327. *Trialkylplumbanes. Part I. Properties of the Trimethylplumbane–Borine–Ammonia System.*

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Potassium borohydride and trimethylchloroplumbane react in liquid ammonia to give trimethyl-lead borohydride ammoniate, which on distillation gives ammonia–borine, ammonia, and trimethylplumbane; the latter reacts with the ammonia to form unstable green ammonium trimethylplumbate, but the plumbane is not recovered by addition of diborane or boron trifluoride. Ammonium trimethylplumbate decomposes first to the red pentamethyldiplumbate and finally to lead, tetramethylplumbane, hydrogen, and methane; it reacts with trimethylchloroplumbane in liquid ammonia to give hexamethyldiplumbane, but does not react with ethylene or diazomethane. Solutions of trimethylplumbane in trimethylamine are less stable than in ammonia.

In a preliminary communication [1] we reported the preparation of trimethylplumbane by reaction of trimethylchloroplumbane with potassium borohydride in liquid ammonia. Preparation by reduction of trimethylchloroplumbane with lithium aluminium hydride in dimethyl ether between −90° and −110° has since been reported, together with some properties of the plumbane.[2,3] The instability of the crude plumbane under our conditions of preparation prompted this investigation of the plumbane–ammonia–borine system; properties and reactions of the pure plumbane will be given in Part II.

Slow removal of solvent ammonia at −78° from an equimolar trimethylchloroplumbane–potassium borohydride mixture left potassium chloride and a white solid which decomposed slowly at 0° and more rapidly at 20° to given hydrogen, methane, ammonia, tetramethylplumbane, and a residue of lead and "ammonia–borine," $(H_3N,BH_3)_n$. In individual experiments the relative amounts of the products other than ammonia–borine varied, but the overall material balance was consistent and indicated an empirical formula $Me_3Pb(BH_4),xNH_3$ ($x \nless 2$) for the white solid. Decomposition in presence of excess of solvent gave the same products. The absence of trimethylborine or its ammonia adduct from these is notable, since decomposition of the very unstable volatile trimethyl-lead borohydride gave trimethylborine, lead, and hydrogen.[4] Hence co-ordination of ammonia to the borohydride converts the latter into a less volatile solid, increases its stability prevents the re-arrangement necessary to form boron–carbon bonds, and permits instead the ready formation of ammonia–borine; the observed characteristics of the latter were those expected for $(H_3N,BH_3)_n$ rather than for the "diammoniate of diborane," $[(H_3N)_2BH_2]BH_4$.[5] Removal of a borine group from the trimethyl-lead borohydride would give trimethylplumbane; there was therefore the possibility that "Me_3PbBH_4,xNH_3" was a mixture of ammonia–borine and an ammoniated trimethylplumbane (*e.g.*, $NH_3,PbHMe_3$). Careful distillation of the trimethyl-lead borohydride at −5° did yield the plumbane, ammonia, and ammonia–borine in the amounts expected, *i.e.*:

$$Me_3PbBH_4,xNH_3 \longrightarrow PbHMe_3 + (x - 1)NH_3 + H_3N,BH_3$$

These products were separated by fractionation at −100°, giving the plumbane as a liquid. It was then found that mixtures of the plumbane and ammonia were much less stable than either the plumbane alone or the trimethyl-lead borohydride ammoniate. Hence presence of ammoniated plumbane in the latter is unlikely, and decomposition proceeds as given in the equation above.

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[1] Duffy and Holliday, *Proc. Chem. Soc.*, 1959, 124.

[2] Amberger, *Angew. Chem.*, 1960, **72**, 494.

[3] Becker and Cook, *J. Amer. Chem. Soc.*, 1960, **82**, 6264.

[4] Holliday and Jeffers, *J. Inorg. Nuclear Chem.*, 1958, **6**, 134.

[5] Shore and Parry, *J. Amer. Chem. Soc.*, 1958, **80**, 8.

Some information as to the nature of the ammonia–plumbane interaction was obtained from the proton magnetic resonance spectrum of the mixture. A detailed examination of the spectrum of the pure plumbane will be reported in Part II; it is sufficient to note here that two main absorption bands were found, the larger due to the hydrogen atoms of the three methyl groups and the smaller, on the low-field side, to the single hydride-hydrogen atom. Addition of ammonia to the plumbane shifted the latter band nearer to the larger band, suggesting increased shielding of the hydride hydrogen, and this indicated a rapid exchange with the hydrogen atoms of the added ammonia, which could clearly be due to ammoniation: $NH_3 + Me_3PbH \longrightarrow NH_4(PbMe_3)$.

When an equimolar mixture of the plumbane and ammonia was kept at −78°, the originally colourless liquid rapidly became green; loss of 0·5 mol. of methane followed, to give a bright red solid, stable at this temperature. Warming to −45° then gave hydrogen, methane, ammonia, tetramethylplumbane, hexamethyldiplumbane, and lead; the diplumbane, on further warming, gave more tetramethylplumbane and lead, and the overall balance corresponded to Pb_2HMe_5,NH_3. If ammonia was first removed from the red solid at −78°, slow decomposition followed giving finally methane, tetramethylplumbane, and lead, in amounts corresponding to decomposition of Pb_2HMe_5. Trimethylplumbane dissolved in an excess of liquid ammonia at −78°; a green solution was formed immediately, slowly changing to red with evolution of methane and then decomposing further to give more methane, lead, and tetramethylplumbane ($Pb : PbMe_4 = 1 : 1$). These results can be accounted for by the reactions (1—5):

$$Me_3PbH + NH_3 \longrightarrow NH_4[PbMe_3] \text{ (green)} \tag{1}$$

$$NH_4[PbMe_3] \longrightarrow PbMe_2 + MeH + NH_3 \tag{2}$$

$$NH_4[PbMe_3] + PbMe_2 \longrightarrow NH_4[Pb_2Me_5] \text{ (red)} \tag{3}$$

$$NH_4[Pb_2Me_5] \longrightarrow Pb + PbMe_4 + MeH + NH_3 \tag{4}$$

or

$$2NH_4[Pb_2Me_5] \longrightarrow Pb + PbMe_4 + Pb_2Me_6 + 2NH_3 + H_2 \tag{5}$$

The alternative elimination of methane from the $[PbMe_3]^-$ anion by ammonolysis to give, *e.g.*, $[PbMe_2NH_2]^-$, postulated for solutions of potassium trimethylplumbate in ammonia,[6] seems improbable in presence of ammonium ion. Although polylead anions are known (*e.g.*, Pb_9^{4-}), alkylplumbanes containing more than two lead atoms have not been reported, and further linking of $PbMe_2$ groups to $[Pb_2Me_5]^-$ ions also seems unlikely.

Attempts to remove ammonia from plumbane–ammonia mixtures by addition of acceptors such as diborane or boron trifluoride did not give appreciable amounts of plumbane, probably because the heat of the ammonia–borine reaction produced too rapid a decomposition of remaining ammonium trimethylplumbate. The plumbane–ammonia mixture did not react with diazomethane, ethylene, or methyl chloride; reaction with at least one of these might have been expected, since the hydride-hydrogen atom of the plumbane must be fairly labile; the absence of reaction is further evidence of the formation of an ammonium salt. This is again supported by the reaction of trimethylchloroplumbane with a solution of trimethylplumbane in liquid ammonia at −78°; the green colour disappeared immediately, but only a trace of methane was formed, the products being hexamethyldiplumbane (appearing finally as lead and tetramethylplumbane) and ammonium chloride in 90% yield: $NH_4[PbMe_3] + Me_3PbCl \longrightarrow Pb_2Me_6 + NH_4Cl$.

A solution of pure trimethylplumbane (free from ammonia) in an excess of trimethylamine decomposed much more rapidly than in ammonia, and only a faint transient red colour was observed before the solution blackened owing to deposition of lead; no break in methane evolution at the stage $MeH : Me_3PbH = 0{\cdot}5 : 1$ was detected and the final ratios were $MeH : Pb : Me_4Pb = 1 : 1 : 1$. Formation of trimethylammonium trimethylplumbate would be easier than that of the ammonium salt, but the subsequent decomposition reactions (2)—(5) would not be expected to occur more readily. In reaction (3) the trimethylplumbate ion is acting as donor to the dimethyl-lead molecule in preference to

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[6] Holliday and Pass, *J.*, 1958, 3485.

ammonia; with trimethylamine, the alternative reaction $Me_3N + PbMe_2 \longrightarrow Me_3N,PbMe_2$ may predominate, preventing formation of much red pentamethyldiplumbate and causing rapid disproportionation of the dimethyl-lead.

Trimethylstannane has been prepared by the reaction[7]

$$Me_3SnNa + NH_4Cl \xrightarrow{NH_3} SnHMe_3 + NaCl + NH_3$$

and trimethylgermane similarly.[8] This type of reaction does not yield trialkylplumbanes, giving, instead, alkanes, lead halides, and R_3Pb compounds.[9] It is now clear that the failure of this method is not due primarily to the instability of the trialkylplumbane, but to the polarity of the molecule in the sense $Me_3Pb^{-}{-}H^{+}$, which makes proton abstraction by solvent ammonia easy but forms a salt less stable than the plumbane itself.

EXPERIMENTAL

Starting Materials.—Ammonia from a cylinder was dried with sodium and stored as gas after fractionation in a high-vacuum system; all other volatile materials were similarly fractionated until correct vapour pressures and infrared spectra were obtained. Potassium borohydride was extracted with liquid ammonia and the extract crystallised. Trimethylchloroplumbane was prepared by reaction of dry hydrogen chloride with tetramethylplumbane in hexane.[10]

All experiments were conducted with a high-vacuum apparatus, and reaction tubes were only opened to atmosphere for treatment of involatile residues. Tetramethylplumbane was estimated by weight after condensation in a weigh-bulb at −196°, lead by precipitation as chromate, and boron as boric acid by titration in presence of mannitol.

Potassium Borohydride–Trimethylchloroplumbane Reactions (Units are mmoles unless otherwise stated).—Reaction times and temperatures varied between 3 min. at −75° to 191 hr. at −33°. In a typical experiment, potassium borohydride (0·99) was added to trimethylchloroplumbane (0·99) in about 9 ml. of liquid ammonia at −33°; shaking gave a white precipitate, with no further change after 191 hr. at −33°, and no non-condensable gas. After slow removal of solvent at −78° the white solid left decomposed slowly at 0° and steadily at 20°, giving after 24 hr. methane (0·15), hydrogen (0·36), tetramethylplumbane (0·66), and ammonia (1·26) as volatile products. A further 24 hr. at 20° gave hydrogen (0·04) only. Water (5 ml.) was condensed into the tube at −196°; hydrolysis at 100° for 20 hr. then gave hydrogen (2·72), ammonia (0·83), and boric acid (0·92), with lead (0·26) in the residue. Hence recovery ratios relative to Pb = 1·00 were $CH_3 : H : NH_3 = 3{\cdot}01 : 1{\cdot}04 : 1{\cdot}37$ before hydrolysis and $H : B : NH_3 = 2{\cdot}96 : 1{\cdot}00 : 0{\cdot}90$ after hydrolysis; overall H = 4·00. No loss of potassium or chloride ion occurred from the residue.

Separation of trimethylplumbane–ammonia and its decomposition. After initial reaction between trimethylchloroplumbane (0·99) and potassium borohydride (0·98), solvent was removed and the white product held at −5°; material volatile at this temperature was distilled off it through a short path and condensed as a white solid at −196°. The latter, when kept at −78°, produced a green solution which slowly changed to a red solid stable at this temperature, with evolution of methane (0·39). Allowing the temperature to rise slowly caused the red solid to darken and decompose with effervescence at −45°. After 6 hr. at 20° the volatile products were methane (0·14), hydrogen (0·12), ammonia (0·75), and tetramethylplumbane (0·26). The residue contained lead and off-white crystals, m. p. 36° (hexamethyldiplumbane has m. p. 38°). Decomposition of the latter was complete at 95°, giving tetramethylplumbane (0·22), and hydrogen (0·07) also appeared here. Hydrolysis of the residue at 100° gave hydrogen (0·12), boric acid (0·07), ammonia (0·05), and lead (0·32). If hydrogen recovered at 95° and by hydrolysis is presumed to come from ammonia–borine (0·07) present as impurity (requiring H, 0·21; found, 0·19), recovery ratios relative to Pb = 1·00 are: overall, $Me : H : NH_3 = 3{\cdot}06 : 0{\cdot}96 : 0{\cdot}94$; red solid, $Me : H : NH_3 = 2{\cdot}57 : 0{\cdot}48 : 0{\cdot}94$.

Decomposition of Trimethylplumbane in an Excess of Liquid Ammonia.—Trimethylplumbane

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[7] Kraus and Greer, *J. Amer. Chem. Soc.*, 1922, **44**, 2629.

[8] Kraus and Flood, *J. Amer. Chem. Soc.*, 1932, **54**, 1635.

[9] Gilman and Bailie, *J. Amer. Chem. Soc.*, 1939, **61**, 731.

[10] Calingaert, Dykstra, and Shapiro, *J. Amer. Chem. Soc.*, 1945, **67**, 190.

(0·71) was condensed at $-196°$ on to ammonia (*ca.* 500) also at $-196°$. A pale green solution was formed as the solvent melted at $-78°$; at this temperature the colour gradually darkened and methane was evolved. After 17 hr. a red solution had been formed and the rate of methane evolution then decreased rapidly; slow evolution continued as the solution again became green, then colourless, lead being deposited. Until the solution became colourless, cooling to $-196°$ to remove methane produced an orange-red solid. Methane evolution ceased (total 0·73) after 190 hr. at $-78°$, with no more produced at $-33°$. In another experiment, the reaction was accelerated by warming to $-33°$ and all the methane was evolved; solvent was then removed and tested to ensure that no tetramethylplumbane had been distilled off. Storage at 20° for 14 hr. then gave tetramethylplumbane (0·18), ammonia (0·01), and non-condensable gas (0·01), with some hexamethyldiplumbane; the diplumbane decomposed at 95°, to give more tetramethylplumbane (0·17), and hydrogen (0·09) was also recovered from ammonia-borine as impurity. The black residue gave on hydrolysis lead (0·36), hydrogen (0·13), boric acid (0·08), and ammonia (0·06). After allowance for ammonia–borine as before, with total Pb = 1·00, ratios were $Pb : PbMe_4 : CH_4 = 0{\cdot}51 : 0{\cdot}50 : 1{\cdot}03$, total Me = 3·02.

Decomposition of Trimethylplumbane in an Excess of Trimethylamine.—The reaction was treated as for the reaction with excess of ammonia (see above); trimethylplumbane (1·17) was added and melting at $-78°$ gave a green solution which immediately blackened with only transient red coloration; methane (0·96) was produced after 3 min., finally 1·14 mol. after 28 hr., the solution then being colourless and lead having been deposited. Solvent was removed as before, leaving tetramethylplumbane (0·29) and hexamethyldiplumbane which gave more tetramethylplumbane (0·31); the amount of lead was 0·57 mol. Hence total Pb being taken as 1·00, ratios were $Pb : PbMe_4 : CH_4 = 0{\cdot}49 : 0{\cdot}51 : 0{\cdot}97$, total Me = 3·01.

Removal of Ammonia from Ammonium Pentamethyldiplumbate.—The diplumbate (0·44) was prepared as described above and held at $-78°$ while ammonia was distilled from it in a closed system to a tube held at $-196°$. The red material began to blacken and non-condensable gas was formed. When no more ammonia could be extracted (172 hr.), evolution of non-condensable gas (methane 0·27; hydrogen 0·07) also ceased; ammonia was removed (1·71). The residue contained tetramethylplumbane (0·48), and the involatile part finally gave more tetramethylplumbane (0·02), lead (0·37), and ammonia–borine (0·10). With Pb = 1·00, ratios from the decomposition were CH_3 : hydride H = 2·56 : 0·47; methane evolved in initial formation of the diplumbate was 0·49 mol.

Ammonium Trimethylplumbate–Trimethylchloroplumbane Reaction.—To a mixture of trimethylplumbane (1·08) and ammonia (~500) trimethylchloroplumbane (1·23) was added at $-78°$; the green colour was immediately discharged and a white precipitate formed; only little methane (0·07) was present and no more was formed at $-33°$. After removal of solvent, partial melting of the residue occurred at 37°, indicating presence of hexamethyldiplumbane; the latter was decomposed to tetramethylplumbane (1·62) and lead (0·52). The hydrolysate yielded ammonium chloride (1·02) and trimethylchloroplumbane (0·17).

In an experiment where trimethylplumbane and ammonia were produced as above, pumping at 10^{-4} mm. gave sufficient transfer of a white solid which sublimed slowly and gave on hydrolysis boron (boric acid) (0·68), hydrogen (2·09 milliequiv.), and ammonia (0·65).

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