219. *Trialkylplumbanes. Part II.*[1] *Some Properties of Trimethyl- and Triethyl-plumbane.*

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Pure trialkylplumbanes R_3PbH (R = Me or Et) have been isolated from the products of reaction of potassium borohydride with trialkylchloroplumbanes in liquid ammonia. Trimethylplumbane decomposes above −37° to give mainly hydrogen and hexamethyldiplumbane; triethylplumbane is more stable. Reaction with hydrogen chloride at low temperatures yields hydrogen quantitatively. Chemical evidence for the polarity of the Pb–H bond is supported by the nuclear magnetic resonance spectrum which suggests the equilibrium $Me_3PbH \rightleftharpoons Me_3Pb^- + Me_3PbH_2^+$.

In Part I[1] we reported the reaction between potassium borohydride and chlorotrimethylplumbane in liquid ammonia and properties of the trimethylplumbane-ammonia-borine-ammonia mixture produced. We now report the separation of the pure plumbane from this mixture at −78° and some of its properties. Triethylplumbane is readily prepared by analogous procedures.

Trimethylplumbane thus prepared had m. p. −104° (Becker and Cook[2] record −106°) and vapour pressures in accord with those reported by Amberger;[3] these workers prepared the plumbane by low-temperature reduction of chlorotrimethylplumbane with lithium aluminium hydride in ether. Our preparation and manipulation of the plumbanes *in vacuo* was advantageous in studying the properties, especially the decomposition, and the danger of detonation on exposure to the atmosphere[2] was minimised. Trimethylplumbane contained in a sealed glass vessel is stable only below −37°; it is clear that the decreasing stability of the hydrides of Group IVb as the Group is descended is operative for both hydrides and trialkyl-metal hydrides, since trimethylstannane is stable at ordinary temperatures. Finholt *et al.*,[4] using the methylstannanes, and Dillard *et al.*,[5] using the ethylstannanes, have demonstrated the validity of Kraus and Greer's[6] hypothesis that the stability of the stannanes increases with the number of alkyl groups. The same applies to the plumbanes; tetramethylplumbane, trimethylplumbane, and dimethylplumbane are stable to *ca.* 110°, −37°, and −50° respectively.

Decomposition of trimethylplumbane above −37° in glass is characterised by deposition of lead and evolution of hydrogen from the clear colourless liquid. On storage at room temperature, the products are hydrogen, methane, lead, tetramethylplumbane, and hexamethyldiplumbane; the diplumbane decomposes to give lead and tetramethylplumbane,[7] and all the lead is finally recovered in these forms when decomposition is completed at 95°. The diplumbane was not reported as a decomposition product by Becker and Cook.[2] About 93% of the hydridic hydrogen is recovered as hydrogen, the remainder as methane; no ethane is found. This seems to preclude formation of methyl radicals, and if the first step in the decomposition is assumed to be homolysis of the lead–hydrogen bond (as suggested by Becker and Cook), reactions (1—8) account for the observed products.

$$Me_3PbH \longrightarrow Me_3Pb + H\cdot \qquad (1)$$

$$H\cdot + H\cdot \longrightarrow H_2 \qquad (2)$$

$$Me_3PbH + H \longrightarrow Me_3Pb\cdot + H_2 \qquad (3)$$

$$\geqslant PbMe + H \longrightarrow \geqslant Pb\cdot + MeH \qquad (4)$$

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[1] Part I, Duffy and Holliday, *J.*, 1961, 1678.

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

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

[4] Finholt, Bond, Wilzbach, and Schlesinger, *J. Amer. Chem. Soc.*, 1947, **69**, 2692.

[5] Dillard, McNeill, Simmons, and Yeldell, *J. Amer. Chem. Soc.*, 1958, **80**, 3607.

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

[7] Calingaert, Soroos, and Shapiro, *J. Amer. Chem. Soc.*, 1942, **64**, 462.

$$2Me_3Pb\cdot \longrightarrow Me_3Pb\cdot PbMe_3 \qquad (5)$$

$$2Me_3Pb\cdot \longrightarrow Me_4Pb + Me_2Pb \qquad (6)$$

$$3Me_2Pb \longrightarrow Pb + Me_3Pb\cdot PbMe_3 \qquad (7)$$

$$2Me_3Pb\cdot PbMe_3 \longrightarrow Pb + 3Me_4Pb \qquad (8)$$

Most of the hydrogen atoms react as in (2), but some remain to react with any methyl-lead compound to give methane (4) or with the plumbane to give hydrogen (3). Trimethyl-lead radicals either dimerise (5) or disproportionate (6), and the immediate decomposition of dimethyl-lead produced by the latter reaction accounts for the early appearance of metallic lead at —37°; reaction (8) is slow below room temperature. There is no evidence for the formation of pentamethyldiplumbane, although ammonium pentamethyldiplumbate $NH_4[Pb_2Me_5]$ is formed on decomposition of ammonia–trimethylplumbane.[1] However, the suggested reaction by which the pentadimethyldiplumbate ion is formed requires addition of the trimethylplumbate *anion* to dimethyl-lead, and the corresponding addition of trimethylplumbane to dimethyl-lead, if it occurs at all, is more likely to yield methane and tetramethylplumbane than to give pentamethyldiplumbane, *i.e.*:

$$Me_3PbH + Me_2Pb \longrightarrow Me_4Pb + MeH$$

The decomposition of triethylplumbane follows a similar course to that of the trimethyl compound, beginning slowly at ~0°; decomposition was completed at 60° and formation of the unstable hexaethyldiplumbane was therefore not observed.

We have previously reported[8] the reaction of trimethylplumbane with hydrogen chloride:

$$Me_3PbH + HCl \longrightarrow Me_3PbCl + H_2$$

Except at very low temperatures, the heat of this reaction causes concomitant thermal decomposition of the plumbane, and the reaction products then also include methane and other chloromethylplumbanes. Thus a slow reaction at —112° gave a 96% yield of chlorotrimethylplumbane, but a reaction at —78° was rapid and gave only a 78% yield, the analysis suggesting that the remaining lead was present as dichlorodimethylplumbane. As expected, the corresponding reaction of the triethylplumbane was less affected by decomposition, and a reaction at —112° gave 100% yield of chlorotriethylplumbane with no evidence of thermal decomposition.

Becker and Cook[2] reported that reaction of trimethylplumbane with ethylene in 2,2′-dimethoxyldiethyl ether at 0° and 500 lb./sq. in. gave a 92% yield of ethyltrimethylplumbane. We have found no evidence for uptake of ethylene at pressures near 1 atm. and temperatures between —78° and 0°, in presence or absence of dimethyl ether. Together with the lack of reaction of ammonium trimethylplumbate with ethylene under similar conditions,[1] these observations suggest that presence of a solvent of either weak or strong proton affinity is of minor importance in promoting reaction of the plumbane with ethylene.

The properties of trimethylplumbane recorded here and in Part I indicate that the Pb–H bond is polar so that the hydridic hydrogen is acidic in character. A study of the high-resolution nuclear magnetic resonance spectrum at low temperatures confirms this; the low-field chemical shift of the hydric hydrogen atom is more than 100 c./sec. to the low-field side of the hydride resonance band in stannanes at 40 Mc./sec. and it is inferred that this hydrogen atom is in a region of low electron density and protonic in type. The ^1H high-resolution nuclear magnetic resonance spectrum of trimethylplumbane recorded at 40·00 Mc./sec. at —70° is shown in the Figure; the chemical shifts of the absorption bands from methylene chloride as external reference are —69, 44, 164, 200, 213, and 232 c./sec. Band 4 is assigned to the methyl groups attached to the lead atom, and bands 3 and 6, symmetrically displaced about band 4, are assigned to a doublet arising from methyl

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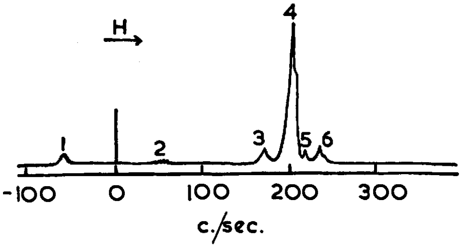
[8] Duffy and Holliday, *Proc. Chem. Soc.*, 1959, 124.

groups attached to ^{207}Pb atoms (of natural abundance 21·1% and with spin-number $I = \frac{1}{2}$). None of the remaining bands in the spectrum is of sufficient intensity to account alone for the hydridic hydrogen atoms (such a band would have one-ninth of the intensity of band 4). Since the chemical evidence for the existence of trimethylplumbane is conclusive, the ^1H resonance spectrum indicates that there are two types of hydridic hydrogen atoms present, probably giving rise to bands 1 and 2; these would result from the existence of the equilibrium

$$2Me_3PbH \rightleftharpoons [Me_3Pb]^- + [Me_3PbH_2]^+$$

If the rate processes involved in this equilibrium were sufficiently slow, two absorption bands would be detected for the hydridic hydrogen atoms, and band 1 could thus be assigned to the protonic hydrogen. If the hydrogen atom attached directly to the lead interacted *via* spin–spin coupling with the nine methyl-hydrogen atoms, then a multiplet of ten bands would result. Such coupling would have the effect of broadening the absorption line to such an extent that it would not be readily detectable. The weak band 2 might be due to such an absorption. On the basis of this argument the methyl absorption band would be a doublet (from the trimethylplumbane) overlapped by a singlet (from the trimethyl-lead anion), and this is not inconsistent with the spectrum where a somewhat broad asymmetrical band (4) is observed for the methyl absorption. Band 5 is possibly due to the methyl groups of an intermediate alkyl-lead decomposition product.



The low-temperature ^1H resonance spectrum of a mixture of trimethylplumbane and ammonia was also obtained at 40·00 Mc./sec. The low-field band in this spectrum (at +81 c./sec. from methylene chloride reference) is at higher field and of greater intensity than the low-field band in the plumbane spectrum. This suggests that the band is due to both ammonia- and hydridic-hydrogen atoms involved in a rapid exchange for the equilibrium

$$Me_3PbH + NH_3 \rightleftharpoons NH_4^+[PbMe_3]^-$$

This supports the chemical evidence for the existence of ammonium trimethylplumbate discussed in Part I.

EXPERIMENTAL

Units below are mmoles unless otherwise stated.

The preparation of starting materials and general technique have been described in Part I. The ^1H high-resolution nuclear magnetic resonance spectra were obtained by means of a Varian V3400B spectrometer operating at 40·00 Mc./sec. Samples were contained and spun in glass tubes of 5 mm. outside diameter. Low temperatures were obtained and maintained by using a thermostat-controlled probe similar to that described by Brownstein.[9] The spectra were calibrated by the side-band technique.[10]

Isolation of Pure Trimethylplumbane from the Plumbane-ammonia–Borine-ammonia Mixture.—After reaction of equimolar amounts of potassium borohydride and chlorotrimethylplumbane in liquid ammonia, the latter was slowly distilled off at −78°. The reaction vessel was

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[9] Brownstein, *Canad. J. Chem.*, 1959, **37**, 1119.

[10] Arnold and Packard, *J. Chem. Phys.*, 1951, **19**, 1608.

then connected to the pumps through a U-tube at −196° and warmed to −5°; a mixture of the solid plumbane, ammonia, and ammonia-borine distilled into the U-tube over a 10-cm. path; the continuous evacuation prevented accumulation of small amounts of decomposition products which would have impeded rapid distillation and accelerated decomposition, and distillation was assisted by frequent shaking of the reaction vessel. After 2 hr. the U-tube was warmed to −110° and distillation continued; ammonia then sublimed out of the U-tube and pumping was continued until separation of ammonia was achieved. When distillation was complete (4 hr.) the U-tube was warmed to ∼20° and the then volatile material quickly collected at −196°; this was finally fractionated through a −78° trap and the middle fraction retained; the overall yield was ∼75%.

Triethylplumbane.—This was prepared by a similar method, with the intermediate temperature of the U-tube at −85° instead of −110° because of the lower volatility of the plumbane; ammonia could then be removed more rapidly. Yields were 25—30%.

Decomposition of Trimethylplumbane.—In a typical experiment trimethylplumbane (1·5) was condensed at −196° into a seal-off tube. Storage at −78° for 6 days produced no visible change in the clear colourless liquid and no non-condensable gas was formed. With a slow controlled rise of temperature, blackening and gas evolution began at −37°. After 24 hr. at −33° blackening had increased and decomposition was completed at 20° for 24 hr. At this stage, a considerable mount of solid of m. p. 36—38° was observed (hexamethyldiplumbane has m. p. 38°), and this was decomposed at 95°. Products were then: CH_4, 0·11; H_2, 0·68; Me_4Pb, 1·08; NH_3, 0·00; Pb, 0·38; all the hydrogen appeared before heating to 95°. Hydrolysis of the residue gave no hydrogen, ammonia, or boric acid. These values give Pb : Me : H = 1·00 : 3·04 : 1·01.

Decomposition of Triethylplumbane.—A similar procedure was used. Production of hydrogen and blackening was slow at 0°, but decomposition was rapid on warming to 60°. After removal of volatile products, heating at 95° for 2 hr. gave no further decomposition. Products were: H_2, 0·33; C_2H_6, 0·08 (with possibly trace of C_4H_{10}); Et_4Pb, 0·540; Pb, 0·22. These give Pb : Et : H = 1·00 : 2·95 : 0·97.

Reaction of Trimethylplumbane with Hydrogen Chloride.—Trimethylplumbane (1·0) was collected as a film at the base of a reaction vessel. Hydrogen chloride (1·91) was condensed about 4 cm. above the plumbane at −196° and the vessel shaken at −112° for 2 hr. Products were flakes of white solid, H_2 0·70, and methane 0·02. A further 2 hr. at −112° gave H_2 0·18 and CH_4 0·01. Reaction was completed at −78°; total non-condensable gases were then H_2 1·01 and CH_4 0·05. Hydrogen chloride (0·85) was recovered, and the white solid gave organolead ion 1·04 and chloride 1·08 mg.-ion; there were no other products. Hence the reaction ratio is 1·0 : 1·06, and a residue of Me_3PbCl 1·00 and Me_2PbCl_2 0·04 is indicated.

Reaction of Triethylplumbane and Hydrogen Chloride.—The procedure was similar. From triethylplumbane (∼1·0) and hydrogen chloride (1·88), hydrogen chloride (1·04) was recovered, and hydrogen (0·83) was the only volatile product. The residue contained organolead ion 0·83 and chloride 0·84 mg.-ion only. Hence the reaction $Et_3PbH + HCl = Et_3PbCl + H_2$ is quantitative.

Reaction of Ethylene and Trimethylplumbane.—From ethylene (1·83) and trimethylplumbane in a sealed glass vessel, with pressure of ethylene ∼1 atm., ethylene(1·82) was recovered after 5 weeks at −78°, and the plumbane decomposed normally on warming. No reaction occurred in a similar experiment at −46°. Using ethylene (1·90) and trimethylplumbane (1·07) and warming from −46° to 0° in 50 min. gave normal decomposition products of the plumbane and ethylene (1·88). Similar experiments in dimethyl ether gave no evidence of reaction.

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