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.

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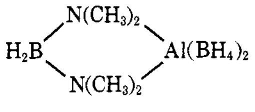
Reaction of Diborane with Tris(dimethylamino)alane. Isolation of a New B–N–Al Heterocycle and a New Compound with a B–N–B–N–B Skeleton

Sir:

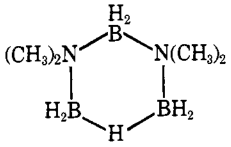
Tris(dimethylamino)alane reacts with excess diborane in diethyl ether at room temperature to form $[(CH_3)_2NBH_2]_2$, μ-$(CH_3)_2NB_2H_5$, $[(CH_3)_2NAl(BH_4)_2]_2$, and two new compounds which we formulate to be $H_2B[N(CH_3)_2]_2Al(BH_4)_2$ and $H_2BN(CH_3)_2BH_2N(CH_3)_2BH_3$.

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.

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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).