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THE REACTION OF TETRAMETHYLLEAD WITH DIBORANE

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Trialkyllead alkoxides and diborane react in diethyl ether at −78° to give, initially, trialkyllead borohydride and alkoxydiboranes[1], but no reaction occurs between tetramethyllead and diborane in absence of solvent[2]. We have therefore re-examined this latter reaction in ether-type solvents, and of these 1,2-dimethoxyethane proved to be the most suitable, since with other ethers (*e.g.* tetrahydrofuran) adduct formation leads to formation of alkoxydiboranes[3]. Tetramethyllead has been shown[4] to be a useful reagent for the methylation of boron–halogen compounds, the other reaction product then being (usually) trimethyllead halide. The products to be expected from the reaction with diborane would therefore be expected to be alkylboranes or alkyldiboranes and either trimethyllead borohydride or trimethylplumbane; at ordinary temperatures both of these would yield ultimately lead, hydrogen, tetramethyllead and possibly a small amount of methane[4].

Reaction of tetramethyllead and diborane in 1,2-dimethoxyethane did not occur below room temperature; at this temperature a slow evolution of hydrogen and deposition of metallic lead occurred. The reaction rate, as measured by rate of hydrogen evolution, soon became even slower and after many days, using excess tetramethyllead, the reaction reached only 83% completion as represented by the equation:

$$2\,B_2H_6 + 3\,Me_4Pb \rightarrow 4\,Me_3B + 6\,H_2 + 3\,Pb$$

The hydrogen evolved contained a trace of methane, and the ratio (hydrogen evolved)/(lead deposited) was always about 2 at any stage in the reaction and irrespective of whether excess tetramethyllead was used or not; this suggests that the reaction was a stepwise replacement of the diborane atoms by methyl groups, *i.e.*

$$B_2H_6 + Me_4Pb \rightarrow Me_3PbH + B_2H_5Me$$

or in general

$$B_2H_{6-x}Me_x + Me_4Pb \rightarrow B_2H_{5-x}Me_{x+1} + Me_3PbH$$

the trimethylplumbane decomposing to give hexamethyldiplumbane

$$4\,Me_3PbH \rightarrow 2\,Me_6Pb_2 + 2\,H_2$$

Since decomposition of hexamethyldiplumbane is catalysed by diborane[1], lead is then formed by the reaction

$$2\,Me_6Pb_2 \rightarrow 3\,Me_4Pb + Pb$$

In reactions where tetramethyllead was not in excess, rapid fractionation of the reaction mixture permitted isolation of some 1,1-dimethyldiborane and trimethyldiborane. With excess tetramethyllead, the only product isolated was trimethylborane which was present in appreciable quantity after long reaction times. But the virtual cessation of reaction at 83% theoretical implies that only five of the diborane hydrogens have been replaced, *i.e.* formation of a mixture of overall composition Me_5B_2H. It would be expected that reaction would be difficult beyond the stage when tetramethyldiborane $Me_4B_2H_2$ has been formed, since then further reaction would require attack on the bridge hydrogen atoms. But tetramethyldiborane is known to undergo disproportionation[5]:

$$3\ Me_4B_2H_2 \rightarrow 2\ Me_3B + 2\ Me_3B_2H_3$$

and this would permit further methylation of the trimethyldiborane thus formed. Tetramethyldiborane is, however, stabilized with respect to disproportionation in presence of an appreciable concentration of trimethylborane[6]; hence when the disproportionation and further methylation produce a mixture of trimethylborane and tetramethyldiborane which is stable, removal of trimethylborane is necessary before methylation can proceed further. The 83% extent of reaction therefore implies that the stable mixture has the composition $[2\ Me_3B + Me_4B_2H_2]$, with $Me/B/H = 5/2/1$.

Observation of the ^1H nuclear magnetic resonance spectrum of the reaction mixture after 1 h showed an intense band centre at $\tau \sim 9.1$ ppm, *i.e.* in the region expected for the protons of lead-attached methyl groups. Superimposed on this band were three peaks, which were compared with the spectrum obtained by Flitcroft and Kaesz[7] for trimethylplumbane. An intense peak at τ 9.16 ppm was assigned to the methyl hydrogens of trimethylplumbane, and a less intense peak at a separation of $\sim$1 c/s to the coupling of the lead-attached hydrogen with the methyl groups. A third peak at τ 9.07 was tentatively assigned to the hydrogens of hexamethyldiplumbane, since such a peak would be expected to be on the low field side of the broad band due to tetramethyllead. The observed coupling constant $J(^{207}Pb\text{–}CH_3)$ was 61.9 c/s for trimethylplumbane (*cf.* 66.7). Observation of the spectrum at later stages in the reaction showed disappearance of the trimethylplumbane peaks, and after 20 h the tetramethyllead band became a sharp single band at τ 9.12 ppm. Substitution of methyl groups in diborane was confirmed by movement of the peak due to the bridging hydrogens from τ 10.53 in diborane to 9.65 ppm, and this was concomitant with the disappearance of the peaks at τ 6.04 and 6.22 ppm assigned to the terminal hydrogens of diborane and the methyldiboranes $Me_xB_2H_{6-x}$ $(x = 1\text{–}3)$[8].

The above observations confirm that the reaction is essentially a stepwise replacement of hydrogen atoms in B_2 entities $B_2H_{6-x}Me_x$ rather than in adducts of the type [solvent$\cdot BH_{3-x}Me_x$]. Treatment of (dimethylamino)borane and bis(dimethylamino)borane with tetramethyllead in 1,2-dimethoxyethane gave no reaction, as expected if BX_3 species do not undergo reaction.

EXPERIMENTAL

Tetramethyllead, kindly supplied by Associated Octel Ltd., was dried and fractionated to the correct vapour pressure (24 mm at 20°). Diborane was prepared by reaction of tin(II) chloride and sodium borohydride; pure samples of the amino-

TABLE 1

RESULTS OF 5 REACTIONS OF TETRAMETHYLLEAD ITH DIBORANE

<table>
<tr><th rowspan="2">B_2H_6 added</th><th rowspan="2">Me_4Pb added</th><th rowspan="2">Time (days)</th><th colspan="5">Products</th><th rowspan="2">% reaction</th></tr>
<tr><th>H_2</th><th>Pb</th><th>$Me_2B_2H_4$</th><th>$Me_3B_2H_3$</th><th>Me_3B</th></tr>
<tr><td>1.25</td><td>1.64</td><td>3</td><td>1.22</td><td></td><td></td><td colspan="2">⏟</td><td>32</td></tr>
<tr><td>1.54</td><td>5.35</td><td>9</td><td>3.23</td><td>1.59</td><td></td><td colspan="2">0.40</td><td>70</td></tr>
<tr><td>1.46</td><td>1.48</td><td>14</td><td>2.50</td><td>1.19</td><td>0.21</td><td>0.30</td><td></td><td>57</td></tr>
<tr><td>0.75</td><td>5.83</td><td>18</td><td>1.88</td><td>0.92</td><td></td><td></td><td></td><td>83</td></tr>
<tr><td>1.54</td><td>5.35</td><td>40</td><td>3.84</td><td></td><td></td><td></td><td>0.91</td><td>83</td></tr>
</table>

boranes were kindly supplied by Dr. M. P. Brown. All reactions were carried out on a millimole scale and reaction products were separated *in vacuo*. Nuclear magnetic resonance spectra were recorded on a Varian V4300B high resolution spectrometer, using tetramethylsilane as external reference ($\tau = 10$ ppm).

Table 1 shows the results of five typical experiments; methylated boranes were identified by hydrolysis, degradation with propionic acid and infrared spectra. All quantities are in mmole.

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SUMMARY

Tetramethyllead and diborane react at room temperature in 1,2-dimethoxyethane to produce methyldiboranes and trimethylplumbane, the latter decomposing to give lead, tetramethyllead and hydrogen. Methylation of diborane appears to stop when much tetramethyldiborane has been formed; the latter disproportionates and forms some trimethylborane. The (dimethylamino)boranes Me_2NBH_2 and $(Me_2N)_2$-BH do not react with tetramethyllead.

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