References and Notes

(1) (a) C. J. Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill, New York, N.Y., 1962, p 267; (b) D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *J. Am. Chem. Soc.*, **83,** 4161 (1961).

(2) (a) D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *J. Am. Chem. Soc.*, **92,** 3342 (1970); (b) J. M. Andrews, D. Coucouvanis, and J. P. Fackler, *Inorg. Chem.*, **11,** 493 (1972); (c) J. J. Mayerle, S. E. Denmark, B. V. DePamphilis, J. A. Ibers, and R. H. Holm, *J. Am. Chem. Soc.*, **97,** 1032 (1975).

(3) B. A. Averill, T. Herskovitz, R. H. Holm, and J. A. Ibers, *J. Am. Chem. Soc.*, **95,** 3523 (1973), and references therein.

(4) T. B. Rauchfuss and D. M. Roundhill, *J. Am. Chem. Soc.*, **97,** 3386 (1975), and references therein.

(5) P. Hemmerich in "The Biochemistry of Cooper", J. Peisach, P. Aisen, and W. E. Blumberg, Ed., Academic Press, New York, N.Y., 1966, p 15.

(6) (a) J. R. Herriot, L. C. Sieker, and L. H. Leusen, *J. Mol. Biol.*, **50,** 391 (1970); C. W. Carter, Jr., S. T. Freer, Ng. H. Xuong, R. A. Alden, and J. Kraut, *ibid.*, **38,** 381 (1971); (c) L. C. Sieker, E. Adman, and L. H. Jensen, *Nature (London)*, **235,** 40 (1972).

(7) (a) D. Coucouvanis, F. J. Hollander, R. West, and D. Eggerding, *J. Am. Chem. Soc.*, **96,** 3006 (1974); (b) D. Coucouvanis, D. G. Holah, and F. J. Hollander, *Inorg. Chem.*, in press.

(8) B. N. Figgis, "Introduction to Ligand Fields", Interscience, New York, N.Y., 1967, Chapter 9.

(9) W. A. Eaton and W. Lovenberg in "Iron-Sulfur Proteins", Vol. II, W. Lovenberg, Ed., Academic Press, New York, N.Y., 1973, Chapter 3.

(10) Voltammetric studies were conducted in acetonitrile with $(Pr_4N)_4PF_6$ as the supporting electrolyte. A detailed electrochemical study of these complexes is currently in progress.

(11) A crystal structure determination of this complex is currently under way.

(12) A. Davison and E. S. Switkes, *Inorg. Chem.*, **10,** 837 (1971).

(13) M. R. Churchhill, J. Cooke, J. Wormald, A. Davison, and E. S. Switkes, *J. Am. Chem. Soc.*, **91,** 6518 (1969).

(14) Preliminary studies show that various 1,1-dithio complexes undergo metathesis reactions with the thiophenolate ion. An interesting metathetical reaction is observed with the $(Ph_4P)_4Cu_8(Dts)_6$ cluster. Analytical data on the crystalline product indicates the stoichiometry $(Ph_4P)_4Cu_6(SPh)_{12}{}^{4-}$.

(15) On sabbatical leave 1974–1975 from Lakehead University, Thunderbay, Ontario, Canada.

(16) Alfred P. Sloan Fellow, 1972–1974. To whom correspondence should be addressed.

D. G. Holah,[15] D. Coucouvanis*[16]

Department of Chemistry, University of Iowa
Iowa City, Iowa 52242

Received July 28, 1975

Photosensitized Decomposition of Diazopropene. Intermolecular Reactions of Vinylmethylene

Sir:

We have studied the triplet-photosensitized decomposition of diazopropene (**1**) and have observed intermolecular abstraction reactions. These results are compatible with triplet vinylmethylene (**2**-*T*) as reactive intermediate. This species may abstract chlorine or hydrogen atoms but apparently prefers hydrogen abstraction over either chlorine abstraction or addition to olefinic double bonds. These reactions are the first examples of intermolecular reactions of a simple vinylmethylene and provide a systematic approach to its reactivity in the triplet state.

Vinylmethylene and many of its derivatives have triplet ground states.[1] However, the pyrolysis or photolysis of their precursors (diazo compounds, diazirines, 3*H*-pyrazoles, or cyclopropenes) yields only intramolecular addition or insertion products,[2] which are most reasonably rationalized via the corresponding singlet states. In an attempt to study intermolecular reactions of vinylmethylene and to test the reactivity pattern of its triplet state, we have studied the benzophenone-sensitized decomposition of diazopropene[3] in the presence of simple chlorinated substrates (CCl_4, $CHCl_3$), saturated hydrocarbons, and olefins.

The benzophenone-sensitized decomposition[5] of **1** in tetrachloromethane produced the geometric isomers, **3** and **4**, in comparable yields totaling >50%.[6] The formation of these products can be rationalized on the basis of a mechanism involving chlorine abstraction by **2**-*T* and coupling of the resulting radicals, chloroallyl and trichloromethyl (pair A). A radical pair mechanism is supported by the strong nuclear spin polarization[7] (Figure 1), which was observed when the irradiation was carried out in an NMR spectrometer. We found enhanced absorption for the allylic and the terminal olefinic protons of products **3** and **4** and emission for the internal olefinic protons. The additional enhanced-absorption signals, three doublets at 4.8, 5.4, and 5.5 ppm, were assigned to a third tetrachlorobutene isomer, **5**. Since we failed to isolate this product, it must either be formed in trace amounts only or it must be unstable under the reaction conditions.

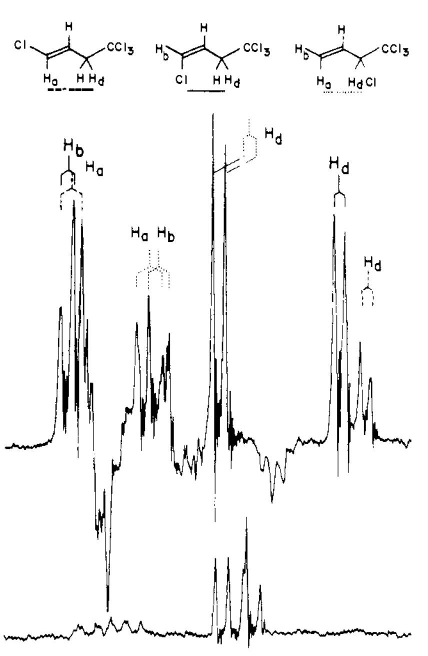
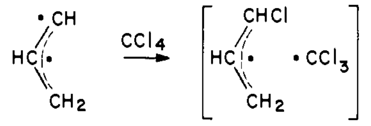
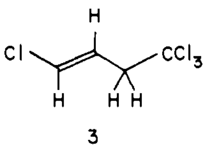


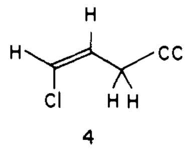
Figure 1. ^{1}H NMR spectrum (60 MHz) of diazopropene in tetrachloromethane containing benzophenone-d_{10} (bottom) and CIDNP spectrum observed during uv irradiation of this solution (top).



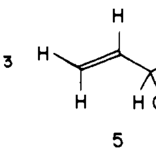
2 PAIR A



3



4



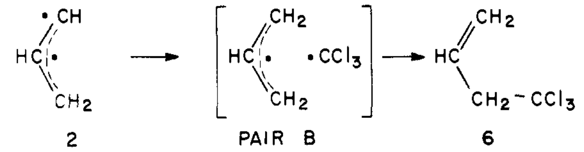
5

The signal direction of a CIDNP spectrum is determined by four parameters and may be used to derive the initial spin multiplicity of the intermediate radical pair and its immediate precursor. For the formation of **3**, **4**, and **5** from pair A we assign these parameters as follows. The 1-chloroallyl radical should have a spin density distribution similar to that of the allyl radical ($a_{1,3} < 0 < a_2$). Its g factor should be somewhat higher than that of the allyl radical ($g = 2.0026$),[8] but certainly considerably smaller than that of the trichloromethyl radical ($g = 2.0091$),[9] hence, $\Delta g < 0$. Given these parameters and the assumed coupling mechanism ($\epsilon > 0$), the observed signal directions indicate that pair A was generated in the triplet state ($\mu > 0$). The identification of the precursor is somewhat problematic since it is difficult to rule out the participation of the diazo compound in an excited state.[10] Nevertheless, we view the formation of pair A in terms of the simplest (and most attractive) mechanism, i.e., as an abstraction reaction of triplet vinylmethylene.

Products of abstraction-recombination reactions also were observed when vinylmethylene was generated in hydrocarbons; for example, the triplet-sensitized decomposition of **1** in cyclohexane yielded allylcyclohexane. The observation of CIDNP effects during the reaction support the assumption of a radical pair mechanism. In contrast, the direct photolysis of **1** failed to produce either intermolecular products or CIDNP effects. These results are compatible with **2**-*T* as an intermediate in the photosensitized decomposition of **1** and indicate that this species abstracts hydrogen atoms from hydrocarbons.

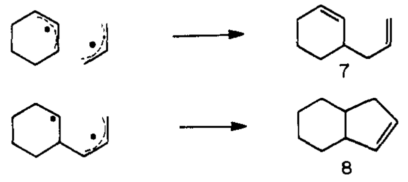
Having found evidence that vinylmethylene may abstract both hydrogen and chlorine atoms, we investigated the question of selectivity. In earlier work we had shown that triplet methylene, in reactions with substrates bearing hydrogen and chlorine atoms, displays a pronounced preference for hydrogen abstraction.[11] If triplet vinylmethylene displays similar selectivity, its reaction with trichloromethane should yield only one primary coupling product, and accordingly, a relatively simple CIDNP spectrum. On the other hand, if **2**-*T* is less selective or if it has a preference for chlorine abstraction, three additional primary coupling products are possible and a complex CIDNP spectrum is expected.

The benzophenone-sensitized decomposition of **1** in trichloromethane produced 4,4,4-trichlorobut-1-ene, **6**, as major product,[12] and the CIDNP experiment showed enhanced signals for all protons of this product: a weak, featureless emission (5.5–6.0 ppm) for the internal proton, three broad absorption signals (5.1, 5.25, and 5.4 ppm) for the terminal olefinic protons, and one absorption doublet (3.55 ppm) for the allylic protons. The direction and relative magnitude of these signals reflect the hyperfine coupling patterns of the allyl radical and suggest a mechanism involving coupling of a triplet-generated radical pair, B. In addition, two emission signals (2.15 and 4.85 ppm) were observed; these apparently represent an "escape" product,[7] possibly hexa-1,5-diene. This CIDNP spectrum is considerably simpler than one expected for chlorine abstraction and, therefore, supports the concept of a selective intermediate.



Although triplet carbenes readily abstract hydrogen atoms from saturated substrates, it has been argued[13] that addition is preferred in their reaction with olefins. Hydrogen abstraction, though observed in the cases of phenylmethylene[14] and diphenylmethylene,[15] was considered unusual. The ratios of addition to abstraction products observed in some of these systems may not correctly represent the reactivity of the triplet methylene, since it is difficult to rule out the participation of the singlet state. The vinylmethylene system is not affected by this restriction, since the singlet state does not undergo intermolecular reactions.[2] Consequently, the observed product ratio is not distorted by singlet-derived products.

The photosensitized decomposition of **1** in cyclohexene yielded a mixture of two hydrocarbons. The major product was identified as 3-allylcyclohex-1-ene (**7**), formed most likely *via* hydrogen abstraction and coupling of the resulting radicals.[16] The second product, as yet unidentified, was found in less than one-tenth the yield of **7**. Whether this material is the addition product, **8**, or not—it appears clear that addition to olefinic double bonds is not an important process for the intermediate derived from diazopropene.



This conclusion and the abstraction reactions of phenylmethylene and diphenylmethylene are not at odds with the addition reactions reported earlier. In our opinion, the balance between addition and abstraction reactions of triplet carbenes is not as one-sided as assumed.[13] We consider both hydrogen abstraction and addition typical reactions of triplet carbenes with olefins.

Acknowledgment. We are indebted to Dr. A. A. Lamola for informing us of his unpublished work on vinylmethylene and for suggesting its study by CIDNP techniques.

References and Notes

(1) (a) Vinylmethylene: R. S. Hutton, M. L. Manion, H. D. Roth, and E. Wasserman, *J. Am. Chem. Soc.*, **98**, 4680 (1974); O. L. Chapman, M. Chedekel, J. Pacansky, N. Rosenquist, and R. S. Sheridan, private communication. (b) Methyl-substituted vinylmethylenes: R. S. Hutton, M. L. Manion, H. D. Roth, and E. Wasserman, unpublished results. (c) 1,2-Benzovinylmethylene: G. L. Closs, L. R. Kaplan, and V. I. Bendall, *J. Am. Chem. Soc.*, **89**, 3376 (1967); (d) Phenyl- and carbalkoxy-substituted vinylmethylenes: G. E. Palmer, J. R. Bolton, and D. R. Arnold, *ibid.*, **96**, 3708 (1974).
(2) (a) G. L. Closs, L. E. Closs, and W. A. Böll, *J. Am. Chem. Soc.*, **85**, 3796 (1963); G. L. Closs, W. A. Böll, H. Heyn, and V. Dev, *ibid.*, **90**, 173 (1968); (b) E. J. York, W. Dittmar, J. R. Stevenson, and R. G. Bergman, *ibid.*, **95**, 5680 (1973); (c) H. D. Hartzler in "Carbenes", Vol. 2, R. A. Moss and M. Jones, Jr., Ed., Wiley, New York, N.Y., 1975, p 43.
(3) Diazopropene was prepared by addition of α-nitroso-α-allylurea[4] to a 10% solution of KOH in 2-(2-methoxyethoxy)ethanol and purified by bulb-to-bulb vacuum transfer.
(4) Cf. the procedure for nitrosomethylurea, F. Arndt, "Organic Syntheses", Collect. Vol. 2, Wiley, New York, N.Y., 1943, p 461.
(5) Solutions containing 0.1 *M* diazopropene (λ_{max} 490 nm, $\epsilon \sim 20$; λ_{min} 350 nm, $\epsilon < 2$) and 0.1 *M* benzophenone (λ_{max} 346 nm, $\epsilon \sim 120$) were irradiated (Osram 200-W high pressure mercury lamp) through a Corning No. 7-51 filter. Under these conditions >95% of the incident light was absorbed by the sensitizer.
(6) Determined by NMR spectroscopy.
(7) (a) A. R. Lepley and G. L. Closs, Editors, "Chemically Induced Magnetic Polarization", Wiley, New York, N.Y., 1973; (b) H. D. Roth, *Mol. Photochem.*, **5**, 91 (1973).
(8) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).
(9) A. Hudson and H. A. Hussain, *Mol. Phys.*, **16**, 199 (1969).
(10) P. P. Gasper and G. S. Hammond in ref 2c, p 207.
(11) H. D. Roth, *J. Am. Chem. Soc.*, **93**, 4935 (1971); **94**, 1400 (1972).
(12) In over 50% yield as determined by NMR spectroscopy.
(13) W. J. Baron, M. R. DeCamp, M. E. Hendrick, M. Jones, Jr., R. H. Levin, and M. B. Sohn in ref 2c, Vol. 1, 1973, p 1.
(14) R. A. Moss and U.-H. Dolling, *J. Am. Chem. Soc.*, **93**, 954 (1971).
(15) G. L. Closs and L. E. Closs, *Angew. Chem., Int. Ed. Engl.*, **1**, 334 (1962); G. L. Closs, *Top. Stereochem.*, **3**, 194 (1968).
(16) The abstraction of hydrogen atoms from cyclohexene by vinylmethylene has been observed previously, A. A. Lamola, private communication.

Marcia L. Manion, Heinz D. Roth*
Bell Laboratories
Murray Hill, New Jersey 07974

Received July 17, 1975