Tetrahedron. Vol. 33, pp 211 to 215. Pergamon Press 1977. Printed in Great Britain

CIDNP STUDY OF THE PHOTOREDUCTION OF BENZOPHENONE WITH SECONDARY ALCOHOLS

J. A. DEN HOLLANDER,* A. J. HARTEL and P. H. SCHIPPERS
Department of Theoretical Organic Chemistry, University of Leiden, P.O. Box 75, Leiden, The Netherlands

(*Received in UK* 29 *April* 1976; *Accepted for publication* 2 *August* 1976)

Abstract—CIDNP has been studied during the photoreduction of benzophenone in the presence of isopropanol and benzhydrol. Since the hydrogen transfer reaction of the dimethyl hydroxy methyl radical with benzophenone competes with geminate recombination of radical pairs, the rate of this reaction step could be determined from CIDNP experiments. A discussion is given about the unexpected net CIDNP effects observed during the photoreduction in the presence of benzhydrol. There is no evidence that this polarization arises by a triplet mechanism.

Since the original discovery of Ciamician and Silber[1] of the action of light on the reduction of benzophenone many investigations have been devoted to the elucidation of the mechanism of this photoreaction.[2,3] It has been established that the primary step of the photoreduction is a hydrogen abstraction reaction of triplet benzophenone from the alcohol (used as a solvent), followed by a hydrogen transfer reaction (Scheme 1).

$$\mathrm{ArAr'CO^{(T)} + RR'CHOH \rightarrow ArAr'\dot{C}OH + RR'\dot{C}OH}$$

$$\mathrm{RR'\dot{C}OH + ArAr'CO \rightarrow ArAr'\dot{C}OH + RR'CO}$$

Scheme 1.

The diarylhydroxy methyl radicals formed can combine to pinacol.

Some aspects of the photoreduction are still the subject of discussions. Recently it has been found that the ketyl radicals show electron polarization (CIDEP) immediately after their formation.[4] CIDNP studies of the photoreduction of benzophenone with hydrocarbons as hydrogen donors have been reported some years ago.[5] In addition CIDNP studies have been presented of the photoreduction of acetophenone with phenol[6] and of benzophenone with amines.[7]

Although it is generally accepted that the published CIDNP spectra can be readily interpreted by the Radical Pair Theory,[8] it has nevertheless been proposed recently that for photochemical reactions a triplet mechanism contributes to CIDNP,[9] by analogy to the triplet mechanism of CIDEP.[10] This mechanism has been successfully applied to the interpretation of electron polarization in solution. Since electron polarization is known to occur during the phororeduction of benzophenone this system is chosen to investigate the possible occurrence of a triplet mechanism of CIDNP.

We studied the photoreduction of several benzophenones with a variety of aliphatic alcohols and aldehydes as hydrogen donor. As a representative example we will discuss the photoreduction of benzophenone in the presence of isopropanol and of benzhydrol. Both the mechanistic aspects of the photoreduction and the possible occurrence of a triplet mechanism of CIDNP received attention. In particular the hydrogen transfer reaction (Scheme 1) has been studied.

Photoreduction of benzophenone in the presence of isopropanol

Figure 1 shows the NMR spectra of 0.05 M benzophenone and 0.1 M isopropanol in hexadeutero benzene. During UV irradiation CIDNP is observed for the parent compounds benzophenone (o-H(7.65–7.95 ppm) and p-H(6.75–7.20 ppm), A) and isopropanol (C$\underline{H}_3$ (0.90 ppm, A), C$\underline{H}$ (3.60–3.90 ppm, E), O$\underline{H}$ (0.70 ppm, E)) and for the products acetone (1.55 ppm, E) and benzopinacol (o-H (7.30–7.55 ppm, E + E/A) O$\underline{H}$ (2.80 ppm, E)). After irradiation the benzophenone has disappeared, and in the NMR spectra benzopinacol, acetone and the excess isopropanol show up. The polarizations of both isopropanol and acetone are readily explained by the reaction sequence given in Scheme 2. The polarizing pair is the diphenylhydroxy methyl/dimethylhydroxy methyl radical pair (Pair I). (ESR parameters diphenylhydroxy methyl:[11] $g = 2.00298$, $A_H(\text{o-H}) = -3.23$ Gauss, A_H (p-H) $= -3.69$, $A_H(\text{m-H}) = 1.24$, and $A_H(\text{OH}) = 3.42$; for the dimethylhydroxy methyl radical:[22] $g = 2.00309$ and $A_H(CH_3) = +19.57$ Gauss). The polarizations observed for the parent compound isopropanol establish that the radical pair can disproportionate to isopropanol and benzophenone, this in contrast to Weiner's assumption[3] that this process can be eliminated. We did not observe the cage product proposed by this author. The regeneration of parent compounds need not be in conflict with the high quantum yield measured for this photoreduction, since the disproportionation will have a low efficiency for a triplet radical pair. The emissions observed for the OH and methine proton of isopropanol demonstrate that the hyperfine interaction for the OH proton of the diphenylhydroxy methyl radical is positive (indicating that the OH proton is predominantly out of the plane of the molecule) and that of the dimethylhydroxy methyl radical negative (OH in the plane of the molecule).

The polarizations observed for the protons of benzopinacol and benzophenone are not easily interpreted according to Scheme 2. The polarizations of these compounds being similar to those obtained during the irradiation of benzophenone in the presence of benzhydrol suggests a common origin (cf. Section 4).

Hydrogen transfer reaction

The emission observed for acetone during the photoreduction of benzophenone in the presence of isopropanol

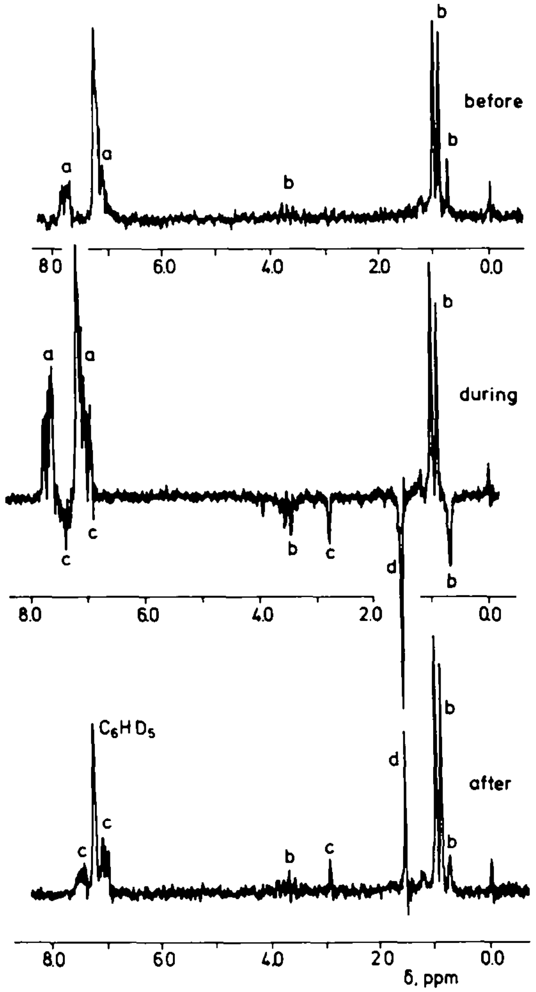


Fig. 1. 60 Mc NMR spectra obtained before, during and after UV irradiation of 0.05 M benzophenone and 0.1 M isopropanol in C_6D_6 (a) benzophenone, (b) isopropanol, (c) benzopinacol; (d) acetone.

is caused by singlet-triplet evolution in Pair I. Its lifetime is limited by the rapid hydrogen transfer reaction of the dimethylhydroxy methyl radical with benzophenone (Scheme 2). Therefore the enhancement factor for the acetone signal reflects the lifetime of this radical and can be used for determination of the rate of the transfer reaction. The radical disappears with the pseudo first order rate k determined by the benzophenone concentration and the second order rate constant k_t of the transfer reaction:

$$k = k_t[B] \qquad (1)$$

in which [B] represents the benzophenone concentration.

$$Ph_2CO \xrightarrow{h\nu} Ph_2CO^{(S_1)} \rightarrow Ph_2CO^{T}$$

$$\big\downarrow {\scriptstyle Me_2CHOH}$$

$$Me_2CHOH + Ph_2CO \leftarrow \overline{Me_2\dot{C}OH \quad Ph_2\dot{C}OH}$$

$$\big\downarrow {\scriptstyle Ph_2CO}$$

$$Me_2CO + Ph_2\dot{C}OH$$

$$Ph_2\dot{C}OH + Ph_2CO \rightleftarrows Ph_2CO + Ph_2\dot{C}OH$$

Scheme 2.

We showed[13] that the recombination probability of a triplet radical pair for a nuclear state |n⟩ is given by:

$$P_{T_n} = \frac{1}{6}\lambda m\sqrt{(2\pi)}\{\sqrt{(\sqrt{(k^2+4a_n^2)}+k)}-\sqrt{(2k)}\} \qquad (2)$$

in which k is the total rate of scavenging for the radical pair; λ is the recombination probability during a singlet collision of the radical pair; a_n the singlet-triplet mixing coefficient determined by g-factor difference and hyperfine interactions; and $m \simeq 10^{-6}\,sec^{1/2}$. For the escape product acetone we obtain for the formation probability:

$$D_{T_n} = 1 - P_{T_n}. \qquad (3)$$

For a multispin system the total probability of finding a certain nuclear spin state of a given nucleus can be evaluated by summing over all spin states of the other nuclei:

$$D_{T\alpha} = \Sigma'_{n'}(1 - P_{T\alpha n'})$$
$$D_{T\beta} = \Sigma'_{n'}(1 - P_{T\beta n'}). \qquad (4)$$

The theoretical enhancement factor for the nucleus under consideration is now given by:

$$V = \frac{D_{T\alpha} - D_{T\beta}}{D_{T\alpha} + D_{T\beta}}\,\frac{2kT}{g_N\beta_N H_0}. \qquad (5)$$

Experimental enhancement factors were determined according to Lehnig and Fischer.[14] We monitored the acetone signal by repetitive scanning before, during and after irradiation of the sample (Fig. 2). The signal intensity measured after irradiation is I_0. Using this intensity and the total irradiation time t′ we correct the intensities measured during irradiation for product formation. The light was attenuated and only a small amount of benzophenone disappears during irradiation, the corrected intensities during irradiation (I) are now constant over the irradiation time. The enhancement factor is determined by:

$$V = \frac{It'}{I_0T_1}. \qquad (6)$$

T_1 is the spin-lattice relaxation time for the product during irradiation. The relaxation time was determined from the buildup of the acetone signal after the admission of light had been started, and was found to be 12(±1) sec. We found no significant dependence on the benzophenone concentration for this relaxation time, and we used in the analysis a constant value for T_1.

We determined the enhancement factor for acetone as formed during the photoreduction with 0.2 M isopropanol in hexadeutero benzene as a function of the benzophenone concentration. To study the isotope effect the experiment was carried out using isopropanol-OH and isopropanol-OD. The theoretical curve for the enhancement factor (as a function of the benzophenone concentration) as given by eqns (1)–(5) was fitted to the experimental points by a least squares procedure, yielding values for the rate constant k_t for the transfer reaction and for the product (λ m) (Table 1). In the least squares fit all nuclei were taken into account (Fig. 3).

The results show that the product (λ m) is the same for the two systems within experimental error. This is

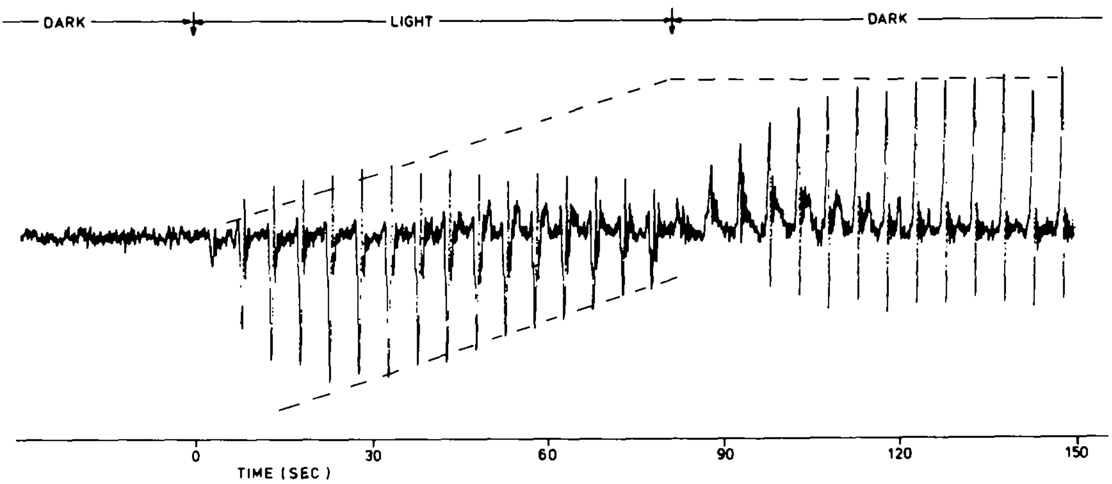


Fig. 2. The acetone signal before, during and after irradiation. The intensity during irradiation has been corrected for product formation (broken lines).

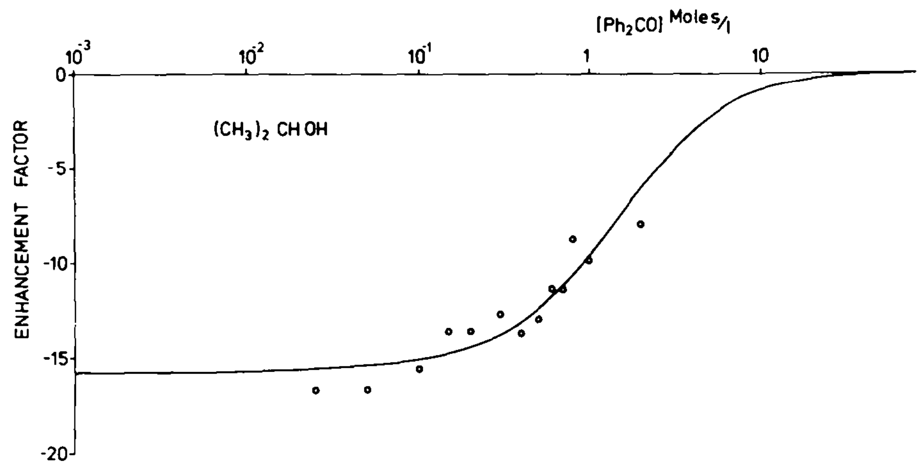


Fig. 3. Experimental enhancement factors of acetone during the irradiation of benzophenone with 0.2 M isopropanol-OH. The curve represents the theoretical calculations using optimized parameters.

Table 1. Rate constants of the hydrogen transfer reaction

hydrogen donor	$\log k_t (M^{-1} sec^{-1})$	$(\lambda m)(sec^{1/2})(\times 10^{-6})$
isopropanol-OH	8.44 (±0.06)	1.07 (±0.04)
isopropanol-OD	8.18 (±0.07)	1.08 (±0.04)

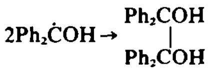
according to expectation since the deuterium substitution can have only a minor influence on both the diffusive behaviour (reflected by m) and the reactivity parameter λ for the disproportionation reaction. The ratio of the rate constants for the hydrogen and for the deuterium transfer reaction is found to be 1.8. This low value of the isotope effect on the rate constant is not unreasonable in view of the high rate of the transfer reaction. The values found are much higher than those reported for aqueous solution.[15] The difference is probably due to hydrogen bond formation of the dimethylhydroxy methyl radicals in aqueous solution.

Variation of acetone CIDNP intensity with 1,4-benzoquinone concentration in isopropanol during irradiation has been reported by Vyas *et al.*[16] These authors, however, did not analyse their data. CIDNP intensities cannot be used in our analysis, but if the decay of the curve is due to the hydrogen transfer reaction of dimethylhydroxy methyl with 1,4-benzoquinone the rate of this reaction is in the order of $10^9\ M^{-1}\ s^{-1}$. This value is not unreasonable in view of the reported values.[15]

Photoreduction of benzophenone in the presence of benzhydrol

During the irradiation of benzophenone and benzhydrol in hexadeutero benzene we obtained the NMR spectrum of Fig. 4. We observe enhanced absorption for the phenylprotons of the parent compound benzophenone and emission for the phenylprotons and the hydroxylproton of the product pinacol. These observations cannot be explained by Scheme 3. Recombination of a symmetrical radical pair can only give rise to multiplet effects in CIDNP[18] and not to the net effects observed. The polarizations for benzophenone and for benzopinacol are

$$Ph_2CO \xrightarrow{h\nu} Ph_2CO^{(S_1)} \rightarrow Ph_2CO^{T} \xrightarrow{Ph_2CHOH} 2Ph_2\dot{C}OH$$



$$2Ph_2\dot{C}OH \rightarrow \begin{array}{c} Ph_2COH \\ | \\ Ph_2COH \end{array}$$

$$Ph_2\dot{C}OH + Ph_2CO \rightleftarrows Ph_2CO + Ph_2\dot{C}OH$$

Scheme 3.

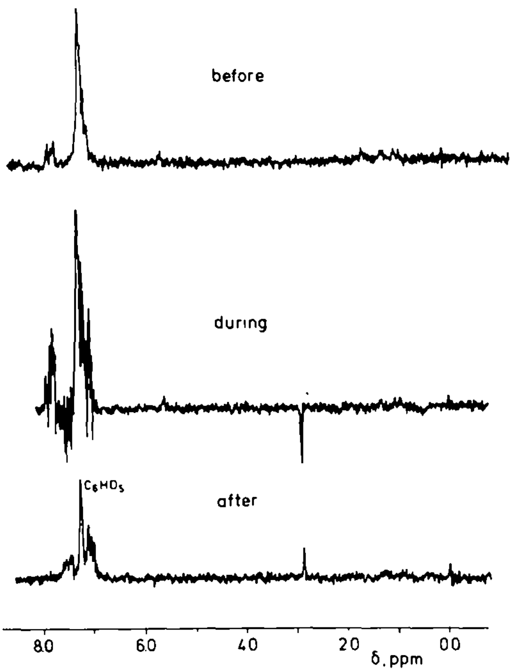


Fig. 4. 60 Mc NMR spectrum obtained before, during and after the irradiation of 0.05 M benzophenone with 0.05 M benzhydrol in C_6D_6 (CH benzhydrol 5.57 ppm, OH benzopinacol 2.85 ppm).

similar for the present system and for the photoreduction of benzophenone in the presence of isopropanol (Section 2), which suggests that the polarizations in the two systems have a common origin.

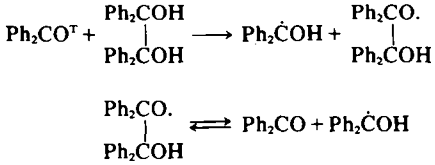
We checked the possibility that the polarizations observed could be due to radicals formed by reaction of triplet benzophenone either with ground state benzophenone or with the solvent deutero benzene[17] by performing an experiment in the absence of either benzhydrol or isopropanol. We failed to detect polarizations, indicating that such reactions were unimportant under our conditions. Moreover, in the presence of a hydrogen donor the benzophenone was consumed within a few minutes, whereas in the absence of a hydrogen donor we could not detect products in the NMR spectrum after the limited irradiation time used for these experiments.

We found some dependence of the CIDNP signals on the solvent used (we tried C_6F_6, $CFCl_3$ and $CFCl_2$–CF_2Cl). The OH emission for benzopinacol was only detected for C_6D_6 solutions, but net effect in the aromatic region was also observed for other solvents.

Polarizations observed during photoreactions of p-benzoquinones, diazanaphthalenes and pyruvic acid have been ascribed recently to a triplet mechanism,[9] and not to the well established radical pair mechanism of CIDNP.[8] Especially the pyruvic acid system bears some analogy with the photoreduction of benzophenone in the presence of benzhydrol. We performed low-field CIDNP experiments for the OH proton of benzopinacol in order to check this possibility,[16] but we did not succeed in this attempt.

In our view the polarizations in the present system should on the basis of the observed opposite polarization for the phenyl protons of benzophenone and those of benzopinacol be ascribed to a radical pair mechanism. This opposite polarization, while it is a basic consequence of the radical pair mechanism for recombination and escape products,[18] is not easily explained by a triplet mechanism. The OH emission for the pinacol is impossible to explain by a triplet mechanism, since this nucleus is not present in the triplet benzophenone molecule. A cross-relaxation mechanism could be responsible for this emission, but such a mechanism is unlikely.[19]

Therefore we are of opinion that the observation of net CIDNP effects in the present system shows that radicals other than the diphenylhydroxy methyl radical occur. Presently it is not possible to identify this intermediate radical. It is clear however that it must be a short living radical occuring in much lower concentration than the diphenylhydroxy methyl radical, because in the ESR spectra only the latter radical shows up. One possibility is the radical proposed by Pitts et al.[2] (Scheme 4). Another possibility is the complex formation of the diphenylhydroxy methyl radical with benzophenone proposed by Schenck et al.[3] We also performed an experiment of benzophenone in the presence of the corresponding pinacol ("Umpinakolisierung"[3]). Also in this case the hydroxyl proton of the pinacol showed emission during the irradiation; the primary step is hydrogen abstraction from the pinacol (Scheme 5).



$$Ph_2CO^T + \begin{array}{c} Ph_2COH \\ | \\ Ph_2COH \end{array} \longrightarrow Ph_2\dot{C}OH + \begin{array}{c} Ph_2CO\cdot \\ | \\ Ph_2COH \end{array}$$

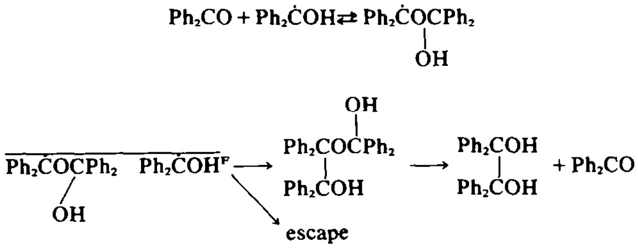
$$\begin{array}{c} Ph_2CO\cdot \\ | \\ Ph_2COH \end{array} \rightleftharpoons Ph_2CO + Ph_2\dot{C}OH$$

Scheme 5.

The intermediate appearing in this scheme offers another possible explanation for the observed effects. However, this radical is likely too short-lived to affect the CIDNP in the products.

CONCLUSION

CIDNP offers the possibility to study the dynamical properties of short-lived radical intermediates. By measuring the enhancement factor for acetone formed



$$Ph_2CO + Ph_2\dot{C}OH \rightleftharpoons \begin{array}{c} Ph_2\dot{C}OCPh_2 \\ | \\ OH \end{array}$$

$$\overline{\begin{array}{c} Ph_2\dot{C}OCPh_2 \\ / \\ OH \end{array} \quad Ph_2\dot{C}OH}^{F} \longrightarrow \begin{array}{c} OH \\ | \\ Ph_2COCPh_2 \\ | \\ Ph_2COH \end{array} \longrightarrow \begin{array}{c} Ph_2COH \\ | \\ Ph_2COH \end{array} + Ph_2CO$$

$$\searrow \text{escape}$$

Scheme 4.

during the photoreduction of benzophenone in the presence of isopropanol we determined the rate constant of the hydrogen transfer reaction of the dimethylhydroxy methyl radical with benzophenone. In benzene solution this transfer is found to be much faster than the values reported for hydrophilic solutions, which may reflect the difference in solvatation for the radical in the two solvents.

From the CIDNP experiments we found evidence that the dimethylhydroxy methyl radical can react with the diphenylhydroxy methyl radical to the starting material isopropanol and benzophenone, a novel reaction step. CIDNP found during the irradiation of benzophenone with benzhydrol revealed the presence of short-lived radical intermediates other than the diphenylhydroxy methyl radicals. No evidence for the occurrence of a triplet mechanism for CIDNP was found.

Acknowledgements—We thank Prof. F. J. Adrian for communicating results prior to publication. We wish to thank the Netherlands Organization for the Advancement of Pure Research (Z.W.O.) for financial support.

REFERENCES

[1] G. Ciamician and P. Silber, *Ber. Dtsch. Chem. Ges.* **33**, 2911 (1900); **34**, 1541 (1901).

[2] J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald and R. B. Martin, *J. Am. Chem. Soc.* **81**, 1068 (1959); A. Beckett and G. Porter, *Trans. Farady Soc.* 2038 (1963); J. G. Calvert and J. N. Pitts, Jr., *Photochemistry*, pp. 532–536. Wiley, New York (1966).

[3] G. O. Schenck, M. Cziesla, K. Eppinger, G. Matthias and M. Pape, *Tetrahedron Letters* 193 (1967); N. Filipescu and F. L. Minn, *J. Am. Chem. Soc.* **90**, 1544 (1968); G. O. Schenck, G. Koltzenburg and E. Roselius, *Z. Naturforsch.* **24b**, 222 (1969); S. A. Weiner, *J. Am. Chem. Soc.* **93**, 425, 6978 (1971).

[4] P. W. Atkins, *Org. Magn. Res.* **5**, 239 (1973).

[5] G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.* **91**, 4550 (1969).

[6] S. M. Rosenfeld, R. G. Lawler and H. R. Ward, *Ibid.* **95**, 946 (1973).

[7] H. D. Roth and A. A. Lamola, *Ibid.* **96**, 6270 (1974); H. D. Roth and M. L. Manion, *Ibid.* **97**, 6886 (1975).

[8] R. Kaptein, *Advances in Free-Radical Chemistry* (Edited by G. H. Williams). Elek Science, London (1975); G. L. Closs, *Advances in Magnetic Resonance* (Edited by J. S. Waugh). Academic Press, New York (1974).

[9] J. Bargon and K.-G. Seifert, *Ber. Bunsen-Gesells.* **78**, 1180 (1974); G. Vermeersch, N. Febvay-Garot, S. Caplain and A. Lablache-Combier, *Tetrahedron Letters* 2991 (1975); H. M. Vyas and J. K. S. Wan, *Chem. Phys. Letters* **34**, 470 (1975); K. Y. Choo and J. K. S. Wan, *J. Am. Chem. Soc.* **97**, 7127 (1975); H. M. Vyas and J. K. S. Wan, *Can. J. Chem.* **54**, 979 (1976).

[10] J. K. S. Wan, S.-K. Wong and D. A. Hutchinson, *Acc. Chem. Res.* **7**, 58 (1974).

[11] R. Wilson, *J. Chem. Soc* (B), 84 (1968).

[12] R. Livingston and H. Zeldes, *J. Chem. Phys.* **44**, 1245 (1966).

[13] J. A. den Hollander, *Chem. Phys.* **10**, 167 (1975).

[14] M. Lehnig and H. Fischer, *Z. Naturforsch.* **25a**, 1963 (1970); R. Kaptein, *J. Am. Chem. Soc.* **94**, 6251 (1972).

[15] D. A. Nelson and E. Hayon, *J. Phys. Chem.* **76**, 3200 (1972); P. S. Rao and E. Hayon, *Nature* **243**, 344 (1973); E. Hayon and M. Simic, *Acc. Chem. Res.* **7**, 114 (1974).

[16] H. M. Vyas, S.-K. Wong, B. B. Adeleke and J. K. S. Wan, *J. Am. Chem. Soc.* **97**, 1385 (1975).

[17] D. I. Schuster and T. M. Weil, *Ibid.* **95**, 4092 (1973); D. I. Schuster and T. M. Weil, *Mol. Photochem.* **6**, 69 (1974); R. S. Davidson and R. Wilson, *Ibid.* **6**, 231 (1974).

[18] R. Kaptein, *Chem. Comm.* 732 (1971).

[19] F. J. Adrian, *Chem. Phys. Letters* **26**, 437 (1974); G. L. Closs, *Ibid.* **32**, 277 (1975); F. J. Adrian, H. M. Vyas and J. K. S. Wan, *J. Chem. Phys.* **65**, 1454 (1976).