quite reasonable. The value of ρ_4 is closer to that for $NiBr_4^{-2}$, 4560 cm.$^{-1}$, than would have been expected if the distortion were neglected. However, it is still rather high, a fact that we must ascribe to the larger covalency of the more electronegative copper ion. The ratio ρ_2/ρ_4 is 0.9, in consonance with previous experimental determinations which suggest this ratio is considerably smaller than the value of 2 or 3 predicted by Hartree-Fock metal ion functions.[5]

The predicted splitting of the T_2 state is very large and the ground state is non-degenerate as required by the Jahn-Teller theorem. Ballhausen and Liehr[6] have correctly pointed out that even tetrahedral $CuBr_4^{-2}$ is strictly not a case to which this theorem applies since the spin-orbit splitting alone (*ca.* 1000 cm.$^{-1}$) provides a non-degenerate ground state. Comparison with the but slightly distorted $ZnBr_4^{-2}$ ion suggests that spin-orbit coupling is insufficient to stabilize the $CuBr_4^{-2}$ ion against further distortion than already is provided by the lattice.

Acknowledgment.—This research was supported by the National Science Foundation.

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(6) C. J. Ballhausen and A. D. Liehr, *J. Mol. Spectry.*, **4**, 190 (1960).

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T. S. PIPER

RECEIVED JUNE 25, 1962

The Preparation of a Series of Compounds Containing the Pentachloroalkoxoniobate (IV) Anion

Sir:

We wish to report the preparation of a new class of niobium(IV) compounds. In particular, pyridinium pentachloromethoxoniobate(IV), (py)$_2$-[Nb(OCH$_3$)Cl$_5$], has been prepared by the electrolytic reduction of $NbCl_5$ dissolved in anhydrous methanol (saturated with anhydrous HCl), followed by the addition of a hot methanol solution of pyridinium chloride. The compound, which results after cooling for several hours, is obtained as a red-brown, spiny, crystalline agglomerate.

Anal. Calcd. for (pyH)$_2$Nb(OCH$_3$)Cl$_5$: C, 28.61; H, 3.27; Cl, 38.45; Nb, 20.13. Found: C, 28.67; H, 3.30; Cl, 38.21; Nb, 20.21.

In agreement with the formulation Nb(OCH$_3$)-Cl$_5^{-2}$, the infrared spectrum reveals no absorption characteristic of the OH group, but does show an intense band at 1095 cm.$^{-1}$ which is not due to pyridinium ion, but is typical of the C–O stretching mode in alkoxides. Furthermore, the spectrum indicates the presence of pyridinium ion and not ligand pyridine.[1]

Magnetic studies indicate Curie–Weiss paramagnetism (Table I) and verify the presence of the niobium(IV) ion, with 4d^1 configuration.

TABLE I

Temp., °K.	$\chi'_M \times 10^6$	θ	μ_{eff}
299	1020	61°	1.72
196	1425		
77	2700		

The compound is extremely sensitive to air, turning blue and then white. It is soluble in water and gives an immediate brown coloration and then slowly deposits a brown hydrous oxide. It is soluble with decomposition in alcohols. In dimethylformamide, solution is accompanied by a violet color which changes quickly to blue. It is insoluble in dimethyl sulfoxide and common organic solvents, such as benzene, ethers, and ketones.

By varying the organic base and the solvent, a series of methoxy, ethoxy, and isopropoxy compounds has been obtained. They are similar, except in color, to (py)$_2$[Nb(OCH$_3$)Cl$_5$], and will be described in detail in a later publication. Further work will include an investigation of the distinct color differences in these compounds and the preparation of the analogous bromides, iodides, and thiocyanates.

(1) N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp *J. Inorg. Nucl. Chem.*, **18**, 79 (1961).

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CARL H. BRUBAKER, JR.

RECEIVED JULY 25, 1962

Mechanism of Alkylborane Isomerization[1]

Sir:

I wish to present evidence which suggests that an intramolecular bridge hydrogen tautomerism

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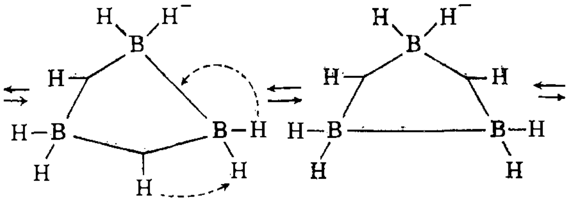
(1) Presented at the American Chemical Society Regional Meeting, Los Angeles, Calif., December, 1960.

mechanism accounts for alkylborane isomerization more satisfactorily than the previously suggested dissociation–association mechanism.

Hydrogen tautomerism and intramolecular rearrangement have been observed to take place in many electron-deficient boron containing compounds. Examples are: $Al(BH_4)_3$,[2] $B_3H_8^-$,[3] $B_3H_7:O(C_2H_5)_2$,[3] B_6H_{10},[3,4] $B_2H_7^-$,[4,5] $B_4H_6:N(CH_3)_3$,[5] and $B_{10}H_{14}$:cineole[5,6]; the B^{11} n.m.r. spectra of $B_{10}H_{13}^-$[7] and $(CH_3)_2NB_2H_5$.[8]

We suggest that the bridge hydrogen tautomerism mechanism in $B_3H_8^-$ and $(CH_3)_2NB_2H_5$ is relevant to alkylborane isomerization.

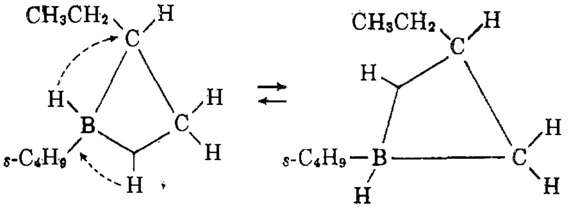
The hydrogens in $B_3H_8^-$ may be considered to migrate about the molecule ion in the following manner



I

The B^{11} n.m.r. spectra of μ-dimethylaminodiborane at several temperatures are compatible with the bridge hydrogen tautomerism mechanism about the boron–boron–nitrogen skeleton although other processes also have been suggested.[8]

One might speculate that an electron-deficient (and isoelectronic) system of boron, carbon, and hydrogen atoms also could tautomerize. For example, di-2-butylborane could rearrange *via* a tautomeric process.



This intermediate structure was suggested previously to account for the *cis* addition of BH_3 groups to the double bond in the hydroboration of olefins.[9] However, the dissociation–association mechanism was considered to account for the alkylisomerization.[10]

The bridge hydrogen tautomerism mechanism explains several observations with respect to alkylborane isomerization which are not satisfactorily explained by the dissociation–association mechanism.

(1) The bridge hydrogen tautomerism mechanism requires that R_2BH be present. Unusually rapid isomerization has been reported[11] in cases where the olefin is too bulky to allow the formation of the trialkylborane.

(2) The addition of a small amount of diborane should increase (*via* rapid alkyl-hydrogen exchange[12]) the concentration of R_2BH present in the system. Subsequent rapid alkyl-hydrogen exchange would allow *all* alkyl groups to exist "part time" in R_2BH molecules and alkylborane isomerization consequently should be speeded up. Such an effect for diborane has been reported.[13]

(3) Alkylborane isomerization proceeds at 160° (*ca.* 1 hr.) in diglyme, whereas 215° (20–50 hr.) is necessary[14] in the absence of diglyme. Diborane and diglyme react reversibly to form diglyme: BH_2^+ and $B_2H_7^-$.[5,15]

It is probable that the diglyme–diborane equilibrium is such that the last traces of diborane are not easily removed, therefore a small amount of diborane is retained which catalyzed the isomerization reaction as in (2), above.

It is probable that alkylaluminane isomerization[16,17] and certain rearrangements and hydrogen migration in carbonium ions also take place *via* a bridge hydrogen tautomerism mechanism.

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(7) This conclusion also was made independently by Dr. R. L. Williams, Admiralty Materials Laboratory, Dorset, England.

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RECEIVED FEBRUARY 23, 1962

The Reaction of Dioxygen Difluoride with Tetrafluoroethylene

Sir:

Dioxygen difluoride, O_2F_2, discovered by Ruff and Menzel,[1] melts at −163.5° to a red liquid; it