Diazenyl Radicals: A ^{15}N CIDNP and Radical Trapping Study of Unsymmetric Diazenes

Ned A. Porter,* George R. Dubay, and John G. Green

Contribution from the Paul M. Gross Chemical Laboratories, Duke University, Durham, North Carolina 27706. Received May 31, 1977

Abstract: The decomposition of phenylazotriphenylmethane, *N*-cumyl-*N'*-phenyldiazene, phenylazoisobutyronitrile, and *N*-cumyl-*N'*-1-norbornyldiazene was studied by ^{15}N CIDNP. The CIDNP spectra support the one-bond cleavage decomposition mechanism for all of these diazenes. This mechanism requires the intermediacy of diazenyl radicals R–N=N·. Independent evidence for the phenyldiazenyl radical was obtained by trapping that species with triphenylmethyl. Thus, decomposition of *cis*-*N*-cumyl-*N'*-phenyldiazene in the presence of triphenylmethyl led to 1.3% of the unsymmetric diazene, phenylazotriphenylmethane, that was formed by the combination of the diazenyl radical and triphenylmethyl.

Since the early studies of Gomberg on triphenylmethyl radicals, unsymmetric diazenes have been used as a source of free radicals.[1] The mechanism of radical formation from these diazenes has been studied extensively, but it has only been in the past 10 years that a firm understanding of diazene decomposition has been attained. Several methods have been used to study the mechanism of diazene decomposition. Ramsperger,[2] Crawford,[3] Engel,[4] Rüchardt,[5] and others[6] have used a kinetic approach for the study of azo decomposition. Stereochemical[7-9] and isotope studies,[10] solvent viscosity effects,[11] and pressure effects[12] have also provided information about diazene decomposition.

The weight of evidence presented thus far suggests that unsymmetric diazenes bearing a phenyl group decompose by initial scission of one carbon–nitrogen bond leading to a nitrogen-containing phenyldiazenyl radical. Stereochemical studies[7,9] and ^{1}H CIDNP[13] studies all support the intermediacy of a phenyldiazenyl radical. [1]H CIDNP suffers somewhat from the complexity of spectra obtained and other nuclei (particularly ^{15}N) show promise[14,15] in simplifying the interpretation of spectra.

Although aryldiazenyl radicals have thus been implicated by a variety of experimental techniques, no successful scavenging experiment of the diazenyl radical by an externally added radical trap has been reported. Hammond and Garst[16] attempted, unsuccessfully, to trap the phenyldiazenyl radical with externally added triphenylmethyl radical. Their experiment involved measuring the rate of decomposition of phenylazotriphenylmethane (**1**) in the presence of added triphenylmethyl radical. No "common radical" rate retardation of **1** decomposition was detected.

We report here on the ^{15}N and ^{13}C CIDNP spectra obtained during decomposition of several unsymmetric diazenes. Further, we report the first successful trapping of the phenyldiazenyl radical by an externally added radical trap.

Results and Discussion

Syntheses of ^{15}N-Labeled Compounds. Syntheses of ^{15}N-labeled compounds were, in general, patterned after previously reported schemes.[17-20] Thus **1, 2, 3,** and **4** could be prepared
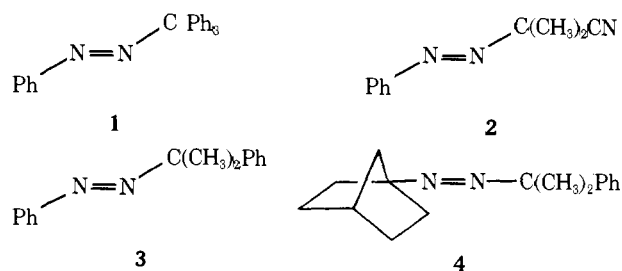
labeled at any of the nitrogens with ^{15}N by established syntheses as reported in the Experimental Section.

The trans diazenes **2, 3,** and **4** synthesized by the methods described (vide supra) were converted to the cis isomers[7,15,21] by low-temperature photolysis. *cis*-**2** and -**3** were stable at temperatures below 0 °C, and *cis*-**4** was stable below about −55 °C. *cis*-**2** and -**3** were purified by low-temperature chromatography on silica gel. *cis*-**4** could not be separated from the trans isomer present in the photoequilibrated mixture and photolysis mixtures containing cis:trans ratios of approximately 60:40 were used in the studies reported here. Although efforts were made to detect the cis isomer of **1** during the low-temperature photolysis of the trans isomer, we could find no evidence for the existence of this species.

^{15}N NMR Chemical Shifts in Diazenes. The ^{15}N chemical shift data for several cis and trans diazenes are presented in Table I. Two generalizations can be made from these data. First, a diazene nitrogen attached to an aryl substituent absorbs upfield from the absorption due to nitrogen bonded to an alkyl group. Thus, for the trans diazenes, all of the nitrogens bonded to the phenyl group (Np) absorb in the range of 120–140 ppm downfield from [15]NO$_3^-$ whereas nitrogens attached to alkyl substituents are found in the range 135–180 ppm downfield from the standard. The second generalization suggested from Table I is that cis diazenes absorb at lower field than the corresponding trans isomer. In fact, with every compound studied, the signal due to the cis diazene was found downfield at least 8 ppm from the absorption of the corresponding trans isomer and in most cases the absorption in the cis diazene was shifted downfield 18–25 ppm from the trans compound.

We also note that the [15]N–[15]N coupling constant is larger for cis isomers than for trans. [15]N double labeled trans-**1**, -**2**, and -**3** all had [15]N–[15]N coupling constants of 17 Hz. The corresponding cis isomers of **2** and **3** had [15]N–[15]N coupling constants of 21 Hz.

CIDNP. Phenylazotriphenylmethane (**1**) was prepared as a monolabeled compound with ^{15}N adjacent to the phenyl group (Np) and as a double-labeled compound with ^{15}N present at both positions in the azo linkage (Np and NT). In Figure 1 are presented (a) the ^{15}N spectrum of doubly labeled **1** in benzene at 30 °C and (b) a spectrum of the same sample taken at 60 °C after azo decomposition has begun. As seen in the figure, signal enhancement is observed as the temperature of the sample is raised and decomposition begins.

Thus, enhanced absorption is observed for both NT and Np nitrogens and, in addition, an emission is observed at 66.5 ppm upfield from [−]NO$_3$. **1** labeled only at Np gives a ^{15}N CIDNP spectrum consisting only of an absorption at −145 ppm due to the uncoupled Np and an emission at +66.5 ppm.

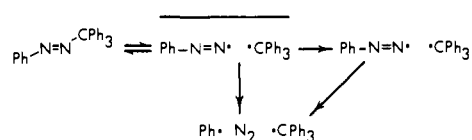The observed CIDNP spectrum can be rationalized on the basis of the mechanism presented in Scheme I. This mecha-

Ph–N=N–CPh$_3$

1

Ph–N=N–C(CH$_3$)$_2$CN

2

Ph–N=N–C(CH$_3$)$_2$Ph

3

N=N–C(CH$_3$)$_2$Ph

4

Table I. ^{15}N Chemical Shifts for Azo Compounds

Structure	Chemical shifts (NO$_3^-$ std)	
$Ph-^{15}N_1=N-Ph$	$^{15}N_1 = -130^a$	
$Ph-^{15}N_1=^{15}N_2-\bigcirc-OH$	$N_1 = -120.4^a$ $N_2 = -132.7^a$	
$Ph-^{15}N_P=^{15}N_T-C(Ph)_3$	$N_P \doteq -145$ $N_T = -169$	
	trans	cis
$Ph-^{15}N_P=^{15}N_I-C(CH_3)_2C\equiv N_N$	$N_N = 118$ $N_P = -135$ $N_I = -137$ $? = -184$	$N_N = 108$ $N_P = -154$ $N_I = -144$
$Ph-^{15}N_P=^{15}N_C-C(CH_3)_2Ph$	$N_P = -132$ $N_C = -170$	$N_P = -161$ $N_C = -194$
$^{15}N_B=N-C(CH_3)_2Ph$	$N_B = -158$	$N_B = -176$

^{a} M. Witanoski, L. Stefaniak, and H. Jonuszewski, "Nitrogen Chemical Shifts in Organic Compounds", in "Nitrogen NMR", M. Witanoski and G. Webb, Ed., Plenum Press, New York, N.Y., 1973.

Scheme I

$$Ph-N=N^{CPh_3} \rightleftharpoons Ph-N=N\cdot \ \cdot CPh_3 \longrightarrow Ph-N=N\cdot \ \cdot CPh_3$$
$$\downarrow \qquad \nearrow$$
$$Ph\cdot \ N_2 \ \cdot CPh_3$$

nism, which is now generally accepted[11,12] for decomposition of 1, involves initial cleavage of one carbon–nitrogen bond leading to the phenyldiazenyl-triphenylmethyl radical pair.

The simple rules developed by Closs, Kaptein, and Oosterhoff[22,23] for predicting the polarization of CIDNP spectra must be modified when considering ^{15}N polarization.[15] Because of the negative gyromagnetic ratio of ^{15}N, the nuclear states of ^{15}N atoms are inverted relative to those of nuclei with positive gyromagnetic ratios. Thus, an additional minus sign is introduced into the rules developed[22,23] for nuclei with positive gyromagnetic ratios. The rule for nuclei with negative γ then becomes

$$\Gamma = -\mu\epsilon\Delta g a_i \qquad (1)$$

where μ, ϵ, Δg, and a_i are identical with the parameters defined earlier.[22,23]

In the example above, μ is negative since the radical pair derives from a singlet precursor, ϵ is positive for the re-formed azo compound since it is a cage product, and Δg is negative.[24] The ^{14}N hyperfine coupling constants for the phenyldiazenyl radical have been calculated[25] and the relationship shown below[26] (eq 2) can be used to relate a_{14N} to a_{15N}.

$$a_{15N} = [(\mu/I)_{15}/(\mu/I)_{14}]a_{14N} \qquad (2)$$

By the use of eq 2 and the ^{14}N calculated[25] hyperfine values, we calculate ^{15}N a values of -19.4 and -9.1, respectively, for the nitrogen adjacent to the phenyl ring and the one most distant from the phenyl substituent. Substituting the values of μ, ϵ, Δg, and a_i in eq 1 leads to the prediction that the ^{15}N CIDNP spectrum should consist of N_P and N_T observed in enhanced absorption with $^{30}N_2$, the escape product, observed in emission. The spectrum predicted on the basis of the mechanism outlined in Scheme I is thus observed experimen-
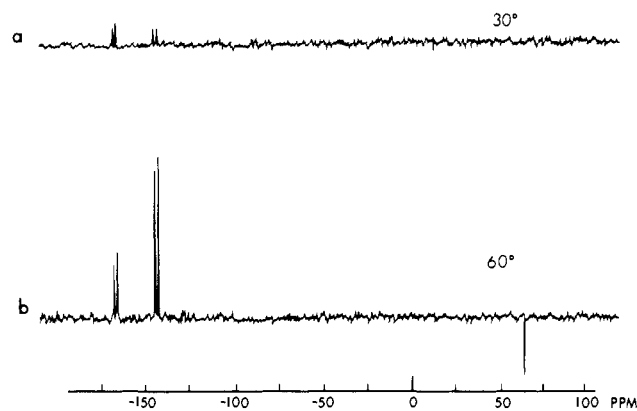

Figure 1. ^{15}N NMR spectra obtained from N_P and N_t labeled 1 (a) at 30 °C in benzene and (b) the same sample at 60 °C.
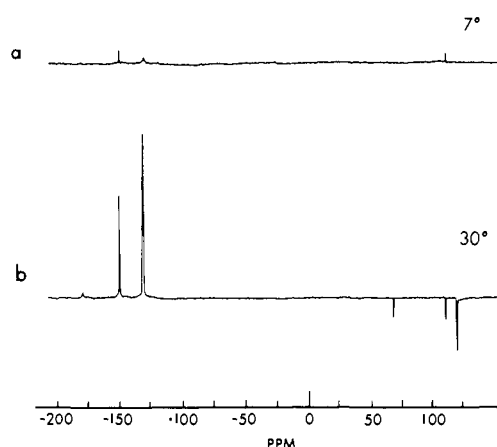

Figure 2. ^{15}N NMR spectra obtained from N_P and N_n labeled cis-2 (a) at 7 °C in benzene and (b) the same sample at 30 °C.

tally. Both diazene nitrogens are observed in enhanced absorption and $^{30}N_2$, which absorbs at +66.5 ppm ($^{15}N_3^-$ standard), is observed in emission.[27] Further, the intensity of the polarization observed for the diazene nitrogens qualitatively reflects the magnitude of the hyperfine coupling constant for those nuclei. Thus, the calculated a for N_P is twice the value of the a of N_T and the intensity of the signal due to N_P is some 2.6 times the value of the N_T signal.

For decomposition of 2, phenylazoisobutyronitrile, ^{15}N CIDNP spectra could be obtained by observation during photolysis of the trans diazene in the NMR probe or by observation during thermal decomposition of the cis isomer. Cis diazenes are considerably less stable than their trans isomers and decomposition of cis-2 is rapid at 30 °C. In Figure 2 are presented (a) the spectrum of cis-2 taken at 7 °C in benzene and (b) the same sample warmed to 30 °C. The cis-2 used in this study was doubly labeled: one ^{15}N at N_p, the nitrogen adjacent to the phenyl substituent, the other at N_N, the nitrile nitrogen. Quite obviously, significant enhancement of the signal accompanies decomposition. Enhanced absorption signals at -154 and -138 ppm are observed and these signals are due to N_p of cis- and trans-2, respectively. The nitrile nitrogens at +108 and +118 ppm (cis and trans, respectively) are observed in emission, as is $^{29}N_2$ at +66.5 ppm.

The CIDNP spectrum obtained from decomposition of cis-2 can be rationalized by consideration of the mechanism shown in Scheme II. On the basis of this scheme, and assuming (a) that g for the cyanoisopropyl radical is larger than that for the diazenyl radical[28] and (b) that the nitrile ^{15}N has a negative hyperfine coupling constant,[29] one can predict the experi-
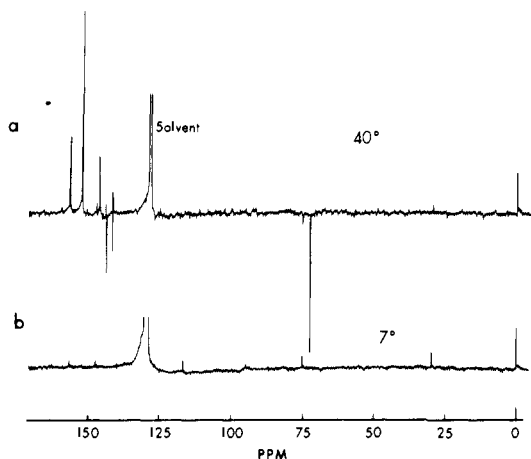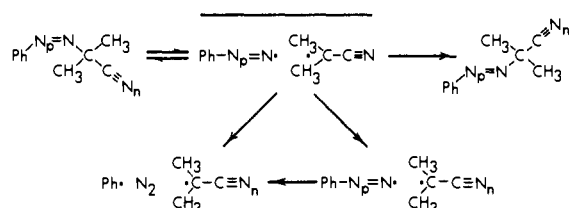
Figure 3. ^{13}C NMR spectra obtained from *cis*-**3** (a) at 40 °C and (b) 7 °C before decomposition has begun.

Table II. ^{13}C CIDNP Data for Decomposition of *cis*-**3**

Chem shift	Polarization	Assignment[a]
156.9 ± 0.3	A	C_p in *cis*-**3**
152.8	A	C_p in *trans*-**3**
147.6	A	C_A in *cis*-**3**
146.4	A	C_A in *trans*-**3**
143.6	E	C_α in α-methylstyrene
141.8	E	C_p in biphenyl
141.6	A	C_A in α-methylstyrene
75.3	E	C_C in *cis*-**3**
72.7	E	C_C in *trans*-**3**

[a] See Scheme IV for identification of atoms in **3**, α-methylstyrene, and biphenyls.

Scheme II

mentally observed spectra by the use of the modified rules discussed earlier.

A very weak absorption was repeatedly observed at −184 ppm in decompositions of N_p-labeled *cis*-**2**. Very few nitrogen compounds, other than diazenes, are known that absorb in this region. This new weak absorption, then, probably is due to a diazene-type product, formed from a cage reaction of the initially formed radical pair. At least two possibilities exist for this new compound as shown in Scheme III. The ketenimine

Scheme III
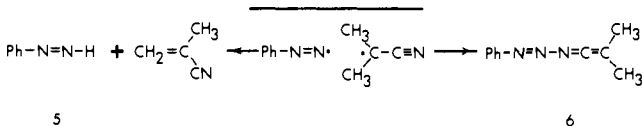
6 seems the more likely of the two possibilities to us since the −184 ppm absorption is not observed in other systems that could also form phenyldiazene (**5**) by disproportionation.[14] Formation of ketenimines is an established cage reaction of cyanoisopropyl radicals, a ketenimine being one of the major cage products formed from two cyanoisopropyl radicals.[30] At this time, we have no other data that we can bring to bear that concerns the structure of the species responsible for the −184 ppm absorption, and the proposal of structure **6** is thus a tentative one.

Direct photolysis of *trans*-**2** in the spectrometer probe (benzene solvent, ∼30 °C) produced ^{15}N CIDNP spectra directly analogous to spectra obtained by thermal decomposition of the cis isomer. An induction period for maximum polarization was observed and further, spectra obtained immediately after photolysis was stopped continued to show substantial polarization. This suggests that one mechanism for polarization involves trans–cis isomerization of **2** followed by thermal decomposition of *cis*-**2**. We have no evidence, however, that indicates that this is the sole mechanism operating, and direct photolysis of *trans*-**2** giving the radical pair may be coincident with the isomerization pathway.

The diazene **3** behaves chemically very much like compound **2**. Thus, decomposition of the cis isomer of **3** or direct photolysis of a sample of the trans isomer of **3** in the NMR probe produces a ^{15}N CIDNP spectrum.[14] The spectrum consists of enhanced absorption of both diazene nitrogens, N_p and N_c, and, in ^{15}N double-labeled **3** (N_p and N_c), the polarization of the N_p nitrogen is some 2.5–3 times that of the polarization due to N_c. Thus, the spectrum obtained from **3** also supports the conclusion that $a_{N_p} > a_{N_c}$.

A ^{13}C CIDNP spectrum obtained from decomposition of *cis*-**3** is presented in Figure 3 and in tabular form in Table II. Scheme IV presents a mechanism, similar to those proposed earlier for **1** and **2**, that is consistent with the ^{15}N and ^{13}C CIDNP spectra.

Scheme IV
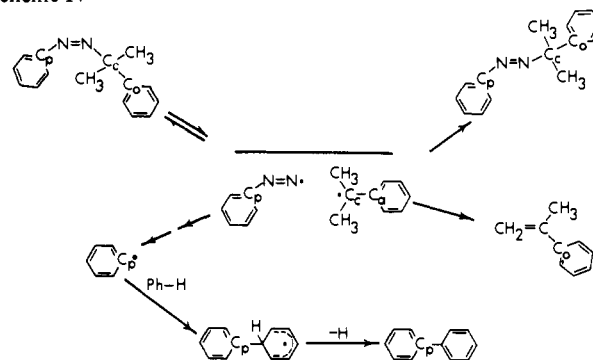
Scheme IV accounts for all of the features of the ^{13}C CIDNP spectrum if one makes the following reasonable assumptions: (a) Cumyl radicals have a larger g value than that of the phenyldiazenyl radical[13] and (b) C_p and C_c have positive hyperfine coupling values and C_A a negative one.[25,31] We should make particular note of the polarization observed for biphenyl. Polarization of C_p occurs at the initial phenyldiazenyl–cumyl radical pair. This polarization is maintained throughout three subsequent steps before the ultimate escape product, biphenyl, is formed. "Memory effects" of this type have been observed in previous studies.[32] It is also of interest that the decomposition of **3** has now been studied by ^{1}H, ^{13}C, and ^{15}N CIDNP and all of these studies point to the same mechanism, that is, homolytic one-bond scission leading to the phenyldiazenyl–cumyl radical pair. Thus, the weight of this evidence, along with the other classical mechanistic studies on **1**, **2**, and **3**,[7,9,11,12,25] leads inevitably to the conclusion that the phenyldiazenyl radical is a discrete, metastable intermediate in aryl-alkyldiazene decomposition.
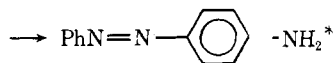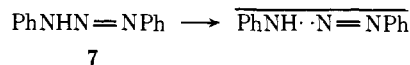
Evidence presented for dialkyldiazene decomposition is somewhat more ambiguous and the only alkyldiazenyl radical for which compelling evidence exists[33] is the methyldiazenyl radical. Kinetic studies suggest[4,5] that there is asymmetric stretching of C–N bonds in the transition state for unsymmet-

ric dialkyldiazenes but that, with the exception of extreme cases, simultaneous cleavage of both C–N bonds occurs in the decomposition. The dialkyldiazene **4** was prepared and studied since the 1-norbornyldiazenyl radical would represent an extreme case, it being particularly unstable.[34]

Photolysis of *trans*-**4** at −125 °C with 366-nm light produced a change in the UV–vis spectrum. A new absorption appeared at longer wavelength and an isosbestic point at 387 nm was maintained during the photolysis. This behavior is typical of aryl-alkyldiazenes and the new absorption observed with λ_{max} 416 nm is due to *cis*-**4**. Photolysis of the mixture at 416 nm caused the new peak to disappear with a concomitant increase in the trans absorption vanished, indicating that *cis*-**3** is unstable above these temperatures. Owing to the instability of *cis*-**4**, no attempts were made to isolate this compound free of the trans isomer. Rather, by photolysis of the trans compound at 366 nm (−125 °C), a mixture containing as much as a 2:1 ratio of *cis*-:*trans*-**4** (^{1}H NMR analysis) was used for further studies.

The decomposition of *cis*-**4** was carried out in cyclopropane solvent at −40 °C in the NMR. The ^{15}N CIDNP spectrum that results[15] is remarkably similar to the spectra obtained from **1**, **2**, and **3**. Enhanced absorption of signals due to the labeled nitrogen (N_b, adjacent to the norbornyl) is observed for both the cis and trans diazenes and, as well, [29]N_2 is observed in emission. Thus, the ^{15}N CIDNP evidence suggests that **4** decomposes via a diazenyl radical mechanism, as do the aryl-substituted compounds, **1**–**3**.

Previously published ^{15}N CIDNP studies by Lippmaa[35] on the decomposition of triazenes are of interest when compared to our results. Decomposition of the doubly labeled triazene, **7**, gave rise to the polarized rearrangement product, *p*-ami-

$$PhNHN = NPh \longrightarrow \overline{PhNH \cdot \cdot N = NPh}$$

7

$$\longrightarrow PhN = N - \hspace{-2pt}\langle\!\!\bigcirc\!\!\rangle\!\!- NH_2^*$$

noazobenzene (polarization indicated by an asterisk) 1. addition to polarized signals from this rearrangement product, a strong emission was observed approximately 66 ppm upfield from NO_3^-. [29]N_2 was discounted as a possible cause of this emission since argon purging did not eliminate the signal. In our studies with **1**–**4** we have observed strong emission signals at +66.5 ppm, the now accepted chemical shift for [29]N_2, and we suggest[14] that [29]N_2 should not be ruled out as a source of polarization in published triazene[35] and diazonium experiments.[36]

Diazenyl Radical Trapping. The evidence pointing to the intermediacy of phenyldiazenyl radicals in decompositions of aryl-alkyldiazenes prompted us to attempt to trap this species with a stable radical scavenger. *cis*-**3** was chosen as a source of the phenyldiazenyl radical since it is easily purified and its chemistry has been extensively studied.[7] Thus, a benzene solution 0.01 M in *cis*-**3** and 4.4 × 10⁻³ M in triphenylmethyl[16,37,38] radical was let stand under N_2 for 5 h at 25 °C (99% decomposition of *cis*-**3**). The total concentration of triphenylmethyl plus dimer[38] was 9.0 × 10⁻² M and the monomer concentration was calculated from the known equilibrium constant (K = 2.1 × 10⁻⁴).[39] After decomposition of *cis*-**3** was complete, excess triphenylmethyl radical was converted to peroxide by exposure to air at room temperature and the diazene products were then analyzed by high-pressure liquid chromatography. *trans*-**3** was formed in 35% yield and phenylazotriphenylmethane (**1**), the expected trapping product, was formed in 1.3% yield. Both of these diazenes were shown to be stable to both the conditions of the *cis*-**3** decomposition and the workup and analysis.

Two mechanisms can be written to account for the conver-

Scheme V
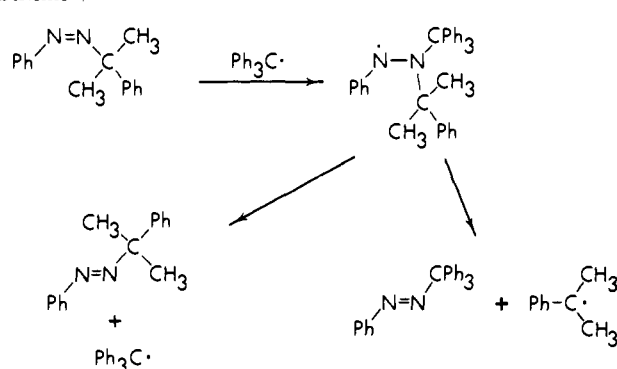
sion of *cis*-**3** to **1**. The first is presented in Scheme V (mechanism 1). In this mechanism, addition of triphenylmethyl to *cis*-**3** yields a hydrazyl radical, **8**, which can undergo β-scission to yield either **1** or *trans*-**3**. The second mechanism is presented in Scheme VI (mechanism 2).

The mechanism outlined in Scheme VI is analogous to the

Scheme VI
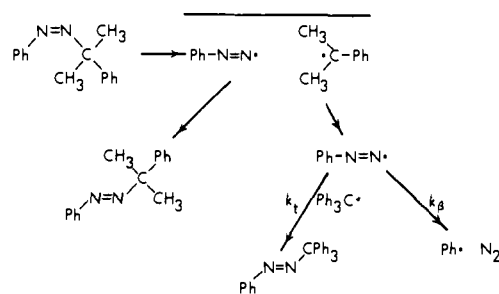
one suggested from the CIDNP experiments discussed earlier. The mechanism must be modified, however, by the presence of the added scavenger, triphenylmethyl. Escape of the phenyldiazenyl radical from the initial pair is followed by entrapment of the radical by triphenylmethyl to yield **1** or by β-scission of Ph–N=N· to yield the phenyl radical and molecular nitrogen.

Four pieces of evidence would appear to rule out mechanism 1 (Scheme V) from serious consideration:

1. The evidence presented from ^{1}H, ^{13}C, and ^{15}N CIDNP studies is consistent with mechanism 2 (vide supra). A hydrazyl radical mechanism would not lead to CIDNP polarizations like those observed.

2. Kinetic studies of *cis*-**3** decomposition in the presence of triphenylmethyl show that the rate of *cis*-**3** decomposition is independent of triphenylmethyl radical concentration, but mechanism 1 requires that the kinetics of *cis*-**3** decomposition should be dependent on triphenylmethyl concentration. If **1** were formed by mechanism 1 competing with mechanism 2 to a small extent, we would be unable to distinguish this minor bimolecular side reaction kinetically. However, one would expect that the hydrazyl radical, if formed, would partition itself primarily to *trans*-**3** and triphenylmethyl rather than **1** and the cumyl radical. Thus, one would expect that **1** formation would be a minor pathway in Scheme V and that *trans*-**3** formation by this pathway would be kinetically detectable.

Actually, the percent yield of *trans*-**3** formed when triphenylmethyl radical is present (35%) is reduced from the yield of *trans*-**3** formed when no triphenylmethyl radical has been added (48%). This result conforms to the previously observed pattern of reduced amounts of coupling product formed[40] when scavenger is added to systems analogous to that shown in Scheme VI. This reduction in the yield of coupling product with added triphenylmethyl requires that some of the *trans*-**3** formed in the reaction is due to radicals that have escaped their site of formation and thus are scavengeable.

3. No hydrazyl type products have been found in the product mixtures.

4. Other workers have ruled out bimolecular decomposition in analogous diazene decomposition.[4] In this published work,[4] even the extremely reactive methyl radical did not lead to bimolecular decomposition so it seems reasonable to conclude in the present case that the stable triphenylmethyl radical is not reacting in a bimolecular fashion with the diazene. In fact, chemical behavior of this type would be unprecedented for triphenylmethyl.

With Scheme VI as the format, the ratio of rate constants k_β/k_T can be estimated as in the equation

$$\frac{k_\beta}{[Ph_3C\cdot]k_t} = \frac{[100 - (\mathbf{1}) - (trans\text{-}\mathbf{3})]}{(\mathbf{1})} \quad (3)$$

where $[Ph_3C\cdot]$ represents the concentration of triphenylmethyl radical and (**1**) and (*trans*-**3**) represent the percent yields of these two products. In this way, the fraction k_β/k_T is calculated to be 0.22. If one assumes a diffusion-limited value of k_T (10^9 s^{-1}) then k_β would be on the order of 2×10^8 s^{-1}; 10^8 s^{-1} should thus be considered as an upper limit for k_β since k_T may well be less than the diffusion controlled value.

The trapping and CIDNP experiments reported here are totally consistent with our earlier studies of unsymmetric phenylazoalkanes. The evidence for the intermediacy of phenyldiazenyl radicals is thus substantial and these species should be considered to be potential intermediates in diazonium, triazene, and diazene chemistry.

Experimental Section

^{13}C and ^{15}N NMR spectra were taken with a Brüker HFX-10 spectrometer. ^1H spectra were taken with a JEOL-MH-100 spectrometer. Visible and ultraviolet absorption spectra were obtained on a Cary 15 spectrometer and analytical high-performance liquid chromatography was done with a Water Associates, Inc. ALC 202 with a 254-nm UV detector.

^{15}N-enriched aniline and $\cdot NaNO_2$ were used without further purification. Column chromatography was carried out by the use of Woelm neutral alumina (activity I). *tert*-Butyl hypochlorite was obtained from Pierce Chemical Co.

^{15}N-**Labeled Phenylhydrazine.**[18] Phenylhydrazine was prepared (60% yield) labeled at either or both nitrogens by reported procedures.[18] Labeled nitrogen was introduced by using [^{15}N]aniline or [^{15}N]sodium nitrite (97% enriched).

[^{15}N]*N*-**Phenyl-*N'*-triphenylmethylhydrazine.** Labeled phenylhydrazine was dissolved in a THF solution containing 1 equiv of triphenylmethyl chloride and 3 equiv of triethylamine.[41] The reaction mixture was refluxed for 2 h and the product hydrazine was oxidized "in situ" without purification since the overall yield of **1** was better by this technique.

[^{15}N]**Phenylazotriphenylethane (1).** To the [^{15}N]*N*-phenyl-*N'*-triphenylmethylhydrazine-THF solution, 15 mL of aqueous NaHCO$_3$ (saturated) was added. One milliliter of 30% H$_2$O$_2$ was added and the reaction mixture was stirred for 3 h at room temperature. The organic phase was then separated from the aqueous phase and the aqueous phase was extracted with 25 mL of benzene (25 °C). Both organic fractions were combined and the solvents were stripped. A yellow oil remained. Ethanol (95%, 15 mL) was added to the oil and this solution was stirred. **1** crystallized from this solution after 30 min of stirring. Product yield for the final two steps was 50%. Material prepared in this way was identical with commercial **1** in every respect.

trans-**Phenylazoisobutyronitrile (2).** The procedure of Ford and Rust[20] was used.[21] Diazene nitrogen labeled **2** was thus available from ^{15}N-labeled phenylhydrazine (vide supra). The nitrile nitrogen of **2** could be labeled via [^{15}N]acetone cyanohydrin, prepared as described[42] from KC^{15}N.

trans-**1-Cumyl-2-phenyldiazene (3).** The synthesis of *trans*-1-cumyl-2-phenyldiazene (3) was modified[7] so that labeled ^{15}N could be more readily incorporated. The following procedure is typical of experiments carried out with or without labeled compounds.

A solution of 0.50 g of α-phenylisobutyryl chloride[43] was dissolved in 6 mL of acetone. After the solution was cooled at 0 °C in an ice

bath, 0.25 g of KN$_3$ was added followed by 0.5 mL of water. The suspension was stirred for 4 h at 0 °C. The reaction mixture was filtered and the solvent removed (>20 °C). The residue was dissolved in ether and dried over Na$_2$SO$_4$. After the Na$_2$SO$_4$ was filtered off, the ether was removed leaving a colorless, pleasant-smelling oil, the acyl azide: IR 1710, 2130 cm^{-1}; ^1H NMR δ 1.56 (s), 7.25 (m). The residue was dissolved in about 50 mL of dry benzene and the solution refluxed for 3 h. The benzene was removed and the cumyl isocyanate distilled at 62–63 °C (2.1 mm). For crucial preparations, the isocyanate was usually not isolated but used directly in benzene solution, IR 2230 cm^{-1}. Isolated yields of 80% were typical. For preparations of unlabeled isocyanate, an excess of NaN$_3$ was used.

N-**Cumyl-*N*-phenylurea.** Using cumyl isocyanate prepared as in the previous section, 1 equiv of aniline in benzene was converted to urea which crystallized out of solution (mp 189–191 °C, reported 190–192 °C).[7] Product could be used directly or recrystallized from benzene. Typical yields were 73%, although labeled compounds tended to give lower (65%) yields based on KN$_3$. Yields of 90% (based on isocyanate) were usually obtained from distilled materials. Product obtained in this way was identical in every respect with previously prepared and analyzed *N*-cumyl-*N*-phenylurea.[7]

1-Cumyl-2-phenyldiazene (3). To 25 mL of *tert*-butyl alcohol saturated with sodium acetate 0.5 g of *N*-cumyl-*N*-phenylurea was added. The suspension was stirred for 20–30 min. To the slurry, 1.2 g of *tert*-butyl hypochlorite was added dropwise. The solution was stirred at room temperature for 30 min. Next, a solution of 1.2 g of potassium *tert*-butoxide in 16 mL of *tert*-butyl alcohol was added and the resulting orange suspension stirred for 30 min. The reaction was quenched in about 100 mL of water and extracted three times with 50-mL portions of hexane. The hexane was washed with several portions of water and dried over K$_2$CO$_3$. The hexane was removed and the oil chromatographed on alumina (hexane, then 1% ether in hexane). **3** prepared in this way was identical with previously prepared and analyzed **3** in every respect,[7] yield 45%.

1-Isocyanatonorbornane. Using 0.99 g of 1-norbornanecarboxylic acid,[44] 1.01 g of the corresponding acid chloride was prepared by reaction with 3.0 g of SOCl$_2$.[45] With 274 mg of KN$_3$, 526 mg of acid chloride was converted to the azide (2100 and 1680 cm^{-1}) in acetone-water (5 mL:0.5 mL). The azide was extracted into benzene and dried over MgSO$_4$. The benzene solution was refluxed for 2–3 h and the isocyanate so obtained was reacted directly with cumylamine to give yields of 70–85% *N*-cumyl-*N'*-(1-norbornyl)urea. The isocyanate exhibited IR peaks at 2250 cm^{-1}.

N-Cumyl-*N'*-(1-norbornyl)urea: the urea (mp 215–216 °C) prepared as outlined above had the following analytical characteristics: ^1H NMR (CDCl$_3$) δ 1.28, 1.44, 1.64 (m, 16 H), 2.08 (m, 1 H), 4.5 (s, 1 H), 4.9 (s, 1 H), 7.2–7.6 (m, 5 H); IR (KBr) 3250 (N–H), 1650 cm^{-1} (C=O). Anal. Calcd for C$_{17}$H$_{22}$N$_2$O: C, 74.96; H, 8.88; N, 10.28. Found: C, 74.94; H, 8.66; N, 10.12.

trans-**1-Cumyl-2-(1-norbornyl)diazene (4).** *N*-Cumyl-*N'*-norbornylurea (0.49 g) was mixed with 10 mL of *tert*-butyl alcohol; then after 20 min 0.85 g of *tert*-butyl hypochlorite was added. A total of 1.07 g of potassium *tert*-butoxide in 13 mL of *tert*-butyl alcohol was added all at once after 20 min and the mixture let stand for 30 min. The reaction was quenched in ice water and the product was bulb-to-bulb distilled at 0.05–0.03 mm and 80–85 °C giving a 76% yield of azo compound: ^1H NMR (CCl) δ 1.46 (s, 6 H), 1.5–1.9 (m, 10 H), 2.3 (m, 1 H), 7.1–7.4 (m, 5 H); IR (CCl$_4$) 1600 cm^{-1} (N=N); UV-vis (isooctane) 366 nm (ϵ 29). Anal. Calcd for C$_{16}$H$_{19}$N$_2$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.41; H, 9.27; N, 11.74. ^{13}C NMR (CCl$_4$) shifts relative to Me$_4$Si δ 26.6, 29.9, 32.0, 35.8, 51.7, 71.0, 82.5, 125.6, 125,0, 127.7.

For the preparation of ^{15}N-labeled **4**, potassium azide (99% enriched) was used to prepare the 1-isocyanatonorbornane. The final diazene product was 50% enriched because of the loss of ^{15}N as $^{29}N_2$ in the Curtius rearrangement.

Cis Diazenes. Cis diazenes were prepared by photolyzing solutions of the trans isomer with a 1000-W Hg–Xe arc lamp at low temperature. For **1**, no cis isomer could be detected by UV at temperatures as low as -125 °C. The equilibrium between *cis*- and *trans*-**2** was established by photolysis at -76 °C in Freon III. The isomers were separated by 0 °C column chromatography on neutral alumina, the trans eluting with 1:3 ether–pentane and the cis with 99:99:2 ether–pentane-acetone. *cis*-**3** was prepared as previously described.[7] The equilibrium between *cis*- and *trans*-**4** was established at -125 °C (pentane–liquid N$_2$ slush) in cyclopropane solvent. The identity of

the cis isomers of **2-4** was established[7,21,15] by ^1H and ^{15}N NMR and UV spectroscopy.

NMR Measurements. Shifts of the ^{15}N-labeled compounds were determined either directly or indirectly relative to ^{15}N-NO_3^- (5.4 M $^{15}NH_4^-$ $^{15}NO_3$ in 2 M HNO_3). The shifts of the cis compounds were determined relative to internal trans isomer and related to the $^{15}NO_3^-$ standard indirectly. The accuracy of the former method is ±1 ppm and of the latter ±2 ppm.

Spectra were taken in 4K of computer memory during CIDNP runs. This allowed two spectra to be taken with minimal delay. This affords a resolution of nearly 1 Hz for the normal 5000-Hz spectra.

CIDNP from Cis Diazene Thermolysis. The spectrum of the cis diazene to be thermolyzed was obtained some 30 °C below the thermolysis temperature. The temperature was then increased rapidly to the desired thermolysis temperature, the instrument was retuned to compensate for the temperature change, and the CIDNP spectrum was then accumulated in 200-500 transients. A spectrum was also obtained after themolysis was completed. CIDNP could be obtained during photolysis of the trans isomer by water-filtered high-intensity light (1000-W Hg-Xe) transmitted into the NMR probe by means of a quartz fiber light pipe.

Triphenylmethyl Radical Trapping Experiments. A sample of *cis-***3** (0.25 g) was used as a source of phenyldiazenyl radicals. *cis-***3** was placed in a glovebag (N_2) with a benzene solution of trityl which had been prepared in the glovebag[16,29,40] and cooled to 10 °C. The glovebag was purged with high-purity N_2 gas. The entire 50-mL sample of triphenylmethyl (4.4×10^{-4} M) in benzene was combined with cold, crystalline *cis-***3.** The reaction mixture was warmed to room temperature and then stirred overnight to ensure complete reaction.

After the reaction was completed, excess triphenylmethyl was destroyed by slowly bubbling air through the solution for 1 h. Triphenylmethyl peroxide was removed by filtration of the reaction mixture and the solvent was then stripped (25 °C, high vacuum, if necessary).

Control experiments were performed by making the following change in experimental procedure. Triphenylmethyl was prepared as above, but it was not added directly to the *cis-***3.** Trityl radicals were trapped by O_2 (g) in air and the solution was filtered; the filtered solution was added to *cis-***3.** *cis-***3** was thus decomposed in a solution having the same characteristics as the reaction media but without trityl present. The stability of the diazene products in this media was established and comparison kinetics of *cis-***3** decomposition was carried out in this media with and without trityl radical being present.

High-performance liquid chromatography was used for analysis in these trapping experiments. All samples were analyzed on Waters Model 202 HPLC with UV detector (λ 254 nm). Product isolation was achieved by using two different reverse phase column packings and by eluting with different mixtures of CH_3CN and H_2O. Corasil/C^{18} and Corasil/Phenyl column packings utilized for separation were purchased from Waters Associates, Inc.

Conditions used for separation on 4 ft of Corasil/C^{18} were 40% stroke eluting 45% H_2O and 55% CH_3CN. **1** had a retention time under these conditions of 10 min. Yield of **1** was determined by HPLC comparison of product mixtures with standard samples.

Kinetics. Decomposition of *cis-***3** in the presence and absence of trityl radicals in chlorobenzene was carried out in the glovebag. The triphenylmethyl solution was cooled to 0 °C and then a 35-mL aliquot of this solution was added to crystalline *cis-***3** which was held at <0 °C. From this solution six 5-mL aliquots were transferred and sealed in 10-mL tubes. These samples were all held at 0 °C by an ice bath and serum caps were used to seal them.

The glovebag was opened and five of the six samples to be decomposed were placed in the bath of a Forma Temp Jr. at 21.7 ± 0.05 °C. One sample was stored at −20 °C and used as a reference. Successive samples were removed from the bath and immediately cooled to 0 °C and then stored at −20 °C with analysis following as quickly as possible.

Controls were run in an identical manner except that the trityl was scavenged and the peroxide filtered prior to addition of the cold chlorobenzene solution to *cis-***3.** Thus, the rate of decomposition of *cis-***3** could be determined in essentially the same reaction medium with and without triphenylmethyl present.

The rate of disappearance of *cis-***3** was measured by normal phase HPLC using 6 ft of alumina and 8:92 chloroform-isooctane. *cis-***3** could be reproducibly measured under these conditions even at 25 °C.

The concentration of *cis-***3** was quantified for these kinetic runs relative to benzophenone internal standard. Under the conditions described benzophenone eluted after 9 min while *cis-***3** had a retention time of approximately 26 min (flow rate 1.2 mL/min). Reaction rates were calculated by the use of a two-variable linear regression analysis. Nine duplicate trapping samples were analyzed and ten duplicate controls. The rate of decomposition of *cis-***3** in the control experiments was indistinguishable from the rate found in the trapping experiments, $3.3 \pm 0.5 \times 10^{-4}$ s^{-1} (90% confidence limit).

References and Notes

(1) (a) M. Gomberg, *Ber.*, **30**, 2043 (1897); (b) M. Gomberg and H. Berger, *ibid.*, **36**, 1088 (1903).
(2) H. Ramsperger, *J. Am. Chem. Soc.*, **51**, 2134 (1929).
(3) R. J. Crawford and K. Tagaki, *J. Am. Chem. Soc.*, **94**, 7406 (1972).
(4) P. S. Engel and D. J. Bishop, *J. Am. Chem. Soc.*, **97**, 6754 (1975).
(5) J. Hinz, A. Oberlinner, and C. Rüchardt, *Tetrahedron Lett.*, 1973 (1975).
(6) S. Solomon, C. H. Wang, and S. G. Cohen, *J. Am. Chem. Soc.*, **79**, 4104 (1957).
(7) N. A. Porter, and L. J. Marnett, *J. Am. Chem. Soc.*, **95**, 4361 (1973).
(8) K. R. Kopecky, P. M. Pope, and J. Sastre, *Can. J. Chem.*, **54**, 2639 (1976).
(9) R. A. Johnson and S. Seltzer, *J. Am. Chem. Soc.*, **95**, 938 (1973).
(10) S. Seltzer and F. T. Dunne, *J. Am. Chem. Soc.*, **87**, 2628 (1965), and references cited therein.
(11) W. A. Pryor and K. Smith, *J. Am. Chem. Soc.*, **92**, 5403 (1970).
(12) R. C. Neuman, G. D. Lockyer, and M. J. Amrich, *Tetrahedron Lett.*, 1221 (1972).
(13) N. A. Porter, L. J. Marnett, C. H. Lochmüller, G. L. Closs, and M. Shobataki, *J. Am. Chem. Soc.*, **94**, 3664 (1972).
(14) N. A. Porter, J. G. Green, and G. R. Dubay, *Tetrahedron Lett.*, 3363 (1975).
(15) Preliminary accounts of some aspects of this work have appeared: ref 14 and J. G. Green, G. R. Dubay, and N. A. Porter, *J. Am. Chem. Soc.*, **99**, 1264 (1977).
(16) J. F. Garst and G. S. Hammond, *J. Org. Chem.*, **23**, 98 (1958).
(17) S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **77**, 3628 (1955).
(18) A. I. Vogel, "Practical Organic Chemistry", 2nd ed, Longmans, Green and Co., New York, N/Y., 1951, p 608.
(19) [^{15}N]Aniline or Na$^{15}NO_2$ were purchased from Koch Isotopes or Prochem, Ltd.
(20) M. C. Ford and R. A. Rust, *J. Chem. Soc.*, **1297** (1958).
(21) L. D. Smith, Thesis, Duke University, 1974.
(22) See, for example, "Chemically Induced Dynamic Nuclear Polarization", A. R. Lepley and G. L. Closs, Ed., Wiley, New York, N.Y., 1973.
(23) R. Kaptein, *J. Chem. Soc. D*, 732 (1971).
(24) The *g* of the diazenyl radical, a σ radical, has been suggested to be less than 2.0012 (ref 13) and *g* of the triphenylmethyl radical is 2.00266: J. Sinclair and D. Kivelson, *J. Am. Chem. Soc.*, **90**, 5074 (1968).
(25) K. G. Seifert and F. Gerhart, *Tetrahedron Lett.*, 829 (1974).
(26) A. R. Forrester, J. M. Hay, and R. H. Thompson, "Organic Chemistry of Stable Free Radicals", Academic Press, New York, N.Y., 1968, p 27.
(27) The chemical shift of $^{29}N_2$ has been somewhat in question but the report of Bradley et al. establishes it at 67.6 ± 1.5 ppm upfield from NO_3^-. C. H. Bradley, G. E. Hawkes, E. W. Randall, and J. D. Roberts, *J. Am. Chem. Soc.*, **97**, 796 (1975).
(28) O. Bethell and M. R. Brinkman, *Adv. Phys. Org. Chem.*, **10**, 53 (1973).
(30) G. S. Hammond, O. D. Trapp, R. T. Keys, and D. L. Neff, *J. Am. Chem. Soc.*, **81**, 4878 (1959).
(31) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance", Harper and Row, New York, N.Y., 1967, Chapter 6.
(32) E. M. Schulman, R. D. Bertrand, D. M. Grant, A. R. Lepley, and C. Walling, *J. Am. Chem. Soc.*, **94**, 5972 (1972).
(33) A. Tsolis, S. G. Mylonakis, M. T. Nieh, and S. Seltzer, *J. Am. Chem. Soc.*, **94**, 829 (1972).
(34) V. R. Koch and G. J. Gleicher, *J. Am. Chem. Soc.*, **93**, 1657 (1971), and references cited therein.
(35) E. Lippmaa, T. Saluvere, T. Pehk, and A. Olivson, *Org. Magn. Reson.*, **5**, 429 (1972).
(36) N. N. Bubnov, K. A. Bilevitch, L. A. Poljakova, and O. Y. Okhlobystin, *J. Chem. Soc., Chem. Commun.*, 1058 (1972).
(37) G. S. Hammond, A. Ravve, and F. Modic, *Anal. Chem.*, **24**, 1373 (1952).
(38) J. M. McBride, *Tetrahedron*, **30**, 2009 (1974).
(39) R. D. Stevens, "An Electron Spin Resonance Study of Some Triarylmethyl Radicals", Ph.D. Dissertation, Queen Mary College, 1968. We thank Dr. P. Smith for informing us of this reference.
(40) T. Koenig and J. M. Owens, *J. Am. Chem. Soc.*, **96**, 4052 (1974).
(41) The use of triethylamine is a modification of the literature[17] scheme so that excess ^{15}N-labeled phenylhydrazine was not required.
(42) R. F. Cox and R. T. Stormart, "Organic Syntheses", Collect. Vol. II, Wiley, New York, N.Y., 1943, p 7.
(43) L. Barclay, K. Adams, H. Fotte, E. Sanford, and R. Young, *Can. J. Chem.*, **48**, 2763 (1970).
(44) W. R. Boehme, *J. Am. Chem. Soc.*, **81**, 2762 (1959).
(45) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Wiley, New York, N.Y., 1967, p 1159.