Table IV
Quadrupole Polarizability of CH_4

Q, Å^4	Source
1.57	This work
2	IR line broadening in CH_4-Ar[a]
2.71	Proton spin relaxation in CH_4-He[b]
0.88	Proton spin relaxation in CH_4-Ne[b]
0.89	Proton spin relaxation in CH_4-Ar[b]

[a] C. G. Gray, *J. Chem. Phys.*, **50**, 549 (1969). [b] S. Rajan, K. Lalita, and S. V. Babu, *J. Magn. Reson.*, **16**, 115 (1974).

mental data on the induced quadrupole moment. The quadrupole moment Θ of a system of charges e_k located at positions $\mathbf{r}_k$ can be defined, following Buckingham,[30] by eq 17. In our model, the ith atom may be assigned

$$\Theta = {}^1/_2 \sum_k e_k(3\mathbf{r}_k\mathbf{r}_k - \mathbf{r}_k{}^2\mathbf{I}) \tag{17}$$

a charge e_i at position $\mathbf{r}_i + \delta\mathbf{r}_i$ and a charge $-e_i$ at $\mathbf{r}_i$, so that the induced atom dipole moment is $\mu_i = e_i\delta\mathbf{r}_i$. Then the induced quadrupole moment can be expressed in terms of the induced atom dipole moments. Defining the quadrupole polarizability $\mathbf{Q}$ by $\Theta = \mathbf{Q}\cdot\mathbf{E}$, we find

$$\mathbf{Q} = \sum_{i,j}(\frac{3}{2}\mathbf{r}_i\mathbf{B}_{ij} + \frac{3}{2}\overset{\cap}{\mathbf{r}_i\mathbf{B}_{ij}} - \mathbf{I}\mathbf{r}_i\cdot\mathbf{B}_{ij}) \tag{18}$$

where $\cap$ indicates transposition of the first and second coordinate indices of $\mathbf{r}_i\mathbf{B}_{ij}$.

For the CH_4 molecule one scalar quantity Q is sufficient to specify $\mathbf{Q}$ when the H atoms are located at (d,d,d), $(d,-d,-d)$, $(-d,d,-d)$, and $(-d,-d,d)$, where $d = r_{CH}/3^{1/2}$.[30] The value of Q calculated from eq 18 using the atom polarizabilities in Table I is given in Table IV along with experimental values estimated from data on collisional interactions of CH_4 with rare gas atoms. The agreement is encouraging and suggests once again that the atom dipole interaction model is capable of reproducing some of the rather subtle charge distortions experienced by real molecules in electric fields.

Conclusions and Outlook

The variety of molecular properties which are accounted for at least approximately suggests that the atom dipole interaction model is a reasonable facsimile of real molecules. The model is appealing because it requires relatively little information for practical calculations. It is to be expected that further research on this model will lead to refinements and extensions to other properties. For example, Sundberg[31] has recently extended the theory to include effects due to the nonlinear response of atoms to an applied field. Buckingham and Stiles[32] have considered the role of higher multipole interactions in optical rotation. Both of these developments may well have significant effects on the properties discussed here.

Note Added in Proof. An important test of the atom dipole interaction model which was not mentioned above is its application to the collisional polarizability anisotropy of inert gases. Buckingham and Dunmur[33] have applied the model with partial success to this effect as it applies to the density dependence of the Kerr constant. Oxtoby and Gelbart[34] have improved the predictions of atom pair anisotropies in a related context by replacing point polarizabilities with polarizability densities which are spread over the whole atom.

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(30) A. D. Buckingham, *Adv. Chem. Phys.*, **12**, 107 (1967).

(31) K. R. Sundberg, *J. Chem. Phys.*, in press.

(32) A. D. Buckingham and P. J. Stiles, *Acc. Chem. Res.*, **7**, 258 (1974).

(33) A. D. Buckingham and D. A. Dunmur, *Trans. Faraday Soc.*, **64**, 1776 (1968).

(34) D. W. Oxtoby and W. M. Gelbart, *Mol. Phys.*, **29**, 1569 (1975); **30**, 535 (1975).

Chemically Induced Nuclear Spin Polarization in the Study of Carbene Reaction Mechanisms

Heinz D. Roth

Bell Laboratories, Murray Hill, New Jersey 07974

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Among the synthetically useful intermediates of organic chemistry there are four classes with carbon atoms in other than tetravalent states. In three of these, carbanions, carbon radicals, and carbocations, carbon is trivalent. The fourth class is that of the carbenes, intermediates containing one divalent carbon atom with two nonbonding electrons, i.e., with an electron sextet. Formally, the recorded interest in divalent carbon species goes back to Dumas' attempts to dehydrate methanol;[1] of course, these experiments were carried out well before the quadrivalence of carbon was recognized. Authentic carbene reactions were observed as early as three-quarters of a century ago by Buchner and

Heinz D. Roth was born in Germany and studied chemistry at the Universities of Karlsruhe and Koln, where he received a Dr. rer. nat. degree in 1965 (with Emmanuel Vogel). After spending 2 years in William Doering's laboratory at Yale University he joined the Organic Chemistry Research and Development Department of Bell Laboratories. His research interests include the chemistry and structure of carbenes, the reactions of photochemically generated radical ions, and the application of nuclear magnetic resonance techniques to the study of reaction mechanisms.

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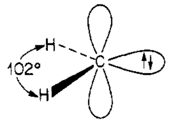
(1) J. B. Dumas, *Ann. Chim. Phys.*, [2] **58**, 28 (1835).

his co-workers in the pyrolysis of ethyl diazoacetate[2] and by Staudinger and his school in the photolysis of ketenes.[3] Renewed interest in carbene chemistry was stimulated by the work of Hine, who postulated dichlorocarbene as an intermediate in the basic hydrolysis of chloroform,[4] and by the work of Doering and Hoffmann, who trapped the postulated species by reaction with cyclohexene.[5] Since then more than 2500 publications dealing with various aspects of carbene chemistry have been published.[6]

Perhaps the most intriguing facet of carbene chemistry is the electronic configuration of the divalent species. Carbenes can exist in two spin multiplicities. In a singlet configuration (**1**) the two nonbonding electrons are paired in an orbital approximating sp^2 character, whereas the fourth orbital, a π orbital, is empty. In a triplet configuration (**2**) the two nonbonding electrons are unpaired, occupying two different orbitals with substantial p character. Singlet carbenes are substantially bent (e.g., $^1CH_2$, $\theta = 102°$),[7] whereas triplet carbenes are closer to linearity although normally still substantially bent (e.g., $^3CH_2$, $\theta = 136°$).[8] Linear structures (**3**), although suggested for several triplet methylenes,[9] appear to be exceptions, e.g., dianthrylmethylene,[10] rather than the rule.



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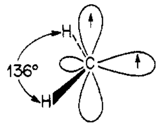

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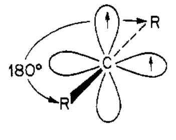

3

Among the characteristic reactions of carbenes are addition to unsaturated bonds and "insertions" into single bonds, such as C–H, C–O, C–Cl, or O–H. To delineate the exact mechanism of one of these reactions typically involves: proving that the reaction indeed proceeds via a carbene; differentiating between one-step (concerted) mechanisms and alternative two-step sequences involving biradicals or radical pairs; and determining the spin multiplicity of the reacting carbene, which might or might not be that of the ground state. Classical mechanistic criteria, particularly the fate of stereochemistry, chirality, or an isotopic label, have been instrumental in establishing the exact mechanisms for reactions of various carbenes with several types of substrates. The spin multiplicity of a carbene can be assigned by spectroscopic techniques under "extreme" conditions. Molecular spectroscopy has been used to identify singlet or triplet carbenes generated by flash photolysis of dilute gaseous systems, and to determine the structures of these species.[11] ESR spectroscopy is a powerful tool for studying carbenes with triplet ground states at low temperatures in inert matrices.[12]

The spin multiplicity of reacting carbenes has been inferred from chemical evidence. Skell and Woodworth introduced the stereospecificity of carbene additions to olefins as a criterion for the spin multiplicity.[13] This method is based on three assumptions: (a) that singlet carbenes exclusively undergo concerted additions; (b) that triplet carbenes add to olefins in a two-step mechanism; and, most importantly, (c) that, in the intermediate 1,3-biradical, rotation is faster than intersystem crossing. Other criteria for the spin multiplicity of a reacting carbene are based on the elegant demonstration by Doering and co-workers that the insertion of methylene into the C–H bond proceeds with retention of absolute configuration[14] and, in the case of allylic C–H bonds, without scrambling of an isotopic label.[15] These reactions are considered characteristic for singlet carbenes whereas "insertions" with loss of optical purity or with scrambling of an isotopic label are ascribed to triplet methylenes. The postulate of Skell and Woodworth and similar assumptions have been extremely fruitful and have prompted much experimental work over more than a decade. DeMore and Benson have criticized the practice of assigning carbene spin multiplicities on the basis of chemical criteria. In their view, the excess energy and not the spin multiplicity of a carbene determines the course of its reaction; retention of stereochemistry or optical purity indicates an intermediate with little or no excess energy, not necessarily a singlet; the loss of optical purity, the scrambling of a label, or randomization of stereochemistry indicates a hot intermediate, not necessarily a triplet carbene.[16] In recent years, theoretical calculations have been directed toward determining the structure, the relative energies, and the reaction mechanisms of simple methylenes. These studies have successfully reproduced the structures of $^1CH_2$ and $^3CH_2$[17] and tend to support the addition and insertion mechanisms[18] proposed by Skell and Doering and their co-workers. Nevertheless, the application of the above-mentioned chemical criteria for assigning spin multiplicities to reacting carbenes is not completely satisfactory.

The CIDNP Method

In the years since 1967, a new technique for the study of radical reactions has been developed. This technique, chemically induced dynamic nuclear polarization (CIDNP), is based on the substantially enhanced NMR signals, in absorption (A) or emission (E), shown by some products of radical reactions immediately after

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(2) E.g., E. Buchner and Th. Curtius, *Ber.*, **18**, 2377 (1885); E. Buchner, *ibid.*, **29**, 106 (1896); **31**, 2241 (1898).

(3) E.g., H. Staudinger and O. Kupfer, *Ber.*, **44**, 2197 (1911); **45**, 501 (1912); H. Staudinger and R. Endle, *ibid.*, **46**, 1437 (1913).

(4) J. Hine, *J. Am. Chem. Soc.*, **72**, 2438 (1950); cf. A. Geuther, *Justus Liebigs Ann. Chem.*, **123**, 121 (1862).

(5) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 2162 (1954).

(6) (a) W. Kirmse, "Carbene Chemistry", 2nd ed, Academic Press, New York, N.Y., 1971; (b) "Carbenes", M. Jones, Jr., and R. A. Moss, Ed., Wiley, New York, N.Y.: Vol. 1, 1973; Vol. 2, 1975.

(7) G. Herzberg and J. Shoosmith, *Nature (London)*, **183**, 1801 (1959); G. Herzberg, *Proc. R. Soc. London, Ser. A*, **262**, 291 (1961).

(8) E. Wasserman, W. A. Yager, and V. J. Kuck, *Chem. Phys. Lett.*, **7**, 409 (1970).

(9) R. M. Etter, H. S. Skovronek, and P. S. Skell, *J. Am. Chem. Soc.*, **81**, 1008 (1959); R. A. Bernheim, R. J. Kempf, J. V. Gramas, and P. S. Skell, *J. Chem. Phys.*, **43**, 196 (1965).

(10) E. Wasserman, V. J. Kuck, W. A. Yager, R. S. Hutton, F. D. Greene, V. P. Abegg, and W. M. Weinshenker, *J. Am. Chem. Soc.*, **93**, 6335 (1971).

(11) G. Herzberg, "The Spectra and Structures of Simple Free Radicals", Cornell University Press, Ithaca, N.Y., 1971.

(12) A. M. Trozzolo and E. Wasserman in ref 6b, Vol. 2, 1975, p 185.

(13) P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956); **81**, 3383 (1959).

(14) L. E. Helgen, Ph.D. Dissertation, Yale University, 1965.

(15) W. von E. Doering and H. Prinzbach, *Tetrahedron*, **6**, 24 (1959).

(16) W. B. DeMore and S. W. Benson, *Adv. Photochem.*, **2**, 217 (1964).

(17) J. F. Harrison in ref 6a, Chapter 5, p 159.

(18) (a) R. C. Dobson, D. M. Hayes, and R. Hoffmann, *J. Am. Chem. Soc.*, **93**, 6188 (1971); (b) N. Bodor, M. J. S. Dewar, and J. S. Wasson, *ibid.*, **94**, 9095 (1972); N. Bodor and M. J. S. Dewar, *ibid.*, **94**, 9103 (1972).

their formation.[19] The theory underlying this effect depends critically on two selection principles, the nuclear-spin dependence of intersystem crossing in a radical pair and the electron-spin dependence of the rates of radical pair reactions such as coupling or disproportionation. Combined, these selection principles result in characteristic nonequilibrium populations in the nuclear spin levels of in-cage reaction products (which are formed exclusively from pairs with singlet multiplicity) and in complementary nonequilibrium populations in the spin levels of free-radical ("escape") products, whose formation is electron spin independent. The quantitative theory of CIDNP is developed to a stage where the intensity ratios of CIDNP spectra can be computed on the basis of reaction and relaxation rates and of characteristic parameters of the radical pair (initial spin multiplicity, μ), of the individual radicals (electron g factors, hyperfine coupling constants, a), and of the products (spin–spin coupling constants, J).[20] Kaptein has summarized this theory in two simple rules,[21] which allow one to predict the qualitative features of a CIDNP spectrum, signal direction or "multiplet phase", from μ, Δg ($=g_i - g_j$), the *signs* of a and J, and factors allowing for the type of reaction (ϵ) and the relative position of the nuclei in the radical pair (σ). On the basis of these rules, one can derive one of the polarization-determining parameters from signal direction or multiplet phase, if the complementary parameters are known.

In the area of carbene chemistry one might envision the use of the CIDNP technique for the investigation of two reaction types: the additions of carbenes to olefins proceeding via 1,3 biradicals and abstraction–recombination reactions. Nuclear spin polarization has been observed in some biradical reactions.[22] However, there appears to be a critical chain length below which biradical polarization cannot be observed; in only one case has (weak) polarization been induced in a biradical where less than four C–C bonds separate the unpaired electrons.[23] Therefore, polarization cannot be expected for the addition of triplet carbenes to olefins. In contrast, abstraction–coupling reactions should lend themselves readily to study by the CIDNP technique. Indeed, Closs and co-workers have used the reaction of diphenymethylene with toluene, which is known to proceed via hydrogen abstraction and to involve the triplet state, as a test case for the predictive power of the radical pair mechanism.[24]

We have studied potential abstraction reactions of methylene and of several simple β,γ-unsaturated derivatives: vinyl-, carbomethoxy-, cyano-, and acetylmethylene, as well as several phenylmethylenes and cyclohexadienylidenes. In these studies we could identify the spin multiplicity of methylenes in several reactions and establish their reactivity patterns in the singlet and the triplet states.

Reactions of Carbenes with Carbon–Hydrogen Bonds

The most characteristic reaction of methylene is the unique insertion into carbon–hydrogen bonds, discovered for ethers by Meerwein and co-workers[25] and established for hydrocarbons by Doering and co-workers.[26] All available evidence supports a one-step mechanism for the solution reaction of (singlet) methylene.[14,15] The CIDNP technique offers a test for contributions by a two-step, abstraction–recombination mechanism.

The reaction of methylene with toluene may serve as an example. We found that nuclear spin polarization can be induced in methyl–benzyl pairs regardless of their initial spin multiplicity. Thus, the photolysis of 1-phenylazomethane in benzene gave rise to E/A polarized ethylbenzene[27] whereas the benzophenone-sensitized decomposition of diazomethane in toluene produced an A/E multiplet effect.[28] In the light of these results, the failure to observe ethylbenzene polarization in the direct photolysis of diazomethane in toluene[28] eliminates the possibility that radical pairs are involved in the reaction of singlet methylene with toluene. We consider these results as indirect evidence for the one-step insertion mechanism previously proposed by Doering and co-workers[14,15] and as a confirmation that the spin multiplicity and not the excess energy determines the mechanism of a carbene reaction in solution. Similar results were observed for the reactions of several substituted carbenes with simple hydrocarbons such as cyclohexane, cyclohexene, or benzene.

In order to study the reactivity of triplet carbenes, we used the triplet-photosensitized decomposition of the precursor diazo compounds. The ensuing reactions are often formulated via energy transfer and loss of nitrogen from the resulting triplet diazo compounds.

$$\text{sens}\ (T_1) + RR'C{=}N_2\ (S_0) \rightarrow \text{sens}\ (S_0) + RR'C{=}N_2\ (T_1)$$

$$RR'C{=}N_2\ (T_1) \rightarrow RR'C\colon\ (T) + N_2$$

However, an alternative reaction sequence amounting to "chemical sensitization"[29] cannot, a priori, be eliminated. In this mechanism, the triplet sensitizer abstracts a hydrogen atom from the substrate and one of the resulting radicals induces the decomposition of the diazo compound.

$$\text{sens}\ (T_1) + SH \rightarrow \cdot\text{sensH} + S\cdot$$

$$\cdot\text{sensH} + RR'C{=}N_2 \rightarrow \text{sens} + RR'\dot{C}H + N_2$$

$$S\cdot + RR'C{=}N_2 \rightarrow RR'\dot{C}S + N_2$$

We could differentiate between these mechanisms by using benzaldehyde (4) as sensitizer.[30,31] Photoexcited

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(19) (a) A. R. Lepley and G. L. Closs, Ed., "Chemically Induced Magnetic Polarization", Wiley, New York, N.Y., 1973; (b) R. Kaptein, *Adv. Free-Radical Chem.*, **5**, 319 (1975); (c) H. D. Roth, *Mol. Photochem.*, **5**, 91 (1973).

(20) (a) G. L. Closs, *Adv. Magn. Reson.*, **7**, 157 (1974); (b) J. H. Freed and J. B. Pedersen, *ibid.*, **8**, 1 (1976).

(21) R. Kaptein, *Chem. Commun.*, 732 (1971).

(22) R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **12**, 16 (1971); G. L. Closs, *J. Am. Chem. Soc.*, **93**, 1546 (1971); G. L. Closs, *Ind. Chim. Belge*, **36**, 1064 (1971); G. L. Closs and C. E. Doubleday, *J. Am. Chem. Soc.*, **94**, 9248 (1972); R. Kaptein, R. Freeman, and H. D. W. Hill, *Chem. Phys. Lett.*, **26**, 104 (1974).

(23) S. L. Buchwalter and G. L. Closs, *J. Am. Chem. Soc.*, **97**, 3857 (1975).

(24) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **91**, 4549 (1969); G. L. Closs and A. D. Trifunac, *ibid.*, **92**, 2186 (1970).

(25) H. Meerwein, H. Rathjen, and H. Werner, *Chem. Ber.*, **75**, 1610 (1942); H. Meerwein, H. Disselnkotter, F. Rappen, H. van Rintelen, and H. van de Vloed, *Justus Liebigs Ann. Chem.*, **604**, 151 (1957).

(26) W. von E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chauduri, *J. Am. Chem. Soc.*, **78**, 3224 (1956).

(27) M. L. Schilling and H. D. Roth, unpublished results.

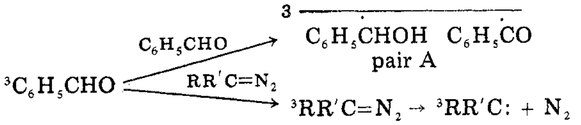
(28) H. D. Roth, *J. Am. Chem. Soc.*, **94**, 1761 (1972).

(29) L. Horner and H. Schwarz, *Tetrahedron Lett.*, 3579 (1966).

(30) H. D. Roth and M. L. Manion, *J. Am. Chem. Soc.*, **97**, 779 (1975).

(31) H. D. Roth and M. L. Manion, *J. Am. Chem. Soc.*, **98**, 3392 (1976).

4 is known to abstract hydrogen from ground-state 4 producing the radical pair, hydroxybenzyl–benzoyl (pair A) and resulting in strongly polarized benzaldehyde.[32] Pair A is also formed upon photolysis of benzoin (5), and strong benzaldehyde polarization is observed in this reaction as well.[32] The attempt to differentiate between energy transfer and chemical sensitization is based on the following considerations. Since hydrogen abstraction by triplet 4 is a bimolecular reaction and is likely to be considerably slower than diffusion controlled, it could be suppressed by efficient energy transfer to an added diazo compound. In contrast, the cleavage of triplet 5 to yield pair A is unimolecular and relatively efficient, and, therefore, less likely to be affected by a diffusion-limited interaction with the diazo compound.



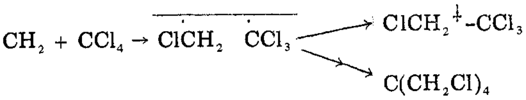
$$ {}^{3}C_6H_5CHO \xrightarrow{C_6H_5CHO} \underset{\text{pair A}}{{}^{3}\overline{C_6H_5\dot{C}HOH \quad C_6H_5\dot{C}O}} $$

$$ {}^{3}C_6H_5CHO \xrightarrow{RR'C{=}N_2} {}^{3}RR'C{=}N_2 \rightarrow {}^{3}RR'C: + N_2 $$

Addition of diazo compounds, e.g., methyl diazoacetate[30] or diazoacetone,[31] efficiently quenched the polarization generated in benzaldehyde solutions but failed to substantially affect the polarization generated in benzoin solutions. This result suggests that the main effect of the diazo compound does not lie in the reaction with pair A (which is formed from 4 *and* 5) but in preventing the formation of pair A from triplet 4. We interpret these results as evidence for energy transfer from triplet 4 to the diazo compounds and, consequently, as evidence for the intermediacy of triplet carbenes.

Reactions of Carbenes with Carbon–Halogen Bonds

The reactions of many carbenes with a wide range of chlorine-bearing substrates have been studied.[33] In most cases, the products of these reactions are derived from one molecule each of reactant and substrate. However, Urry and Eiszner reported a remarkable exception, the unique photoreaction of diazomethane with tetrachloromethane. This reaction affords pentaerythrityl tetrachloride (7),[34] the formation of which requires four molecules of diazomethane per molecule of CCl_4. The formation of 7 has been explained plausibly with a ten-step radical chain mechanism.[34] When we carried out this reaction in the probe of an NMR spectrometer we observed CIDNP signals of several minor products, most prominently that of 1,1,1,2-tetrachloroethane (6, E),[35] a coupling product derived from the primary radical pair. The observed signal directions indicate that singlet methylene is involved in the abstraction reaction that leads to the polarized products and, more importantly, that it initiates the free-radical chain reaction leading to 7.



$$ CH_2 + CCl_4 \rightarrow \overline{Cl\dot{C}H_2 \quad \dot{C}Cl_3} \rightarrow ClCH_2{}^{\text{⸸}}\text{-}CCl_3 $$

$$ \overline{Cl\dot{C}H_2 \quad \dot{C}Cl_3} \rightarrow C(CH_2Cl)_4 $$

(Throughout this account, a dagger (†) indicates CIDNP absorption, an inverted dagger (⸸) CIDNP emission.)

These results and the observation of polarized methyl 2,3,3,3-tetrachloropropionate upon photolysis of methyl diazoacetate in tetrachloromethane[36] were the first indications to suggest *abstraction* reactions for *singlet* carbenes in solution. Because of the significance of this assignment, it was imperative to confirm independently the analysis of the CIDNP parameters and to assess whether the postulated abstraction reaction is a major pathway or an unimportant side reaction. The unusually high enhancement factor[35] of 6 confirms that a substantial portion of this product is represented by the CIDNP signal. The correct assignment of the precursor multiplicity was confirmed by the triplet-sensitized reaction. Designed to alter one of the polarization-determining parameters, μ, this experiment yielded polarized products with altered signal directions. Consequently, there is little doubt that chlorine abstraction is a major reaction of singlet methylene.

Surprising as the association of a singlet carbene with an abstraction reaction appeared at first, our subsequent studies showed that chlorine abstraction is a general reaction, not only of singlet methylene but of many other singlet carbenes as well. The choice of substrate is not limited to aliphatic halocarbons; singlet methylene was found to abstract even the chlorine atom of chlorobenzene.[37]

$$ {}^{1}CH_2 + C_6H_5Cl \rightarrow {}^{1}\overline{C_6H_5\cdot \quad \cdot CH_2Cl} \rightarrow C_6H_5\text{-}CH_2{}^{\dagger}Cl $$

In addition to coupling, the radical pairs produced by carbenes may form products by "disproportionation". This reaction leads to the formation of an olefin and a methane derivative and amounts to β elimination of the elements of HCl by the carbene from the substrate.[38]

Selectivity of Singlet and Triplet Carbenes

The almost complete lack of selectivity displayed by (singlet) methylene in its solution reactions with primary, secondary, and tertiary C–H bonds prompted its classification as "the most indiscriminate reagent known in organic chemistry".[26] However, in reactions with haloalkanes, methylene was found to display a relatively high degree of discrimination; in the reaction with 2-chloro-2-methylpropane, attack on chlorine accounted for 60% of the isolated products, even though the hydrogen atoms outweigh the halogen statistically, 9:1. When these studies were carried out, the spin multiplicity of the reacting carbene could not be determined and was not discussed.[39] However, we have often found that chlorinated substrates may induce the intersystem crossing of carbenes by a heavy-atom effect. Accordingly, results such as the formation of racemic 1-chloro-2-methylbutane from optically active 2-chlorobutane[40] would be ascribed to triplet methylene. The results of our CIDNP studies clearly indicate that the singlet state of methylene is involved in the chlorine

(32) M. Cocivera and A. M. Trozzolo, *J. Am. Chem. Soc.*, **92**, 1772 (1970); G. L. Closs and D. R. Paulson, *ibid.*, **92**, 7229 (1970).

(33) Reference 6a, Chapter 11, Section VI, p 442.

(34) W. H. Urry and J. R. Eiszner, *J. Am. Chem. Soc.*, **73**, 2977 (1951); W. H. Urry, J. R. Eiszner, and J. W. Wilt, *ibid.*, **79**, 918 (1957).

(35) H. D. Roth, *J. Am. Chem. Soc.*, **93**, 1527 (1971).

(36) (a) M. Cocivera and H. D. Roth, *J. Am. Chem. Soc.*, **92**, 2573 (1970); (b) H. D. Roth, *Ind. Chim. Belge*, **36**, 1068 (1971).

(37) H. D. Roth unpublished results.

(38) H. D. Roth, *J. Am. Chem. Soc.*, **94**, 1400 (1972).

(39) V. Franzen, *Justus Liebigs Ann. Chem.*, **627**, 22 (1959).

(40) W. von E. Doering, private communication.

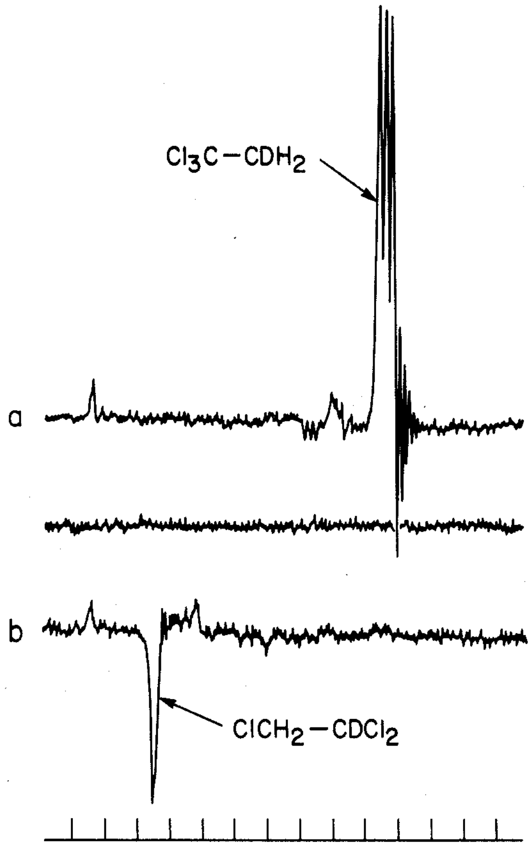
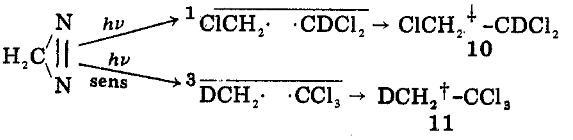


Figure 1. ^1H NMR spectra (60 MHz) of diazirine solutions in deuteriotrichloromethane during triplet-sensitized (a) and direct (b) photolysis. A spectrum of the same region without irradiation is shown between traces a and b.

abstraction and, thus, establish a preference of singlet methylene for attack on halogen. This preference is in full agreement with the electrophilic nature generally ascribed to singlet methylene and reflects the favorable interaction between a Lewis acid and a Lewis base. Nevertheless, this type of selectivity has not been associated with singlet methylene before.

An investigation of triplet methylene revealed that this species, though involved occasionally in chlorine abstraction,[35] shows a strong preference for hydrogen abstraction. This feature is aptly demonstrated in the photosensitized decomposition of diazirine in deuteriotrichloromethane. This experiment (Figure 1a) produced strongly polarized 1,1,1-trichloro-2-deuterioethane (**11**), a product initiated by hydrogen abstraction, but showed no indication of 1,1,2-trichloro-1-deuterioethane (**10**), the product resulting from chlorine abstraction. In contrast, **10** was formed upon direct photolysis as indicated by a strong CIDNP signal (Figure 1b).[41] Similar results were observed during the photosensitized decomposition of diazomethane and several substituted diazo compounds in a variety of substrates.[42] Additional selective reactions of several singlet and triplet carbenes will be discussed in the following section.

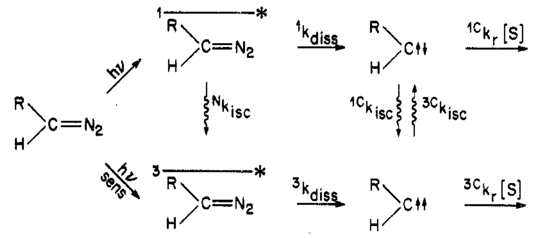


$$\mathrm{H_2C}\begin{matrix}\mathrm{N}\\ \| \\ \mathrm{N}\end{matrix}\begin{matrix}\xrightarrow{h\nu} {}^1\overline{\mathrm{ClCH_2\cdot\ \ \cdot CDCl_2}} \rightarrow \mathrm{ClCH_2}^{\downarrow}\text{-}\mathrm{CDCl_2} \\ \qquad\qquad\qquad\qquad\qquad \mathbf{10} \\ \xrightarrow[\text{sens}]{h\nu} {}^3\overline{\mathrm{DCH_2\cdot\ \ \cdot CCl_3}} \rightarrow \mathrm{DCH_2}^{\uparrow}\text{-}\mathrm{CCl_3} \\ \qquad\qquad\qquad\qquad\qquad \mathbf{11}\end{matrix}$$

Intersystem Crossing in Carbene Reactions

In many carbene reactions, the spin multiplicity of the reacting species is not that of the ground state. This observation is most simply explained by assuming that the rate of reaction of these species is faster than their rate of intersystem crossing to the ground state. Actually, the generation and the decay of carbenes are determined by several rate constants, some of which are shown in the following scheme.

The chemical fate of an excited-singlet diazo compound depends on the rate of several competing processes, inter alia, dissociation ($^1k_{diss}$) and intersystem crossing ($^Nk_{isc}$). If the dissociation is fast, a singlet carbene results, whose fate again depends on several competing rates, including those of reaction ($^{1C}k_r$[S]) and intersystem crossing ($^{1C}k_{isc}$).



Triplet diazo compounds can be generated by intersystem crossing from the excited-singlet states or, directly, by triplet energy transfer from a photosensitizer. Their dissociation ($^3k_{diss}$) generates triplet carbenes. For a diazo compound, the triplet state lies appreciably below the excited singlet state. Therefore, intersystem crossing from triplet to excited singlet should not compete prominently with dissociation. For a carbene, however, the triplet may lie above or below the singlet or the two states may be nearly degenerate so that intersystem crossing ($^3k_{isc}$) may compete with the reaction ($^{3C}k_r$[S]) of these species. This discussion is somewhat simplified since we have neglected intramolecular rearrangements of excited diazo compounds (e.g., diazoacetone) or carbenes (e.g., vinylmethylene) and bimolecular reactions of photoexcited diazo compounds.

The carbene reactions discussed so far in this Account represent limiting cases, where the dissociation of the excited diazo compound and the reaction of the resulting carbenes are substantially faster than the competing intersystem crossing processes. Thus, the direct photolysis of diazomethane, diazoacetonitrile, or methyl diazoacetate[35,36] resulted exclusively in the reactions of the respective singlet carbenes, whereas the photosensitized decomposition of these diazo compounds led to typical reactions of triplet methylenes.[27,30,35]

The case of diphenyldiazomethane is different. Here, direct irradiation leads to reactions of triplet diphenylmethylene, indicating that in this system the intersystem crossing of either the excited-singlet precursor or of singlet diphenylmethylene is competing efficiently with the dissociation or the bimolecular reaction of these species. Several authors have suggested that the reactions of diphenylmethylene with several substrates occur from the singlet state. However, all CIDNP signals observed in reactions of di-

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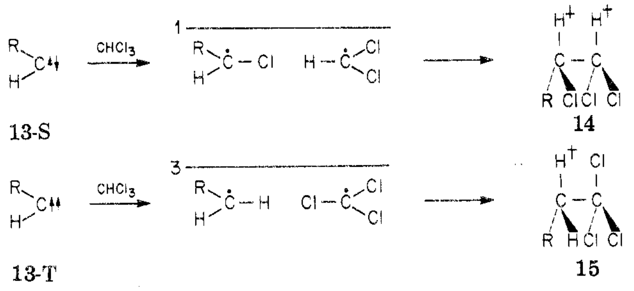
(41) H. D. Roth, *J. Am. Chem. Soc.*, **93**, 4935 (1971).
(42) M. L. Manion and H. D. Roth, *J. Am. Chem. Soc.*, **93**, 6919 (1975).

phenylmethylene involve the triplet state.[24,43,44]

For several monosubstituted carbenes, however, we found evidence that their reaction with a given substrate involves the singlet and the triplet state. In contrast to the reactions of methylene, we found four diazo compounds for which either the direct irradiation or the photosensitized decomposition resulted in both hydrogen and chlorine abstraction from trichloromethane.

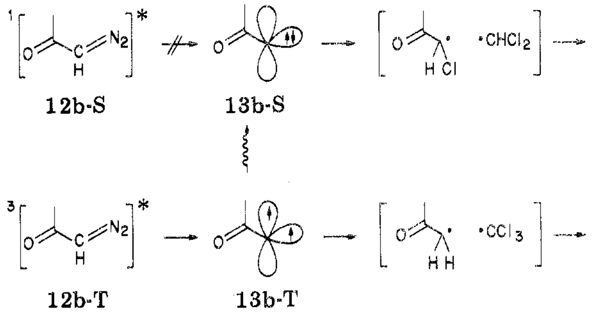
Trichloromethane appears to be ideally suited as a probe for simultaneous hydrogen and chlorine abstraction by monosubstituted carbenes, because the respective products can be identified readily in the presence of each other. Chlorine abstraction will result in the formation of 2-substituted 1,1,2-trichloroethanes (**14**) which show pairs of doublets, whereas the 2-substituted 1,1,1-trichloroethanes (**15**) resulting from hydrogen abstraction show sharp singlets. Since the CIDNP signal direction provides a built-in check for the precursor multiplicity, we can in each case determine whether we are dealing with nonselective reactions of one spin state or with simultaneous selective reactions of singlet and triplet states. We have studied the cases of diazotoluene, diazoacetone, methyl diazoacetate, and diazoacetonitrile. In all four cases, the CIDNP spectra document that the intermediate carbenes are selective. Hydrogen abstraction is due to a triplet precursor, whereas the corresponding singlet carbenes preferentially abstract chlorine.



a, R = C_6H_5; b, R = $COCH_3$; c, R = $COOCH_3$; d, R = CN

The direct irradiation of diazotoluene (**12**, R = C_6H_5) in $CHCl_3$ produced 1,1,2-trichloro-2-phenylethane (**14a**) via **13a**-S and 1,1,1-trichloro-2-phenylethane (**15a**) via **13a**-T. These results suggest that the intersystem crossing to the triplet manifold competes with reactions in the singlet manifold. However, our results do not allow us to decide whether intersystem crossing occurs in the diazo compound or in the carbene.[27]

The case of diazoacetone (**12**, R = $COCH_3$) allows more specific conclusions. Here, no intermolecular product and no polarization was observed upon direct photolysis, but photosensitized decomposition in $CHCl_3$ resulted in a polarization pattern similar to that discussed for the photolysis of **12a**. Again, hydrogen abstraction by a triplet precursor and chlorine abstraction by a singlet precursor were indicated. Since reasonable mechanistic alternatives can be eliminated,[31] we formulate these reactions via **13b**-T and **13b**-S, respectively. The study of diazoketone–ketocarbene systems is complicated by the fact that direct photolysis results in the Wolff rearrangement, an intramolecular reaction producing ketenes. This rearrangement has been formulated via singlet acylcarbenes as intermediates.[45] Our finding that no polarization was observed upon direct photolysis of **12b** eliminates the relaxed-singlet carbene (**13b**-S) as an intermediate in the Wolff rearrangement of **12b** and, simultaneously, eliminates the excited-singlet diazo compound (**12b**-S) as a precursor for the singlet carbene. Apparently, **13b**-S is formed from the triplet carbene by intersystem crossing which competes efficiently with the hydrogen abstraction reaction.



The intersystem crossing from **13b**-T to **13b**-S rules out the possibility that **13b**-S lies appreciably above **13b**-T but it is not sufficient to establish which state is the ground state. Minimum requirements for such an assignment are the independent generation of singlet and triplet state and intersystem crossing exclusively in one direction.

The two carbenes discussed so far could be generated directly in only one spin multiplicity. In contrast, carbomethoxycarbene (**13c**) can be generated independently in the singlet or in the triplet state by, respectively, the direct photolysis or the photosensitized decomposition of methyl diazoacetate (**12c**). In this system, only chlorine abstraction was observed upon direct photolysis (Figure 2b), whereas the sensitized decomposition revealed hydrogen abstraction (by **13c**-T) and chlorine abstraction (by **13c**-S; Figure 2a) under conditions where direct absorption of the diazo compound was ruled out.[27] Since intersystem crossing from the triplet state of the diazo compound to the (higher lying) excited-singlet state is unlikely, it appears that intersystem crossing occurs from **13c**-T to **13c**-S. At the same time the results of the direct photolysis show conclusively that intersystem crossing from **13c**-S to **13c**-T is not significant.[27]

It is tempting to interpret these results as evidence for a singlet ground state. However a kinetic analysis of this system shows that such a conclusion is not warranted. Our data allow a comparison between the competing rates of intersystem crossing and of reaction, and between the ratios of these rates for each spin state: ${}^{3C}k_{isc}/{}^{3C}k_r >> {}^{1C}k_{isc}/{}^{1C}k_r$. From this relation one can derive the relative magnitude of ${}^{3C}k_{isc}$ and ${}^{1C}k_{isc}$ if the relative rates of reaction can be measured or estimated reliably. The singlet will indeed be the ground state if ${}^{3C}k_r$ and ${}^{1C}k_r$ are of comparable magnitude.

An examination of the transition states of the two reaction types does not support such an assumption. The rate of the electrophilic attack of a singlet carbene on a chlorocarbon should depend markedly on the

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(43) D. Bethell, J. Hayes, and A. R. Newall, *J. Chem. Soc., Perkin Trans. 2*, 1307 (1974).

(44) G. L. Closs in ref 6b, Vol. 2, 1975, p 159.

(45) H. Meier and K.-P. Zeller, *Angew. Chem., Int. Ed. Engl.*, 14, 32 (1975).

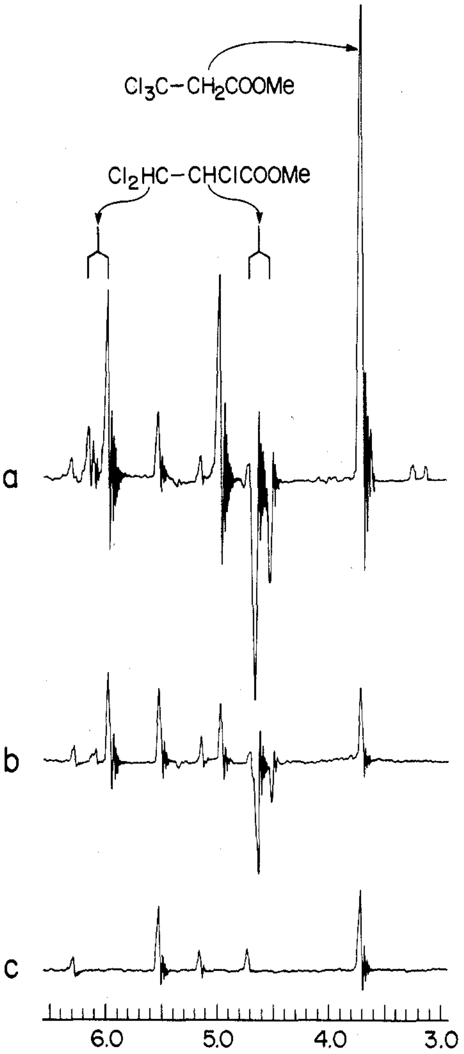
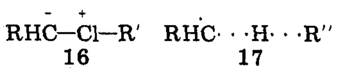


Figure 2. ^1H NMR spectrum of methyl diazoacetate in trichloromethane (c) and CIDNP spectra observed during direct (b) and photosensitized (c) decomposition of the diazo compound.

nature of the α substituent. For carbenes with electron-withdrawing substituents (COOR, $COCH_3$, CN) the energy of the transition state (or the intermediate) of structure **16** should be substantially reduced. On the other hand, the hydrogen abstraction by a triplet methylene is not expected to show a similar substituent effect. Rather, the energy of the transition state (**17**) should depend largely on the dissociation energy of the C–H bond of the substrate. Considering the relatively strong C–H bond of trichloromethane (D_{C-H} = 96 kcal/mol), it is quite reasonable that hydrogen abstraction should be slow. Given an appreciable difference between $^{1C}k_r$ and $^{3C}k_r$ (e.g., two orders of magnitude), it is possible that no intersystem crossing is observed from singlet to triplet state even if the carbene has a triplet ground state.



$$RH\overset{-}{C}-\overset{+}{Cl}-R' \quad RH\dot{C}\cdots H\cdots R''$$

16 17

This conclusion is borne out by the results obtained with cyanomethylene (**13d**), which is known to be a ground-state triplet.[9] We found that **13d**-T generated by photosensitized decomposition of diazoacetonitrile (**12d**) did undergo intersystem crossing in competition with hydrogen abstraction. In contrast, the direct irradiation failed to produce any polarization indicating a triplet precursor. Accordingly, any significant intersystem crossing from **13d**-S to the lower lying **13d**-T is ruled out.[27]

Although the observed intersystem crossing from triplet to singlet state is not sufficient to establish singlet ground states for the carbenes, **13b-d**, our finding nonetheless allows an important insight into these systems: the singlet states of acetylmethylene, carbomethoxycarbene, and cyanomethylene cannot lie significantly above the corresponding triplet states, since intersystem crossing to a higher lying state cannot occur at competitive rates if the singlet–triplet splitting is substantially larger than about 5 kcal/mol.

Conclusion

This Account is an attempt to illustrate the value of the CIDNP method as a mechanistic criterion in the chemistry of carbenes. This technique, judiciously applied, has been a key tool in elucidating several facets of carbene reactivity. We were able to show: (a) that singlet carbenes may undergo abstraction reactions (although they react with C–H bonds by insertion only), (b) that singlet carbenes have a preference for chlorine abstraction whereas triplet carbenes preferentially abstract hydrogen, (c) that energy transfer is involved in the photosensitized decomposition of several diazo compounds, and (d) that trichloromethane is a useful substrate for studying carbenes that undergo intersystem crossing in competition with bimolecular reactions. The potential of the CIDNP method does not appear to be exhausted with these achievements, and we hope that this technique will continue to contribute to the understanding of carbene reactions and of their mechanisms.

I am indebted to many colleagues who have contributed to the work discussed here; the initial experiments were carried out in collaboration with Michael Cocivera, a pioneer in photo CIDNP; for much of this work I used a modified NMR spectrometer under the patient guidance of Saul Meiboom and Richard Hewitt; in the studies of unsaturated carbenes I enjoyed the capable collaboration of Marcia Manion-Schilling; throughout this research I had the benefit of expert advice and stimulating discussions with E. A. Chandross, A. A. Lamola, A. M. Trozzolo, and E. Wasserman.