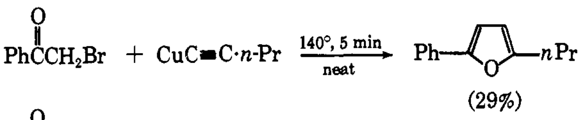
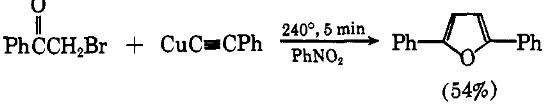

(4)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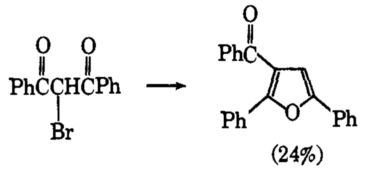
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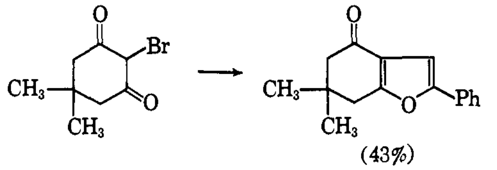
(7)

furans[2] and benzo[*b*]thiophenes[5] from *o*-halophenols and thiophenols and with the conversion of *o*-halopyridinols (pyridones) to furopyridines.[2,6] Reactions 4–7 suggest the possibility of a synthesis of unusual heterocyclic systems from a variety of carbonyl derivatives.

Acknowledgment. The authors are grateful to the National Institutes of Health (AI04132) for generous support.

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(5) A. M. Malte and C. E. Castro, *J. Am. Chem. Soc.*, **89**, 6770 (1967).

(6) A general synthesis of a wide array of furo[3,2-*b*]pyridines and furo[3,2-*c*] pyridines will be reported shortly. The keto tautomer is the dominant form of "hydroxypyridines" in the solid state and in solution: "Heterocyclic Compounds, Pyridine and its Derivatives," Part 1, E. Klingsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 67.

(7) To whom inquiries should be addressed.

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Preparation and Properties of $B_5H_8^-$ Salts. A New Synthesis of Decaborane(14)

Sir:

Recent reports by Gaines and Iorns[1] and by Onak, Dunks, Searcy, and Spielman[2] on the existence of $B_5H_8^-$ prompt us to describe results of independent studies carried out in this laboratory. We have prepared a number of salts of $B_5H_8^-$, examined its boron-11 nmr spectrum, and investigated some of its reactions, including one which results in the formation of $B_{10}H_{14}$. Initial results are reported at this time.

In a procedure similar to that of Gaines and Iorns,[1] LiB_5H_8 was prepared through the reaction of methyllithium with pentaborane(9). Samples were maintained at −78° to minimize decomposition. Sodium and potassium salts of $B_5H_8^-$ were generated by allowing a metal hydride to react with an equimolar amount of pentaborane(9) in glyme at −50°. An equivalent amount of hydrogen was produced after several hours at this temperature. Onak and co-workers[2] obtained

$$MH + B_5H_9 \xrightarrow{\text{glyme}} H_2 + MB_5H_8(\text{solvate})$$
$$M = Na, K$$

equivalent amounts of hydrogen in analogous reactions, which were carried out at room temperature. However, it seems clear from the present investigation that the nmr spectrum they report for the $B_5H_8^-$ ion is more likely that of a decomposition or rearrangement product. We have found that the sodium and potassium salts of $B_5H_8^-$ decompose rapidly in glyme on approaching room temperature; a light yellow precipitate appears and the high-field doublet in the boron-11 nmr spectrum disappears. On the other hand, samples of LiB_5H_8 in solution show no apparent decomposition for periods of up to 1 hr at room temperature.

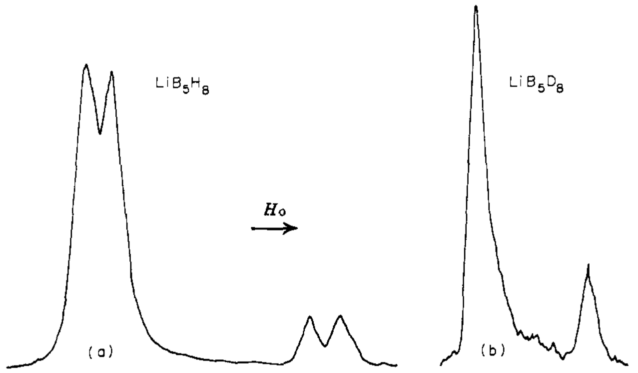

Figure 1. (a) The ^{11}B nmr spectrum (32.1 Mc) of LiB_5H_8 at 35°. Chemical shifts (ppm from $BF_3 \cdot O(C_2H_5)_2$) and coupling constants (cps in parentheses) are 17.0 (127) and 52.7 (156). (b) The ^{11}B nmr spectrum (19.3 Mc) of LB_5D_8 at 23°. Chemical shifts (ppm from $BF_3 \cdot O(C_2H_5)_2$) are 17.8 and 53.7.

Boron-11 nmr spectra of LiB_5H_8, NaB_5H_8, and KB_5H_8, generated and kept at low temperature to prevent decomposition, are simpler than those previously reported.[1,2] They consist of an upfield doublet, assigned to an apical boron, and a low-field doublet, assigned to basal borons. The chemical shift and coupling constant of the high-field doublet are essentially constant over the temperature range −80–35°. However, the low-field doublet in the LiB_5H_8 spectrum is temperature dependent. The chemical shift goes to higher field, and the coupling constant decreases with increasing temperature. From −80 to −60°, the low-field doublet is symmetrical in appearance; from −50 to 0°, it is asymmetric in appearance, resolving to a symmetrical doublet at room temperature (Figure 1a). Asymmetry of the low-field doublet at low temperature is consistent with the earlier report,[1] but in none of the spectra of undecomposed $B_5H_8^-$ salts, over the entire temperature range studied, was a peak at 11.8 ppm observed. This peak might arise from unreacted pentaborane(9) or from decomposition of the specimen.

The boron-11 nmr spectrum of LiB_5D_8 at room temperature is presented in Figure 1b. Two symmetrical singlets, one corresponding to an apical boron and one corresponding to apparently magnetically equivalent basal borons, were seen over the range −80 to 35° in the spectra of the deuterated species. The boron-11 nmr spectra are consistent with a pyramidal

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(1) D. F. Gaines and T. V. Iorns, *J. Am. Chem. Soc.*, **89**, 3375 (1967).

(2) T. Onak, G. B. Dunks, I. W. Searcy, and J. Spielman, *Inorg. Chem.*, **6**, 1465 (1967).

structure derived from that of pentaborane through removal of a proton (most likely a bridge proton) from a basal boron.[1] Apparent equivalence of basal borons at ambient temperature can be accounted for by assuming averaging of chemical shifts through tautomerism, as is used to account for the boron-11 nmr spectrum of hexaborane(10).[3]

Addition of an equivalent quantity of $(CH_3)_4NCl$ to an ether solution of LiB_5H_8 at −78° followed by warming and stirring 48 hr at ambient temperature results in the formation of a pale yellow solid mixture containing LiCl and $(CH_3)_4NB_5H_8$.[4] Lithium chloride was extracted with cold alkaline aqueous solution and the residual $(CH_3)_4NB_5H_8$ was recrystallized from acetone–water solution.

Anal. Calcd for $C_4H_{12}NB_5H_8$: C, 35.5; B, 39.7. Found: C, 36.0; B, 40.0.

A plot of equivalent conductance of $(CH_3)_4NB_5H_8$ in dilute acetonitrile *vs.* the square root of equivalent concentration gave a slope of 301, a reasonable value for a 1:1 electrolyte.[5] A cryoscopic molecular weight measurement determined with a 0.05 *m* solute concentration in acetonitrile is consistent with complete ionization 1:1 electrolyte. *Anal.* Calcd for $(CH_3)_4N^+B_5H_8^-$: mol wt, 68.6; Found: mol wt, 66.6. The X-ray powder diffraction pattern of this salt can be indexed in the cubic system. Though not complex in appearance, the boron-11 nmr spectra of $(CH_3)_4NB_5H_8$ and $(CH_3)_4NB_5D_8$ differ markedly from the spectra of the corresponding alkali metal salts; we are unable to discuss them satisfactorily at the present time. Conceivably the $B_5H_8^-$ ion in the tetramethylammonium salt is a structural isomer of the corresponding ion in the alkali metal salts.

The $B_5H_8^-$ ion appears to be degraded to $B_3H_8^-$ by isopropyl alcohol.

$$(CH_3)_4NB_5H_8 + 6\textit{i}\text{-}C_3H_7OH \longrightarrow (CH_3)_4NB_3H_8 + 3H_2 + 2B(OC_3H_7)_3$$

A solution of $(CH_3)_4NCl$ in isopropyl alcohol was added to an equivalent amount of LiB_5H_8 in diethyl ether at −78°. Upon warming, the solution was stirred for 1 hr and filtered under nitrogen. The white solid isolated was $(CH_3)_4NB_3H_8$ in 75% yield. It was identified by chemical analyses and its boron-11 nmr spectrum. A similar degradation of $(CH_3)_4NB_9H_{12}$ by methanol to give $(CH_3)_4NB_3H_8$ has been reported.[6]

Through tensiometric titrations at −78° in diethyl ether and in glyme, it was determined that alkali metal $B_5H_8^-$ salts react with diborane in equimolar ratios. This reaction appears to produce unsymmetrical cleavage of diborane.

$$B_2H_6 + MB_5H_8 \longrightarrow MBH_4 + B_6H_{10}$$

The alkali metal borohydrides were identified from their boron-11 nmr spectra and their X-ray powder diffraction patterns. For the time being, it is believed that in the reaction cited above a BH_2^+ is inserted into the basal plane of the $B_5H_8^-$ ion, giving a product which is an isomer of normal B_6H_{10}. The nmr spectrum of this new material consists of two doublets: an upfield doublet which is in excellent agreement with that assigned to the apical boron of hexaborane(10) with respect to coupling constant and chemical shift, and a downfield doublet which is some 27 ppm upfield from the value assigned to the basal borons of hexaborane(10).[7] This material will distil away with the solvent diethyl ether from the reaction mixture at −20°. Upon standing at room temperature in solution, it appears to convert at least partially to normal hexaborane(10). The boron-11 nmr spectrum of an ether solution which was permitted to stand at room temperature for 30 min showed that the low-field doublet assigned to hexaborane(10) had appeared, while the doublet some 27 ppm upfield from it had diminished in intensity. The upfield doublet was unchanged.[8]

By refluxing glyme solutions of the B_6H_{10} product obtained from the reaction of diborane with either NaB_5H_8 or KB_5H_8, we have been able to obtain $B_{10}H_{14}$ in 20–30% yields. Decaborane(14) was characterized by its X-ray powder diffraction pattern, its melting point, and its boron-11 nmr spectrum. Efforts are continuing to elucidate the nature of the B_6H_{10} product and to improve the yield of $B_{10}H_{14}$ from the alkali metal $B_5H_8^-$–B_2H_6 systems.

Acknowledgment. We wish to acknowledge, gratefully, the support of this work by the National Science Foundation. We are also grateful to Mr. Frank Parker of the University of Michigan for taking nmr spectra at 32.1 Mc.

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(3) R. E. Williams, *J. Inorg. Nucl. Chem.*, 20, 201 (1961).

(4) A reported attempt to prepare $(CH_3)_4NB_5H_8$ yielded $(CH_3)_4NB_3H_8$; experimental conditions were not given.[2]

(5) R. D. Feltham, and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

(6) B. M. Graybill, J. K. Ruff, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 2669 (1961).

(7) T. P. Onak, H. Landesman, R. W. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

(8) Note Added in Proof. The normal form of hexaborane(10) was isolated from the mixture and identified by its boron-11 nmr spectrum and by its mass spectrum.

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Isomerization of Maleic Acid by Vanadous Ion

Sir:

cis–trans isomerism brought about by a variety of agents such as heat, free radicals, etc., is well known and accounted for by a number of mechanisms.[1] None of these cases, however, involves electron transfer to the double bond through other parts of the molecule. On the other hand, Fraser and Taube suggested,[2] in connection with their work on electron-transfer reactions, that activation of the double bond of maleic acid leading to isomerization may be possible by "remote attack" by the reducing agent on the carboxyl group. The conjugation of the maleic acid molecule and the high reducibility of its double bond are factors that make such an expectation plausible. The present experiments show that this idea was essentially correct though its manifestation in the system in which it was originally reported now seems open to question.[3] When vanadous ion is added to a maleic acid aqueous solution, isomerization to fumaric acid does take place, along with reduction to

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(1) See, for example, R. B. Cundal, *Progr. Reaction Kinetics*, **2**, 165 (1964).

(2) R. T. M. Fraser and H. Taube, *J. Am. Chem. Soc.*, **81**, 5514 (1959); **83**, 2242 (1961).

(3) H. Taube, private communication. It was not found possible to doublicate the positive experimental evidence reported in ref 2.