distortion of the potential energy surface in the crystal as compared to the gas phase. However, at the present time we know of no basis for meaningful estimates of such possible effects.

A primary kinetic isotope effect, $k_2{}^H/k_2{}^D$, in excess of 10^6 rather than a "normal" effect of $\approx 10^2$ at 87°K would provide clear support for a large degree of tunnelling. Unfortunately there are serious problems in obtaining accurate measurements of $k_2{}^D$ under the conditions which apply here. We attempted to measure the decay of $CD_3\cdot$ in CD_3CN at 87°K by esr over a period of 12 hr while the sample was being continuously photobleached, but because of difficulties connected with spectrometer stability, we can only state with confidence at this time that $k_2{}^D$ is definitely less than 5×10^{-4} min^{-1}. Thus $k_2{}^H/k_2{}^D$ exceeds 140 at 87°K. In future work, we hope to be able to devise experiments to measure the actual value of this ratio.

Regardless of which theory applies to the process, hydrogen atom abstraction would seem to be important in the general consideration of free-radical reactions in organic compounds at low temperatures.[13] Progress in this field has been hindered by the experimental difficulty of establishing the reaction path with certainty in the vast majority of systems, so the present result may be of wide significance and we plan to examine other cases of potential interest.

Acknowledgments. It was suggested by Professor W. H. Hamill at the 1970 Gordon Conference on Radiation Chemistry that tunnelling could provide an explanation for hydrogen atom abstraction reactions at low temperatures. Discussions on various facets of this work with Dr. P. J. Ogren, Dr. F. P. Sargent, and Professor J. E. Willard have been helpful. We also thank Professor R. P. Bell for his comments on an earlier version of this paper.

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[13] *Cf.* S. H. Chin and S. I. Weissman, *J. Chem. Phys.*, **53**, 841 (1970); these authors have observed the rapid migration of hydrogen atom vacancies in a solid solution of the free radical bis(trifluoromethyl) nitroxide, $(CF_3)_2NO$, in its hydroxylamine, $(CF_3)_2NOH$, at 110°K.

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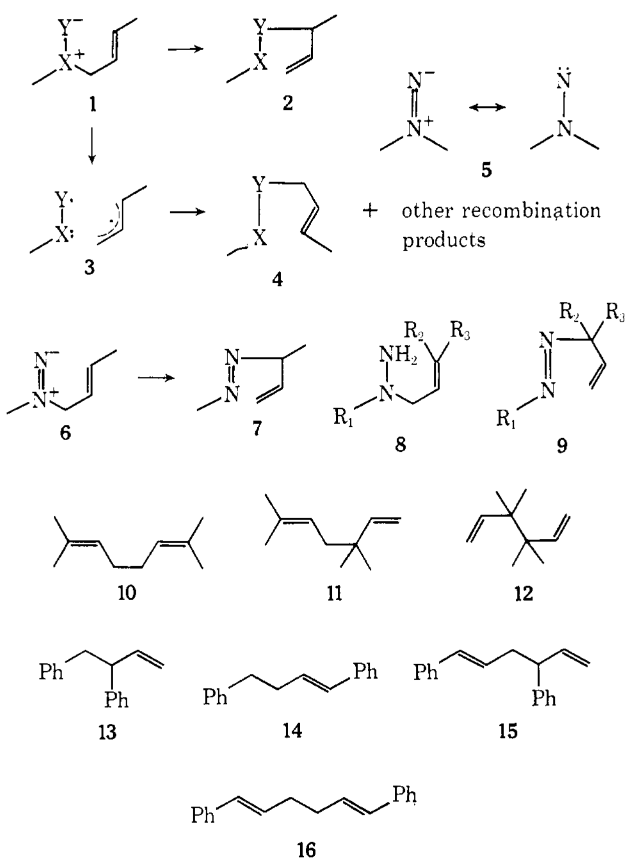
Sigmatropic Rearrangements of Diazenes

Sir:



Recently we have adumbrated[1] a general scheme for ylide rearrangements of type **1** to **2**, and have presented evidence for a duality of mechanism in such processes, namely the facile orbital symmetry conserved[2] process **1** to **2** and the competing homolytic dissociation–recombination path, through **3**, to **4**. This latter process is in general less facile and competes only at high temperatures and in special structural environments with the concerted pathway. Since the diazene function[3] **5** may, in its dipolar form, be described as an ylide, and since the nonbonding electrons on the terminal nitrogen would be ideally located to participate in the suprafacial transformation, **1** to **2**, as in **6** to **7**, we have investigated the properties of such species **6**. Furthermore, as a recent note[4] describes work whose interpretation is in contradiction to our own findings we report here our analysis of this problem.[5]

We prepared a series of allylic hydrazines **8a–g**,[6] Table I, and subjected them to a variety of oxidants, designed to produce the diazene **6**, namely mercuric oxide,[7] lead tetraacetate, manganese dioxide, and *tert*-butyl hypochlorite. The metal oxides at or below 0°, in CCl_4 suspension, produced the allylic azo compounds in

Table I. Hydrazines and Azo Compounds

	R_1	R_2	R_3
a	C_6H_5	CH_3	CH_3
b	C_6H_5	H	H
c	CH_3	CH_3	CH_3
d	CH_3	H	C_6H_5
e	3-Methyl-2-butenyl	CH_3	CH_3
f	Allyl	H	H
g	Benzyl	H	C_6H_5

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[1] J. E. Baldwin, W. F. Erickson, R. E. Hackler, and R. M. Scott, *Chem. Commun.*, 576 (1970).

[2] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

[3] For an excellent review of diazenes see: D. M. Lemal in "Nitrenes," W. Lwowski, Ed., Interscience, New York, N. Y., 1970, Chapter 10.

[4] W. D. Ollis, I. O. Sutherland, and Y. Thebtaranoth, *Chem. Commun.*, 1199 (1970).

[5] An earlier report (C. L. Bumgardner and J. P. Freeman, *J. Amer. Chem. Soc.*, **86**, 2233 (1964)) describes the reaction of diallylamine with difluoramine, a reaction which was presumed to produce the diallyldiazene, to yield *N*-allylpyrazoline. In our case we have isolated the azo compound **9f**, and have observed its slow rearrangement to acrolein allylhydrazone.

[6] The hydrazines were prepared by alkylation with allylic halides or by reduction (Al–Hg) of the corresponding nitrosamines.

[7] An early report (A. Michaelis and K. Luxembourg, *Chem. Ber.*, **26**, 2174 (1893)), described the oxidation with mercuric oxide of **8b** to **9b**. Despite an assertion to the contrary, ref 3, p 390, we have confirmed their observation.

yields of 70%, along with small amounts of hydrocarbons resulting from extrusion of nitrogen and coupling of the residual fragments, *vide infra*. That the diazene **6** was not an intermediate in this hydrocarbon formation was shown by the oxidation with *tert*-butyl hypochlorite (1.0 mol) and triethylamine (1.2 mol) in ether at −78° which cleanly produced the azo compound (9 g) in 87% isolated yield, with no hydrocarbons. It appears that the hydrocarbons formed in these oxidations derive from some secondary pathway involving the metal oxides;[8] however, the major path in all cases is azo compound production. The allylic azo compounds[9] were relatively stable at room temperature, in the absence of acids and bases, and their structures were apparent from spectral data, *e.g.*, **9a** had λ_{max} 263 (ϵ 8500), 410 (ϵ 130); nmr δ 1.45 (s, 6 H), 4.9–6.4 (m, 3 H), 7.2–7.8 (5 H). A chemical proof of constitution for this example was readily obtained by catalytic reduction (Pd/C, atmospheric pressure) to 1-phenyl-2-(2-methylbutyl)hydrazine, readily reoxidized (HgO) to the corresponding azo compounds, and reductively cleaved with zinc in acetic acid to equivalent amounts of aniline and *tert*-pentylamine, identical with authentic samples. Azo compounds (**9a**, **b**, **d**) were sufficiently thermally stable to withstand distillation at high vacuum, and were so purified; however, those (**9e**, **f**, **g**) with two allylic or benzylic substituents were thermally unstable above 50° and decomposed rapidly with nitrogen evolution to yield mixtures of hydrocarbons. Thus the azo compound **9e** was smoothly transformed by thermolysis[10] (75°, 60 min) and by photolysis[11] (quartz filter, high-pressure Hanovia lamp) to the same hydrocarbon mixture of **10**, 63%, **11**, 27%, and **12**, 10%, analyzed by preparative[12] glc and compared with authentic samples of the pure hydrocarbons.[13]

The above results indicate that allylic diazenes **6** do undergo the expected sigmatropic rearrangement to azo compounds **7**, which may decompose further, with nitrogen extrusion, to yield mixtures of hydrocarbons. However, it has recently been claimed[4] that allylic diazenes, as **6**, generated by base-catalyzed decomposition of tosyl hydrazides, *e.g.*, the tosyl derivative of **8g**, are transformed into hydrocarbons, without the intermediacy of the azo compound, as **7**. It is apparent that the temperature conditions used in these reactions (55–60°, 6 hr) are too vigorous to observe the intermediates, which as we have shown are thermally quite labile. Thus, the azo compound **9g** (nmr 4.86 (s, 2 H), 4.92–5.30 (m, 3 H), 5.92–6.56 (m, 1 H), 7.08–7.20 (m, 10 H)), the expected intermediate in the decomposition of the tosyl derivative of **8g**, was smoothly transformed at 80° in CCl_4 solution with approximately first-order kinetics ($t_{1/2}$, 3 min) to a hydrocarbon mixture: **13**, 30%, **14**, 50%, **15**, 6%, **16**, 2.5%, bibenzyl, 9%, and benzaldehyde, 2%, analyzed and separated by preparative glc. The ratio of **13** to **14** is approximately the same as that claimed[4] to result in the tosyl hydrazide decomposition and we believe these results are in accord with the intermediacy of the azo compounds, as **7**. Mechanistically the transformation of the azo compounds to the hydrocarbons might be regarded as a radical dissociation–recombination since apparently all possible recombination products are produced. As we have earlier shown[1,14] such mixtures are commonly found in the radical pathway **1** to **4** of ylide decompositions and are associated with CIDNP[15] in the coupling products. When the azo compound **9g** was rearranged at 140° (diphenyl ether) in the 100-MHz probe, abnormal proton polarizations were observed in the methylene and methine hydrogens of the hydrocarbon product (δ 2.4–3.0), both emission and enhanced absorption.[16] Although we have, as yet, been unable to identify each polarization with specific transitions work is underway to do so. This observation gives strong support for the radical pathway in the second step.

In summary, the above experiments prove that allylic diazenes, produced by a variety of methods from hydrazines, rearrange by a preferred [2,3]-sigmatropic process to allylic azo compounds, which are themselves thermally unstable and with suitable activation extrude nitrogen, *via* a radical pathway, yielding the hydrocarbon coupling products. These data do not exclude the possibility of a prior thermal reversal to the diazene, as **6**, followed by radical formation from that species, and experiments are in hand to resolve this problem.

Acknowledgment. We wish to thank the U. S. Public Health Service, the National Science Foundation, the Petroleum Research Fund, administered by the American Chemical Society, and Eli Lilly and Company for support of this research.

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(8) It seems likely that oxidations with metal oxides and lead tetraacetate proceed by a series of one-electron steps; consequently, the hydrazinyl radical might be a precursor of the diazenes and to a smaller extent of the hydrocarbons. Such a stepwise oxidation is avoided with the hypochlorite.

(9) All new compounds cited here, except where thermal instability precluded, *i.e.*, **9f**, **g**, have given correct analytical data.

(10) S. G. Cohen and C. H. Wang, *J. Amer. Chem. Soc.*, **77**, 2457 (1955).

(11) P. S. Engel and P. D. Bartlett, *ibid.*, **92**, 5883 (1970).

(12) 5% Carbowax for analytical and preparative work.

(13) We thank Dr. R. E. Hackler for these samples.

(14) J. E. Baldwin and R. E. Hackler, *J. Amer. Chem. Soc.*, **91**, 3646 (1969).

(15) H. Fischer and J. Bargon, *Accounts Chem. Res.*, **2**, 110 (1969).

(16) G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, **91**, 4554 (1969).

(17) A. P. Sloan Fellow, 1969–1971.

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Chemical Exchange Broadening and Chemically Induced Dynamic Nuclear Polarization during a Free Radical Initiated Chain Iodine Transfer Reaction

Sir:

It has recently been suggested,[1] on the basis of the observation of chemically induced dynamic nuclear polarization (CIDNP), that rapid iodine atom transfer may take place between alkyl radicals and iodoalkanes. We report here additional evidence from chemical exchange broadening for rapid thermoneutral reactions of this type and present an estimate of the rate constant for the iodine exchange reaction between allyl radical and allyl iodide. Detection and rate estimates for

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(1) H. R. Ward, R. G. Lawler, and R. A. Cooper, *Tetrahedron Lett.*, 527 (1969); A. R. Lepley, *J. Amer. Chem. Soc.*, **91**, 748 (1969).