ance with the theory applied to the C–S bonds. The sodium-coordinated S–O bonds are slightly longer than the noncoordinated S–O bond; however, this difference is hardly significant.

Acknowledgment. The author wishes to thank Dr. Lyle H. Jensen for helpful discussions. Financial support under Grant AM-3288 from the National Institutes of Health is also gratefully acknowledged.

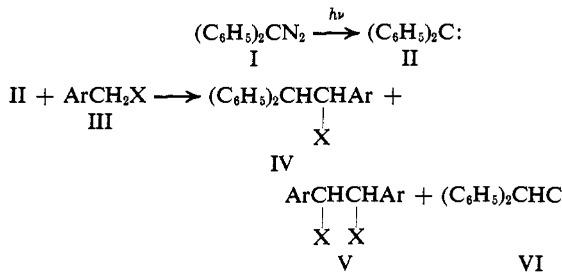
Communications to the Editor

Induced Dynamic Nuclear Spin Polarization in Reactions of Photochemically and Thermally Generated Triplet Diphenylmethylene[1]

Sir:

Several examples of chemically induced dynamic nuclear spin polarization in free radical reactions have been reported.[2] Although no detailed theoretical treatment has been published, a specific mechanism has been proposed to account qualitatively for the observed phenomenon.[2a,3,4] We wish to report the first examples of strong nuclear polarizations resulting from photochemically initiated reactions proceeding through triplet-state intermediates.[5]

Diphenyldiazomethane (I) decomposes photochemically to diphenylmethylene (II), shown by esr spectroscopy to have a triplet ground state.[6] In solvents with benzylic hydrogens (III) the reaction products are triarylethanes (IV), diarylethanes (V), and tetraphenylethane (VI).[7] When a solution of I (1.5% w/v) in toluene (IIIa) was irradiated inside the probe of an nmr spectrometer which had been modified to admit the focused light beam of an Osram 500-W super-high-pressure mercury arc, the spectrum shown in Figure 1β was obtained. Transitions 1–8 are true photo-signals as shown by their collapse within a few seconds after irradiation was ceased, leaving only the methyl-^{13}C peak of toluene as shown in Figure 1α. The signals were regenerated immediately after the light was readmitted. After all diphenyldiazomethane had been consumed (~8-min irradiation) spectrum γ was obtained. Lines 1–8 correspond in chemical shifts and coupling constant to the A_2B spectrum of the benzylic protons in 1,1,2-triphenylethane (IVa). Lines a and b in Figure 1β and 1γ are caused by the benzylic protons of Va and VI, respectively. Equivalently polarized spectra were obtained with mesitylene (IIIb). Solvents with benzylic methylene groups such as methyl phenylacetate (IIIc) and benzyl cyanide (IIId) also gave strongly polarized spectra originating from IVc and IVd, respectively. In the latter compounds the benzylic protons give AB quartets with positive polarizations of lines 1 and 3 and negative polarization for transitions 2 and 4 (labeling the transitions in a sequence of increasing field).



$$(C_6H_5)_2CN_2 \xrightarrow{h\nu} (C_6H_5)_2C: \quad \text{I} \qquad \text{II}$$

$$\text{II} + \underset{\text{III}}{ArCH_2X} \longrightarrow \underset{\text{IV}}{(C_6H_5)_2CH\underset{|}{\underset{X}{C}}HAr} + \underset{\text{V}}{Ar\underset{X}{\underset{|}{C}}H\underset{X}{\underset{|}{C}}HAr} + \underset{\text{VI}}{(C_6H_5)_2CHCH(C_6H_5)_2}$$

a, Ar = C_6H_5; X = H
b, Ar = 3,5-$(CH_3)_2C_6H_3$; X = H
c, Ar = C_6H_5; X = $COOCH_3$
d, Ar = C_6H_5; X = CN

The polarization (P) is defined as $P = (\langle I_z \rangle - \langle I_z \rangle_0)/\langle I_z \rangle_0$ where $\langle I_z \rangle$ and $\langle I_z \rangle_0$ are the expectation values of the nuclear spins in the polarized states and at thermoequilibrium.[8,9] At sufficiently high concentrations (>1% w/v) the photochemical reaction rate is independent of the concentration of I, and the steady-state concentration of polarized IVa is given by $[\text{IVa}^*]_s = nk_LT_1$, where k_L is the zero-order rate for the decomposition of I, n is the fraction of IVa produced (yield), and T_1 is the nuclear spin lattice relaxation time of IVa. Independent measurements of these parameters ($n = 0.40$, $k_L = 4.0 \times 10^{-4}$ M sec^{-1}, $T_1 = 2.2$ sec) gives $[\text{IVa}^*]_s = 3.53 \times 10^{-4}$ M. Intensity comparisons with a standard solution of IVa gives a polarization for lines 1 and 4 of $|P| = 760 \pm 100$.

Polarized spectra of IVb–d were also obtained by thermally decomposing I in IIIb–d at 140° (*e.g.*, Figure 2). The signal-to-noise ratios of these spectra were up to one order of magnitude larger than in the photochemical reaction because larger steady-state concentrations of polarized compounds were easily obtainable by increasing the concentration of I and accelerating the rate of its decomposition. The signs and relative intensities of the various transitions in the polarized spectra were identical with those obtained in the corresponding photochemical reactions.

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

[2] (a) J. Bargon and H. Fischer, *Z. Naturforsch.*, **22a**, 1551, 1556 (1967); (b) H. R. Ward and R. G. Lawler, *J. Am. Chem. Soc.*, **89**, 5518 (1967); (c) H. R. Ward, R. G. Lawler, and H. Y. Loken, *ibid.*, **90**, 7361 (1968); H. R. Ward, R. G. Lawler, and R. A. Cooper, *ibid.*, **91**, 746 (1969); (d) A. R. Lepley, *ibid.*, **90**, 2710 (1968); A. R. Lepley and R. L. Landau, *ibid.*, **91**, 748 (1969); (e) R. Kaptein, *Chem. Phys. Lett.*, **2**, 261 (1968).

[3] R. G. Lawler, *J. Am. Chem. Soc.*, **89**, 5519 (1967).

[4] M. Cocivera, *ibid.*, **90**, 3261 (1968).

[5] Cocivera[4] observed nuclear polarizations originating from photoexcited states of certain quinones without net chemical reaction.

[6] For a summary of references, see G. L. Closs, "Topics of Stereochemistry," Vol. 3, John Wiley & Sons, Inc., New York, N. Y., 1968, pp 198–203.

[7] W. Kirmse and L. Horner, *Ann.*, **625**, 34 (1959).

[8] The polarization equals the spectra enhancement factor (F) when the radiofrequency field amplitude is not markedly altered by resonance of the polarized nuclei. That this condition is met can be seen by comparing the relative intensities of transitions 1 and 4 which, except for different signs, are the same as in the unpolarized compound.

[9] For a review on dynamic nuclear polarization, see K. H. Hausser and D. Stehlik, *Advan. Magnetic Resonance* 3, 79 (1968).

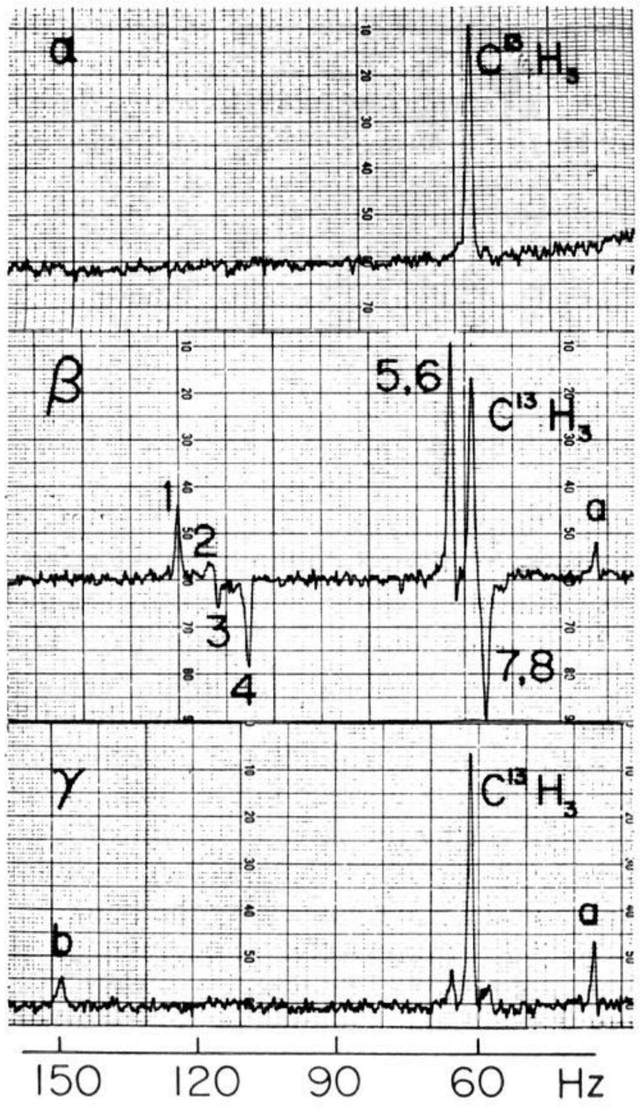
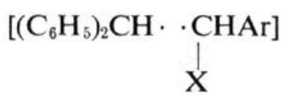


Figure 1. Nmr spectra of a solution of I (0.06 *M*) in toluene at 30°; (α) no light; (β) light admitted; (γ) after 10 min of irradiation. Chemical shifts are in hertz downfield from solvent CH_3.

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.

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.

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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.

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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).