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THE REACTION OF MONOBROMODIBORANE WITH PHOSPHINE

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Monobromodiborane (B_2H_5Br) (1) readily forms a 1:1 adduct with phosphine at -78°. With reactants in equimolar amounts, decomposition occurs at -45° to give diborane and phosphine monobromoborane (PH_3BH_2Br), but with a two-fold excess of phosphine, decomposition gives nearly equimolar amounts of PH_3BH_2Br and phosphine borane (PH_3BH_3). The monobromoborane adduct is stable to 0° at which temperature it slowly polymerises with the evolution of hydrogen.

Reaction of monobromodiborane and phosphine (1:1 addition). In a typical experiment, monobromodiborane (0.66m.mole) and phosphine (0.66m.mole) were distilled into a reaction vessel (approximately 25 ml) on a conventional vacuum line. The reactants were allowed to warm up from -196° to -78° and held at that temperature for one hour. A white solid was formed and the pressure was negligible - as would be expected for the formation of a 1:1 adduct. The pressure remained negligible up to a temperature of -45° when there was a sharp increase with evolution of diborane (0.32m.mole). At this temperature (-45°) the solid changed to a colorless liquid which was stable to 0°. With further increases in temperature, hydrogen was evolved leaving a viscous liquid. No other volatile products were formed. The following series of reactions is consistent with the observations:

$$B_2H_5Br + PH_3 \xrightarrow{-78^\circ} H_3P.\underset{Br}{B}(H).BH_3\ (s)$$

$$H_3P.\underset{Br}{B}(H).BH_3\ (s) \xrightarrow{-45^\circ} \tfrac{1}{2}B_2H_6 + H_3P.BH_2Br\ (l)$$

$$H_3P.BH_2Br\ (l) \xrightarrow{>0^\circ} 1/n(H_2PBHBr)_n\ (l) + H_2.$$

The decomposition of the monobromoborane adduct is analogous to that described for the borane adduct (2), which gives $(H_2BPH_2)_n$ and H_2 on polymerisation, but only under more severe conditions. Under the conditions that result in the polymerisation of PH_3BH_2Br, the adduct PH_3BH_3 readily dissociates into diborane and phosphine.

The experiment was repeated using a standard nmr tube (3) as the reaction vessel. The mixture of monobromodiborane (7.0m.mole) and phosphine (7.0m.mole) gave the expected amount of diborane (3.5m.mole) at -45°. This was distilled off and the tube was sealed. The proton nmr spectrum of the colorless liquid was recorded at -20° on a Varian A-60 and is consistent with the structure PH_3BH_2Br. FIG. 1 shows the expected $-PH_3$ resonance. There is a doublet centered at 5.1 ppm downfield from external TMS, which is the result of coupling between the phosphorus atom and its attached hydrogen atoms (J_{PH} = 405 cps). Coupling of the two hydrogen atoms on boron with those on phosphorus splits each component of the phosphine doublet into a 1:2:1 triplet ($J_{HH'}$ = 6 cps). The $-BH_2'$ resonance is not resolved but appears as a broad 'hump' centered at approximately 1.9 ppm downfield of TMS. However, the integration shows that the ratio of the intensities of the $-PH_3$ and $-BH_2'$ resonances is 3:2. The spectrum must be run below 0° because above this temperature bubbles are formed and the liquid becomes very viscous. All fine structure in the spectrum is lost but a doublet due to hydrogen atoms on phosphorus can still be seen, centered at 5.8 ppm downfield of TMS (J_{PH} = 422 cps). This is at least consistent with the formation of polymers of the type $(PH_2BHBr)_n$.

Reaction of monobromodiborane and phosphine (1:2 addition). In a

typical experiment monobromodiborane (0.65m.mole) and phosphine (1.30m.mole) were distilled into the reaction vessel on the vacuum line. The reactants

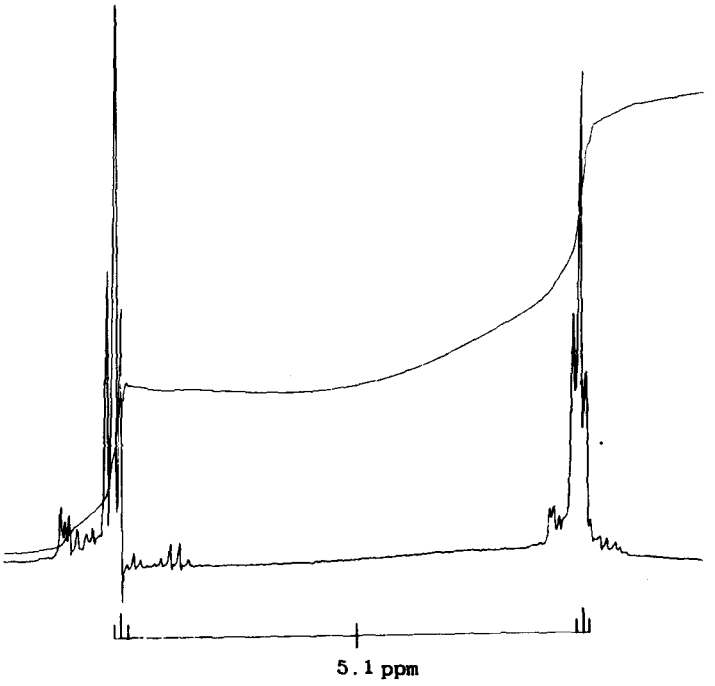

FIG. 1. Proton Nmr, Spectrum of $H_3P.BH_2'Br$

$J_{PH} = 405$ cps $J_{HH'} = 6$ cps

were allowed to warm up from -196° to -78° and held at that temperature for one hour. A white solid was formed and an excess of reactants was indicated by the pressure - as would be expected for the formation of the 1:1 adduct. On warming to -63° the pressure dropped to a negligible value and remained so when the temperature was raised to -23°. However, at -45° part of the solid liquidified - as would be expected for the monobromoborane adduct. Between -23° and 0° there was a sharp rise in the pressure as the solid component decomposed to diborane and phosphine (a total of 0.96m.mole). At room temperature the only volatile species was hydrogen. The following series of reactions is consistent with the observations:

$$B_2H_5Br + PH_3 \xrightarrow{-78^\circ} H_3P.B(H)(Br).BH_3\ (s)$$

$$H_3P.B(H)(Br).BH_3\ (s) + PH_3 \xrightarrow{-63^\circ} H_3P.BH_3\ (s) + H_3P.BH_2Br\ (l)$$

$$H_3P.BH_3\ (s) \xrightarrow{0^\circ} \tfrac{1}{2}B_2H_6 + PH_3$$

$$H_3P.BH_2Br\ (l) \xrightarrow{>0^\circ} 1/n(H_2PBHBr)_n + H_2.$$

The experiment was repeated in a sealed nmr tube using monobromodiborane (2.75m.mole) and phosphine (5.5m.mole) in a 1:2 ratio and stopping the reaction at -23°. The solid and liquid phases were vigorously shaken to give a clear liquid. During this process the tube had to be warmed up for a short time in order to get a completely clear liquid. The proton nmr spectrum was run at -20° and is shown in FIG. 2. It shows the presence of PH_3BH_2Br (cf. FIG. 1). Distortion of the triplets arises from some decomposition to the polymeric form as a result of the need to

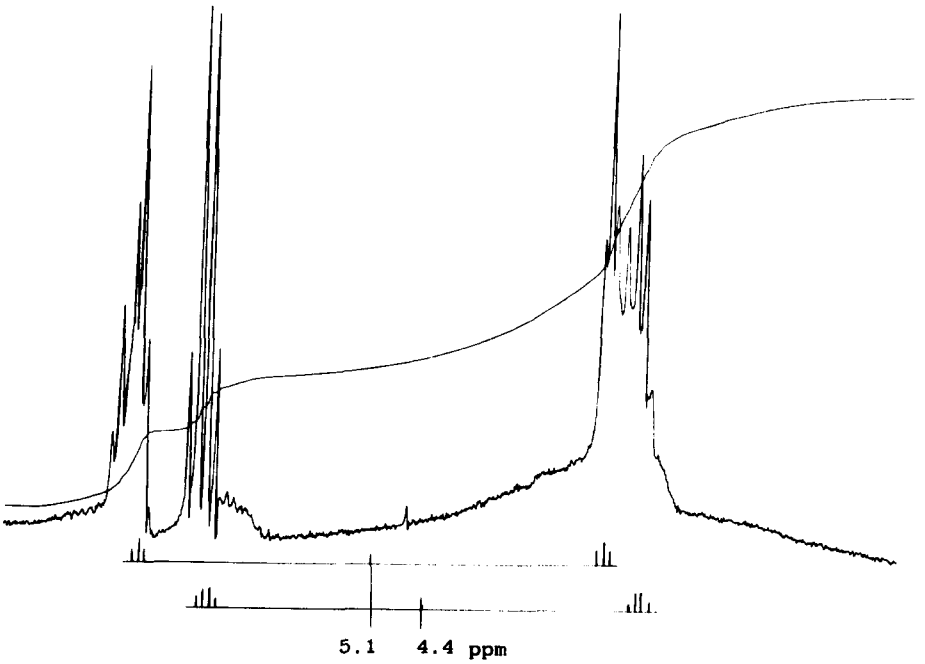

FIG. 2. Proton Nmr Spectrum of $H_3P.BH_3'$ and $H_3P.BH_2'Br$

J_{PH} = 375 cps $J_{HH'}$ = 8 cps

warm the sample for a short time. The $-PH_3$ resonance in PH_3BH_3 is seen as a doublet centered at 4.4 ppm downfield of TMS (J_{PH} = 375 cps). Each doublet is split into a 1:3:3:1 quartet as expected ($J_{HH'}$ = 8 cps). This is in good agreement with the reported spectrum of the pure adduct (4). A comparison of the intensities of the $-PH_3$ resonances for the two adducts indicates that they are formed in approximately equimolar amounts. A trace of PH_3BH_3 is formed in the 1:1 addition as can be seen from FIG. 1.

Discussion

Replacement of one hydrogen atom in PH_3BH_3 by bromine has quite a striking effect on the properties. The J_{PH} coupling constant changes from 375 cps to 405 cps indicating an increase in the 's' character of the P-H bond. The low field shift of the $-PH_3$ resonance to 5.1 ppm from 4.4 ppm, and the increased 'acceptor power' of 'BH_2Br' compared with 'BH_3' (5) may be rationalised by reference to the electronegativity of bromine. Some features of the reactions support this. Thus the monobromoborane adduct is formed more readily than the borane adduct under identical conditions, and its mode of decomposition also suggests a strengthening of the P-B bond when a bromine atom is attached to boron. Further, the adduct PH_3BH_2Br polymerises to give $(PH_2BHBr)_n + H_2$, rather than $(PH_2BH_2)_n + HBr$, although there is no obvious mechanistic reason why hydrogen evolution should be preferred. The formation of stronger P-B(Br) bonds may be a contributory factor. The increased strength of the P-B(Br) bond may also contribute to the non-dissociation of PH_3BH_2Br in conditions that result in the breaking of the P-B bond in the dissociation of PH_3BH_3.

References

1. H. I. SCHLESINGER and A. B. BURG, J. Amer. Chem. Soc. 53, 4321 (1931).
2. E. L. GAMBLE and P. GILMONT, J. Amer. Chem. Soc. 62,717 (1940), and A. B. BURG and R. I. WAGNER, J. Amer. Chem. Soc. 75, 3872 (1953).

3. Varian Associates, Palo Alto, California, U.S.A.

4. R. W. RUDOLPH, R. W. PARRY and C. F. FARRAN, Inorg. Chem. 5, 723 (1966).

5. A. B. BURG and E. S. KULJIAN, J. Amer. Chem. Soc. 72, 3103 (1950).