the levels with $m_j = 0$, and it is indeed possible that the level $m_j = 0$ is more highly populated than either of the $m_j = \pm 1$ levels. Therefore, whenever there are two or more nuclei which give rise to degenerate transitions only, it is only possible to detect that part of the spin polarization which is caused by a deviation of the total Zeeman energy of the spin system from the equilibrium value. A different situation is shown for the polarization of IIb. Analysis of the spectrum as an A$_3$B system with positive vicinal spin coupling constants gives the pattern shown in Figure 3 in which the overpopulation is concentrated in levels with $m_j = 0$ and ± 1. Since emitting and absorbing transitions are not degenerate, it is possible to detect a second kind of spin polarization which cannot be expressed by a spin temperature and corresponds to a deviation of the entropy of the spin states from the equilibrium value. Superimposed on this polarization may be an energy polarization reflecting itself in unequal population of states with m_j of opposite signs. (In the spectra this would be shown in a nonzero integral over the spectrum.) It can be shown that the energy polarization cannot exceed the value of γ_e/γ_n which is 660 for protons with pure scalar electron–nuclear coupling and one-half of that

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[3] G. S. Hammond, W. P. Baker, and W. M. Moore, *J. Am. Chem. Soc.*, **83**, 2795 (1961).

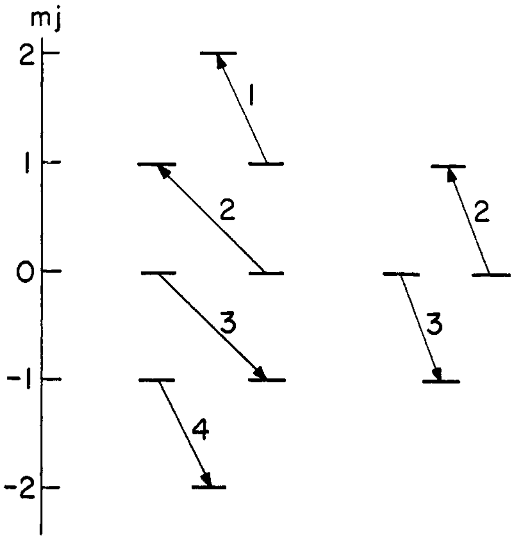

Figure 3. Transition diagram of A_3B system of polarized IIb.

value for a pure dipolar coupling. In contrast, the entropy polarization can theoretically reach magnitudes of $>10^4$.

As in the preceding communication, the spectra reported in the reaction with ethylbenzene cannot be explained by the previously advanced schemes. Also, a quantitative calculation of the electron relaxation time, T_{1_e}, by previously described methods,[4] of benzophenone triplet state shows that the relaxation rate, $1/T_{1_e}$ (10^8 sec^{-1}), is much larger than the known rates of hydrogen abstraction. This again leads to the formation of the radicals in thermal equilibrium before hydrogen abstraction has taken place. This, together with the magnitude of the polarization, emphasizes the need for a new theory on chemically induced dynamic nuclear spin polarization.

These results demonstrate unequivocally that the products II are formed from a paramagnetic precursor, in agreement with the conclusions derived previously from chemical studies.[3] They also point to the potential value of dynamic polarization in mechanistic photochemistry.

(4) Footnote 11 in ref 2.

G. L. Closs, L. E. Closs
Department of Chemistry, The University of Chicago
Chicago, Illinois 60637

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A Mechanism Explaining Nuclear Spin Polarizations in Radical Combination Reactions[1]

Sir:

The preceding communications describe the observation of large nuclear spin polarizations caused by photochemical reactions involving radical combinations.[2] This communication presents a mechanism capable of explaining the observed spectra.

The reactions described have in common that the first paramagnetic species generated is a triplet molecule (T) containing none of the hydrogens causing the polarized spectra. Also, because of very fast electron spin relaxation, $1/\tau_T$, the Zeeman states, $T_{|1,1\rangle}$, $T_{|1,0\rangle}$, and $T_{|1,\bar{1}\rangle}$, of the triplet molecule (T) are in thermoequilibrium before reaction. Rapid molecular rotation and a strong magnetic field (H_0) effectively decouple the spin from the molecular frame and assure quantization of the spin with reference to H_0. The probabilities of hydrogen abstraction (w_a) are assumed to be equal for each Zeeman state yielding a radical pair (RP) whose triplet Zeeman states are being populated according to the equilibrium population (Figure 1). The singlet state, $RP_{|0,0\rangle}$, will be populated by either "intersystem crossing" with probabilities w_j, w_i, and w_jK_z [$K_z = \exp(-g\beta H_0/kT)$], or by separation of the components of the radical pair occurring with probability w_d from each state and recombination of the free radicals with the appropriate spin wave function. Irreversible depopulation of $RP_{|0,0\rangle}$ occurs by product formation with probability w_{se}.

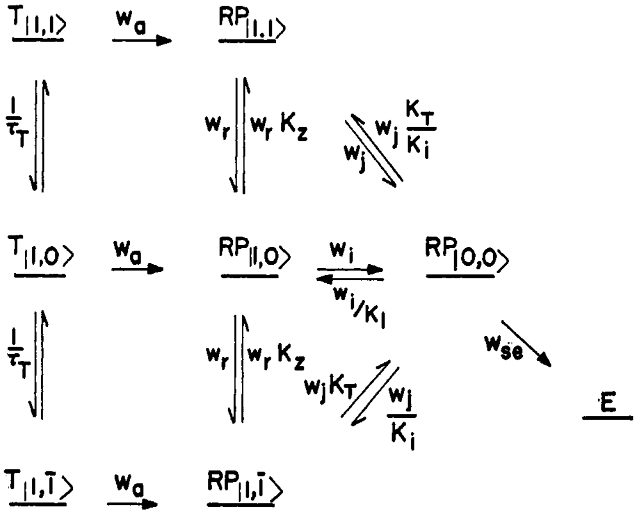

Figure 1. Reaction diagram with electron Zeeman states consisting of a triplet molecule (T), a radical pair (RP), and the radical combination product E.

We consider now the possibility of obtaining nuclear spin polarization from the processes characterized by w_j, w_i, and w_jK_z. For this we assume a radical pair having one proton bonded to each component. The spin-dependent part of the Hamiltonian for a stationary four-spin system can be written as in eq 1, where S, I,

$$\mathcal{H} = (\gamma_e/2\pi)H_0\cdot(S_1 + S_2) + (\gamma_n/2\pi)H_0\cdot(I_1 + I_2) + \mathcal{H}_d + \mathcal{H}_{sc} \quad (1)$$

γ_e, and γ_n are the electron and nuclear spin operators (each of $^1/_2$) and the electron and nuclear magnetogyric ratios, respectively. The first two terms represent the electron and nuclear Zeeman splitting while the next term ($\mathcal{H}_d$) is the sum of all dipolar interactions. The last term includes all scalar interactions and can be written explicitly as eq 2, where A_{jk} is the electron–

$$\mathcal{H}_{sc} = \sum_{j=1}^{2}\sum_{k=1}^{2}A_{jk}(S_j\cdot I_k) + J_{ee}S_1\cdot S_2 + J_{nn}I_1\cdot I_1 \quad (2)$$

nuclear and J_{nn} the nuclear–nuclear spin coupling constant and J_{ee} is the electron–electron scalar exchange coupling constant.[3] Because of its small size the term

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(1) Supported in part by National Science Foundation Grant GP-7043X.

(2) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **91**, 4549, 4550 (1969).

(3) All coupling constants are in hertz.