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).

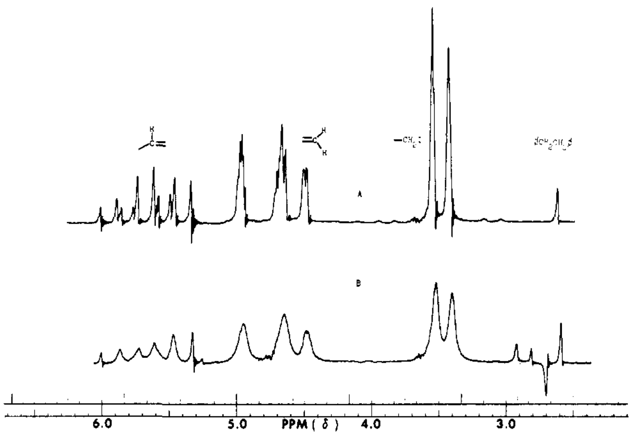
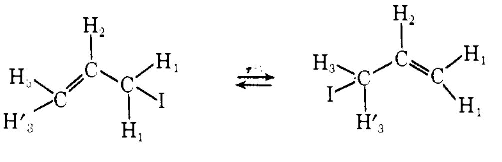


Figure 1. (A) Spectrum of allyl iodide and bibenzyl in *o*-dichlorobenzene solution at 100°. (B) Spectrum taken of 0.5 *M* lauroyl peroxide and 8.3 *M* allyl iodide in *o*-dichlorobenzene at 100°. Absorption assignment is: bibenzyl (δ 2.60); undecyl iodide, H-1 (enhanced signal at δ 2.82); allyl iodide, H-1 (δ 3.46), H-3 (δ 4.5–5.0), and H-2 (δ 5.3–6.0).

such identity reactions by standard chemical and kinetic techniques require tedious double-labeling or racemization experiments.

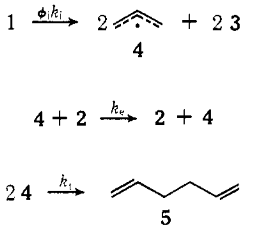
During the reaction of a 0.5 *M* solution of lauroyl peroxide (**1**) and 8.3 *M* allyl iodide (**2**) in *o*-dichlorobenzene at 100°, the nmr spectrum shown in Figure 1B is obtained. The spectrum in Figure 1A is that of a solution of allyl iodide under identical conditions except for the absence of peroxide; addition of molecular iodine to this solution has no effect on the spectrum. Three features of Figure 1B are of interest: (a) the enhanced multiplet at δ 2.70–2.95, (b) the broadening of most of the lines from allyl iodide (while lines from undecyl iodide, **3**, and the bibenzyl standard remain sharp), and (c) the normal width of the two outside lines in the multiplet arising from H-2 of the iodide. The enhanced triplet (a) arises from **3** formed by abstraction of iodine from allyl iodide by undecyl radicals (thus producing allyl radicals). The appearance of enhanced absorption downfield of emission in the multiplet (AE) is consistent with nuclear spin selection in interactions between undecyl radicals in a primary cage.[2] Polarization in undecyl radicals which escape the primary encounter should persist no longer than 10^{-4}–10^{-5} sec, which places a lower limit on the rate with which the iodine transfer from allyl iodide to undecyl radical must occur.

The specific line broadening effects in allyl iodide[3] (b,c) are consistent with the chemical exchange process (eq 1) in the limit of the slow exchange for protons at the 1 and 3 positions and fast or intermediate exchange for the central lines in the H-2 multiplet. The unbroadened outer lines of the H-2 multiplet are typical of the effects arising from modulation of coupling constants by correlated exchange processes. Such alternating line-width effects are commonly observed in esr[4] but in the present case arise from the differences in magnitude of J_{vic} for ethylenic and allylic protons.



(1)

Scheme I



(2i)

(2e)

(2t)

A proper quantitative investigation of these broadening effects[5] unfortunately has so far proven impossible because of complicating overlap with enhanced lines arising from reaction products, formed at higher reaction temperature. Even so, the effects may be analyzed in terms of the simplified reaction (Scheme I) to give an estimate of k_e. From the excess width of the H-1 lines at 100° in the presence of 0.5 *M* **1**, a lifetime, τ, between exchanges of approximately 0.2 sec can be estimated. This lifetime is related to k_e by eq 3. The

$$\tau = 2k_e^{-1}[\mathbf{4}]^{-1} \qquad (3)$$

steady-state concentration of **4** may be estimated from Scheme I if it is assumed: (a) that the observed 47% yield of **3** represents the efficiency, ϕ_i, of production in the initiation step, (b) that the first-order rate constant for decomposition[6] of **1** is 1.5 × 10^{-3} sec^{-1} at 100°, and (c) that the chain transfer (eq 2e) is terminated primarily by dimerization of allyl radicals with a rate constant[7] of 10^{10} M^{-1} sec^{-1}. Support for c is found in the isolation of 65% of the theoretical amount of the dimer **5** based on the amount of **3** formed.[8] The steady-state expression 4 yields an allyl radical concentration of 3 × 10^{-7} *M* during the time that the spectrum in Figure 1B was scanned. This in turn

$$[\mathbf{4}] = \sqrt{\frac{2\phi_i k_i[\mathbf{1}]}{k_t}} \qquad (4)$$

yields a value for k_e of 3 × 10^7 M^{-1} sec^{-1}.

A lower limit to k_e may also be obtained within the framework of Scheme I by using the limit of detect-

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[2] R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, 4, 214 (1969).

[3] A similar broadening effect in the allyl iodide lines can be observed during the decomposition of benzoyl peroxide and of propionyl peroxide in allyl iodide–*o*-dichlorobenzene solutions.

[4] P. D. Sullivan and J. R. Bolton, *Advan. Magn. Resonance*, **4**, 39 (1970). See pp 41–43 of this reference for a description of the selective broadening of the inner lines of a spin–spin multiplet.

[5] If a careful measurement of the shape of the spectrum were possible over a wide temperature range it should in principle be possible, by numerical simulation for example, to distinguish between two-jump and four-jump models for the exchange. Equations 2 and 5 also predict that the broadening due to interaction of the nuclei with the unpaired electron should become pronounced at lower allyl iodide concentrations. Verification of this prediction has not been possible, however, because of overlap of the pertinent allyl iodide lines at lower concentrations with enhanced signals from reaction products.

[6] C. E. H. Bawn and R. G. Halford, *Trans. Faraday Soc.*, **51**, 780 (1955).

[7] The bimolecular rate constant for dimerization of benzyl radicals under similar conditions has been reported to be 4 × 10^9 M^{-1} sec^{-1} [R. D. Burkhart, *J. Amer. Chem. Soc.*, **90**, 273 (1968)]. A larger value is chosen for allyl to compensate both for its smaller size (and larger diffusion coefficient) and ability to dimerize at either end. Uncertainty in k_t, however, is sure to contribute the largest error to this estimate of k_e.

[8] Other product yields, based on the starting lauroyl peroxide concentration, were: *n*-undecane, 2%; 1-undecene, 3%; 1-tetradecene, 2%; *n*-docosane, 23%; undecyl laurate, 6%; and lauric acid, 3%. Addition of undecyl and allyl radicals to *o*-dichlorobenzene also occurs to give products of undetermined structure in modest amounts.

ability of approximately 0.25 Hz for the excess broadening of the outer lines of the H-2 multiplet by dephasing of H-2 spins in **4** *via* the known hyperfine interaction[9] ($a = 4.06$ G) with the unpaired electron in the allyl radical. Such broadening effects are well known in nmr spectra of molecules undergoing rapid exchange with small amounts of paramagnetic species[10] and give rise to a contribution to the nmr line width, $T_{2,\mathrm{ex}}^{-1}$, given by eq 5 (assuming the lifetime, τ_R, of the radical is less than the relaxation time of the unpaired electron).[10b] Thus, $\tau_\mathrm{R} \leqslant 1 \times 10^{-8}$ sec or $k_\mathrm{e} \geqslant 1 \times 10^{7}$

$$T_{2,\mathrm{ex}}^{-1} = \frac{2}{\tau}\frac{(a\tau_\mathrm{R})^2/4}{[1 + (a\tau_\mathrm{R})^2/4]} \tag{5}$$

M^{-1} sec^{-1} which is in excellent agreement with the previous estimate and is *independent* of the estimate of allyl radical concentration.

The estimate of the rate constant for thermoneutral iodine atom transfer thus shows that this process, at least for the allyl system, proceeds at a rate several orders of magnitude faster than radical recombination. If such rates also are characteristic of nonconjugated alkyl radicals,[11] they can easily explain the transfer of nonequilibrium nuclear spin populations to alkyl iodide reagents undergoing free-radical reactions.

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(9) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(10) (a) E. deBoer and H. van Willigen, *Progr. Nucl. Magn. Spectrosc.* 111 (1967); (b) C. S. Johnson, Jr., *J. Chem. Phys.*, **39**, 2111 (1963).

(11) The rate constant for abstraction of iodine from 1-iodopropane by methyl radical in the gas phase may be estimated indirectly to be 4×10^5 M^{-1} sec^{-1} at 100° [D. M. Tomkinson and H. O. Pritchard, *J. Phys. Chem.*, **70**, 1579 (1966)]. The 100-fold acceleration reported here for allyl is in accord with the lower carbon-iodine bond energy in allyl iodide [F. P. Lossing, K. U. Ingold, and J. H. S. Henderson, *J. Chem. Phys.*, 22, 1489 (1954)].

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Rearrangements of Dihydrodicyclopentadiene Derivatives in Phosphoric Acid. 1,4-Hydride Shifts

Sir:

In 1948 the dehydration of 9-*exo*-hydroxytetrahydro-*exo*-dicyclopentadiene (I) with orthophosphoric acid was reported to give 1,2-dihydro-*exo*-dicyclopentadiene (II).[1] Later the product was found to be 9,10-dihydro-*exo*-dicyclopentadiene (III).[2] The behavior of several compounds related to I in phosphoric acid under a set of standardized conditions has now been studied, and we wish to report that alcohols I and IV and alkenes II and V afford III and 9,10-dihydro-*endo*-dicyclopentadiene (VI) in very nearly a constant ratio.

Products were identified by retention times using gas–liquid partition chromatography on a 5 ft × 1/8 in., 10% diisodecyl phthalate on 60–80 Chromosorb W column at 50° and 25 ml/min helium flow rate and by their nmr traces.[3] Peak areas were determined by weighing the excised graph paper and product mixture compositions were calculated assuming equivalent thermal conductivities for the isomers.

The reaction of alcohol I with phosphoric acid (1:1 by weight) at 150° for 30 min gave a mixture of alkenes containing 65% III and 25% VI, and alcohol IV gave 67% III and 25% VI. Alkene II under the same conditions gave 63% III and 23% VI while alkene V yielded 67% III and 20% VI. In each reaction, small amounts (9–14%) of the alkanes, *endo*- and *exo*-tetrahydrodicyclopentadienes, were observed. On dilution of alcohol IV with H_3PO_4 and $CHBr_3$, as an immiscible cosolvent, to concentrations of 6×10^{-4} M, a constant amount of olefin (98%) was obtained in a ratio of 9:1 (*cf.* Table I). The product alkenes III and VI were found to be completely stable under the conditions employed. At 180° and 60 min, however, VI did rearrange to give 14% III, the most stable of the four dihydrodicyclopentadienes.

Table I

Concn of IV, mol l.$^{-1}$	% III	% VI	% saturated
9.4 (1:1 by wt)^a	67	25	8
1.2^a	73	17	10
1.2 in H_3PO_4 + 1 ml of $CHBr_3$^{b}	67	20	13
0.12	68	16	16
0.012^a	51	6	43
0.012 in H_3PO_4 + 5 ml of $CHBr_3$^{b}	85	10	5
0.012 in H_3PO_4 + 10 ml of $CHBr_3$^{a,b}	84	10	6
0.012 in H_3PO_4 + 20 ml of $CHBr_3$^{a,b}	82	11	7
0.0012^a	56	6	38
0.0012 in H_3PO_4 + 5 ml of $CHBr_3$^{a,b}	89	9	~2
0.0006 in H_3PO_4 + 5 ml of $CHBr_3$^{a,b}	89	9	~2

[a] Average value of duplicate runs; deviation from mean ±1%. [b] The addition of $CHBr_3$ as an immiscible cosolvent greatly increases the effective dilution factor. The slow diffusion of organic alcohol into H_3PO_4 from $CHBr_3$ greatly enhances the dilution effect over the apparent dilution factor.

These results may be rationalized by a reaction scheme (Scheme I) involving equilibrated tautomeric ions (VII and VIII) or by a common intermediate IX. The endo ring fused reactants IV and V give cation VII or IX in which a 1,2 alkyl shift is competitive with an intermolecular or an intramolecular hydride shift. The exo ring fused reactants I and II give cation VIII or IX in which a 1,3 hydride shift is competitive with a 1,2 alkyl shift. Dilutions to concentrations of 10^{-3}–10^{-4} M have been used to minimize intermolecular hydride shifts.[4] Our dilution studies show a limiting amount of olefin VI which at these concentrations would be expected to arise only from an intramolecular hydride shift.

We have also dehydrated 9-*exo*-hydroxy-2,2-dimethyl-9,10-dihydro-*endo*-dicyclopentadiene (X)[5,6] at 150° for

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(1) H. A. Bruson and T. W. Riener, *J. Amer. Chem. Soc.*, **70**, 2809 (1948).

(2) P. von R. Schleyer and M. M. Donaldson, *ibid.*, **78**, 5702 (1956); P. Wilder, Jr., and G. T. Youngblood, *ibid.*, **78**, 5706 (1956).

(3) S. Cesca, M. L. Santostasi, W. Marconi, and N. Palladino, *Ann. Chim.* (*Rome*), **55** (7), 704 (1965).

(4) P. von R. Schleyer, *Angew. Chem.*, **81**, 539 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 529 (1969).

(5) H. C. Brown and P. Geoghegan, *J. Amer. Chem. Soc.*, **89**, 1522 (1967).

(6) C. F. Culberson and P. Wilder, Jr., *J. Org. Chem.*, **26**, 4289 (1961).