THE REACTION OF ALUMINIUM BOROHYDRIDE WITH TIN AND LEAD TETRAMETHYL

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Abstract-Tin and lead tetramethyl do not react with diborane but both react vigorously with aluminium borohydride giving solid products which decompose ultimately to tin or lead, hydrogen, methylated boranes and methyl aluminium borohydride, MeAl(BH₄)₂. No dimethyl aluminium borohydride or trimethyl aluminium are found. The nature of the decomposition products suggests the intermediate formation of compounds such as Me₂Sn(BH₄)₂ and Me₃PbBH₄, but there is no evidence for replacement of more than two methyls by borohydride groups. Possible explanations are given for the limitations observed in the replacement of borohydride by methyl groups, and vice versa.

BOROHYDRIDES of several metals have been prepared by various methods, e.g. by the reaction of the metal hydride or alkyl with diborane^(1,2) or by metathetic reactions, involving a metal alkyl⁽³⁾ or other metal compound^(4,5) and another borohydride, usually that of lithium or aluminium. The object of the present work was to investigate the possibility of preparing covalent borohydrides of tin and lead by the reaction of either diborane or aluminium borohydride on the appropriate tetra-alkyl compound—the latter being chosen, since they are typical tetracovalent compounds and the alkyl groups are known to be replaceable by a wide variety of other groups.

EXPERIMENTAL

All manipulations were carried out in a Stock-type vacuum apparatus as described by SANDERSON.⁽⁶⁾ Aluminium borohydride was prepared (1) by the reaction of equimolar amounts of lithium aluminium hydride and boron trichloride in ether;⁽⁷⁾ the aluminium borohydride was displaced from its etherate by treatment with aluminium chloride in benzene and then fractionated until pure (v.p. at $20^{\circ}C = 286$ mm). (2) By heating together solid aluminium chloride and a mixture of potassium borohydride and lithium chloride, essentially the method of SCHLESINGER and BROWN,⁽⁵⁾ who found that lithium borohydride gave better yields by this method than did sodium or potassium borohydride-hence the addition of lithium chloride in the present procedure. The yield by this method was about 50 per cent, together with some diborane. The latter was more conveniently prepared by reduction of boron trichloride in ether by lithium aluminium hydride.⁽⁸⁾ Tin and lead tetramethyl were prepared from the appropriate chloride and Grignard reagent, and fractionated in the vacuum apparatus until pure. Stannane was prepared by reduction of stannic chloride by ethereal lithium aluminium hydride.

In an experiment, measured amounts of each reactant were condensed together in a tube at liquid-nitrogen temperature; the tube was sealed and reaction allowed to proceed under particular conditions of time and temperature. The tube was then cooled again and opened to the vacuum system, when any non-condensable gas was taken off, identified and measured, using a Töpler pump,

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⁽⁷⁾ H. I. SCHLESINGER and A. E. FINHOLT Hydrides and Borohydrides of Light Elements. NRL Report No. C-3147 (1947).

⁽⁸⁾ A. E. FINHOLT, A. C. BOND and H. I. SCHLESINGER J. Amer. chem. Soc. 69, 1199 (1947).

gas burette and combustion tube for this purpose. Excess of either reactant was then removed at the lowest possible temperature, and then the temperature was raised and volatile materials taken off, fractionated and analysed, as follows:

Methyl aluminium borohydride was identified (1) by its v.p.-temperature curve⁽⁷⁾ and (2) by hydrolysis, yielding aluminium (as hydroxide), methane and hydrogen in the ratio 1:1:8 as required by the equation:

$$MeAl(BH_4)_2 + 9H_2O = CH_4 + 8H_2 + Al(OH)_3 + B(OH)_3$$

Diborane, and mixtures of diborane and methylated boranes $(BH_{3-x}Me_x)_2$, including trimethyl boron, were determined by (1) hydrolysis, giving the B : H ratio and (2) reaction with excess trimethylamine,⁽⁹⁾ the trimethylamine taken up being equivalent to the boron (e.g. $B_2H_4Me_2 + 2Me_3N$

= $2Me_3N\cdot BH_2Me$). The results of (1) and (2) together then gave the mean composition of the mixture, i.e. the mean value of x in $(BH_{3-x}Me_x)_2$.

Non-volatile materials were analysed by thermal decomposition or hydrolysis followed by measurement of volatile or gaseous products as described above; the residues were finally analysed for aluminium and boron, and tin or lead, as appropriate.

RESULTS AND DISCUSSION

Diborane did not react with tin or lead tetramethyl, nor with stannane. However, aluminium borohydride reacted vigorously on warming excess of it with either tetramethyl compound from -190° C to ordinary temperature, forming a white solid which darkened rapidly. By more cautious warming, unreacted aluminium borohydride could be removed at -60° C, together with a little hydrogen; the reaction ratio Al(BH₄)₃/M Me₄ (M = Pb, Sn) varied between 1 : 1 and 2 : 1, though approaching the latter figure more closely with tin tetramethyl.

On warming further to -20° C, the lead reaction yielded a volatile fraction containing lead; this was removed, but decomposed rapidly, giving lead, methylated boranes, hydrogen, and the substance methyl aluminium borohydride, MeAl(BH₄)₂. No further separation of volatile material could be effected from the original reaction mixture, because it decomposed rapidly above -20° C, yielding similar products to those obtained from the volatile fraction. Tin tetramethyl reacted similarly, again yielding methyl aluminium borohydride, hydrogen, methylated boranes and tin. Under all the conditions of reaction investigated, varying temperature, reaction time and reactant ratio, no products other than these were obtained.

In particular, the following were sought for, but never found as such: dimethyl aluminium borohydride, trimethyl aluminium, hydrocarbons and borohydrides of tin and lead.

The absence of dimethyl aluminium borohydride, Me_2AlBH_4 , is not surprising; it is known to be unstable, decomposing very easily to give boron trimethyl as a product, indicating a transfer of methyl groups from aluminium to boron. It is therefore plausible to suppose that the methylated boranes found in the present experiments were formed from the decomposition of compounds such as $Me_vPb(BH_4)_{4-v}$, or $Me_vPb(BH_3Me)_{4-v}$. In several experiments it was in fact found that in the volatile tin-containing fraction the ultimate products (other than methyl aluminium borohydride) were Sn, $B_2H_4Me_2$ and H_2 , in the ratio 1 : 1 : 2, suggesting

 $Me_2Sn(BH_4)_2 = Sn + B_2H_4Me_2 + 2H_2$

Dimethyl tin borohydride might then originate by a reaction

 $2\mathrm{Al}(\mathrm{BH}_4)_3 + \mathrm{SnMe}_4 = \mathrm{Me}_2\mathrm{Sn}(\mathrm{BH}_4)_2 + \mathrm{MeAl}(\mathrm{BH}_4)_2,$

(9) H. I. SCHLESINGER, N. W. FLODIN and A. B. BURG J. Amer. chem. Soc. 61, 1078 (1939).

i.e. a 2 : 1 reactant ratio, as found. In some of the lead tetramethyl experiments, a similar Pb : $B_2H_4Me_2$: H_2 ratio indicated that the volatile lead compound might be $Me_2Pb(BH_4)_2$. In one experiment where the reaction time was very short, the products of decomposition of the volatile lead-containing fraction were Pb : BMe_3 : $2H_2$, suggesting Me_3PbBH_4 , trimethyl lead borohydride. In other experiments, the decomposition product ratios did not correspond to any one methyl lead borohydride, and it is probable that here a mixture (e.g. $Me_2Pb(BH_4)_2 +$ $Me_2Pb(BH_3Me)_2$) was formed. Moreover, it is significant that in all the reactions, methyl aluminium borohydride, which would be expected to distil off with unchanged aluminium borohydride, at -60° C, did not appear until the temperature was raised to between -30 and -20° C. This suggests that the white solid originally formed was made up of compounds containing both lead (or tin) and aluminium, and that these then decomposed to give methyl aluminium borohydride and methyl-lead (tin)-borohydride compounds of the kind suggested above.

One further fact is important. After separation of all the methyl aluminium borohydride from the reaction products, the Pb/B or Sn/B ratio in the remainder was never greater than 2. This clearly indicates that the unstable methyl lead or tin borohydrides formed never contained more than two BH_4 (or BH_3Me) groups in the molecule—there was no evidence at all for the formation of (e.g.) $MePb(BH_4)_3$ or $Pb(BH_4)_4$.

It is necessary therefore to explain why one, but not two, borohydride groups in aluminium borohydride can be replaced by methyl groups without loss of stability (with respect to decomposition) and without the appearance of dimerized molecules (methyl aluminium borohydride is monomeric⁽⁷⁾): and also why not more than two methyl groups can be replaced by BH₄ (or BH₃Me) groups in tetramethyl tin or lead, any such replacement producing an unstable compound. The nature of the metalborohydride bond in covalent borohydrides has been considered only in the case of aluminium borohydride. Analysis of the infra-red spectrum of the latter agrees with a hydrogen bridge model for the structure in which the six bridge hydrogen atoms are at the vertices of a trigonal prism rather than at the vertices of an octahedron.⁽¹⁰⁾ LONGUET-HIGGINS,⁽¹¹⁾ using the trigonal model, suggested that there are three trigonal Al-B σ -bonds formed from the sp^2 hybrid orbitals of the aluminium and boron. Three π -bonds can then be formed by overlap of the three hybrid pd^2 orbitals of the aluminium with the remaining p-orbitals of the boron atoms, the bridge protons being situated at the antinodes of these bonds. Using this concept of the structure, the replacement of one borohydride by a methyl group can be considered. If the new Al-C σ -bond is formed by combination of an aluminium sp^2 with a carbon sp^3 hybrid orbital, no rearrangement of the remaining Al-B σ -bonds is required. Two π -bonds may then be formed from two pd hybrid orbitals of the aluminium and the p-orbitals of the boron atoms. If overlap is sufficiently good here, then the stability of the Al-B bonds may be comparable with those in aluminium borohydride itself; moreover, no dimerization is expected, since the aluminium has no suitable orbital available. Replacement of a second borohydride group to give dimethyl aluminium borohydride, with the Al—C and Al—B σ -bonds formed as before, requires that the single π -bond be formed by overlap of a p-orbital of

⁽¹⁰⁾ W. C. PRICE J. chem. Phys. 17, 1044 (1949).

(11) H. C. LONGUET-HIGGINS J. chem. Soc. 141 (1946).

aluminium with a similar p-orbital of boron, i.e. a $p_{\pi}-p_{\pi}$ bond. Although this type of bond may occur in diborane, in this case the greater aluminium-boron distance is likely to preclude strong overlap, and this may explain the instability of dimethyl aluminium borohydride and its ready decomposition with rupture of both Al-B and B-H bonds. Moreover, if complete conversion of aluminium borohydride to trimethyl aluminium (or more correctly, to Al₂Me₆) is considered, the aluminium orbitals must rearrange and assume sp^3 hybridization. At the temperature used in the present experiments it is quite likely that this conversion would be extremely slow, in view of the energy required for rearrangement—hence the absence of trimethyl aluminium in the reaction products.

In tin and lead tetramethyl, the metal-carbon bonds are formed from sp^3 hybrid orbitals from each atom, and since the inner *d*-levels are fully occupied in the tin or lead, further increase in covalency is difficult. However, with σ -bonds from sp^3 hybrid atomic orbitals, weak π -bonding is possible using d^2 hybrid orbitals, giving two angular π -bonds. It is possible that the outer orbitals of tin or lead can be used in this way, in compounds such as Me₂Sn(BH₄)₂; if so, the maximum number of possible π -bonds is two, thereby restricting replacement of methyl by borohydride groups, as already noted. This is in contrast to the ability of some group IV*a* elements (e.g. Zr, Hf) to form tetra-covalent borohydrides M(BH₄)₄; but here the metal-boron σ -bonds may be formed by hybridization of *s*, *p* and *d* atomic orbitals, and low-energy *d*-orbitals are also available for π -bond formation.

These arguments are, in the absence of much structural evidence, necessarily speculative; in particular, further information regarding the structure of methyl aluminium borohydride would be welcome.

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