While the physical, spectroscopic, and chemical evidence presented suggests strongly that the compounds which we report here do indeed contain the silacyclopropane ring, ultimate proof of this will be given only by an X-ray crystal-structure determination. We are continuing work in this area. The ring cleavage and ring insertion reactions of III, VIII, and IX are under investigation. Other bulky substituents are being examined for their application in the stabilization of the SiC_2 ring and extension of this new chemistry to other metallacyclopropanes also is in progress. Prelimiary results suggest that the germacyclopropane ring can be stabilized in similar fashion.[10]

Acknowledgments. The authors are grateful to the U. S. Air Force Office of Scientific Research (NC)-OAR for generous support of this work (Grant No. AF-AFOSR-72-2204), to Dr. D. D. Traficante for the ^{13}C nmr spectra, Professor G. E. Maciel for the ^{29}Si nmr spectra, Dr. C. Hignite for the high-resolution mass spectra, and Dr. Kurt L. Loening for advice on nomenclature.

(10) D. Seyferth and M. Massol, unpublished work.

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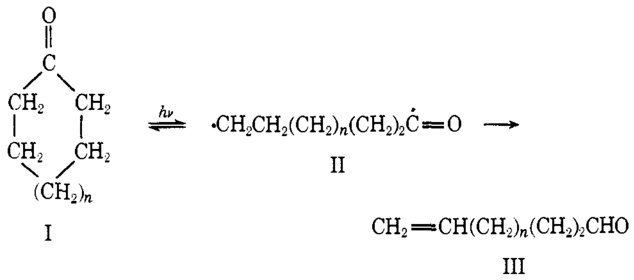
Chemically Induced Dynamic Nuclear Spin Polarization Derived from Biradicals Generated by Photochemical Cleavage of Cyclic Ketones, and the Observation of a Solvent Effect on Signal Intensities[1]

Sir:

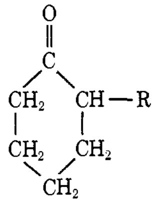
Previously we have given a qualitative discussion of the theory of chemically induced dynamic nuclear spin polarization (CIDNP) applied to reactions proceeding through diradical intermediates.[2] The important difference of CIDNP derived from biradicals and the much more common radical pair based CIDNP is the absence of diffusive separation of the correlated electron spins in the former.[3] To observe CIDNP in either system it is necessary that one of the triplet substates be nearly degenerate with the zero-order singlet state for a time sufficiently long for the wave function to evolve. In radical pairs at high fields the rapidity of diffusive separation assures a vanishing scalar exchange coupling ($2J$) between the components of the pair, leading to degeneracy of T_0 ($|1,0\rangle$) and S ($|0,0\rangle$) states. Mixing between these states *via* the small hyperfine interactions does not involve any change in the z components of the nuclear spin angular momentum. A competitive process such as diffusion is therefore necessary to observe polarization *via* spin selection.

In biradicals, however, it is possible that the mean singlet–triplet splitting, $\langle 2J \rangle$, approaches the electron Zeeman splitting ($g\beta H_0 \sim \langle 2|J| \rangle$) and leads to near degeneracy between the $T_\pm$ ($|1,1\pm\rangle$) and S states. According to the selection rule, $\Delta(m_z)_s = -\Delta(m_z)_I$, $T_\pm$–S mixing leads to net nuclear spin flips and thus does not require diffusion or other competitive processes. Some flexibility to meet the required conditions is given by the possibility of adjusting the magnetic field to the residual exchange coupling in the biradical. However, a further restriction is imposed by the requirement to generate the biradical from a triplet precursor because only then does a net intersystem crossing occur between the biradical and the product ground state. These rather severe limitations are the reasons that only very few biradical reactions have been reported to exhibit CIDNP signals.[2,4]

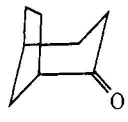
In this communication we wish to give examples of simple biradicals which meet the conditions specified above and give CIDNP spectra in their products.[5] When the cyclic ketones Ib–Ie were irradiated in chloroform, strong emission signals were observed for the reactants (Ib–Ie) and their products (IIIb–IIIe).[6]



a, $n = 1$
b, $n = 2$
c, $n = 3$
d, $n = 4$
e, $n = 5$



IVa, R = CH_3
IVb, R = C_6H_5



V

Specifically the signals were assigned to the α and β protons of I and the olefinic and aldehyde protons of III. A typical spectrum, that of irradiated cycloheptanone (Ib), is shown in Figure 1. The fact that all transitions are in emission, regardless of the absolute signs of the hyperfine coupling of the corresponding protons in II, constitutes good evidence for T_-–S

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[1] Supported by grants from the Petroleum Research Fund (3965-C4), administered by the American Chemical Society, and the National Science Foundation (GP 18719X).

[2] G. L. Closs, *Ind. Chem. Belg.*, **36**, 1064 (1971); see also G. L. Closs, *J. Amer. Chem. Soc.*, **93**, 1546 (1971); J. F. Garst, R. M. Cox, J. T. Barbas, R. D. Roberts, J. I. Morris, and R. C. Morrison, *ibid.*, 92, 5761 (1970).

[3] For recent reviews on CIDNP see: G. L. Closs, *Proc. Int. Congr. Pure Appl. Chem., XXIIIrd, Spec. Lect.*, **4**, 19 (1971); H. R. Ward, *Accounts Chem. Res.*, **5**, 18 (1972); R. G. Lawler, *ibid.*, **5**, 25, (1972); R. Kaptein, Dissertation, Leiden, 1971; H. Fischer, *Fortschr. Chem. Forsch.*, 24, 1 (1971).

[4] R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **12**, 16 (1971), have observed signals arising from large biradicals. In these cases, however, competing, spin independent, intermolecular reactions were possible and thus the normal T_0-S mixing mechanism can account for the observed spectra.

[5] The ^{13}C CIDNP spectra of an almost identical series of compounds have recently been observed by R. Kaptein (private communication).

[6] The ketones were irradiated inside a modified probe of an HA-60 nmr spectrometer with the condensed beam of a 1000-W xenon–mercury lamp (optics, $f = 1$). Although a quartz insert and nmr tube gave somewhat more intense spectra, the effect was also observable in Pyrex equipment.

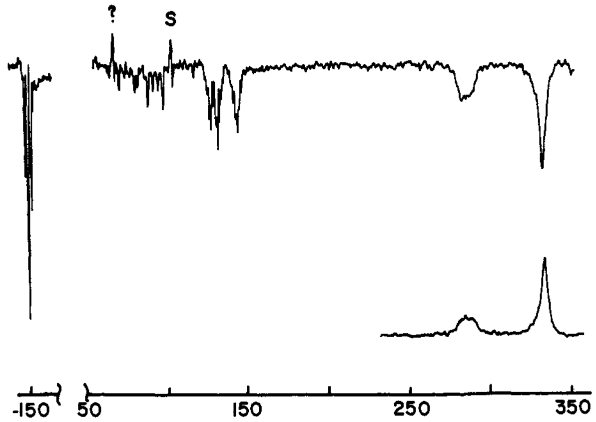

Figure 1. Spectra of 0.14 *M* cycloheptanone in chloroform at 60 MHz: lower trace, dark spectrum; upper trace, spectrum obtained during irradiation. Chemical-shift scale is in hertz from $CHCl_3$. S denotes ^{13}C satellite of solvent.

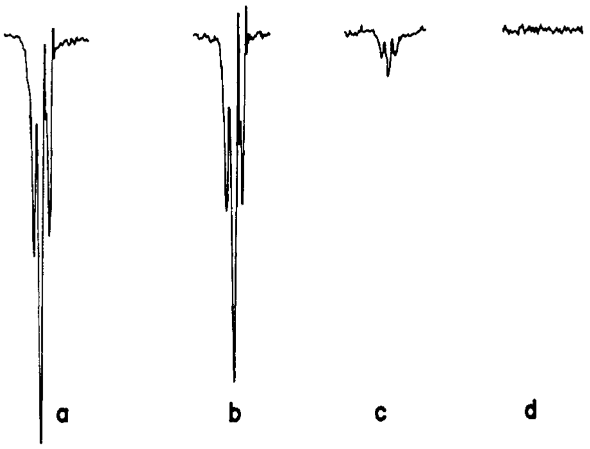

Figure 2. Aldehyde proton signal of IIIb in: (a) $CHCl_3$; (b) CH_2Cl_2; (c) cyclohexane; (d) benzene.

intersystem crossing in II. As has been pointed out previously,[2] $T_\pm$–S mixing, in contrast to T_0–S mixing, does not depend on the signs of the hyperfine couplings nor on any differences in the *g* factor of the individual electron spins.

Comparison of the signal intensities of the olefinic and aldehyde protons in III with those of the α and β protons in I, after correction for the nuclear relaxation times, is a direct measure of the ratio of forward and return reaction. For Ib a value of 3 ± 1:1 was found in favor of regenerating starting material.[7,8]

Most interesting is the observation of a strong solvent effect on the signal intensities. Figure 2 shows that the intensities of the aldehyde proton in IIIb decrease with the solvent sequence $CHCl_3$, CH_2Cl_2, C_6H_{12}, with no observable signal in benzene. In chloroform–benzene mixtures, 1 *M* benzene results in a sixfold reduction in signal intensity while the reaction rate is only diminished by a factor of two. We believe this effect to be a reflection of the average singlet–triplet splitting between the zero-order states.[9] Solvent–diradical interaction may lead to preferential stabilization of either the singlet or triplet state. At present we prefer not to speculate on the nature of this interaction.

As expected, variation of ring size and structure has a large influence on the CIDNP signal intensities. While cyclohexanone (Ia) showed no detectable emission, very weak aldehyde proton emissions were observable from 2-methyl- (IVa) and 2-phenylcyclohexanone (IVb). The maximum signal intensity was observed for cycloheptanone (Ib), with decreasing intensities for Ic–e. Presumably this is at least in part[10] a reflection of the decreasing singlet–triplet splitting with increasing chain length of the biradical. A maximum signal is expected for the intermediate with the closest match of the Zeeman and singlet–triplet splittings.

That the average exchange coupling is not only dependent on the formal length of the chain but also on structural features is demonstrated rather convincingly by the strong signals obtained from bicyclo[3.2.1]-octanone (V) which gives a 1,6 diradical, and the weak but easily detectable signal from camphor in which a 1,5 diradical is the intermediate. The bridging in the biradicals derived from the latter two compounds is presumably preventing an easy approach of the two ends.

Determination of the magnetic field dependence of signal intensities should give information in the scope and limitations of CIDNP as a tool to study biradicals. Such experiments are in progress.

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[7] The large uncertainty may have its origin in the fact that the relaxation times prevailing during the reaction can be expected to differ substantially from those measured on the static compounds. The reason for this discrepancy is the presence of a relatively high steady-state concentration of free radicals during the reaction.

[8] P. J. Wagner and R. W. Spoerke, *J. Amer. Chem. Soc.*, **91**, 4437 (1969), deduced the reversibility of the reaction by quantum yield studies; see also W. C. Agosta and W. L. Schreiber, *ibid.*, **93**, 3947 (1971).

[9] A solvent dependence of the magnitude of exchange interactions has previously been noted by S. Glarum, *J. Chem. Phys.*, **47**, 1374 (1967).

[10] The type I cleavage becomes less pronounced with increasing ring size of the cyclic ketones and therefore part of the reduction in signal intensities must be attributed to a diminished quantum yield.

Detection of Trace Amounts of Sodium by Fluorescence Emission Excited by a Continuous Wave Organic Dye Laser

Sir:

Organic dye lasers have been used by several workers to increase the detectability of trace amounts of materials.[1-6] The high intensity of a continuous wave (cw) dye laser concentrated in a line width comparable to atomic and ionic absorption widths combined with its highly directional properties and tunability makes it an excellent source for fluorescence excitation.[7] In this communication, we describe the use of a cw organic

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[1] N. C. Peterson, M. J. Kurylo, W. Braun, A. M. Bass, and R. A. Keller, *J. Opt. Soc. Amer.*, **61**, 746 (1971).

[2] R. A. Keller, E. F. Zalewski, and N. C. Peterson, *ibid.*, **62**, 319 (1972).

[3] R. J. Thrash, H. Von Weyssenhoff, and J. S. Shirk, *J. Chem. Phys.*, **55**, 4659 (1971).

[4] M. B. Denton and V. H. Malmstadt, *Appl. Phys. Lett.*, **18**, 485 (1971).

[5] L. M. Fraser and J. D. Winefordner, *Anal. Chem.*, **43**, 1694 (1971); **44**, 1444 (1972).

[6] J. Kuhl and G. Marowsky, *Opt. Commun.*, **4**, 125 (1971).

[7] For a review of cw dye lasers, see A. L. Bloom, *Opt. Eng.*, **11**, 5 (1972), and references cited therein.