American Chemical Society, and the National Science Foundation (Grant No. MPS 73-05016) at Princeton University and the National Science Foundation (Grant No. GP 33142X) at Texas A&M University for support of this work. We are grateful to Dr. D. M. Collins and Professor B. L. Shapiro for helpful advice.

References and Notes

(1) (a) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84,** 959 (1975); (b) R. Ugo, *Catal. Rev.*, **11,** 225 (1975).
(2) F. A. Cotton, *Chem. Soc. Rev.*, **4,** 27 (1975).
(3) M. H. Chisholm and W. Reichert, *J. Am. Chem. Soc.*, **96,** 1249 (1974).
(4) M. H. Chisholm, F. A. Cotton, B. A. Frenz, W. Reichert, and L. W. Shive, *J. Chem. Soc., Chem. Commun.*, 480 (1974).
(5) M. H. Chisholm, F. A. Cotton, B. A. Frenz, W. W. Reichert, L. W. Shive, and B. R. Stults, *J. Am. Chem. Soc.*, **98,** 4469 (1976).
(6) M. H. Chisholm, M. W. Extine, and W. W. Reichert, *Adv. Chem. Ser.* **No. 150,** 273 (1970).
(7) M. H. Chisholm, F. A. Cotton, C. A. Murillo, and W. W. Reichert, *J. Am. Chem. Soc.*, in press.
(8) M. H. Chisholm, F. A. Cotton, M. W. Extine, B. R. Stults, and J. M. Troup, *J. Am. Chem. Soc.*, **97,** 1242 (1975).
(9) M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, **97,** 5625, (1975).
(10) M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *J. Am. Chem. Soc.*, **98,** 4477 (1976).
(11) M. H. Chisholm, F. A. Cotton, M. W. Extine, M. Miller, and B. R. Stults, *J. Am. Chem. Soc.*, **98,** 4486 (1976).
(12) M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *J. Am. Chem. Soc.*, **98,** 5683 (1976).
(13) M. H. Chisholm, F. A. Cotton, M. W. Extine, M. Miller, and B. R. Stults, *Inorg. Chem.*, **15,** 2244 (1976).
(14) M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *Inorg. Chem.*, **15,** 2252 (1976).
(15) M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, in press.
(16) M. H. Chisholm, F. A. Cotton, M. W. Extine, M. Millar, and B. R. Stults, *Inorg. Chem.*, in press.
(17) R. J. Klingler, W. Butler, and M. D. Curtis, *J. Am. Chem. Soc.*, **97,** 3535 (1975).
(18) Thus there exists the potential for the catalytic hydrogenation of acetylenes to olefins. In the cluster compounds $Ni_4(CN\text{-}t\text{-}Bu)_4(RC{\equiv}CR)_3$ which contain acetylenic moieties bridging nickel atoms, this catalysis has been achieved. M. G. Thomas, E. L. Muetterties, R. O. Day, and V. W. Day, *J. Am. Chem. Soc.*, **98,** 4645 (1976).
(19) (a) A. Nakamura and N. Hagahara, *Nippon Kagaku Zasski*, **84,** 344 (1963); A. Nakamura, *Mem. Inst. Sci. Ind. Res. Osaha Univ.*, **19,** 81 (1962); (b) W. I. Bailey, Jr., and F. A. Cotton, unpublished work.
(20) W. I. Bailey, Jr., F. A. Cotton, J. D. Jamerson, and J. R. Kolb, *J. Organomet. Chem.*, **121,** C23 (1976).
(21) There is one reported structure[22a] of an allene bridging two metal atoms that are not bonded to each other, and, of course, several examples[22] of allenes serving as two-electron, 1,2-dihapto ligands have been structurally characterized.
(22) (a) P. Racanelli, G. Pantini, A. Immirzi, G. Allegra, and L. Porri, *Chem. Commun.*, 361 (1969); (b) T. Kashawagi, N. Yasuoka, N. Kasai, and M. Kukudo, *ibid.*, 317 (1969); (c) T. G. Hewitt, K. Anzenhofer, and J. J. DeBoer, *ibid.*, 312 (1969).
(23) The nature of this compound, which is virtually insoluble in all the usual spectroscopic solvents, is uncertain. It does not appear to be formed by reaction of allene with $Cp_2Mo_2(CO)_4$(allene), but, rather, competitively upon reaction of allene with $Cp_2Mo_2(CO)_4$. Its elemental analysis is consistent with the formula $Cp_2Mo_2(CO)Q_4C_3H_4$ and its IR spectrum has bands at 1945, 1920, 1905, 1840, and 1720 cm^{-1}. The compound is essentially nonvolatile, although at 300 °C, ions corresponding to $Cp_2Mo_2(\text{allene})^+$ and $Cp_2Mo_2(\text{allene})(CO)_2{}^+$ together with weaker ions of *m/e* considerably greater than $Cp_2Mo(CO)_2(\text{allene})^+$ were observed in the mass spectrum. It has been shown by direct comparison that the compound is not $Cp_2Mo_2(CO)_4(MeCCH)$.
(24) The space group used was *Pn*, a nonstandard setting of *Pc*. Unit cell dimensions: $a = 10.932$ (2) Å, $b = 7.776$ (2) Å, $c = 10.015$ (1) Å, $\beta = 107.82$ (2)°, $V = 810.6$ Å^3. $d_{calcd} = 1.943$ for $Z = 2$ and FW = 474.18. A total of 2041 unique reflections with $0° < 2\theta(\text{Mo K}\alpha) \leq 55°$ were collected at 23 ± 2°. The structure was solved and refined by full-matrix least-squares using only the 1306 reflections with $I > 3\sigma(I)$. All C, O, and Mo atoms were treated anisotropically and anomalous scattering by Mo was included. Final *R* values were, $R_1 = 0.030$ and $R_2 = 0.046$.
(25) D. M. Grant, J. Hirst, and H. S. Gutowsky, *J. Chem. Phys.*, **38,** 470 (1963).
(26) Cf. G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley, New York, N.Y., 1972, p 25, et seq.

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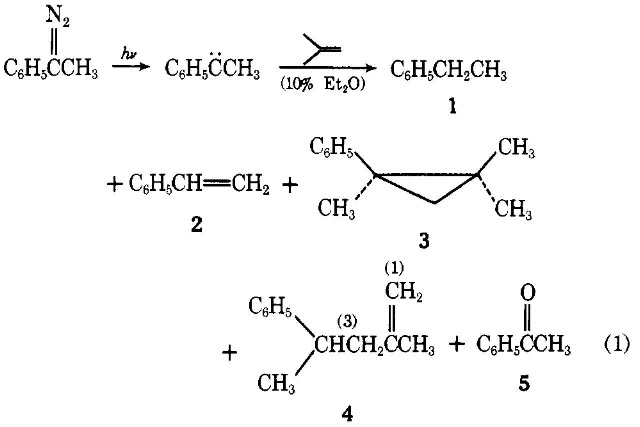
Reactions of Methylphenylcarbene and Phenylcarbene in Isobutene Matrices: Origins of the "Insertion" Products

Sir:

Phenylcarbene reacts with frozen *cis*-butene matrices (−196 °C) to yield olefins which apparently arise by abstraction-recombination reactions of the triplet carbene.[1] These observations, characterized as "most remarkable",[2] have led us to examine reactions of the title carbenes with isobutene matrices. Not only has our earlier finding of matrix-fostered olefin formation been confirmed, but using $(CH_3)_2C{=}^{13}CH_2$ matrices, we have obtained an even more remarkable glimpse into the origins of the olefins.

Equation 1 and Table I summarize the products from photolytically generated $PhCCH_3$ and isobutene.[4] Photolyses (6–8 h) were conducted in Pyrex tubes at 3000 Å, using the procedures described in ref. 1. Isobutene was degassed, and residual diazoalkane was destroyed with maleic anhydride.[5] Products **2–5** were identified by GC (18 ft × 0.25 in. 15% Carbowax 20M column, 160 °C) comparisons with authentic samples, and by GC-MS techniques. Ethylbenzene was identified by NMR. The identity of **4** was substantiated by GC comparisons with authentic **4** on three different 100 ft Golay columns (Apeizon-L, SF-96, Carbowax K-1540, all at 130 °C). Products were stable to all photolytic conditions. Authentic **3** was prepared from 1-bromo-1-phenyl-2,2-dimethylcyclopropane[6] with methyl iodide and methyllithium.[7] To prepare 2-methyl-4-phenyl-1-pentene (**4**),[8] 3-phenylbutanoic acid was converted to 4-phenyl-2-pentanone with methyllithium, and the ketone was treated with triphenylphosphonium methylide.



1-Phenyldiazoethane was photolyzed in a matrix (−196 °C) of $(CH_3)_2C{=}^{13}CH_2$,[9] to clarify the origin of **4**. ^{13}C NMR analysis of unlabeled **4** revealed resonances for C(1) and C(3) at δ ($CDCl_3$, Me_4Si) 112.0 and 37.8, respectively.[11] In the ^{13}C NMR spectrum of product **4** derived from the labeled isobutene matrix, the signal of C(3) was prominent; calculations indicated that >96% of the ^{13}C label was at C(3).

A parallel series of experiments was carried out with phenylcarbene, generated from phenyldiazomethane,[1,5] eq 2. In isobutene solutions (0 °C, −120 °C), addition product **6**[5]

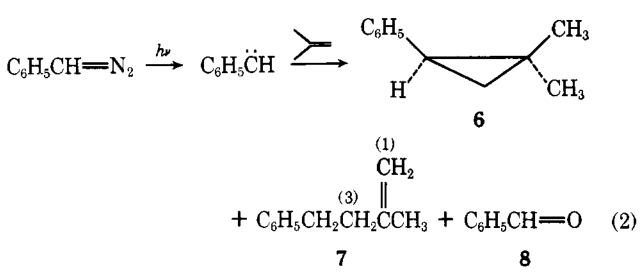


Table I. Product Distributions (%) from $PhCCH_3$ and Isobutene as a Function of Temperature[a]

Temp, °C	**1**	**2**	**3**	**4**	**5**
−40	5.6	26.	40.	—	28.
−70[b]	—	32.	47.	—	22.
−100	11.	7.9	44.	—	37.
−120	4.7	14.	38.	0.2	42.
−160[c]	7.3	20.	47.	1.8	24.
−196[c]	17.	42.	8.0	22.	11.

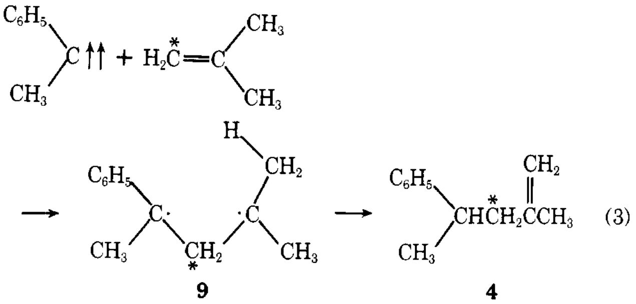
[a] Values are corrected for detector response, are relative to **2,** and are normalized to 100%. Averages of duplicate runs are tabulated; reproducibility was generally <±2%. [b] Photosensitized with benzophenone ($NiSO_4$–$CoSO_4$ filter). Little **1** was detected, but it has been observed in similar experiments.[4a] [c] Solid isobutene matrices were formed; ~10 vol % of diethyl ether was added to provide a uniform matrix. (Ether was present in the solution runs too.) An additional product, $C_{12}H_{18}O$ (exact mass determination), was isolated. It is assumed to result from "insertion" of $PhCCH_3$ at the α-position of diethyl ether; see below.

was dominant and alkene **7** could not be detected, but in a matrix, at −196 °C, the yield of **7**[12] *exceeded* that of **6**, 1.26:1. (Diethyl ether was generally omitted in phenylcarbene experiments. Product ratios were independent of its presence or absence, and toluene was not observed in any of these experiments.) Photolysis of phenyldiazomethane in a labeled isobutene matrix (−196 °C) gave **7** which, by ${}^{13}C$ NMR analysis,[11] contained 20% of the label at C(1) and 80% at C(3).[13]

The behavior of $PhCCH_3$ and PhCH generated in −196 °C isobutene matrices parallels that of PhCH in 2-butene matrices;[1] viz., compared to their behavior in liquid isobutene, both carbenes exhibit marked decreases in cyclopropane formation (**3** and **6**), and dramatic enhancement of alkene products (**4** and **7**). Also striking are the high relative yield of styrene from $PhCCH_3$ at −196 °C and, most importantly, the near-regiospecific label result in the conversion of $(CH_3)_2C{=}{}^{13}CH_2$ to **4.**

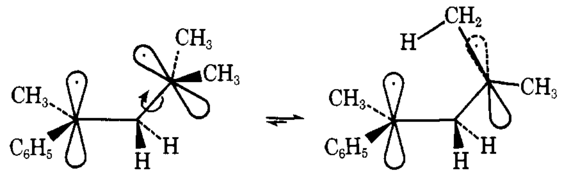
Why do matrices foster alkene formation? Assuming rapid and reversible singlet-triplet equilibria for $PhCCH_3$ and PhCH,[1,4a,14] singlet reactions may be geometrically more demanding than triplet reactions because, in the former, *two* bonds form "simultaneously", whereas, in the latter reactions, these bonds form sequentially. Although not crucial in the liquid phase, where the normally faster singlet reactions prevail, the restricted mobility enforced by the solid matrix may place a premium on reactant orientation, and favor reaction from the orientationally less-demanding triplet side of the spin state equilibrium. Thus matrix-restricted, singlet $PhCCH_3$ gives mainly the intramolecular product, styrene, and intermolecular reaction is damped; the yield of **3** (or **6**) falls. Triplet products, conversely, are exalted.

What is the origin of **4**?[15a] The label result can be explained by the addition-H-shift mechanism of eq 3.[15b] Triplet addition affords the well-stabilized triplet diradical **9.** If addition occurs along the trajectory described for $^{3}(CH_2)$ + ethylene,[16] then **9** will form in highly congested conformation **9A,** for which models reveal severe methyl-methyl and methyl-phenyl oppositions. Despite proper orbital alignment for closure, bond rotations will likely be faster than spin inversion,[14,17a] and **9A** should relax to less-congested conformer **9B,** which is properly aligned for H migration. Although, after spin inversion, some **3** will form from **9A,** much **4** will form from the more prevalent **9B.**[17b]



(3)

9 **4**



9A **9B**

An abstraction-recombination origin for **4** demands that abstraction occur at C(3) of isobutene, but that all collapse of the $C_6H_5\dot{C}HCH_3$, $\dot{C}H_2C(CH_3){=}CH_2$ radical pair occur at C(1). Although not impossible, such an exclusive "antimemory" effect seems less cogent than the mechanism of eq 3.

Alkene formation form PhCH and $(CH_3)_2C{=}{}^{13}CH_2$ is not label-specific. ^{3}(PhCH) should be more reactive than $^{3}(PhCCH_3)$, and the diradical formed by the former's addition to isobutene should be less stabilized than **9.** Therefore, abstraction-recombination and addition-H-migration mechanisms may well be competitive in PhCH-isobutene matrix reactions, accounting for label-scrambled **7.**[18] (Abstraction-recombination may, in fact, be dominant in PhCH-2-butene matrix reactions.[1]) We are continuing our studies of novel matrix-carbene reactions.[19]

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References and Notes

(1) R. A. Moss and U-H. Dolling, *J. Am. Chem. Soc.,* **93,** 954 (1971).
(2) W. J. Baron, M. R. DeCamp, M. E. Hendrick, M. Jones, Jr., R. H. Levin, and M. B. Sohn in "Carbenes", Vol. I., M. Jones, Jr., and R. A. Moss, Ed., Wiley, New York, N.Y., 1973, p 68. Note that the alternative mechanism there offered has been experimentally excluded.[3]
(3) R. W. Shaw, Ph.D. Thesis, Princeton University, 1973; private communication from Professor M. Jones, Jr.
(4) Earlier studies of $PhCCH_3$–olefin reactions include: (a) Y. Yamamoto, S-I. Murahashi, and I. Moritani, *Tetrahedron,* **31,** 2663 (1975); (b) I. Moritani, Y. Yamamoto, and S-I. Murahashi, *Tetrahedron Lett.,* 5697 (1968); (c) H. Kristinsson, *ibid.,* 2343 (1966); (d) G. L. Closs and J. J. Coyle, *J. Org. Chem.,* **31,** 2759 (1966).
(5) G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.,* **86,** 4042 (1964).
(6) R. A. Moss and R. Gerstl, *Tetrahedron,* **22,** 2637 (1966).
(7) K. Kitatani, T. Hiyama, and H. Nozaki, *J. Am. Chem. Soc.,* **97,** 950 (1975).
(8) This compound exhibited GC purity, and IR, NMR, and exact mass spectral characteristics in accord with the assigned structure.
(9) Labeled isobutene was prepared from acetone and $(C_6H_5)_3P{=}{}^{13}CH_2$.[10] The ylide was made from $(C_6H_5)_3P^+CH_3,I^-$ synthesized from CH_3I containing 12.5 ± 0.6 atom % ${}^{13}C$. NMR analysis ($=CH_2$ satellite and parent absorptions) showed the isobutene to contain 11.6 ± 0.2 atom % ${}^{13}C$ at the methylene carbon; isobutene recovered after photolysis showed 11.9 ± 0.1 atom % ${}^{13}C$ at this position.
(10) G. Wittig and U. Schöllkopf, *Org. Synth.,* **40,** 66 (1960).
(11) Complete analyses of the ${}^{13}C$ NMR spectra will appear in the Ph.D. Thesis of M. A. Joyce.
(12) 2-Methyl-4-phenylbutene-1, **7,**[8] was prepared from hydrocinnamic acid by a sequence analogous to that employed for **4.**
(13) Chemical shifts for **7** were δ ($CDCl_3$, Me_4Si): C(1), 110.2; C(3), 34.3.
(14) Reviews: P. P. Gaspar and G. S. Hammond in "Carbenes", Vol. II. R. A. Moss and M. Jones, Jr., Ed., Wiley, New York, N.Y., 1975, p 207 ff; G. L. Closs, *Top. Stereochem.,* **3,** 193 (1968).
(15) (a) Control experiments show that, with diethyl ether absent, little ethylbenzene forms. The principal origin of **1** is probably $^{3}(Ph\ddot{C}CH_3)$ + H· → $Ph\dot{C}HCH_3$ (+ H·) → **1,** with each H· coming from the α-positions of ether molecules. Under matrix conditions, recombination of the initial $Ph\dot{C}HCH_3$, $CH_3\dot{C}HOC_2H_5$ radical pair competes well with diffusion. Importantly, α-phenylethyl radical is not a precursor of **4;** photolysis of *tert*-butyl 2-phenylperpropionate in isobutene matrices gave **1, 2,** and α-phenylethyl *tert*-butyl ether, but no **4.** (b) A similar mechanism has been offered for 3-methyl-1-butene formation in the gas phase reactions of $^{3}(CH_2)$ and 2-butenes, but the mechanistic assignment is not definitive: D. F. Ring and B. S. Rabinovitch, *Int. J. Chem. Kinet.,* **1,** 11 (1969); C. McKnight and F. S. Rowland, *J. Am. Chem. Soc.,* **88,** 3179 (1966); and R. W. Carr, Jr., and

G. B. Kistiakowsky, *J. Phys. Chem.*, **70**, 118 (1966).
(16) N. Bodor, M. J. S. Dewar, and J. S. Wasson, *J. Am. Chem. Soc.*, **94**, 9095 (1972).
(17) (a) R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 1475 (1969). (b) We have established that no more than ~5% of the alternative H migration occurs from **9** to form 2-phenyl-4-methylpent-1-ene. We suspect we know why this process competes so poorly with **9** → **4**. Additional experiments are planned.
(18) If the recombinations of benzyl–isobutenyl radical pairs were random, the label result would suggest 40% of an abstraction–recombination mechanistic component. Incursion of a matrix-imposed (normal) memory effect would reduce this contribution.
(19) Preliminary experiments reveal matrix-engendered alkene formation from fluorenylidene and *cis*-2-butene; M. A. Joyce, unpublished work.

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A ^{15}N CIDNP Investigation of Dialkyl Azo Compounds: Evidence for *tert*-Alkyl Diazenyl Radicals

Sir:

Although azoalkanes have been studied for some 40 years, the mechanism of their decomposition is still a matter of some controversy.[1] The evidence for the one-bond mechanism (eq 1) in arylazoalkane decomposition is extensive.[2-5] Stereochemical[2] and CIDNP[3] studies as well as investigations of rate vs. viscosity[4] and pressure[5] all point to the intermediacy of phenyldiazenyl radicals. Alkyldiazenyl radicals, however, have proved to be much more elusive and the two-bond mechanism (eq 2) has been accepted (but not necessarily proven) for most dialkyl azo compounds.

Scheme I

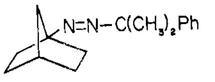
$$R{-}N{=}N{-}R' \rightleftarrows R{-}N{=}N\cdot \cdot R' \rightarrow R\cdot\ N_2 \cdot R' \qquad (1)$$

$$R{-}N{=}N{-}R \rightarrow R\cdot\ N_2 \cdot R' \qquad (2)$$

Kinetic studies by Engel[6] and Ruchardt[7] point to asymmetric stretching of C–N bonds in the transition state for unsymmetric dialkyl azo compounds. They conclude that, with the exception of extreme cases, the two-bond mechanism applies for dialkyl azo compounds. Kinetic methods only provide information about the transition state, however, and both authors note that care must be exercised in using rate data as evidence for or against the intermediacy of diazenyl radicals.

CIDNP has been used successfully in studies of azo compound decomposition. ^{1}H, ^{13}C, and ^{15}N CIDNP studies[3] have supported the one-bond mechansim for decomposition of *cis*- or *trans*-phenylazoalkanes, but, to date, no CIDNP evidence favoring the one-bond mechanism for dialkyl azo compounds has been presented. We report here a ^{15}N CIDNP study that provides the first direct spectroscopic evidence supporting the intermediacy of an alkyldiazenyl radical.

Compound **1** was chosen for study,[8] since the cumyl and 1-norbornyl radicals differ significantly in their stabilities.[9,10] Recently, the symmetric bis-1-norbornyl azo compound has been shown to be particularly resistant to photochemical radical formation—photoisomerization being preferred.[11]



Photochemical decomposition of *trans*-**1** in cyclopropane (25 °C, sealed tube) or benzene leads to products expected from homolytic cleavage. Norbornane (5%), dicumyl (40%), and α-methylstyrene were isolated by gas chromatography and identified. Photolysis of **1** (366 nm.) at −125 °C in cyclopropane produced *cis*-**1**. The existence of *cis*-**1** was supported by low temperature ^{1}H and ^{15}N NMR as well as UV-visible spectroscopy. Thus, *trans*-**1** labeled with ^{15}N at the nitrogen adjacent to the norbornyl group absorbs 154-ppm downfield from $^{15}NO_3^-$, whereas the cis compound absorbs further downfield at 168 ppm. Similarly, in the ^{1}H NMR, the singlet due to the six protons of the cumyl methyl group for *trans*-**1** are found at δ 1.4, whereas the same protons absorb at δ 1.9 for the cis isomer. λ_{max} for the cis isomer is found at longer wavelength than for the trans. Thus, the n–π^* absorbance of *trans*-**1** (λ_{max} 355 nm) is shifted to longer wavelength (λ_{max} 416 nm) upon low temperature photolysis with an isosbestic point maintained at 387 nm during the photolysis. The photoequilibrium concentration of the cis isomer can be favored by photolysis at 366 nm and the trans isomer is favored by photolysis at 415 nm, where the absorbance of the cis isomer is dominant.

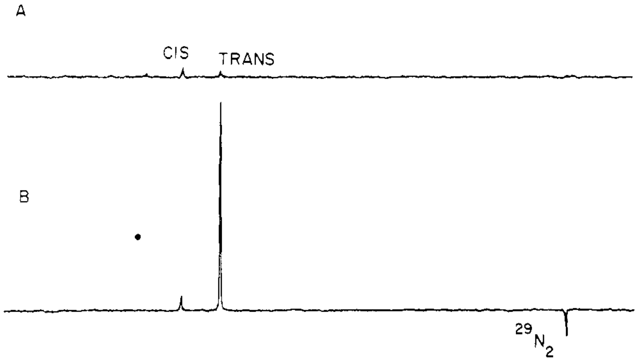


Figure 1. (a) ^{15}N NMR spectrum of a mixture of *cis*- and *trans*-**1** in cyclopropane at −90 °C. (b) ^{15}N CIDNP spectrum obtained by decomposing *cis*-**1** at −40 °C in cyclopropane solvent (**1** is ^{15}N enriched at the azo nitrogen adjacent to the norbornyl group).

A ^{1}H CIDNP spectrum was produced by thermal decomposition of *cis*-**1** at −36 °C in cyclopropane. The major features of the ^{1}H CIDNP are emissions near δ 2.05 and two other emissions at δ 4.8 and 5.2. Comparison with authentic samples reveals that these signals are due to α-methylstyrene (AMS). The alkyl region of the CIDNP spectrum was extremely complex and was partially buried in the cyclopropane solvent peak, making further analysis of the spectrum impossible.

Thermal decomposition of ^{15}N labeled *cis*-**1** at −40 °C in a ^{15}N Bruker HFX-10 spectrometer produced the spectrum shown in Figure 1. The spectrum consisted of polarized signals due to *cis*- and *trans*-**1**.[12] In addition, a strong emission for $^{29}N_2$ was observed 66.5-ppm upfield from $^{15}NO_3^-$. The ^{15}N CIDNP spectra reported here are consistent with the mechanism shown in Scheme II.

The initially formed 1-norbornyldiazenyl–cumyl radical pair can recombine to form *cis*- and *trans*-**1** that are polarized. Further, diffusion and β cleavage of the alkyldiazenyl radical yields $^{29}N_2$, showing polarization that is inverted, as expected, relative to the azo return products.[13] The ^{15}N CIDNP spectra are thus consistent with the radical pair theory of CIDNP developed by Closs, Kaptein, and Oosterhoff.[13,14] We note that due to the negative gyromagnetic ratio of ^{15}N, the simple CKO rules[13,15] must be modified, since the energy of a nuclear state depends directly on the gyromagnetic ratio. Thus, an additional minus sign is introduced into the CKO rules developed[13,15] for nuclei with positive gyromagnetic ratios.[16]

The ^{15}N CIDNP spectrum obtained from **1** is directly analogous to ^{15}N CIDNP spectra obtained from unsymmetric phenylazoalkanes.[17] Thus, decomposition of *cis*-phenylazocumene[17] resulted in enhanced absorption of the azo nitrogens and emission due to $^{29}N_2$. Since phenylazoalkanes are known