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THE GENERATION AND SOME REACTIONS OF METHYLBORYLENE

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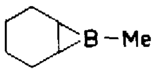
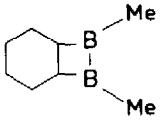
We wish to report the generation of a hitherto unknown species, viz. methylborylene, CH_3B:. The formation of methylborylene was recognized by the products it yielded on reaction with cyclohexene. Methylborylene is generated from methylboron dibromide and a suitable form of potassium, viz. the liquid alloy NaK_5 and the compound C_8K.

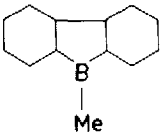
A preliminary reaction showed the $MeBBr_2$-NaK_5 system in cyclohexene to be very reactive, but the reaction was difficult to control. However, when methylboron dibromide was beforehand saturated with carbon dioxide, it proved possible to moderate the reaction. The mixture of reaction products was subjected to combined gas chromatography and exact mass spectroscopy. On the basis of their parent peaks the following species were identified: $C_7H_{13}B$ (I), $C_8H_{16}B_2$ (II), $C_{13}H_{23}B$ (III), $C_{14}H_{26}B_2$ (IV), and $C_8H_{16}B_2O$ (V). Because of the simplicity of the system, the exact masses were correlated with the following tentative structural assignments:



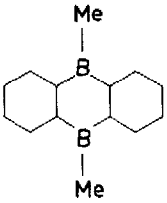
I



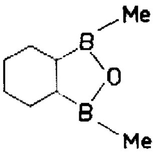
II



III



IV



V

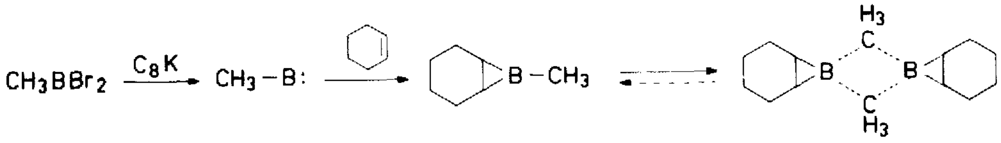
The oxygen-containing species V may be expected to result from unintented oxidation and/or hydrolysis. Later on, V was isolated and its structure ascertained by means of PMR and GCMS.

The reactions of C_8K with methylboron dibromide and cyclohexene (equimolar amounts) in boiling benzene were easy to control and yielded a mixture containing two main components. According to PMR data one of these was $MeBBr_2$; GCMS indicated $C_7H_{13}B$ (I) to be the other main component. It appeared impossible to separate the two components by vacuum distillation (b.p. $MeBBr_2$: 62°): for the mixture the rather high boiling range of 80-90°/0.6 mm was observed.

In a following experiment the excess $MeBBr_2$ was converted into Et_2MeB with ethyllithium. Vacuum distillation yielded a very air-sensitive product boiling at 64-66°/0.2 mm. Elementary analysis: found C 77.19, H 11.82; calc. for $C_7H_{13}B$ (I) C 77.85, H 12.13. I and IV have, of course, the same elementary composition. Since the CCMS data pointed to I, but the high boiling point rather suggested IV, we performed a molecular weight determination by ebulliometry in benzene: aver. found: 202; calc. for I: 108, for IV: 216. This points rather to compound IV than to I; however, GCMS analysis of the distillate showed a very high base peak at m/e=108 (I), whereas a peak at m/e=216 (IV) was notably absent. In addition a low peak at m/e=84 indicated the presence of a small amount of Et_2MeB.

It thus appears that the compound in question occurs as a - maybe somewhat dissociating - dimer $(C_7H_{13}B)_2$ which under the harsher circumstances prevailing under GCMS conditions manifests itself as the monomer $C_7H_{13}B$ (I). There are no reasons to assume that this compound has structure IV since in the experiments with NaK_5 the presence of both I and IV was indicated by their parent peaks, demonstrating that I and IV can exist independent of each other in the mass spectrometer. Furthermore, it is very unlikely that IV should be completely broken down in the mass spectrometer (into two units I) to the effect that its parent peak cannot be detected, whereas I, containing a highly strained three-membered ring, remains partially intact.

The results obtained with C_8K can now be rationalized by the following sequence of reactions:

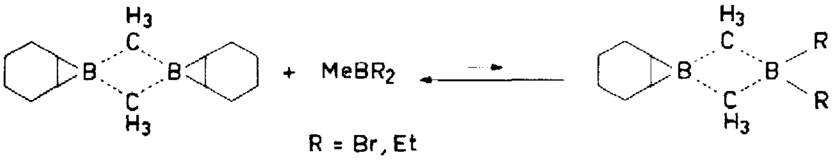


I Ia

The molecular weight found must, therefore, be ascribed to the dimer Ia of compound I, 7-methyl-7-borabicyclo[4.1.0]heptane. This dimer represents the first example of a simple boron-carbon compound in which boron has attained tetra-coordination by means of forming two boron-carbon two electron-three center bonds.

Evidence for the (distorted) tetrahedral surroundings of the boron atoms in the dimer Ia follows from its PMR spectrum: the single methylboron peak (at δ=0.72 ppm) is quite sharp, whereas methylboron peaks in three-coordinated boron compounds are broad due to the quadrupole moment of the boron atom.

The difficulty of separating $MeBBr_2$ and Et_2MeB from Ia could be due to the occurrence of the following equilibria:



The available evidence strongly indicates that the primary reaction product I (or its dimer Ia) can react further with methylborylene and/or cyclohexene to give the series of reaction products II to V.