

Figure 1. (a) The $(\text{LiSiMe}_3)_6$ hexamer. (b) A schematic view of the "folded-chair" conformation of Li_6 in $(\text{LiSiMe}_3)_6$.

clo[1.1.0.]butan-1-yl lithium-tetramethylenediamine (2.74 Å).⁵ The second distance is between lithium atoms meta to each other on the edge of the ring and averages 3.27 Å (av esd 0.04 Å), which is much greater than the observed bond distance and slightly over twice the van der Waals radius (1.55 Å). Thus, it is clear that there is no significant interaction except between adjacent lithium atoms.

Each Me_3Si group, is located centrally above a triangular face on the periphery of the Li_6 ring, with three nearly equal lithium-silicon bond distances of average value 2.68 Å (av esd 0.03 Å). Thus the silicons form a nonbonded hexameric ring which is reciprocal to the Li_6 ring. The equivalence of the lithium-silicon bonds implies each silicon participates equally in bonding to each of the three lithium atoms in a delocalized molecular orbital over these centers. One may initially postulate the direct bonding of each lithium to the two adjacent lithiums and to three silicon atoms. The silicons not only serve as bridges along the edges of the ring but also serve to bridge the meta lithium atoms of the rings resulting in the folded configuration observed.

In order to better understand the conformation of the hexameric Li_6 ring, it is instructive to consider the fact that any hexameric conformation involving six symmetry-equivalent atoms and six symmetry-equivalent bonds can be derived from an undistorted octahedron by compressing the octahedron along a $\bar{3}$ axis of the octahedron. The extreme examples are the undistorted octahedron and the planar benzene ring. One may characterize the conformation of such a crown or chair-type ring system by the bond angles along the periphery, by the dihedral angle between the back and the seat of the chair, or by the ratio between the closest nonbonded distances within the ring and the bonded distances. In Table I we have presented such data for the octahedron, for the Li_6 hexamer, for cyclohexane, and for benzene. It will be noted that the Li_6 chair conformation is much closer to the octahedron than to a cyclohexane structure and may be thought of in a "folded chair" conformation.

Certainly this structure may have significant implications concerning the bonding and reactivity of these derivatives. Additional speculation awaits further refinement of the structure and rigorous calculations, both of which are currently in progress, and will be reported at a later date in a full paper.

Trimethylsilyllithium was prepared by cleavage of bis(trimethylsilyl)mercury as previously described.⁶ The crystals for the X-ray structural determination were grown from hot cyclohexane and were loaded into thin-walled capillaries in an argon filled drybox which were then sealed.

Crystals of $(\text{LiSiMe}_3)_6$ are monoclinic, $P2_1/a$ with lattice constants $a = 18.902$ (4) Å, $b = 14.078$ (3) Å, $c = 13.933$ (3) Å, $\beta = 89.60$ (2)°, and $Z = 4$. Intensity data

Table I. Comparison of Conformational Parameters in Hexamers

| | Dihedral angle, back to seat (deg) | Bond angle (deg) | Ratio non-bonded: bonded | Symmetry |
|--------------------------|------------------------------------|------------------|--------------------------|----------|
| Octahedron | 54.7 | 60.0 | 1.0 | O_h |
| $(\text{LiSiMe}_3)_6$ | 70.5 | 74.6 | 1.21 | D_{3d} |
| | | (av esd, 1.0°) | | |
| Cyclohexane ^a | 130.7 | 111.6 | 1.64 | D_{3d} |
| Benzene | 180.0 | 120.0 | 1.732 | D_{6h} |

^a E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley, New York, N. Y., 1965, p 454.

were collected by a θ - 2θ scan on a Syntex diffractometer with graphite monochromated $\text{Mo K}\alpha$ radiation to a value of $\sin \theta/\lambda < 0.423$. The structure was solved by application of the Sayre equation and Fourier techniques. The present discrepancy factors are

$$R = \frac{\sum |F_o - F_c|}{\sum |F_o|} = 0.080$$

and

$$R_w = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2} = 0.103$$

for 1671 data. The contributions of the 56 hydrogen atoms have not yet been included in the calculation. The asymmetric unit contains two independent halves of $(\text{LiSiMe}_3)_6$ hexamers located about crystallographic inversion centers. Thus each molecule possesses $C_i - \bar{1}$ crystallographic symmetry and $D_{3d} - \bar{3}2m$ idealized molecular symmetry.

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† NOTE ADDED IN PROOF. Since submission of this communication, R. Zenger, W. Rhine, and G. Stucky, *J. Amer. Chem. Soc.*, **96**, 6048 (1974), have reported the structure of cyclohexyllithium. This derivative crystallizes as a hexamer of approximately S_6 symmetry with the six lithium atoms in the same configuration as shown in $(\text{LiSiMe}_3)_6$. In addition to the obvious distinction between the bridging ligands, a second significant difference appears to be present, that is, the suggested interaction between the α -hydrogen atoms of the cyclohexyl groups and the lithium framework which leads to stabilization of the hexamer. This type of interaction is highly unlikely in LiSiMe_3 hexamers.

Theodore F. Schaaf, William Butler
Milton D. Glick, John P. Oliver*

Department of Chemistry, Wayne State University
Detroit, Michigan 48202

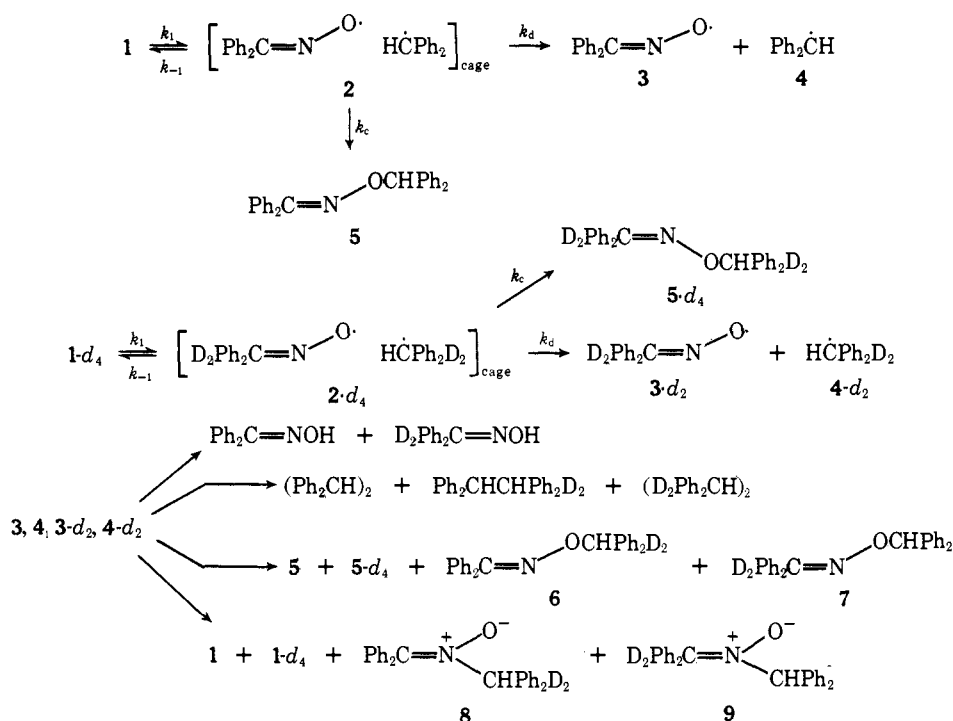
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Determination of the Rate Constant for Homolysis of a Nitrene Carbon-Nitrogen Bond via Crossover Measurements of Isotopically Labeled Substrates. Kinetic Properties of Caged Amibent Radicals¹

Sir:

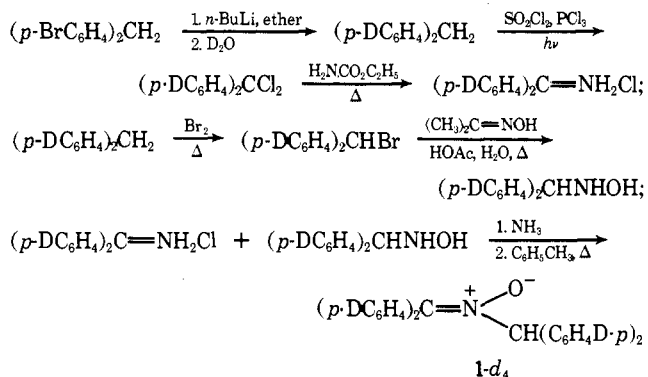
Methods of estimating true unimolecular homolytic rate constants for systems exhibiting cage return are attracting increasing interest.² An accompanying concern is an understanding of the competitive rates of primary processes involving the perturbation and destruction of the initially formed caged radicals.^{2,3}

Scheme I



In previous reports we presented evidence for the intermediacy of benzhydryl and iminoxy radicals in the thermalolysis of α, α -diphenyl-*N*-benzhydryl nitronone (**1**).⁴⁻⁶ We now describe a study of the simultaneous decomposition of this nitronone and its tetra-deuterated analog **1-d₄**. The results of this study permit an evaluation of the rate constant for homolysis of the C-N bond and ratios of rate constants for the competing paths for destruction of the caged radicals.

The deuterated nitronone was prepared by the sequence



Mass spectrometric analysis of **1-d₄** showed it to possess an average of 3.80 deuterium atoms per molecule in good agreement with combustion analysis.

A mechanism which accounts for the solution thermalolysis of **1** and **1-d₄** is shown in Scheme I.

Decompositions of mixtures of **1** and **1-d₄** in diethylcarbitol (DEC) were interrupted after partial completion. The nitronone and *O*-benzhydryloxime (*O* ether) fractions were quantitatively separated (chromatography over florilisil and alumina) and subjected to mass spectrometric analyses. The degree of intramolecularity, α ,⁷ for each fraction isolated can be determined using the expression

$$\alpha = 1 - 2X_{365}$$

in which X_{365} is the mole fraction of crossover species

(m/e 365) in the isolated nitronone or *O* ether fraction. It should be noted that *O* ether formation is irreversible.

After partial decompositions of **1** and **1-d₄**, the reisolated nitronone as well as the product *O* ether exhibited "crossover species." Suitable controls demonstrated that crossover did not occur during separation procedures. The ratio, millimoles of intermolecularly formed nitronone/millimole of intermolecularly formed *O* ether (r) in decompositions interrupted after short reaction times, was evaluated. Thus 0.182 mmol of an equimolar mixture of **1** and **1-d₄** (0.0183 *M* in DEC) was allowed to undergo 10% decomposition at 144°. The nitronone remaining at this point amounts to 0.164 mmol. Mass spectral analysis shows that, of this, 0.0044 mmol is derived from intermolecular recombination of radicals. The intermolecularly formed *O* ether produced under these conditions is 0.0077 mmol. The ratio, r , is then 0.58. A similar analysis of products from a run stopped after 20% reaction (at which point 93.5% of the recovered nitronone still possessed its original isotopic distribution) yields a value $r = 0.70$. The ratio, k_{-1}/k_c , is the ratio of the rate of collapse of the caged radical pair (**2** or **2-d₄**) at nitrogen to the rate of collapse at oxygen. The value of r will approach this ratio as the per cent decomposition of nitronone approaches zero, assuming that the geminate and kinetically free radicals have similar ratios for recombination at nitrogen to oxygen. The ratio k_d/k_c [(100% - yield of intramolecularly formed *O* ether)/(yield of intramolecularly formed *O* ether)] is determined from runs involving 100% decomposition of nitronones. In the complete decomposition of an equimolar mixture of **1** and **1-d₄** (0.0185 *M* in DEC) the total yield of *O* ether was 60.4%. Its degree of intramolecularity, α , was 0.325. Thus the yield of intramolecularly formed *O* ether is 19.6%. This gives a value for $k_d/k_c = 4.10$. Thus of the caged radical pairs generated in step k_1 , approximately 11% collapse back to nitronone (k_{-1}), 17% collapse to *O*-benzhydryloxime (k_c), and 71% become free radicals via diffusion leading to nitronone, *O* ether, and other products (via dimerization, hydrogen atom abstraction, etc.).

The homolysis rate constant, k_1 , can be evaluated from the data in Table I. The first-order rate constant, k' , for the

Table I. Partial Decomposition of 1-1-d₄ Mixtures in DEC at 144°

| % reaction | t, min | Initial mixture 1 + 1-d ₄ (mmol) | Total nitronne remaining (mmol) | Nitronne remaining with isotopic composition 1 + 1-d ₄ (mmol) ^a | f, fraction of original 1 + 1-d ₄ re-maining |
|------------|--------|---|---------------------------------|---|---|
| 10 | 61 | 0.1823 | 0.164 | 0.160 | 0.878 |
| 20 | 129 | 0.0908 | 0.0727 | 0.0680 | 0.749 |
| 30 | 204 | 0.0577 | 0.0404 | 0.0344 | 0.596 |
| 50 | 391 | 0.0548 | 0.0274 | 0.0229 | 0.418 |

^a These values correspond to $\alpha \times$ mmol of total nitronne remaining.

disappearance of nitronne of original composition 1 + 1-d₄ can be derived from the reaction steps in Scheme 1 making the steady-state approximation for the caged radical pairs 2 and 2-d₄. The integrated first-order rate law is given in eq

$$k' = k_1(k_c + k_d)/(k_c + k_d + k_{-1}) \quad (1)$$

2. The ratio $[1 + 1-d_4]_t/[1 + 1-d_4]_0$ is equal to f in Table

$$\ln \frac{[1 + 1-d_4]_0}{[1 + 1-d_4]_t} = k't \quad (2)$$

I. Thus $\log f = -k't/2.303$. Indeed, a plot of $\log f$ vs. t is linear passing through the origin. The slope leads to a value of $k' = 3.64 \times 10^{-5} \text{ sec}^{-1}$. The true homolysis rate constant, k_1 , can then be obtained from eq 3, which is a rearranged form of eq 1. Using a value of 0.58 for k_{-1}/k_c ⁸ and

$$k_1 = k'(1 + k_d/k_c + k_{-1}/k_c)/(1 + k_d/k_c) \quad (3)$$

$k_d/k_c = 4.10$ (*vide supra*), $k_1 = 4.05 \times 10^{-5} \text{ sec}^{-1}$. The spectroscopically (uv) determined observed first-order rate constant for 1 in diethylcarbitol at 144° is $2.93 \times 10^{-5} \text{ sec}^{-1}$.

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- The fraction of the O ether product or the fraction of recovered nitronne not formed by a statistical recombination of iminoxy and benzhydryl radicals. This expression assumes that 1 and 1-d₄ were present in equimolar amounts in the original mixture.
- The average of r (assumed equal to k_{-1}/k_c) determined at 10 and 20% decomposition is 0.64. Our estimated standard error of r at 10% reaction is $\pm 23\%$ yielding a value of $r = 0.58 \pm 0.13$. The estimated error of r at 20% reaction is 8% giving a value of $r = 0.70 \pm 0.06$. The error is principally due to uncertainty in α_N at early stages of decomposition. The total amount of O ether formed at 10% reaction was 0.0121 mmol of which 0.077 mmol was scrambled. At 20% reaction the corresponding

quantities were 0.0106 and 0.0067 mmol. Starting nitronne concentrations, but not the weights of 1 + 1-d₄, were constant for these individual experiments. Using the rate constant, k' , for rate of disappearance of nitronne of original composition 1 + 1-d₄, these values of r can be corrected giving values of 0.56 and 0.61, respectively. The average of these two values was used in calculating k_1 . The corrected value of r at 30% reaction is 0.54.

Jose A. Villarreal, Edward J. Grubbs*

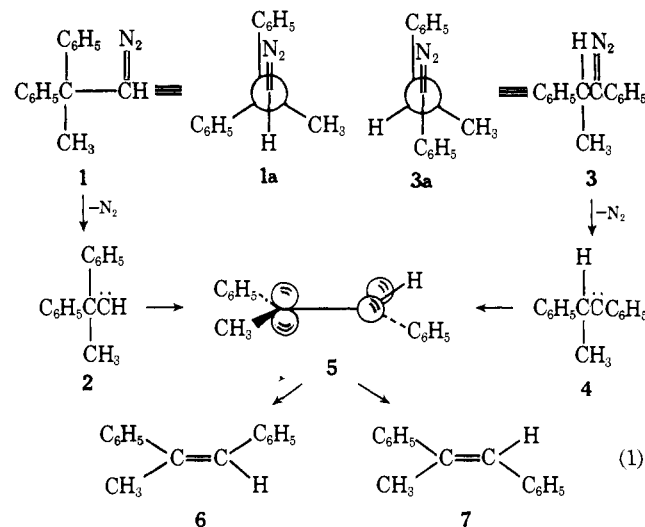
Department of Chemistry, San Diego State University
San Diego, California 92182

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The Case against the Phantom Singlet as a Common Intermediate in Carbenic Decompositions of 1-Diazo-2,2-diphenylpropane and 1-Diazo-1,2-diphenylpropane

Sir:

The mechanisms of carbenic rearrangement are subjects of interest.¹ Recently 1-diazo-2,2-diphenylpropane (1) and 1-diazo-1,2-diphenylpropane (3) have been reported² to decompose thermally or photochemically to (*Z*)- and (*E*)-1,2-diphenyl-1-propenes (6 and 7) having the same *cis/trans* ratio of 0.66 ± 0.2 . Carbenes 2 and 4 are presumed to rearrange by migration of different groups, phenyl in 2 and hydrogen in 4, to give the same ratio of 6 and 7 *via* a common intermediate, the phantom singlet 5.² Intermediate 5 could arise by orthogonal migration of phenyl in 1a and hydrogen in 3a upon loss of nitrogen; overlap of the p orbitals of 5 during rotation of 90° leads preferentially to the thermodynamically favored isomer 7.²



We should now like to summarize our studies of (1) thermolysis of 1 and 3 as generated *in situ* from 2,2-diphenylpropionaldehyde tosylhydrazone (8)³ and 1,2-diphenylpropanone tosylhydrazone (9),³ (2) carbenic and cationic decomposition of pure 1 under various conditions, and (3) aprotic diazotization of 2,2-diphenylpropylamine (10). The present results differ significantly from those reported previously² and rule out phantom singlet 5 as a common intermediate in rearrangement of 2 and 4.

It has now been found that the sodium salt of 8 thermolyzes at 160° in diglyme to 6 (45–47%) and 7 (33–35%) along with 1,1-diphenylcyclopropane (11, 19%). The ratios of 6:7 in six such pyrolyses range from 1.29 to 1.42:1.⁴ Thus the major product of phenyl migration in decomposition of 1, a presumed intermediate, is 6, the less stable stilbene, rather than 7. Furthermore there is produced 11, the product of in-