$p$-$(CD_3)_3CCH_2$.—The effect that $\gamma$-deuterium substitution exerts on the principal band of $p$-neopentylnitrobenzene and $p$-neopentylaniline is the smallest one observed. However, in each successive determination on H and D compounds, $\nu_{max}$ for neopentylaniline was consistently less than that for its $\gamma$-$d_4$ derivative. The difference spectrum of Figure 2 shows this even more clearly. For neopentylnitrobenzene in heptane, no difference was found in the average of determinations on a Beckman DU, but, in determinations on the Cary Model 14 spectrometer, $\nu_{max}$ for the $\gamma$-$d_9$ derivative was consistently smaller by a tiny amount. The differential absorption curve of Figure 1 shows a rather weak maximum and minimum, but has the shape required for a shift to lower energy of the transition of the D compound.

In previous articles, it has been pointed out that the lowest energy conformation of neopentylbenzenes is probably one in which a portion of two of the terminal methyl groups somewhat overhang one side of the ring (see also ref 28).[10d,e] It was suggested that part of the enhanced effectiveness of the $p$-neopentyl substituent in electronic transitions, both of the type represented by eq 1 and that represented by eq 2, may be due to a polarization across space of these terminal methyl groups (the $h\nu$ order in both instances is neop $<$ $t$-Bu, $CH_3 < H$). However, the observed opposite effect of $\gamma$ deuterium on the principal band of $p$-neopentylnitrobenzene and $p$-neopentylaniline is difficult to reconcile with this suggestion. If the effect of $\gamma$-D substitution is transmitted through the bonding electrons, then the effect would be expected to be very small in any event.

As regards the effect of $\gamma$-D substitution on chemical transitions, $\gamma$-$d_9$ neopentyl methanesulfonate hydrolyzes somewhat slower than the normal compound in water: $k_H/k_D = 1.017$.[42,43] On the other hand, $\gamma$-$d_9$ may slightly increase the rate of solvolysis of $\alpha$-methylneopentyl brosylate: $k_H/k_D = 0.979 \pm 0.017$ in 43% ethanol at 40°; $k_H/k_D = 0.986 \pm 0.014$ in 95% trifluoroacetic acid at 10°.[44]

**Registry No.**—Nitrobenzene, 98-95-3; aniline, 62-53-3; nitrobenzene-$p$-$d$, 13122-36-6; aniline-$p$-$d$, 13122-28-6; $p$-nitrotoluene-$\alpha$-$d_3$, 23346-24-9; $p$-toluidine-$\alpha$-$d_3$, 23346-25-0; $p$-methylanisole-$\alpha$-$d_3$, 23346-26-1; $p$-neopentylnitrobenzene-$\alpha$-$d_2$, 23346-27-2; isobutylene-$d_8$, 20762-54-3; $t$-butyl chloride-$d_9$, 918-20-7; $p$-neopentylnitrobenzene-$\gamma$-$d_9$, 23346-29-4; $p$-neopentylaniline-$\gamma$-$d_9$, 23359-82-2.

**Acknowledgment.**—The authors thank Dr. R. G. Minton for preparing and purifying some of the deuterium compounds. Financial support of the Office of Ordnance Research, U. S. Army, also is gratefully acknowledged.

[42] M. J. Blandmer and R. E. Robertson, *Can. J. Chem.*, **42**, 2137 (1964).

[43] Decreased branching in the alkyl substituent decreased $k_H/k_D$ in the hydrolysis of alkyl methanesulfonates; for isobutyl-$\gamma$-$d_6$, $k_H/k_D = 0.968$, and for $n$-propyl-$\gamma$-$d_3$, $k_H/k_D = 0.924$.

[44] W. M. Schubert and P. H. LeFevre, *J. Amer. Chem. Soc.*, **91**, 7746 (1969).

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# Kinetics and Stereochemistry of the Gas-Phase Addition of HBr to Methyl-Substituted Allenes

REX Y. TIEN AND PAUL I. ABELL

*Department of Chemistry, University of Rhode Island, Kingston, Rhode Island 02881*

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The kinetics and stereochemistry of the gas-phase, photocatalyzed addition of HBr to allene, methylallene, 1,1-dimethylallene, 1,3-dimethylallene, and tetramethylallene have been investigated. The rate expression is the same for all: rate of adduct formation = $k[HBr]I_0^{1/2}$. Reactivities relative to allene are 1:1.36:1.31:1.56:1.65 for the compounds as listed. The products, with one minor exception, involve addition of the bromine atom to the center carbon of the allenic system.

The free-radical addition of HBr to simple olefins reaction has been investigated in both solution and gas phases for many years. The general picture that has emerged is that the bromine atoms add to that carbon of the olefinic bond which will yield the most stable radical. In the gas-phase reaction, this radical contains the energy of the new carbon–bromine bond, and may readily dissociate to starting olefin and bromine atom, or be collisionally deactivated to thermal equilibrium, whereupon it may abstract a hydrogen from HBr to give the alkyl bromide product.[1,2]

The situation is more complex with cumulative bond systems. The addition of a radical or atom to the terminal (more electronegative[3]) carbon of an allene produces a vinyl radical. If addition of a radical takes place at the center carbon, however, the radical structure can acquire allylic resonance stabilization by rotation through 90°.[4] The question arises as to whether this rotation can occur fast enough so that this stabilization becomes kinetically important. An examination of the kinetics of the reaction of allene with HBr demonstrated that the initial reaction of the bromine atom with the allene is at the center carbon, and is apparently irreversible.[5] The kinetics does not disclose whether there may be a reversible terminal carbon attack, but only that all of the product of kinetic importance is from reaction at the center carbon.

The stereochemistry of free-radical attack on allene and alkyl-substituted allenes has been investigated for other radials than bromine atoms. Methyl radicals,[6] trifluoromethyl radicals,[6] and trichloromethyl[7] attack exclusively at the terminal carbon, while fluorine

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[1] R. Field and P. I. Abell, *Trans. Faraday Soc.*, **65**, 743 (1969).

[2] K. T. Wong and D. A. Armstrong, *Chem. Commun.*, **12**, 353 (1966).

[3] B. Pullman, *J. Chim. Phys.*, **55**, 790 (1958).

[4] E. I. Heiba, *J. Org. Chem.*, **31**, 776 (1966).

[5] P. I. Abell and R. S. Anderson, *Tetrahedron Lett.*, **40**, 3901 (1964).

[6] H. Meunier and P. I. Abell, *J. Phys. Chem.*, **71**, 1430 (1967).

[7] H. Van de Ploeg, J. Knotnerus, and A. Bickel, *Rec. Trav. Chim. Pays-Bas*, **81**, 775 (1962).

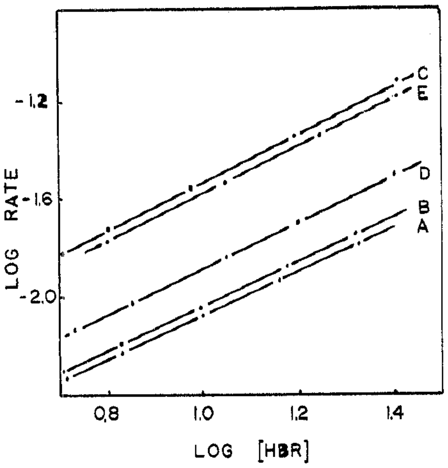

Figure 1.—Rate dependence on HBr concentration at constant allene concentration: A, allene (propadiene); B, methylallene (1,2-butadiene); C, 1,1-dimethylallene (3-methyl-1,2-butadiene); D, 1,3-dimethylallene (2,3-pentadiene); E, tetramethylallene (2,4-dimethyl-2,3-pentadiene).

atoms,[8] gas-phase Br atoms,[5] and $PH_2$ radicals[9] react at the center carbon. Thiyl radicals,[10] trimethyltin radicals,[11] and liquid-phase Br atoms[12] attack at both sites. Heiba and Haag[12] have suggested that attack at terminal carbons may be reversible for the latter radicals, and center-carbon attack irreversible.

Investigation of the various methyl-substituted allenes in their reaction with HBr was undertaken in the hope that the relative energetics and stereochemistry might throw light on the reaction. If the initial attack by bromine atom on the center carbon is indeed irreversible, then the kinetics and thermodynamics will relate to the structure and reactivity of the allylic radicals thus formed.

## Results

The various allenes were allowed to react with hydrogen bromide in a cylindrical quartz reaction vessel, irradiated with a 100-W, medium-pressure mercury arc lamp. Kinetic rates were determined by the pressure drop as followed by a quartz spiral manometer and optical lever. Products were isolated by gas chromatography and identified by retention time and/or spectral evidence.

The determination of the kinetic rate expression was by measurement of the change in pressure during a run at constant temperature. When the concentration (pressure) of allene or substituted allene was varied from 15 to 75 Torr and the concentration of HBr was held constant, it was found that the rates did not change, and therefore the allene did not enter into the rate expression. However, when the concentration of HBr was varied from 15 to 75 Torr while the allene concentration was held constant, there was a direct correlation of rate with pressure of HBr. When log (HBr pressure) was plotted *vs.* log (reaction rate), a straight line was obtained for each allene. These plots had slopes of unity, indicating a first-order dependence on HBr concentration (Figure 1).

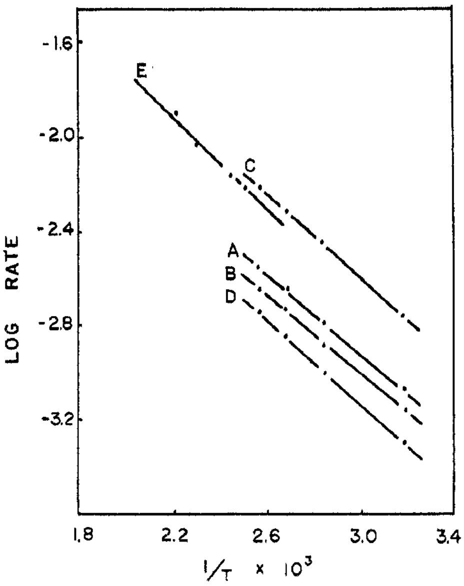

Figure 2.—Arrhenius plots for the addition of HBr to allenes: A, allene (propadiene); B, methylallene (1,2-butadiene); C, 1,1-dimethylallene (3-methyl-1,2-butadiene); D, 1,3-dimethylallene (2,3-pentadiene); E, tetramethylallene (2,4-dimethyl-2,3-pentadiene).

The dependence of rate on light intensity was obtained by using a calibrated set of Corning 7-54 ultraviolet light filters. Using a variety of conditions of temperature, pressure, and ratio of allenes to HBr, plots of log (relative rate) *vs.* log (light intensity) gave straight lines of slope 0.50 ± 0.04. The experimental rate expression then becomes

$$\text{rate} = k_{\text{exptl}}[\text{HBr}]I_a^{1/2}$$

It is to be noted that this is an initial rate, and not an integrated rate over a reaction carried nearly to completion.

The activation energies were obtained by kinetic runs at a series of temperatures between 40 and 120°. These are shown in Figure 2 and summarized in Table I.

TABLE I

ACTIVATION ENERGY OF HBr–ALLENE REACTIONS

| Allene | $\Delta E^{\ddagger}$, kcal/mol |
|---|---|
| Propadiene | −3.43 |
| 1,2-Butadiene | −3.44 |
| 3-Methyl-1,2-butadiene | −4.17 |
| 2,3-Pentadiene | −4.06 |
| 2,4-Dimethyl-2,3-pentadiene | −4.23 |

Relative reactivities for the various allenes were obtained by competition experiments with allene for a limited amount of HBr. Analysis of the products by gas chromatography gave the results shown in Table II.

The products of the reactions of the individual allenes with HBr were separated by gas chromatography and identified by nmr and ir spectroscopy. The products and relative amounts are given in Table III, and the spectroscopic data used in structure assignment are given in Table IV.

In general the reactions were very clean and the kinetics very straightforward. The reactions proceeded

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[8] C. Baumgardner and K. McDaniel, *J. Amer. Chem. Soc.*, **91**, 1032 (1969).

[9] H. Goldwhite, *J. Chem. Soc.*, 3901 (1965).

[10] K. Greisbaum, A. Oswald, E. Quiram, and W. Naegele, *J. Org. Chem.*, **28**, 1952 (1963).

[11] H. Kuivila, W. Rahman, and R. Fish, *J. Amer. Chem. Soc.*, **87**, 2835 (1965).

[12] E. I. Heiba and W. O. Haag, *J. Org. Chem.*, **31**, 3814 (1966).

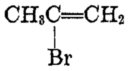
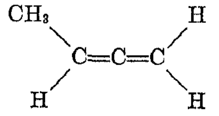
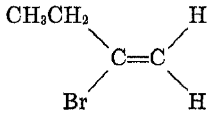
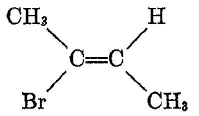
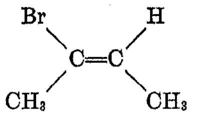
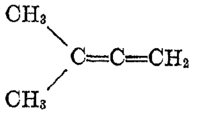
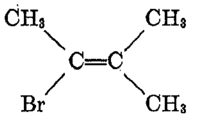
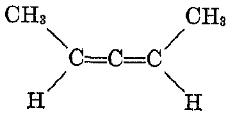
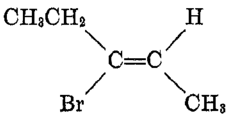
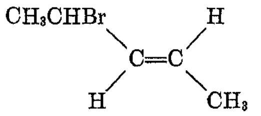
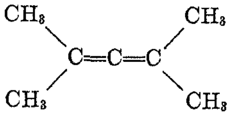
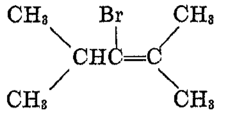
Table II

Relative Reactivities of Allenes toward HBr

| Allene | 60° | 90° | 120° | $\Delta(\Delta E^{\ddagger})$ *vs.* $C_3H_4$, kcal/mol |
|---|---|---|---|---|
| Propadiene (standard) | 1.00 | 1.00 | 1.00 | 0.00 |
| 1,2-Butadiene | 1.36 | 1.36 | 1.35 | 0.063 |
| 3-Methyl-1,2-butadiene | 1.31 | 1.31 | 1.32 | −0.037 |
| 2,3-Pentadiene | 1.56 | 1.55 | 1.53 | 0.017 |
| 2,4-Dimethyl-2,3-pentadiene | 1.65 | 1.66 | 1.66 | 0.042 |

Table III

HBr–Allene Adducts

| Allene | Yield, % | Product distribution: Compd | Product distribution: % |
|---|---|---|---|
| $CH_2{=}C{=}CH_2$ | 98 |  $CH_3C(Br){=}CH_2$ | 100[a] |
|  | 98 |  | 6.5[a] |
|  |  |  | 83[a] |
|  |  |  | 10.5[a] |
|  | 97 |  | 100[a] |
|  | 96 |  | 94[b] |
|  |  |  | 6[b] |
|  | 89 |  | 100?[a] |

[a] All products were separated on a 4-9-ft column of 20% dinonyl phthalate on Chromosorb P (60–80 mesh). The retention times for the products are in the order listed. [b] Products were separated on an 8-ft column of a 20% mixture of di-2-ethylhexyl sebacate and dimethylsulfolane on Chromosorb Z.

rapidly to give monoaddition products, and reaction times were short. No products involving addition of 2 mol of HBr were observed. The separation of the products in the tetramethylallene experiments was not very efficient, and there may be some minor products hidden under the single product peak observed.

In only one case was there any product other than material from center-carbon attack by bromine atoms. The minor product from 1,3-dimethylallene was unexpected, but the nmr spectrum leaves little doubt that the structure assignment is correct.

## Discussion

The experimental kinetic rate expression indicates that the rate-determining step in the addition of HBr to allenes is the hydrogen abstraction step in the scheme below, and, of the various conceivable termination steps, the radical dimerization shown is the important one. The addition of the bromine atom to the center carbon is irreversible, and probably has only a small, or no, activation energy. Therefore, the process should be one of trapping bromine atoms almost as rapidly as they are formed by photolysis of the HBr, and then the more leisurely hydrogen abstraction process follows. Because no appreciable concentration of bromine atoms exists at any given instant, the termination steps involving bromine atoms which are found in reactions with simple olefins[13–15] cannot be involved here.

$$\mathrm{HBr} \xrightarrow{h\nu} \mathrm{H}\cdot + \mathrm{Br}\cdot$$

$$\mathrm{Br}\cdot + \text{allene} \xrightarrow{k_2} \text{bromoallyl radical}$$

$$\text{bromoallyl radical} + \mathrm{HBr} \xrightarrow{k_3} \text{product} + \mathrm{Br}\cdot$$

$$2 \text{ bromoallyl radicals} \xrightarrow{k_t} \text{dimer}$$

If one compares the experimental rate expression with that derived from steady-state assumptions

$$\text{rate} = \left(\frac{k_2}{k_t}\right)^{1/2} I_0^{1/2}$$

it is apparent that the experimental expression can be rewritten in the form of an Arrhenius expression

$$k_{\text{exptl}} = \left(\frac{A_2}{A_t}\right)^{1/2} I_0^{1/2} e^{\frac{-(E_2 - E_{t/2})}{RT}}$$

Thus the experimenal activation energy, $\Delta E^{\ddagger}$, of Table I is equated with $E_2 - E_{t/2}$. It is to be presumed from many atom additions to olefins that $E_2 = 0$. Accordingly, $\Delta E^{\ddagger} = -E_{t/2}$, and the activation energy as observed is one-half of the termination activation energy. It is somewhat surprising to find activation energies of the order of 6–9 kcal/mol for the dimerization of free radicals, but, when it is recalled that the allyl resonance energy is *ca.* 10 kcal/mol,[16] this is not an unreasonable value. It is unfortunate that the *A* factor for the reaction cannot be simplified similarly, but, since none of the individual terms in the nonexperimental part of the expression above are known, the experimental *A* factor is meaningless.

The differences in reactivities of the various allenes (Table II) must be ascribed to some factor which is not temperature dependent. The increased reactivity with increased methyl substitution no doubt reflects the increased hyperconjugative resonance stabilization in the corresponding bromoallyl radicals. However, since the various bromoallyl radical intermediates can only go on to form products by hydrogen abstraction, the relative reactivity values indicate the ease with which they are formed and are not related to how they behave after formation. All this adds up to implication of the

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(13) P. I. Abell, *Trans. Faraday Soc.*, **60**, 2214 (1964).

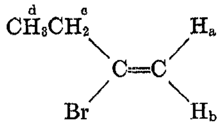
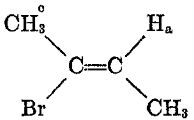
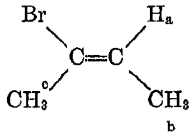
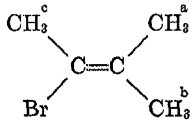
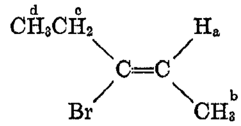
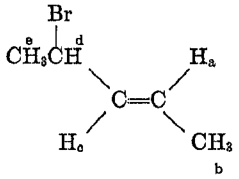
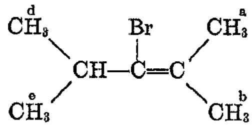
(14) R. J. Field and P. I. Abell, *ibid.*, **65**, 743 (1969).

(15) P. I. Abell and P. K. Adolf, *J. Chem. Thermo.*, **1**, 333 (1969).

(16) D. M. Golden, N. A. Gac, and S. W. Benson, *J. Amer. Chem. Soc.*, **91**, 2136 (1969).

TABLE IV

ANALYTICAL DATA FOR HBr–ALLENE ADDUCTS

| Compd | Registry no. | Nmr[a] Peak position, ppm, and coupling constants | Nmr[a] Peak ratios | Concn in $CCl_4$, % | Ir, $cm^{-1}$ |
|---|---|---|---|---|---|
|  | 23074-36-4 | a, 5.53 (s)<br>b, 5.34 (s)<br>c, 2.44 (q)<br>d, 1.12 (t)<br>$J_{a,b}$ = 1.10 cps<br>$J_{c,d}$ = 7.0 cps | 1<br>1<br>2<br>3 | 50 | 3000 s, 1645 s, 1450 s, 1425 s, 1360 s, 1320 s, 1278 s, 1250 s, 1149 s, 1120 s, 1070 w, 912 w, 850 s |
|  | 3017-68-3 | a, 5.67 (q)<br>b, 1.69 (d)<br>c, 2.25 (s)<br>$J_{a,b}$ = 7.0 cps | 1<br>3 | 50 | 3010 s, 1670 m, 1451 s, 1420 s, 1281 s, 1138 s, 1115 s, 980 w, 947 s, 852 s |
|  | 3017-71-8 | a, 5.81 (m)<br>b, 1.70 (d)<br>c, 2.20 (s)<br>$J_{a,b}$ = 7.0 cps | 3<br>1<br>3 | 50 | 3010 s, 1668 m, 1450 s, 1428 s, 1281 s, 1139 s, 1115 s, 997 w, 948 s, 851 s |
|  | 3017-70-7 | a, 1.78 (s)[b]<br>b, 1.85 (s)[b]<br>c, 2.25 (s) | 3<br>3<br>3 | 50 | 3000 s, 1670 s, 1475 s, 1372 s, 1220 s, 1128 s, 1029 s, 981 m, 789 s |
|  | 23068-94-2 | a, 5.68 (q)<br>b, 1.69 (d)<br>c, 2.43 (q)<br>d, 1.08 (t)<br>$J_{a,b}$ = 7 cps<br>$J_{c,d}$ = 7 cps | 1<br>3<br>2 | 50 | 3002 s, 1660 s, 1450 s, 1371 s, 1300 s, 1120 s, 995 w, 927 m, 879 s, 797 s |
|  | 23068-95-3 | a, 5.62 (q)<br>b, 1.69 (d)[b]<br>c, 5.73 (m)<br>d, 4.60 (5)<br>e, 1.80 (d)[b]<br>$J_{a,b}$ = 6.5 cps<br>$J_{c,d}$ = 4.0 cps<br>$J_{d,e}$ = 7.0 cps | 1<br>3<br>1<br>1<br>3 | 50 | 3000 s, 1670 s, 1450 s, 1285 s, 1191 m, 1045 s, 995 m, 960 s, 893 m, 788 s |
|  | 23074-38-6 | a, 1.74 (s)[b]<br>b, 1.84 (s)[b]<br>c, 4.84 (m)[b]<br>d, 0.97 (d)[b]<br>e, 1.03 (s)[b]<br>$J_{a,b}$ = 7 cps<br>$J_{c,d}$ = 3 cps<br>$J_{c,e}$ = 3 cps | 3<br>3<br>1<br>3<br>3 | 50 | 3020 s, 1650 s, 1452 s, 1290 s, 1130 s, 1114 s, 998 m, 957 m, 851 s, 790 s |

[a] s, singlet; d, doublet; q, quartet; m, multiplet. [b] Overlap.

Arrhenius *A* factor or entropy term as the most reasonable explanation for the reactivity differences. The decrease in entropy that must accompany this increase in relative reactivity probably can be ascribed to increased rotational freedom in going from the allene to the bromoallyl radical. Because of the composite nature of the *A* factor, more detailed speculation is fruitless.

The determination of the orientation of addition was unambiguous, with one exception. The attack of the bromine atom is effectively on the central carbon of the allenic system. If there is attack on the terminal carbons, it is not kinetically important under our reaction conditions, but can be invoked as an explanation for the small dependence of product distribution on HBr concentration in the addition of HBr to 1,3-dimethylallene. The ratio of center to terminal carbon attack drops from 94:6 down to 85:15 with a tenfold increase in the HBr/allene ratio (1:1 to 10:1). This may well reflect the reversibility of attack at the terminal carbons, because a more statistical process becomes possible when the chain-transfer step is rendered more likely.

One observes much the same sort of situation with the formation of three products from methylallene. The temperature dependence of product distribution (6.5% of nonterminal hydrogen atom abstraction at 40°, 9.7% at 120°) suggests that there is a loss of selectivity with increased temperature. This is not observed with 1,1-dimethylallene, because there is never enough loss of selectivity with increased temperature to produce any detectable nonselective product. Thus one sees here the expected behavior of free radicals—loss of selectivity with increased temperature. This behavior is seldom observed with reactions as sensitive to structural alteration as HBr addition.

## Experimental Section

The hydrogen bromide was CP grade from Matheson Co. The allenes, except 1,1-dimethylallene, were commercial chemicals; allene came from Matheson Co., the others from the Chemical Samples Co. 1,1-Dimethylallene was prepared by the method of Doering[17] and Hoffman.[18] All compounds were degassed before use and dried thoroughly over phosphorus pentoxide. The reaction system was a conventional all-glass apparatus except for the quartz reaction vessel, the quartz spiral Bourdon gauge, and the quartz medium-pressure mercury arc lamp (GE 100 W). Gas chromatography was done on apparatus connected directly to the reaction system, using hydrogen as the carrier gas, and either dinonyl phthalate columns or a mixture of di-2-ethylhexyl sebacate and dimethylsulfolane. Reaction times were short, usually less than 5 min, and were kept to less than 10% reaction in the kinetic runs. Product identification was largely by nmr, using 50% solutions in $CCl_4$ run in a Varian A-60 spectrometer. All gas-phase runs and reactions were carried out at least in triplicate, and under a variety of temperatures and pressures. The yields, relative reactivities, and activation energies are reproducible to *ca.* ±2%.

**Registry No.**—Allene, 463-49-0; methylallene, 590-19-2; 1,1-dimethylallene, 598-25-4; 1,3-dimethylallene, 591-96-8; tetramethylallene, 1000-87-9.

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[17] W. von E. Doering and P. M. LaFamme, *Tetrahedron*, **2**, 75 (1958).

[18] R. Hoffman, *ibid.*, **22**, 521 (1966).

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# N-Nitrenes. IX. The Reaction of 1,1-Dibenzylhydrazine Anions with Tosyl Azide, Oxygen, and Nitrous Oxide

GEN KOGA AND J.-P. ANSELME[1]

*Department of Chemistry, University of Massachusetts, Boston, Massachusetts 02116*

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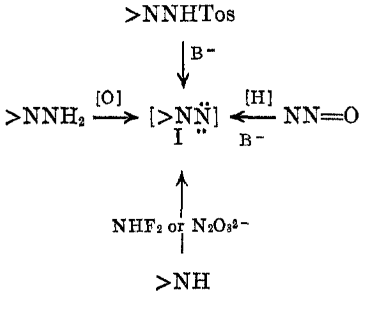
The diazo transfer reaction of tosyl azide to the anion and to the dianion of 1,1-dibenzylhydrazine gives bibenzyl, benzaldehyde dibenzylhydrazone, and 3,3-dibenzyl-1-tosyltriazene. The effect of temperature, the nature of the anion, and the conditions of the reactions, and the mechanisms by which these products are formed, are discussed. Evidence for the participation of N-azidodibenzylamine as an intermediate has been adduced. The reaction of the monoanion of 1,1-dibenzylhydrazine with nitrous oxide and with oxygen results in the formation of the same products (except for the triazene) as are obtained with tosyl azide.

Through the N-nitrene[2] intermediate I, moderate success has been achieved in the gross rationalization of the products formed in a number of reactions[3-8] (Scheme I). The sequence of events between the time the reactants are brought together and the isolation of the products is a matter of conjecture. The questions as to whether or not N-nitrenes are involved and their behavior under the reaction conditions being used are still unresolved.

SCHEME I



In order to eliminate as many parameters as possible, a method which would produce N-nitrenes directly was needed. By analogy with the generation of carbenes and nitrenes from the corresponding diazo alkanes and azides, N-azides (II) should give N-nitrenes (I) by loss of elemental nitrogen.

$$>\overset{-}{C}-\overset{+}{N}\equiv N \longrightarrow\ >C: + N_2 \tag{1}$$

$$-\underset{-}{\overset{-}{N}}-\overset{+}{N}\equiv N \longrightarrow -\ddot{N}: + N_2 \tag{2}$$

$$\underset{\text{II}}{>N-\underset{-}{\overset{-}{N}}-\overset{+}{N}\equiv N} \longrightarrow \underset{\text{I}}{>N-\ddot{N}:} + N_2 \tag{3}$$

A major portion of our research effort has been devoted to the development of new and mild methods of preparation of azides. Presumably, these techniques could be applied to the preparation of N-azides. The formation of azides and diazo alkanes[9] by the *diazo transfer* reaction to the anions of the appropriate amine derivatives has been reported.[10] Diazo alkanes were obtained from the reaction of oxygen and tosyl azide with anions of hydrazones[11] and by the *azido transfer* reaction of tosyl azide to ketimine anions.[10c]

We are now reporting the results of our investigations of the reactions of the monoanion and of the dianion of 1,1-dibenzylhydrazine with tosyl azide.

## Results

The monoanion and the dianion of 1,1-dibenzylhydrazine were prepared by addition of the appropriate

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[1] To whom all inquiries should be addressed. Fellow of the Alfred P. Sloan Foundation.

[2] In this discussion, it is by no means implied that the involvement of N-nitrenes as fully developed entities has been proven.

[3] For a summary, see C. G. Overberger, J.-P. Anselme, and J. G. Lombardino, "Organic Compounds with Nitrogen-Nitrogen Bonds," The Ronald Press Co., New York, N. Y., 1966, p 89.

[4] C. G. Overberger, M. Valentine, and J.-P. Anselme, *J. Amer. Chem. Soc.*, **91**, 687 (1969).

[5] L. A. Carpino, *J. Org. Chem.*, **30**, 736 (1965), and previous papers.

[6] (a) D. M. Lemal, *et al.*, *J. Amer. Chem. Soc.*, **85**, 1944 (1963); (b) *ibid.*, **86**, 2395 (1964).

[7] (a) C. L. Bumgardner, K. J. Martin, and J. P. Freeman, *ibid.*, **85**, 97 (1963); (b) C. L. Bumgardner and J. P. Freeman, *ibid.*, **86**, 2233 (1964).

[8] D. M. Lemal and T. W. Rave, *ibid.*, **87**, 393 (1965).

[9] Diazo alkanes can formally be considered as N-nitrenes (iii) and can be viewed as arising from N-azidimines (III).

$$\underset{\text{III}}{>C=N-N_3} \xrightarrow{-N_2} \underset{\text{i}}{>C=\overset{+}{N}=\overset{-}{N}} \longleftrightarrow \underset{\text{ii}}{>\overset{-}{C}-\overset{+}{N}\equiv N} \longleftrightarrow \underset{\text{iii}}{>C-\underset{\cdot\cdot}{\ddot{N}}-N}$$

[10] (a) G. Koga and J.-P. Anselme, *Chem. Commun.*, 446 (1968); (b) J.-P. Anselme and W. Fischer, *Tetrahedron*, **25**, 855 (1969); (c) J.-P. Anselme, W. Fischer, and N. Koga, *ibid.*, **25**, 89 (1969).

[11] (a) W. Fischer and J.-P. Anselme, *J. Amer. Chem. Soc.*, **89**, 5312 (1967); N. Koga and J.-P. Anselme, unpublished results. (b) W. Fischer and J.-P. Anselme, *Tetrahedron Lett.*, 877 (1968).