trialkylboranes. We are continuing to explore these possibilities.

[8] National Science Foundation Predoctoral Fellow, 1970–1972.
[9] Postdoctorate research associate on Grant No. GM 10937 from the National Institutes of Health.

Herbert C. Brown,* M. Mark Midland,[8] Alan B. Levy[9]
Richard B. Wetherill Laboratory, Purdue University
Lafayette, Indiana 47907
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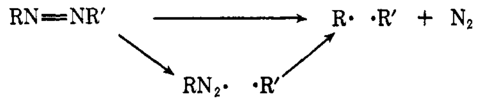
Application of Chemically Induced Dynamic Nuclear Polarization to a Study of the Decomposition of Unsymmetric Azo Compounds[1]

Sir:

The mechanism of the thermal and photochemical decomposition of azo compounds has been the focus of several recent investigations.[2–5] The development of the radical pair theory of CIDNP opened the way for a new and potentially powerful approach to the problem.[6]

Two fundamentally different dissociation mechanisms can be visualized in which the loss of nitrogen may occur either by concerted cleavage of both C–N bonds or by a stepwise process giving rise to an intermediate diazenyl radical (eq 1). Because of the expected differences in the magnetic properties of the initial radical pairs associated with the two mechanisms, CIDNP should be capable of distinguishing between them. In this communication we wish to demonstrate the application of this method to the thermal and photochemical decompositions of azo compounds 1 and 2.



(1)

$PhN{=}NC(CH_3)_2Ph$ **1** $\quad (Ph)_2CHN{=}NCH_2Ph$ **2**

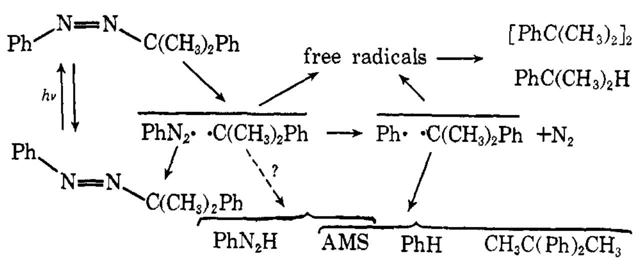
A 0.2 *M* solution of the trans isomer of **1** in benzene was irradiated with ultraviolet light inside an nmr spectrometer probe.[7] The resulting CIDNP spectrum showed enhanced absorption (A) and emission (E) lines identified to arise from dicumyl (weak A), cumene (AE multiplet), 2,2-diphenylpropane (E), α-methylstyrene (E), and benzene (E).[8] In addition, the intensity of the methyl signal of *trans*-**1** is greatly reduced during photolysis (only to increase again after irradiation has been stopped), indicating CIDNP emission during photolysis counterbalanced by normal absorption of the starting material. Product analysis showed dicumyl and biphenyl to be the main products (48 and 20%, respectively), while α-methylstyrene (AMS), cumene, and diphenylpropane were produced in minor amounts. Several high-boiling unidentified products were also present and are presumably formed from radical attack on the solvent.

The possible importance of *cis*-**1** as a key intermediate in the photochemical decomposition of **1** suggested itself by the observation of an induction period of several minutes for the full development of the CIDNP signals. Also, after irradiation had been stopped the signals persisted for a period much longer than the nuclear relaxation times of the products, suggesting the photochemical formation of an intermediate which underwent thermal decomposition. Subsequently, *cis*-**1** was successfully prepared by low-temperature irradiation (−40°) and chromatography (−5°). The crystalline stable solid (48–50° dec) decomposes in benzene solution with a half-life of 10 min at 25° to give 47% *trans*-**1**, 13% dicumyl, and 11% biphenyl with AMS, cumene, and 2,2-diphenylpropane formed in less than 1% yield.

When the thermal decomposition of *cis*-**1** in benzene is followed by nmr, a CIDNP spectrum is obtained (Figure 1) which is almost identical with that observed on photolysis of *trans*-**1** except that the methyl groups of *trans*-**1** are now clearly seen in emission.

From the application of the rules of the radical pair theory[6] and from product analysis, Scheme I emerges as a plausible reaction sequence. The intermediacy of the phenyldiazenyl radical is clearly established by the re-formation of *trans*-**1** as evidenced by its methyl group emission signal. The singlet multiplicity of the radical pair precursor (thermal reaction from ground state) with the known signs of the hyperfine coupling constants in the cumyl radical led to the conclusion that $g_{PhN_2\cdot} < g_{PhC(CH_3)_2\cdot}$. The emission signals obtained from AMS, 2,2-diphenylpropane, and benzene suggest that these products also are derived from reactions of the geminate phenyldiazenyl–cumyl radical pair. For the latter two products, however, it is necessary to invoke a phenyl–cumyl secondary correlated pair (derived from the primary pair by loss of nitrogen). AMS may in principle arise from either pair although the presence of polarized benzene points to the secondary pair as its origin.[9]

Scheme I



Comparison of the signal intensities of AMS and *trans*-**1** (Figure 1) with their relative yields indicates a specific polarization of AMS ~10² times greater than

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[1] Supported by National Science Foundation Grants GP 18719 (G. L. C.) and GP 27650 (N. A. P.).
[2] W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 5403 (1970).
[3] N. A. Porter, M. E. Landis, and L. J. Marnett, *ibid.*, **93**, 795 (1971).
[4] N. A. Porter and P. M. Iloff, *Chem. Commun.*, 1575 (1971).
[5] (a) K. Tagaki and R. J. Crawford, *J. Amer. Chem. Soc.*, **93**, 5910 (1971). (b) For a related study of pentazdienes see J. Hollander and W. P. Neumann, *Angew. Chem.*, **82**, 813 (1970).
[6] For recent reviews see: G. L. Closs, "Special Lectures from XXIIIrd International Congress of Pure and Applied Chemistry," Vol. 4, 1971, p 19, and R. Kaptein, "Chemically Induced Dynamic Nuclear Polarization," Ph.D. Thesis, Leiden, 1971.
[7] *trans*-**1** was synthesized by methods analogous to those previously reported.[3] Elemental analysis and nmr, uv, and ir spectra support the structure.
[8] To detect the benzene signal the reaction was run in dichloromethane.
[9] Disproportionation of the primary pair should give phenyldiazene with the N–H proton in emission. No signal attributable to this compound was found although the fast quadrupole relaxation of the nitrogen would probably erase the CIDNP signal.

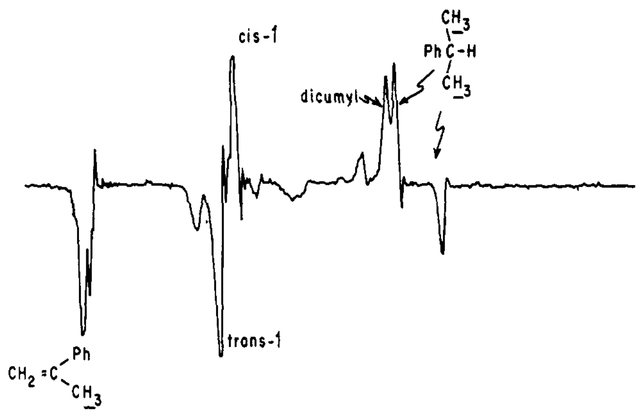

Figure 1. Alkyl region of the CIDNP spectrum obtained during thermal decomposition of *cis*-**1** in benzene at 40°.

for *trans*-**1**. This difference suggests that AMS as well as benzene and diphenylpropane are formed from radicals which have lived as pairs much longer than the pair which leads to *trans*-**1**. This interpretation is supported by the small yield of these products and is in agreement with Scheme I which requires the phenyldiazenyl radical to lose nitrogen before the secondary pair can be formed. Further support for this scheme is derived from scavenging experiments. Addition of $BrCCl_3$ does not affect the intensity of the emission signal of *trans*-**1** but almost completely eliminates the AMS signals. From these observations, one can estimate the rate constant for loss of nitrogen from $Ph\text{-}N_2\cdot$ to fall between 10^7 and 10^9 sec^{-1}.

Even though AMS is a minor product, detailed analysis of its spectrum is most informative. Figure 2 shows the CIDNP spectrum of AMS and the calculated spectrum using the known magnetic parameters of cumyl radical. The best fit is obtained with an apparent Δg of 1.3×10^{-3} and $A_N > 75$ G, establishing an upper limit for the g factor of PhN_2 of 2.0012.[10] Both parameters are consistent with a bent σ radical, a structure expected for PhN_2 which is isoelectronic with the benzoyl radical.[11]

Finally, dicumyl and cumene originate from the free radicals which have escaped the pairs. Most of their net A-type polarization is lost through nuclear relaxation in the free-radical state and the AE multiplet in cumene most likely originates from noncorrelated pairs formed by diffusive encounter of the cumyl and phenylcyclohexadienyl radical pair.[12]

It appears worth noting that the photochemical decomposition of *trans*-**1** proceeds through *cis*-**1** which decomposes thermally under the reaction conditions. The lack of photodecomposition at temperatures where *cis*-**1** is stable is also consistent with the notion that the only photochemical act of consequence at room temperature is trans–cis isomerization.

Results obtained on the decomposition of **1** support the previous claims that suitably substituted azo compounds decompose *via* one-bond scission leading to diazenyl radicals.[2-4] However, a previous CIDNP study of **2** failed to produce any evidence for a radical pair with a finite Δg (only pure multiplet effect spectra were observed) indicating either a concerted mechanism or a lifetime of the diazenyl radical of less than 10^{-10} sec.[13]

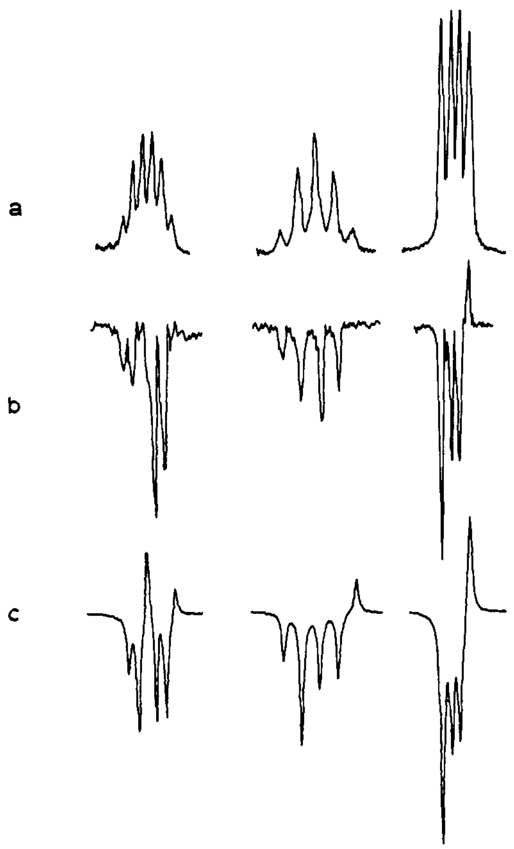

Figure 2. Spectra of AMS: (a) normal spectrum; (b) CIDNP spectrum obtained on photolysis of *trans*-**1**; (c) calculated spectrum with $A_H = 18$, $A_N = 75$ G, $\Delta g = 1.3 \times 10^{-3}$. Discrepancies between b and c must at least in part be attributed to neglect of relaxation in c.

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[10] The apparent Δg is only an upper limit of the Δg in the phenyldiazenyl–cumyl pair because the cumyl radical spends part of its lifetime with the phenyl radical as its partner whose g factor is close to the free electron value.

[11] P. J. Krusic and T. A. Rettig, *J. Amer. Chem. Soc.*, **92**, 722 (1970).

[12] The participation of phenylcyclohexadienyl radical in the formation of cumene was demonstrated by the lack of cumene signals when the reaction was run in hexadeuteriobenzene.

[13] G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, **91**, 4554 (1969); **92**, 2186 (1970).

N. A. Porter,* L. J. Marnett, C. H. Lochmüller
Paul M. Gross Chemical Laboratories, Duke University
Durham, North Carolina 27706

G. L. Closs, Masako Shobataki
Department of Chemistry, The University of Chicago
Chicago, Illinois 60637

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Photoinduced Aromatic Substitution, Addition, and Rearrangement Reactions of Aromatic Ketones[1]

Sir:

The extensive studies on the photochemistry of aromatic ketones have revealed a variety of reactions at the carbonyl function, such as photoreduction, the Paterno–Büchi reaction, and the Norrish type I and II cleavages.[2] We describe in this communication

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[1] Photoinduced Substitution. XI. This research was supported by the National Science Foundation (GP-5715). Part X: W. C. Petersen and R. L. Letsinger, *Tetrahedron Lett.*, 2197 (1971).