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Boron Heterocycles. IV. Relative Stabilities toward Disproportionation and Base-Acceptor Character of 1,3,2-Dioxaborolane and 1,3,2-Dioxaborinane[1]

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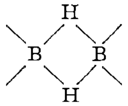
In recent years a number of substituted five-membered rings (dioxaborolanes) of framework OCH_2CH_2OB- and six-membered rings (dioxaborinanes) $OCH_2CH_2CH_2OB-$ have been prepared. In general, these compounds have not been studied in detail; however, there has been appreciable discussion concerning the relative properties of the two ring systems. In particular, relative stabilities and base-acceptor character discussed in terms of relative ring strain have been considered.[2] Of the parent rings, only OCH_2CH_2OBH has been reported previously. The present study is concerned with the relative stabilities toward disproportionation of the rings OCH_2CH_2OBH and $OCH_2CH_2CH_2OBH$, reconsideration of criteria for stability, and relative base-acceptor character.

Experimental Section

A. Synthetic Procedures.—$O(CH_2)_3OBH$ and $O(CH_2)_2OBH$ were prepared according to methods previously described for the preparation of $O(CH_2)_2OBH$,[3] with the exception that CH_2Cl_2 was used as a solvent. *Anal.* Calcd for $O(CH_2)_3OBH$: H (hydridic), 0.24; B, 4.80. Found: H (hydridic), 0.24; B, 4.76.

B. Physical Properties of 1,3,2-Dioxaborinane.—$O(CH_2)_3OBH$ is a clear, viscous liquid at room temperature which is soluble in CH_2Cl_2 and $(C_2H_5)_2O$. Its molecular weight from vapor density measurements at about 15 mm was found at room temperature to be 84 ± 1 (calcd: 85.9).

The mass spectrum showed a parent mass of 85, with no evidence for higher molecular weight dimeric species. Boron-11 nmr spectra gave no evidence for



bridges in solution (CH_2Cl_2).

The infrared spectrum, which was obtained in a 10-cm gas cell with Eastman Kodak IRTRAN-4 windows at 20 mm, is as follows: 2949 (s), 2892 (m, sh), 2575 (s), 1494 (m), 1487 (s), 1440 (s), 1432 (s), 1286 (s), 1218–1236 (vs, br), 1277 (vs), 1217 (vs), 1134 (w), 909 (m), 894 (m), 811–839 (w, br) cm^{-1}, where s = strong, m = medium, w = weak, br = broad, sh = shoulder, and v = very. No evidence for B–H–B bridge absorptions was observed in the spectra of freshly distilled samples.

The following vapor pressure measurements were made according to a previously described procedure:[3] 1.65 (−22.9°), 2.75 (−15.3°), 5.85 (−6.4°), 9.10 (0.0°), 10.45 (1.8°), 12.90 (5.2°), 15.40 (8.6°), 27.60 mm (19.2°). A plot of log P *vs.* $1/T$ was linear in the range studied, allowing reduction of the data to $\log P_{mm} = -2.14 \times 10^3/T + 8.79$. The heat of vaporization was 9.81 ± 0.30 kcal/mole.

C. Disproportionation Studies.—The stoichiometry of disproportionation of 1,3,2-dioxaborolane was established earlier.[3]

$$O(CH_2)_2OBH \rightleftharpoons {}^1/_6B_2H_6 + {}^1/_3O(CH_2)_2OBO(CH_2)_2OBO(CH_2)_2O$$

1,3,2-Dioxaborinane was found to decompose in a like manner. Forward and reverse reactions were observed using methods described previously.[3] Disproportionation products were identified by infrared spectra for B_2H_6 and mass spectrometry and chemical analyses for $O(CH_2)_3OBO(CH_2)_3OBO(CH_2)_3O$.

Rates of disproportionation were studied through the following procedure. A measured quantity of freshly purified heterocycle, either $O(CH_2)_2OBH$ or $O(CH_2)_3OBH$, was distilled into a tube of known volume (about 110 ml), which contained a mercury manometer on a side arm. The bulb had been previously cleaned in alcoholic KOH, then thoroughly rinsed with distilled water, and baked dry. The quantity of heterocycle used was always sufficiently small so that the pressure of heterocycle used was well below the saturation pressure. The bulb was thermostated at 25° and the rate of decomposition was followed by means of a cathetometer. From the equation for disproportionation, the partial pressure of unreacted heterocycle is given by $P_{hot} = {}^6/_5P_{obsd} - {}^1/_5P^0$, where P_{het} = partial pressure of undecomposed heterocycle, P_{obsd} = observed pressure at some given time, and P^0 = initial pressure of the pure heterocycle. Initial pressures were of the order of 20 mm and runs for each heterocycle were made in duplicate. The rate law for the forward disproportionation reaction appears to be second order, giving linear plots of $1/P_{het}$ *vs.* time for a period of about 1 week (about 50% disproportionation). The observed kinetics of disproportionation of $(CH_3O)_2BH$ appears to be second order also.[4] Rate constants were determined from the slopes of the plots and were averaged for each heterocycle. They were found to be $0.9 \pm 0.2 \times 10^{-4}$ mm^{-1} hr^{-1} for $O(CH_2)_2OBH$ and $2.2 \pm 0.3 \times 10^{-4}$ mm^{-1} hr^{-1} for $O(CH_2)_3OBH$.

Samples from which rate data were obtained were allowed to stand at 25° until the systems had come to equilibrium. Equilibrium was detected by plotting pressure *vs.* time and observing a plateau of constant pressure. Constant pressure was observed from 2 to 4 weeks to assure that equilibrium had been achieved. Since the volumes of the reaction tubes were calibrated and since the initial pressure of pure heterocycle was known, it was possible to calculate the equilibrium partial pressure of B_2H_6 and the heterocycle and in turn calculate the equilibrium constant for the disproportionation reaction. For heterogeneous equilibrium with either $O(CH_2)_2OBO(CH_2)_2OBO(CH)_2O$ or $O(CH_2)_3OBO(CH_2)_3OBO(CH_2)_3O$ being the condensed phase, the equilibrium constant was obtained from the expression

$$K_p = \frac{P_{B_2H_6}{}^{1/6}}{P_{O(CH_2)_nOBH}} \qquad n = 2 \text{ or } 3$$

For the homogeneous equilibrium, the equilibrium constant was obtained from the expression

$$K_p = \frac{P_{B_2H_6}{}^{1/6}P_{O(CH_2)_nOBO(CH_2)_nOBO(CH_2)_nO}{}^{1/3}}{P_{O(CH_2)_nOBH}}$$

The vapor pressures of $O(CH_2)_2OBO(CH_2)_2OBO(CH_2)_2O$ and $O(CH_2)_3OBO(CH_2)_3OBO(CH_2)_3O$ were determined with a micro-

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[1] For III, see D. E. Young, G. E. McAchran, and S. G. Shore, *J. Am. Chem. Soc.*, **88**, 4390 (1966).

[2] A. J. Hubert, B. Hargitay, and J. Dale, *J. Chem. Soc.*, 931 (1961).

[3] S. H. Rose and S. G. Shore, *Inorg. Chem.*, **1**, 744 (1962).

[4] H. S. Uchida, H. B. Kreider, A. Murchison, and J. F. Masi, *J. Phys. Chem.*, **63**, 1414 (1959).

TABLE I

EQUILIBRIUM DATA[a]

Compound	10^3P_1, atm	10^3P_2, atm	10^6P_3, atm	K_p[b]	K_p[c]	$\Delta G°_{298}$,[b] kcal/mole	$\Delta G°_{298}$,[c] kcal/mole
$\underline{O(CH_2)_3OB}H$	6.45	3.85	5.8	61.4 ± 0.5	11.0 ± 0.2	−2.4 ± 0.1	−1.4 ± 0.1
$\underline{O(CH_2)_3OB}H$	6.46	3.41	5.8	60.1 ± 0.5	10.8 ± 0.2	−2.4 ± 0.1	−1.4 ± 0.1
$\underline{O(CH_2)_2OB}H$	19	77	3.6	24 ± 2	0.36 ± 0.07	−1.9 ± 0.1	0.60 ± 0.05
$\underline{O(CH_2)_2OB}H$	17	69	3.6	26 ± 2	0.40 ± 0.07	−1.9 ± 0.1	0.54 ± 0.05

[a] P_1 = partial pressure of heterocycle; P_2 = partial pressure of B_2H_6; P_3 = partial pressure of $\underline{O(CH_2)_nOB}O(CH_2)_nO\underline{BO(CH_{2n}O}$. [b] Heterogeneous equilibrium. [c] Homogeneous equilibrium.

manometer and found to be 2.7 × 10^{-3} and 4.4 × 10^{-3} mm, respectively.

D. Lewis Base Adducts.—The adduct $\underline{O(CH_2)_3OB}HN(CH_3)_3$ was prepared in the same manner as $\underline{O(CH_2)_2OB}HN(CH_3)_3$.[3] In a typical reaction, trimethylamine and 1,3,2-dioxaborinane reacted in a 1.07:1.00 molar ratio. The adduct is a white solid which has a vapor pressure of approximately 26 mm at −23°. The infrared spectrum of the gas phase above the solid at room temperature is simply a composite of the spectrum of each component, indicating no interaction in the gas phase. (Adduct formation would shift the B–H stretching frequency, 2575 cm^{-1}, to a significantly lower value.) Vapor density measurements gave an average value of 72 ± 1 for the molecular weight of the gas phase at room temperature. This is consistent with complete dissociation of the adduct (formula wt of $\underline{O(CH_2)_3OB}HN(CH_3)_3$: 145).

Trimethylphosphine adducts of $\underline{O(CH_2)_2OB}H$ and $\underline{O(CH_2)_3OB}H$ were prepared by distilling about 1 mmole of $P(CH_3)_3$ into a bulb which contained about 0.5 mmole of heterocycle at −196°. The bulb was warmed to 0° for several minutes and was then cooled to −45°. Excess $P(CH_3)_3$ was distilled into a trap at −196° and then measured volumetrically. At −45° and below, not all of the $P(CH_3)_3$ could be recovered. Trimethylphosphine and 1,3,2-dioxaborinane reacted in the molar ratio of 1.04:1.00. Reaction of trimethylphosphine and 1,3,2-dioxaborolane was in the molar ratio of about 0.7:1.00. This low ratio is attributed to the tendency of $\underline{O(CH_2)_2OB}H$ to form an intractable glass. Above −45° the adducts were sufficiently unstable so that all of the $P(CH_3)_3$ could be recovered. Vapor density measurements of a 1:1 gaseous mixture of $(CH_3)_3P$ and $\underline{O(CH_2)_2OB}H$ and a 1:1 gaseous mixture of $(CH_3)_3P$ and $\underline{O(CH_2)_3OB}H$ gave values of 75 ± 2 and 81 ± 5, respectively. These values indicated that no adduct formation occurs in the vapor phase (formula wt of $\underline{O(CH_2)_2OB}HP(CH_3)_3$: 148; formula wt of $\underline{O(CH_2)_3OB}HP(CH_3)_3$: 162). Infrared spectra of each gas phase were simply composites of the spectrum of each component.

Results and Discussion

Stability Studies.—Thermodynamic data obtained from the homogeneous vapor phase disproportionation of 1,3,2-dioxaborolane and 1,3,2-dioxaborinane

$$\underline{O(CH_2)_2OB}H(g) \rightleftharpoons {}^1/_6B_2H_6(g) + {}^1/_3\underline{O(CH_2)_2OB}O(CH_2)_2O\underline{BO(CH_2)_2O}(g)$$

$$\Delta G°_{298} = 0.60 \pm 0.05 \text{ kcal/mole}$$

$$\underline{O(CH_2)_3OB}H(g) \rightleftharpoons {}^1/_6B_2H_6(g) + {}^1/_3\underline{O(CH_2)_3OB}O(CH_2)_3O\underline{BO(CH_2)_3O}(g)$$

$$\Delta G°_{298} = -1.4 \pm 0.1 \text{ kcal/mole}$$

and kinetic data obtained from the forward reaction of the disproportionation studies in which the specific rate constants were 0.9 ± 0.2 × 10^{-4} mm^{-1} hr^{-1} for 1,3,2-dioxaborolane and 2.2 ± 0.3 × 10^{-4} mm^{-1} hr^{-1} for 1,3,2-dioxaborinane show that there is essentially little difference between the two rings. The five-membered ring appears to be slightly more resistant toward disproportionation.

On the basis of ease of synthesis from 1,2- and 1,3-diols, Hubert, Hargitay, and Dale[2] believed that the five-membered ring was less stable than the six-membered ring, the principal evidence being a competitive reaction in which $HOCH_2CH_2CH_2OH$ forms the dioxaborinane ring more readily than $HOCH_2CH_2OH$ forms the dioxaborolane ring. However, their criterion for stability and the examples chosen neglected the configurations of the diols from which the boron heterocycles are formed. Thus in ethylene glycol the OH groups are *trans* to each other.[5] This unfavorable arrangement is probably a better reason for their observation than the claim that the five-membered ring is less stable because it is highly strained. The classic work of Broeseken[5] has considered the effect of configuration of 1,2-diols on heterocycle formation with boric acid and has shown that the *cis* arrangement is more favorable.

Base-Acceptor Character.—1,3,2-Dioxaborolane and 1,3,2-dioxaborinane are very weak Lewis acids. Infrared spectra and vapor densities show that the trimethylamine and trimethylphosphine adducts of these heterocycles are completely dissociated in the vapor phase. They cannot be sublimed quantitatively. However, insofar as dissociation pressure can be used as a measure of stability of the adduct, it seems clear that, with respect to base strength, trimethylamine is a stronger base than trimethylphosphine (Table II). The order of apparent base strength N > P is discussed in paper III,[1] which considers the effect of Lewis acid upon apparent base strength.

TABLE II

DISSOCIATION PRESSURES OF ADDUCTS

Adduct	State	Temp, °C	Equilibrium pressure above solid
$\underline{O(CH_2)_2OB}HN(CH_3)_3$	Solid	25	*Ca.* 10 mm, completely dissociated
$\underline{O(CH_2)_3OB}HN(CH_3)_3$	Solid	−23	*Ca.* 26 mm, completely dissociated
$\underline{O(CH_2)_2OB}HP(CH_3)_3$	Solid		Above −45° existence of adducts could not be detected
$\underline{O(CH_2)_3OB}HP(CH_3)_3$	Solid		

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(5) J. Boeseken, *Advan. Carbohydrate Chem.*, **4**, 189 (1949).

Arguments rationalizing weak acceptor character of borate esters in terms of boron-oxygen π bonds are well known and are given elsewhere;[6] however, it is of interest to note that the boron-11 chemical shift data given in Table III for the free heterocycles can be correlated with this rationale, assuming, roughly, that the chemical shift can be considered to be related to the electron density on boron. Chemical shifts for the oxygen-substituted heterocycles occur at significantly higher fields than those for the sulfur-substituted rings $\underline{\mathrm{SCH_2CH_2SB}}\mathrm{H}$ and $\underline{\mathrm{SCH_2CH_2SB}}\text{-}i\text{-}\mathrm{C_4H_9}$ suggesting greater electron density around boron in oxygen-substituted heterocycles. This is consistent with the strong acceptor character of $\underline{\mathrm{SCH_2CH_2SB}}\mathrm{H}$.[7]

TABLE III

BORON-11 NUCLEAR MAGNETIC RESONANCE DATA

Compound	Solvent	J, cps	δ, ppm[a]
$\mathrm{(CH_3O)_2BH}$[b]		141	−26.1
$\underline{\mathrm{O(CH_2)_2OB}}\mathrm{H}$	$\mathrm{CH_2Cl_2}$	173	−28.7
$\underline{\mathrm{O(CH_2)_3OB}}\mathrm{H}$	$\mathrm{CH_2Cl_2}$	170	−25.9
$\underline{\mathrm{S(CH_2)_2SB}}\mathrm{H}$	$\mathrm{C_6H_6}$	140	−61.3
$\underline{\mathrm{S(CH_2)_2SB}}\text{-}i\text{-}\mathrm{C_4H_9}$[c]			−70.0
$\underline{\mathrm{O(CH_2)_2OB}}\mathrm{HN(CH_3)_3}$	$\mathrm{CH_2Cl_2}$	127	−7.5
$\underline{\mathrm{O(CH_2)_3OB}}\mathrm{HN(CH_3)_3}$	$\mathrm{CH_2Cl_2}$	152	−16.6

[a] $\mathrm{BF_3 \cdot O(C_2H_5)_2}$. [b] T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959). [c] M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 1345 (1961).

From the dissociation pressure data in Table II, the five-membered ring is apparently a stronger Lewis acid than the six-membered ring, which is consistent with thermochemical studies of the heats of formation of analogous adducts.[2,8]

It is of interest to note that the orders of donor character of tetrahydrofuran, $\mathrm{(CH_2)_4O}$, and tetrahydropyran, $\mathrm{(CH_2)_5O}$, parallel the order of acceptor character of the boron heterocycles in that the five-membered ring, THF, is a stronger donor than the six-membered ring, THP.[9] Effect of ring size on donor and acceptor character has been accounted for by invoking strain arguments.[2,10,11] However, the only available thermodynamic data suggest that differences in strain energy are very small,[9,12] and other arguments have been invoked to account for the effect of ring size on donor character.[9,13] Essentially, they consider the effect of rehybridization and possible steric factors. The extent to which such arguments are valid has not necessarily been established; however, they can be applied, in principle, to the boron heterocycles as well.

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Some New Cobalt Nitrosyl Complexes

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During our studies[2-4] of aziridine (ethylenimine) complexes, the possibility of forming some unusual nitrosyl compounds was discovered. A variety of interesting nitrosyl complexes of cobalt have now been prepared. These compounds fit the general formula $\mathrm{CoL}_q\mathrm{(NO)}_r\mathrm{X}_s$, wherein L is a ligand other than nitric oxide and X is one of the anions $\mathrm{NO_3^-}$, $\mathrm{Cl^-}$, or $\mathrm{ClO_4^-}$. The compounds fall into two categories. In one category (hereafter class A), q, r, and s have values of 4, 1, and 2, respectively (if L is bidentate, than q = 2). In the other category (hereafter class B), the values of q, r, and s are 2, 2, and 1, respectively.

Experimental Section

Materials.—All materials were obtained commercially. Reagent grade cobalt salts were used without purification. Solid amines were crystallized from appropriate solvents until no further improvement in melting point was obtained. Liquids were distilled prior to use. The amines were distilled over KOH pellets at reduced pressure, and colorless distillates were obtained. Nitric oxide was used as received from Matheson Coleman and Bell.

Procedures.—The compounds were analyzed by Schwarzkopf Microanalytical Laboratory. Infrared spectra were taken in KBr pellets in the range 4000–670 cm^{-1} using a Perkin-Elmer Model 137 spectrophotometer. Magnetic susceptibilities were determined by the Gouy balance technique or pendulum magnetometer at 27–28°. Conductivity measurements were made at 25° in methanol solution on an Industrial Instruments Model RC 16B2 conductivity bridge; the methanol was distilled over Drierite.

Preparations. General.—The reaction vessel consisted of a three-neck flask fitted with a gas inlet tube (extending below the surface of the reaction medium), a dropping funnel, and a gas outlet tube vented to a hood. Reactions were cooled *via* an ice bath, and stirring was accomplished with a Teflon-covered stirring bar and a magnetic stirrer.

Solutions of the appropriate cobalt(II) salt were prepared, filtered, and cooled. The reaction vessel was flushed with $\mathrm{N_2}$. Previously-cooled ligand was added, then the $\mathrm{N_2}$ flow was replaced with NO for the specified period of time. The products were filtered under $\mathrm{N_2}$.

Further details of the preparations may be obtained upon request.[1]

Class A Compounds. Nitrosyltetraaziridinecobalt(II) Chloride Monohydrate, $\mathrm{[Co(C_2H_5N)_4NO]Cl_2 \cdot H_2O}$.—To 10 g of

(1) To whom inquiries should be addressed.

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