not completely, stereospecific manner and with retention of configuration of the olefins. Apparently, however, dual mechanisms are operating in these cases, and the full account is open to studies in the future.[15] Methylenecyclobutane, a higher homolog of **1**, has proved to be stable under the same catalytic conditions.

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(15) Methylenecyclopropane substrates appropriate for the elucidation of the mechanism are not at hand. Attempted reactions of 2,2-dimethylmethylenecyclopropane or isopropylidenecyclopropane with dimethyl fumarate or maleate have failed.

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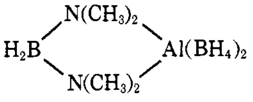
Reaction of Diborane with Tris(dimethylamino)alane. Isolation of a New B–N–Al Heterocycle and a New Compound with a B–N–B–N–B Skeleton

Sir:

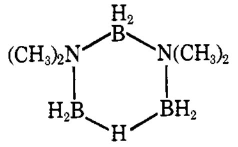
Tris(dimethylamino)alane reacts with excess diborane in diethyl ether at room temperature to form $[(CH_3)_2NBH_2]_2$, μ-$(CH_3)_2NB_2H_5$, $[(CH_3)_2NAl(BH_4)_2]_2$, and two new compounds which we formulate to be $H_2B[N(CH_3)_2]_2Al(BH_4)_2$ and $H_2BN(CH_3)_2BH_2N(CH_3)_2BH_3$.

The first, a colorless crystalline solid produced in 75% yield, passes 0° and stops at −17° under trap-to-trap vacuum line separation. *Anal.* Calcd for $[(CH_3)_2N]_2AlB_3H_{10}$: Al, 17.1; B, 20.9; H (hydrolytic), 6.33; $(CH_3)_2N$, 55.7. Found: Al, 17.5; B, 20.2; H (hydrolytic), 6.20; $(CH_3)_2N$, 55.7. The mass spectrum contains no peaks higher than the monomer parent ion at *m/e* 158. The infrared spectrum shows strong bands at 2510, 2420, and 2340, and at 2120 cm^{-1} (B–H, and Al–H–B stretching, respectively). No absorption characteristic of Al–H stretching is present. The boron-11 nmr spectrum[1] shows a 1:2:1 triplet at −1.6 ppm (J_{BH} = 115 Hz) and a 1:4:6:4:1 quintet at 37.6 ppm (J_{BH} = 89 Hz); the sharp well-resolved signals are in the integrated intensity ratio of 1:2, respectively. The proton nmr spectrum (toluene-d_8) shows a strong relatively sharp $N-CH_3$ singlet and a weaker broad 1:1:1:1 quartet assigned to the BH_2 protons. No proton signal arising from the borohydride groups bonded to aluminum could be detected, probably owing to extreme broadening by interaction with the aluminum-27 quadrupole moment. The cyclic structure shown below is consistent with this information.



This material, although very sensitive to air, moisture, and hydroxylic solvents, only decomposes slowly at room temperature when kept in clean evacuated vessels.

The second compound, a colorless liquid formed in 5–10% yield, passes −17° and stops at −30°. *Anal.* Calcd for $[(CH_3)_2N]_2B_3H_7$: B, 25.4; H (hydrolytic), 5.49; $(CH_3)_2N$, 69.0. Found: B, 25.1; H (hydrolytic), 5.46; $(CH_3)_2N$, 68.7. The mass spectrum is qualitatively similar to that of $[(CH_3)_2NBH_2]_2$ with the exceptions of an envelope associated with the parent ion $[(CH_3)_2N]_2B_3H_7^+$ starting at *m/e* 128 and a peak assigned to $(CH_3)_2NB_2H_5^+$ at *m/e* 71. The boron-11 nmr spectrum of a toluene solution at 30° consists of a sharp 1:2:1 triplet at −6.7 ppm (J_{BH} = 109 Hz) overlapping a very broad triplet centered at 1.6 ppm having twice the intensity of the low-field signal. The broad signal exhibits a temperature dependence characteristic of a $H_2B-H-BH_2$ group,[2,3] resolving into a triplet of doublets at −30° and into a symmetrical 1:5:10:10:5:1 sextet at 60°. The sharp triplet does not change in this temperature range. The proton nmr spectrum at −20° in toluene-d_8 shows a sharp single $N-CH_3$ resonance, two overlapping 1:1:1:1 BH quartets in approximate 1:2 intensity ratio, and a broad B–H–B bridge proton signal at highest field. These data suggest the hydrogen-bridged cyclic structure.



At 75° the compound decomposes to μ-$(CH_3)_2NB_2H_5$ and $[(CH_3)_2NBH_2]_2$ according to

$$H_2BN(CH_3)_2BH_2N(CH_3)_2BH_3 \longrightarrow \mu\text{-}(CH_3)_2NB_2H_5 + {}^1\!/_2[(CH_3)_2NBH_2]_2$$

The chemistry of both new materials and the reactions of diborane with other aminoalane derivatives are under investigation in this laboratory and will be reported more fully at a later date.

Acknowledgment. Support for this work by the National Science Foundation is gratefully acknowledged.

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(1) Boron-11 and proton nmr spectra were obtained using a Varian HA-100 spectrometer equipped with standard accessories. Boron-11 chemical shifts are in parts per million (ppm) relative to diethyl ether–boron trifluoride.

(2) D. F. Gaines and R. Schaeffer, *J. Amer. Chem. Soc.*, **86**, 1505 (1964).

(3) R. F. Schirmer, J. H. Noggle, and D. F. Gaines, *ibid.*, **91**, 6240 (1969).

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A Fair Test for Competitive Cycloadditions. Duality of Mechanism in the Cyclization of 5-Allylcyclohexa-1,3-diene

Sir:

In studies of the intramolecular Diels–Alder reaction, Doering and Krantz[1] have noted that heating 5-allylcyclohexa-1,3-diene (**1**) at 225° leads to tricyclo[3.3.1.0^{2,7}]non-3-ene (**2**), benzene (**3**), 1-allylcyclohexa-1,3-diene (**4**), 2-allylcyclohexa-1,3-diene (**5**), and recovered starting material. This communication deals with the stereochemical fate of the deuterium label in cyclized α,α-dideuterio-5-allylcyclohexa-1,3-diene (**6**) as a convenient probe of mechanism in the range of 184–203°. At 203° equilibrium between **1** and **2** was established by heating either isomer for 48 hr.[2]

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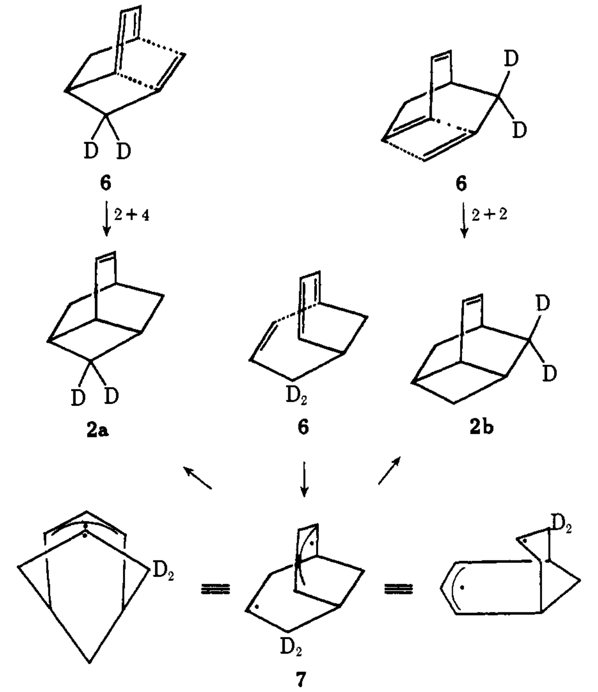
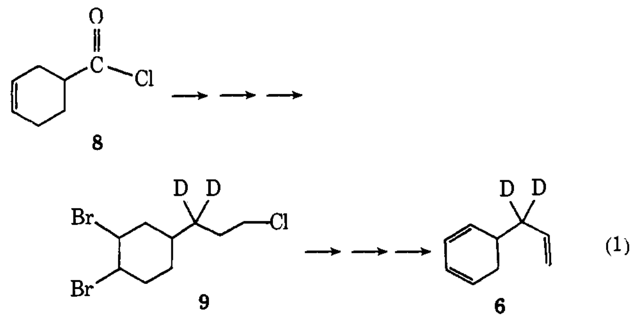
(1) (a) W. von E. Doering and A. Krantz, unpublished results; (b) A. Krantz, Ph.D. thesis, Yale University, New Haven, Conn., 1967; (c) cited by A. Krantz and C. Y. Lin, *Chem. Commun.*, 1287 (1971).

Scheme I



As illustrated in Scheme I three mechanistic possibilities are distinguishable by noting the position of the deuterium label in cyclized **6**. A concerted (or two-stage)[3] [4 + 2] process would lead to deuterium at exclusively the C$_8$ position of **2a**, whereas the concerted (or two-stage) [2 + 2] reaction would fix the deuterium only at the exo and endo positions of **2b**. A stepwise process involving a symmetrical diradical intermediate **7** (or its equivalent[4]) would initially lead to equal amounts of **2a** and **2b**.



(1)

The preparation of **6** was accomplished by a sequence essentially identical with that previously employed in the synthesis of **1** (eq 1).[1,5] Lithium aluminum deuteride (>99% d_4) reduction of the carbonyl chloride[6] **8** (70%), Wiley[7] bromination (87%), Grignard formation, and reaction with ethylene oxide (45%) followed by treatment with thionyl chloride (69%) and then bromine (97%) produced a mixture of trihalides **9**, which after reaction with anhydrous dimethylamine (100°, 76%), oxidation with 30% hydrogen peroxide, and then pyrolysis gave **6** in 60% yield: ir (neat) 3088, 995, 910 (HC=CH$_2$), 2090, 2112, and 2190 cm^{-1} (C–D str); uv (ethanol) λ_{max} 260 nm (ϵ 5580); nmr (CCl$_4$) δ 2.08 (m, 3, allyl), 4.98 (m, 2, =CH$_2$), and 5.78 (b, singlet, 5, olefinic). Mass spectrographic analysis at ionizing voltage of 8.0 eV indicated the isotopic composition of labeled **1** (**6**) to be 97.0% d_2, 2.5% d_1, and 0.5% d_0.

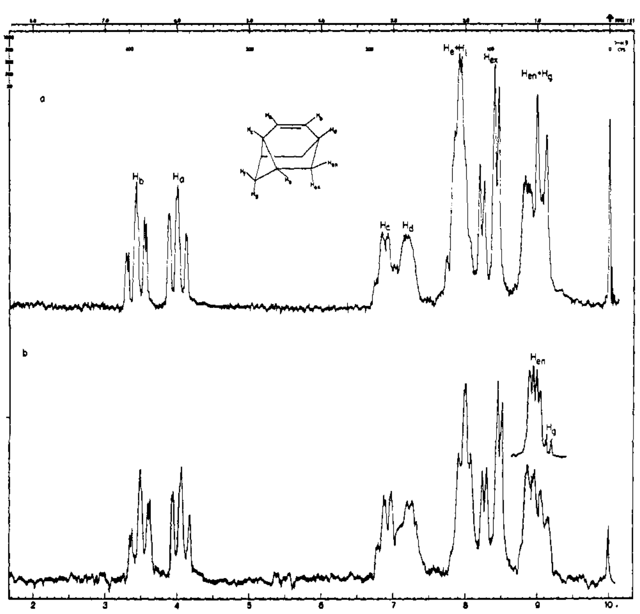


Figure 1. (a) The 60-MHz spectrum of tricyclo[3.3.1.0^{2,7}]non-3-ene. (b) The 60-MHz spectrum of tricyclic product from heating α,α-dideuterio-5-allylcyclohexa-1,3-diene at 193° for 33.5 hr; the H$_{en}$ and H$_g$ signals from the 220-MHz spectrum (not to scale) are shown above the corresponding pattern in the 60-MHz spectrum.

After heating **6** (>99%+ by vpc) in the gas phase (50–80 μl in 250-ml Pyrex tubes sealed under vacuum at $-196°$) at 193 ± 3° for 33.5 hr,[8] the tricyclic product was isolated by vpc and analyzed by nmr spectroscopy. The 60-MHz pmr spectrum of cyclized **6** pictured in Figure 1 (b) differs from the unlabeled variety (**2**)[9] in Figure 1 (a), with respect to resonances in **2** centered at δ 1.0 (m, 3) and 2.07 ppm (H$_f$ + H$_e$, m, 3). The former absorption is derived from signals due to H$_g$ (0.93 ppm, J = 8.0 Hz)[10] and H$_{en}$ (1.11 ppm, dd, J = 12.0 and 6.0 Hz).[11]

The spectrum of cyclized **6** clearly reveals the double doublet pattern of H$_{en}$ protons and shows no obvious absorption due to H$_g$. The resonances at δ 2.07 ppm were reduced in relative intensity by approximately one proton. The remaining peaks were essentially unaffected.

The signal due to H$_{en}$ and H$_g$ protons from the 220-MHz spectrum of cyclized **6** is shown directly above the corresponding absorption in the 60-MHz spectrum in Figure 1 (b). The measured value of 97:3 for the ratio of H$_{en}$:H$_g$ (after correction for the isotopic

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[2] In this work the equilibrium constant at 203° for the cyclization of **1** into **2** was found to be $K = [2]/[1] = 1.38 \pm 0.05$.

[3] R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

[4] See R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *J. Amer. Chem. Soc.*, **92**, 7091 (1970), for a discussion of twixtyls, species which may operationally behave as true intermediates.

[5] Yields are given in parentheses; appropriate spectral data and elemental analyses were obtained for all new compounds.

[6] J. Klein, *Isr. J. Chem.*, **1**, 385 (1963).

[7] G. A. Wiley, R. L. Herskowitz, B. M. Rein, and B. C. Chung, *J. Amer. Chem. Soc.*, **86**, 964 (1964).

[8] Under these conditions labeled **1**, **2**, **3**, and the two unresolvable components **4** and **5** were formed in the ratios 34.0:29.6:5.1:31.3, respectively.

[9] Assignments in **2** are based on spin decoupling experiments and will be detailed in the full paper.

[10] The assignment of the doublet absorption at δ 0.93 ppm to the cyclobutyl proton H$_g$ is consistent with the knowledge that endoid protons of the methylene bridge of bicyclo[3.1.1]hexanes absorb at uncommonly high field. For further examples see K. B. Wiberg and B. A. Hess, *J. Org. Chem.*, **31**, 2251 (1966).

[11] K. Tori, Y. Takano, and K. Kitahanoki, *Chem. Ber.*, **97**, 2798 (1964), have found that protons syn to the ethylenic bridge of bicyclo[2.2.2]octenes generally appear at higher field than those of an anti disposition.

composition of starting material) indicates that under these conditions *ca.* 94 ± 3% of **2** is formed *via* a [4 + 2] cycloaddition.

The position of the label in tricyclic product after heating **6** under a variety of conditions was determined using dmr spectroscopy.[12,13] The results based on the intensity ratio D_f:D_{ex}, 100:0 (184°, 21 hr), 93:7 (193°, 33.5 hr), and 70:30 (203°, 36.5 hr)[14] indicate that at 184° (21 hr) the formation of **2** proceeds exclusively by a [4 + 2] mechanism, but at higher temperatures at least one other pathway intervenes to scramble the label. Assuming that no more than 1% of **2b** is formed at 184°, the [4 + 2] pathway is kinetically favored by at least $-RT \ln k_2/k_1 = 4.576\ (457.2) \log (99) = -4.1$ kcal/mol.[15]

Although the lower energy pathway to **2** must involve a [4 + 2] cycloaddition of **1**, several interpretations of the scrambling of the label between H_{en}–H_{ex} and H_f–H_g proton pairs are possible. Extensive commentary on the scrambling must await the full paper but suffice it to say that the raw kinetic data can encompass a diradical mechanism for this process involving the formation of **7** from **1** (or **2**) followed by rapid coupling to give tricyclic product.[17]

Studies are continuing to test for the involvement of a $[_{\pi}4_s + _{\pi}2_a]$ cycloaddition in the primary formation of **2** and to obtain precise activation parameters for the reactions in this system.

Acknowledgment. Acknowledgment is made to the Research Foundation and the Graduate School of the State University of New York at Stony Brook, to the Research Corporation, and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[12] Dmr spectra were taken on a Bruker HFX-90 nmr spectrometer with a measuring frequency of 13.82 MHz by Mr. W. Schittenhelm of Bruker Scientific Inc., Elmsford, N. Y., to whom I am indebted. Integrations were performed electronically with the aid of a Fabri-Tek 1080 computer.

[13] The D_g and D_{en} resonances coincided in the 13.82-MHz dmr spectra but their combined intensities always equalled the sum of the intensities of the resolved D_f and D_{ex} signals. No other signals were detectable in the dmr spectra of cyclized **6**.

[14] After heating **6** for 36.5 hr at 203°, recovered dideuterio-5-allylcyclohexa-1,3-diene contained 14% of the label in the γ position of the allyl side chain.

[15] Since factors which stabilize products may be important in stabilizing the activated complex leading to products, the [2 + 2] reaction which produces cyclobutanes is usually disadvantaged compared to the [2 + 4] case and the usual reaction course favoring formation of cyclohexenes can be explained without regard to the theory of Woodward and Hoffmann.[16] However, the present result makes clear that even in a competition where the same product could have been formed from either pathway the [4 + 2] cycloaddition is still kinetically favored.

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

[17] The experimentally derived value for the initial rate of formation of **2** (due primarily to a [4 + 2] cycloaddition) at 193° is $k = 6.16 \times 10^{-6}$ sec^{-1}. The computed value of 39.4 ± 3 kcal/mol[18] for the activation energy of formation of **2** from **1** coupled with an A factor estimated[18] at $10^{11.5 \pm 0.5}$ gives $k = 10^{-7}$ sec^{-1} for the slower diradical mechanism.

[18] These parameters were estimated by group additivity methods described by (a) S. W. Benson in "Thermochemical Kinetics," Wiley, New York, N. Y., 1968; (b) S. W. Benson and H. E. O'Neal in "Kinetic Data on Gas Phase Unimolecular Reactions," NSRDS-NBS-21, 1970, U. S. Government Printing Office, Washington, D. C.; (c) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969), and will be discussed in detail in the full paper.

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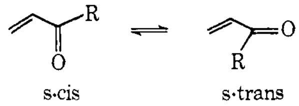
A Simple Method for Assigning Vibrational Frequencies to Rapidly Equilibrating Rotational Isomers

Sir:

Continuing interest in the conformations of organic molecules and related spectral properties[1] prompts us to report a novel and simple method based upon the matrix isolation technique for assigning vibrational frequencies to rapidly equilibrating rotational isomers. Previous workers have employed temperature-dependent infrared spectroscopic studies of gaseous and liquid samples, Raman spectroscopy, and infrared studies of the crystal[2–4] in the determination of vibrational patterns of individual conformers. In our method an immobilized mixture of conformers in an argon matrix at 20.4°K is prepared by rapid freezing of a room temperature equilibrated gas-phase sample. The conformer ratio is then perturbed by photochemical irradiation. Under the conditions of the experiment infrared bands are highly resolved, and the low temperature and rigidity of the matrix prohibit thermal interconversion of conformers corresponding to local energy minima.[5] If the conformer ratio is displaced photochemically, analysis of the changes in the relative intensities of bands allows assignments to be made to the components of the mixture.

The method is illustrated for but-3-en-2-one (**1**) which has been studied spectroscopically and is thought to exist primarily in the s-cis and s-trans forms.[2,6–8] The enthalpy difference between the two rotamers is approximately 0.5 kcal/mol favoring the s-trans form.



1, R = CH_3
2, R = H

Photoirradiation of **1** in an Ar matrix ($M/R = 800$) with nickel sulfate filtered light from a medium pressure mercury arc for periods up to 4.16 hr produced only changes in the relative intensities of bands as shown for a representative region of the infrared spectrum in Figure 1. A number of bands which included the carbonyl absorption at 1690 cm^{-1} previously assigned to the s-trans conformer upon irradiation decreased at identical rates, whereas another set showed a corresponding increase in intensity. The observation of a reciprocal relationship between two sets of bands

[1] (a) N. Oi and J. F. Coetzee, *J. Amer. Chem. Soc.*, **91**, 2473, 2478 (1969); (b) G. J. Karabatsos and D. J. Fenoglio, *ibid.*, **91**, 1124, 3572, 3577 (1969); (c) A. J. Bowles, W. O. George, and D. B. Cunliffe-Jones, *Chem. Commun.*, 103 (1970); (d) W. E. Stewart and T. H. Siddall, III, *Chem. Rev.*, 70, 517 (1970); (e) D. J. Chadwick, J. Chambers, G. D. Meakins, and R. L. Snowden, *Chem. Commun.*, 624, 625 (1971); (f) I. Juchnovski and J. Kaneti, *Tetrahedron*, 27, 4269 (1971); (g) D. D. Faulk and A. Fry, *J. Org. Chem.*, **35**, 364 (1970); (h) R. B. Birge, W. C. Pringle, and P. A. Leermakers, *J. Amer. Chem. Soc.*, **93**, 6715 (1971).

[2] K. Noack and R. N. Jones, *Can. J. Chem.*, **39**, 2201 (1961).

[3] R. Mecke and K. Noack, *Chem. Ber.*, **93**, 210 (1960).

[4] R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960).

[5] At 20°K thermally induced unimolecular reactions with A factors in the range of 10^{13} sec^{-1} and activation energies greater than 1 or 2 kcal/mol would not be observable on the time scale of the experiment.

[6] A. J. Bowles, W. O. George, and W. F. Maddams, *J. Chem. Soc. B*, 810 (1969). (As these authors point out, it is possible that the conformer referred to as s-cis is actually skew or nonplanar.)

[7] P. D. Foster, V. M. Rao, and R. F. Curl, Jr., *J. Chem. Phys.*, **43**, 1064 (1965).

[8] W. G. Fately, R. K. Harris, F. A. Miller, and R. E. Witkowski, *Spectrochim. Acta*, **21**, 231 (1965).