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(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.
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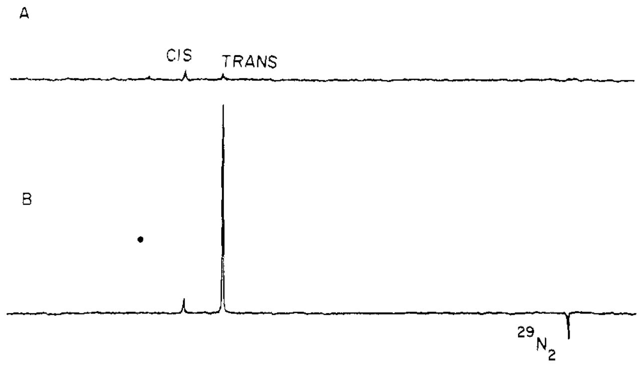


Figure 1. (a) ^{15}N NMR spectrum of a mixture of *cis*- and *trans*-**1** in cyclopropane at −90 °C. (b) ^{15}N CIDNP spectrum obtained by decomposing *cis*-**1** at −40 °C in cyclopropane solvent (**1** is ^{15}N enriched at the azo nitrogen adjacent to the norbornyl group).

A ^{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

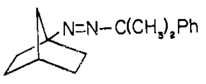
$$R{-}N{=}N{-}R' \rightleftarrows R{-}N{=}N\cdot\ \cdot R' \rightarrow R\cdot\ N_2\ \cdot R' \quad (1)$$

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

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.

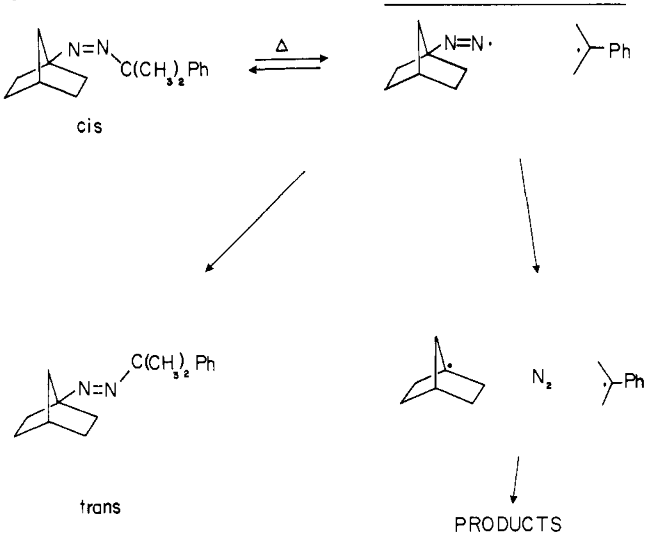
A ^{1}H CIDNP spectrum was produced by thermal decomposition of *cis*-**1** at −36 °C in cyclopropane. The major features of the ^{1}H CIDNP are emissions near δ 2.05 and two other emissions at δ 4.8 and 5.2. Comparison with authentic samples reveals that these signals are due to α-methylstyrene (AMS).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

Scheme II



to decompose via intermediate diazenyl radicals,[2,3] this experiment provides strong support for alkyldiazenyl radicals during azo decomposition.

The proton CIDNP spectrum also supports the mechanism proposed in Scheme II. The vinyl and allylic protons of α-methylstyrene are polarized in the cumyl-1-norbornyldiazenyl radical pair. The AMS emission that results is predicted by the CKO rules[13,15] and is analogous to the results of ^{1}H CIDNP studies on the cumyl-phenyldiazenyl radical pair.[2,3]

Previously, evidence was presented that established the intermediacy of only two diazenyl radicals—the phenyl- and methyl-substituted species.[18] This work suggests that 1-norbornyl diazenyl radical also has a finite lifetime and emphasizes the effectiveness of ^{15}N CIDNP in studies of azo decomposition.

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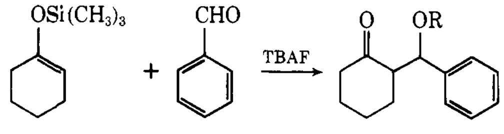
Fluoride Ion Catalyzed Aldol Reaction between Enol Silyl Ethers and Carbonyl Compounds

Sir:

The title reaction[1] exhibits various characteristic features which have not been observed in ordinary aldol reaction[2] involving Lewis acid-complexed enolates[3] or species in hydroxylic solvents.

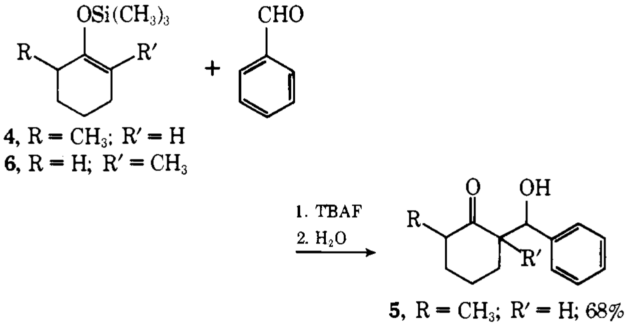
Under the influence of *a catalytic amount* (5–10 mol %) of tetrabutylammonium fluoride (TBAF), the enol trimethylsilyl ether **1** reacted with an equimolar amount of benzaldehyde in THF smoothly at low temperatures, giving the aldol silyl ether **2** in > 80% yield.[4] Workup with aqueous CH_3COOH, dilute HCl, or KF-CH_3OH afforded quantitatively the corresponding aldol **3**. This reaction gives no or very little products arising from undesired dehydration, self-condensation, or polyaldol condensation which frequently takes place under conventional aldol reaction conditions.[2]



1

2, R = Si(CH$_3$)$_3$
3, R = H

This cross aldol reaction finds considerable generality. In place of **1**, enol trimethylsilyl ethers of cyclopentanone, cycloheptanone, diethyl ketone, pinacolone, etc., could be used as well. Enol silyl ethers derived from sterically hindered ketones such as diisobutyl ketone may be equally employable. Both aromatic aldehydes, ArCHO (Ar = C_6H_5, p-$CH_3OC_6H_4$, p-$NO_2C_6H_4$, α-furyl, etc.), and aliphatic aldehydes (heptanal, isobutyraldehyde, 3-phenylpropanal, etc.) are usable, but, in usual, aromatic aldehydes serve as a better receptor (usually 70–95% yield) than aliphatic ones (35–50%). When α,β-unsaturated aldehydes such as cinnamaldehyde or 2-hexenal were used, only 1,2-addition products were formed (50–60%). The catalyzed reaction proceeds regiospecifically. Thus each of the enol silyl ethers **4** and **6** reacted with benz-



4, R = CH$_3$; R′ = H
6, R = H; R′ = CH$_3$

5, R = CH$_3$; R′ = H; 68%
7, R = H; R′ = CH$_3$; 62%