References and Notes

(1) J. M. Pratt, "The Inorganic Chemistry of Vitamin B₁₂", Academic Press, London and New York, 1972.
(2) H. A. O. Hill, "Inorganic Chemistry", G. Eichorn, Ed., Elsevier Scientific Publishing Company, Amsterdam, Oxford, and New York, 1973, p 1067.
(3) V. L. Goedken and J. Molin-Case, *J. Chem. Soc., Chem. Commun.*, 337 (1973).
(4) M. Weiss, Y.-A. Park and V. L. Goedken, to be submitted.
(5) V. L. Goedken, S.-M. Peng, and Y.-A. Park, *J. Chem. Soc.*, **96**, 284 (1974).
(6) V. L. Goedken, J. Pluth, S-M. Peng, and B. Bursten, submitted for publication.
(7) V. L. Goedken and Y.-A. Park, *J. Chem. Soc., Chem. Commun.*, 214 (1975).
(8) M. Gerloch, B. M. Higson, and E. D. McKenzie, *Chem. Commun.*, 1149 (1971).
(9) These magnetic moments are very similar to those reported in ref 8 for which temperature dependent studies suggested an equilibrium between spin singlet and spin triplet states.
(10) K. Bowman, D. P. Riley, D. H. Busch, and P. W. R. Corfield, *J. Am. Chem. Soc.*, **97**, 5036 (1975); D. P. Riley, J. A. Stone, and D. H. Busch, *ibid.*, **98**, 1752 (1976).
(11) The ¹H NMR data of the acetylene and nitrile adducts demonstrate the greater trans-labilizing effect of carbon vs. nitrogen donor atoms. Examination of the proton resonances shows that the pyridine trans to the carbon donor exhibits free rotation; distinction can be made only among the α,β, and γ protons. However, the pyridine trans to the nitrogen donor displays five distinct interpretable resonances. For the latter system, the stronger Co-py bond creates sufficient interaction with the macrocyclic ligand to prevent rotation of the pyridine on the NMR time scale. The NMR spectra require the α- and α'-protons of the pyridine ligand to be directed toward the nonequivalent 2,4-pentanediiminato rings rather than toward the equivalent benzenoid rings.
(12) The x-ray crystal structures of the five-coordinate cobalt(III) iodide complex III and of the acetylene adduct, V, have been completed and are consistent with the conclusions presented in this paper.
(13) D. M. Barlex, J. A. Evans, R. D. W. Kemmitt, and D. R. Russell, *Chem. Commun.*, 331 (1971).
(14) D. M. Barlex, A. C. Jarvis, R. D. W. Kemmitt, and B. Y. Kimura, *J. Chem. Soc., Dalton Trans.*, 2549 (1972).
(15) A. C. Jarvis, R. D. W. Kenneth, B. Y. Kimura, D. R. Russell, and P. A. Tucker, *J. Organomet. Chem.*, **66**, C63 (1974).
(16) D. R. Russell and P. A. Tucker, *J. Chem. Soc., Dalton Trans.*, 1743 (1975).
(17) C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Am. Chem. Soc.*, **83**, 3428 (1961).

Marvin C. Weiss, Virgil L. Goedken*

*Department of Chemistry, University of Chicago
Chicago, Illinois 60637*

Solution Photochemistry of Diazoacetone. Wolff Rearrangement and Acetylmethylene

Sir:

Diazoketones undergo several interesting reactions: intramolecular insertions and additions,[1] the Wolff rearrangement[2] and intermolecular additions, which apparently involve triplet ketocarbenes.[3] In an attempt to delineate the reactivity pattern of triplet acetylmethylene (**2-T**), we studied the photosensitized decomposition of diazoacetone (**1**) in hydrocarbons and chlorinated substrates using chemically induced dynamic nuclear polarization (CIDNP)[4] as a probe for radical pair derived reaction products. Our results suggest that **2-T** may react by hydrogen abstraction or may undergo intersystem crossing to the singlet state (**2-S**). In partially chlorine substituted solvents chlorine abstraction by **2-S** is observed simultaneously with hydrogen abstraction by **2-T**. The fact that chlorine abstraction is not observed upon direct photolysis suggests that **2-S** is not an intermediate in the Wolff rearrangement of **1**.

When solutions of **1** and benzophenone (**3**) in cyclohexane-d_{12} or cyclohexene-d_{10} were irradiated in the probe of an NMR spectrometer[5] they displayed broad emission singlets (∼2.15 ppm) representing the α-methylene protons of α-cyclohexylacetone (**6**) and α-(3-cyclohexenyl)acetone (**7**), respectively. The observation of these effects indicates that the


Figure 1. ¹H NMR spectrum (60 MHz) of diazoacetone (**1**; 0.1 M) in CHCl₃ (bottom) and CIDNP spectrum observed during the photosensitized decomposition (benzophenone, 0.1 M) of **1** in CHCl₃ (top). S denotes the high-field ¹³C satellite of CHCl₃.

products, **6** and **7**, are being formed by coupling of radical pairs, e.g., acetonyl-d_1 (**4**; $g = 2.0045$; $a_H{}^\alpha < 0$)[6] cyclohexyl-d_{11} (**5**; $g = 2.0026$).[7] The observed signal directions suggest that these pairs are formed either directly from a triplet precursor or by an encounter of free radicals. The second mechanism would imply a chain reaction initiated by the sensitizer via hydrogen abstraction from the solvent and propagated by induced decomposition of the diazo compound (chemical sensitization).[8] Since similar CIDNP signals were not observed during the radical induced decomposition of **1** in these solvents,[9] we interpret the observed results as evidence for an energy transfer mechanism with **2-T** as key intermediate.
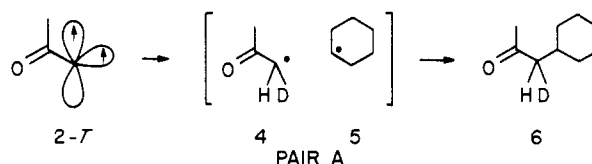

Since triplet carbenes often display a pronounced preference for hydrogen abstraction,[10] we studied the photosensitized decomposition of **1** in trichloromethane. During this reaction we observed indeed a sharp absorption singlet (3.8 ppm) representing the methylene protons of 4,4,4-trichlorobutan-2-one (**9**). The polarization of this product is consistent with coupling of trichloromethyl (**8**; $g = 2.0091$)[11] with acetonyl radicals, generated in pairs by hydrogen abstraction of **2-T** from the solvent.
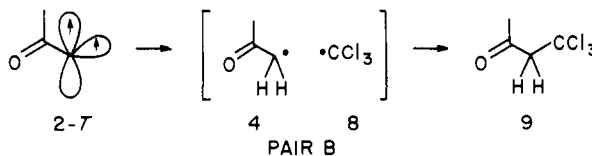
However, this reaction also produced two doublets at 4.55 (emission, E) and 6.05 ppm (enhanced absorption, A; Figure 1), which represent the protons in the 3- and 4-positions of 3,4,4-trichlorobutan-2-one (**12**). This product is most reasonably explained by coupling of pair C, a pair of α-chloroacetonyl (**10**; $g = 2.0070$; $a < 0$)[12] and dichloromethyl radicals (**11**; $g = 2.0080$; $a = -17$ G).[13] An analysis of the net signal directions and of the superimposed E/A multiplet effects[4] indicated that this pair is generated from a singlet precursor.[14] This assignment leaves **9** as the only product derived directly from **2-T** and asserts that this species is selective.

What is the origin of pair C? Inefficient photosensitization and direct photolysis of **1** to yield **2-S** would provide a trivial explanation. However, the irradiation of **1** in the absence of

the sensitizer, though resulting in smooth decomposition, failed to generate any observable nuclear spin polarization. Consequently, the CIDNP effects are linked to the sensitizer. One can envisage several direct mechanisms how the sensitizer could generate pair C in the singlet state. Mechanisms involving diffusion-controlled reactions of the initially excited singlet state of the sensitizer, e.g., energy transfer to, or exciplex formation with the diazo compound, are eliminated because of the short lifetime of this state.[15] Ground-state association of 1 and 3, which might lead to an excited-state complex, is ruled out because neither uv nor NMR spectra show evidence for it. Finally, a mechanism involving an excited-state complex, 14, between sensitizer and trichloromethane,[16] is eliminated because it can form pair C only by a very specific quenching reaction without precedent. Therefore, we conclude that pair C is generated by singlet acetylmethylene, 2-S, which arises via intersystem crossing of 2-T.
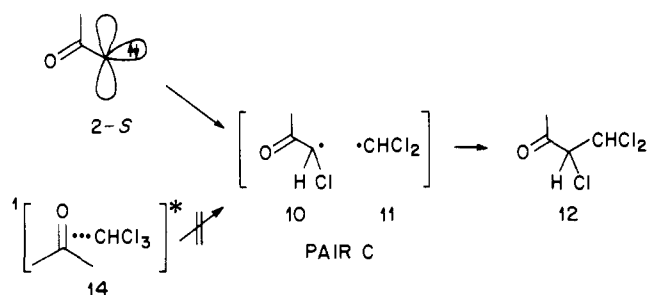
This assignment implies that the intersystem crossing rate of 2-T and its rate of reaction with $CHCl_3$ are of the same order of magnitude. A similar conclusion is suggested for the photosensitized decomposition of 1 in cyclohexane/$CHCl_3$. This reaction led to polarized geminate coupling products initiated via both hydrogen abstraction by 2-T ($\rightarrow$6,9) and via chlorine abstraction by 2-S ($\rightarrow$12). However, we were able to offset the balance between the rates of reaction and of intersystem crossing by choosing appropriate substrates. Only one polarized coupling product, 7, was observed in cyclohexene/$CHCl_3$; apparently, 2-T reacts considerably faster with cyclohexene than with $CHCl_3$ and its overall rate of hydrogen abstraction is substantially greater than its rate of intersystem crossing to 2-S. In contrast, sensitized decomposition of 1 in CCl_4 produced polarized 3,4,4,4-tetrachlorobutan-2-one (13, E), whose signal direction indicated that it was generated predominantly from a singlet precursor. In this case, the intersystem crossing of 2-T is faster than its reaction with CCl_4. This finding confirms that chlorine abstraction by triplet carbenes, though observed occasionally,[10b,17] is not generally favorable.

The conclusion that 2-S is formed during the photosensitized decomposition of 1, and that it reacts with chlorocarbons by chlorine abstraction bears significance for the mechanism of the Wolff rearrangement of 1. The formation of ketenes upon direct irradiation of diazoketones is formulated frequently via singlet ketocarbenes.[2] In the case of 1, the direct photolysis is known to produce methylketene,[3] but we failed to observe any intermolecular products. Consequently, 2-S is eliminated as an intermediate in the Wolff rearrangement of 1 and the mechanistic alternative, methyl migration concerted with loss of nitrogen,[2] must be favored.

In summary, we have investigated the photodecomposition of diazoacetone and have observed reactions of acetylmethylene in the triplet and the singlet state. Acetylmethylene was eliminated as an intermediate in the Wolff rearrangement of diazoacetone. The mechanistic conclusions in this system are more detailed than for most other diazo compounds. Usually, the photoreactions of diazo compounds are discussed as carbene reactions although the participation of excited states of
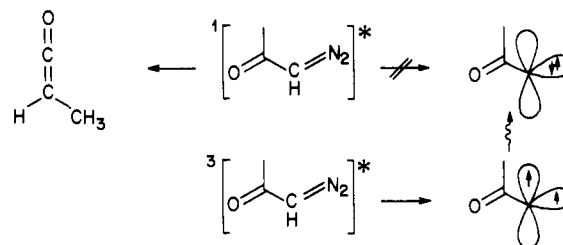
the diazo compound cannot be ruled out. When simultaneous involvement of singlet and triplet carbenes is postulated, it is usually not clear whether intersystem crossing occurs in the diazo compound or, after loss of nitrogen, in the carbene. In the system discussed here, the involvement of excited-singlet diazoacetone is ruled out. Therefore, it is quite clear that 2-S and not 1-S is the precursor for 12 and 13, and that intersystem crossing can only occur from 2-T to 2-S. This observation does not in itself establish 2-S as the lower lying state but it rules out the possibility that 2-S lies appreciably above 2-T. The question, which of these states is the ground state, is currently under investigation.

References and Notes

(1) (a) W. Kirmse, "Carbene Chemistry", 2d ed, Academic Press, New York, N.Y., 1971; (b) W. J. Baron, M. R. DeCamp, M. E. Hendrick, M. Jones, Jr., R. H. Levin, and M. B. Sohn in "Carbenes", Vol. 1, M. Jones, Jr., and R. A. Moss, Ed., Wiley, New York, N.Y., 1973, p 107.
(2) H. Meier and K.-P. Zeller, Angew. Chem., Int. Ed. Engl., 14, 32 (1975).
(3) M. Jones, Jr., and W. Ando, J. Am. Chem. Soc., 90, 2200 (1968).
(4) (a) A. R. Lepley and G. L. Closs, Ed., "Chemically Induced Magnetic Polarization", Wiley, New York, N.Y., 1973; (b) H. D. Roth, Mol. Photochem., 5, 91 (1973).
(5) Solutions containing 0.1 M diazoacetone (λ_{max} 245 nm, ϵ 9 × 10^3; λ_{min} 342 nm, ϵ 18; λ_{max} 367 nm, ϵ 23) and 0.1–0.25 M benzophenone (λ_{max} 346 nm, ϵ 120) were irradiated through a Corning 7-51 filter with the light of an Osram 200-W high pressure mercury lamp.
(6) D. M. Camaioni, H. F. Walter, J. E. Jordan, and D. W. Pratt, J. Am. Chem. Soc., 95, 7978 (1973).
(7) R. W. Fessenden and R. H. Schuler, J. Chem. Phys., 39, 2147 (1963).
(8) L. Horner and H. Schwarz, Tetrahedron Lett., 3579 (1956); cf. A. Padwa and R. Layton, ibid., 2167 (1965).
(9) Cf. H. D. Roth and M. L. Manion, J. Am. Chem. Soc., 97, 779 (1975).
(10) (a) H. D. Roth, J. Am. Chem. Soc., 93, 4935 (1971); 94, 1400 (1972); (b) M. L. Manion and H. D. Roth, ibid., 97, 6919 (1975).
(11) A. Hudson and H. A. Hussain, Mol. Phys., 16, 199 (1969).
(12) In analogy to the carboxychloromethyl radical, K. Mobius, K. Hoffmann, and M. Plato, Z. Naturforsch. A, 23, 1209 (1968).
(13) M. Lehnig and H. Fischer, Z. Naturforsch. A, 25, 1963 (1970).
(14) A third polarized product, 3,4,4,4-tetrachlorobutan-2-one (13), indicated by an enhanced singlet at 4.9 ppm (A), is evidently formed by coupling of ·CCl_3 with α-chloroacetonyl radicals. Since this pair cannot be formed directly by reaction of 1 or 2 with trichloromethane, we explain its formation by a free-radical encounter. The observed signal direction supports this assignment.
(15) A. Nitzan, J. Jortner, and P. M. Rentzepis, Chem. Phys. Lett., 8, 445 (1971).
(16) Cf. J. A. den Hollander, R. Kapstein, and P. A. T. M. Brand, Chem. Phys. Lett., 10, 430 (1971).
(17) H. D. Roth, J. Am. Chem. Soc., 93, 1527 (1971).

Heinz D. Roth,* Marcia L. Manion

Bell Laboratories
Murray Hill, New Jersey 07974

The Thermal Dimer and Ketene Cycloadduct of $\Delta^{1,4}$-Bicyclo[2.2.0]hexene[1]

Sir:

We have previously reported that $\Delta^{1,4}$-bicyclo[2.2.0]hexene (1) disappears spontaneously by a process which appears to obey second-order kinetics.[2] It did not give the expected ring opened product 1,2-dimethylenecyclobutane. We now have investigated the thermal reaction in more detail.

The electrolysis of 1-bromo-4-chlorobicyclo[2.2.0]hexane in dimethylformamide at −15 to −20° gave a solution of 1 which could be extracted into pentane. The pentane solution