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VINYLLEAD COMPOUNDS
II. REACTIONS OF TETRAVINYLLEAD WITH COMPOUNDS CONTAINING BORON–CHLORINE AND BORON–HYDROGEN BONDS

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Reactions of tetraorganotin compounds with boron trihalides to give organoboron halides R_nBX_{3-n}(X = halogen, n = 1 to 3) are well known and have been used for the preparation of aryl-[1], alkyl-[2], perfluoroalkyl-[3], vinyl-[4] and perfluorovinylboron compounds[5]. In general, yields of triorganoborons are low (but *cf.* ref. 5), and diorganoboron fluorides are best prepared by fluorination of the corresponding boron chloride rather than from boron trifluoride[4]; except with aryltin compounds not more than two organic groups are cleaved from the tin. Organolead compounds have been little used in these reactions, although formation of trimethylboron from boron trichloride and tetramethyllead is quantitative at ordinary temperatures[6].

We have found that trivinylboron can be prepared in yields greater than 80% by reaction of boron trichloride with excess tetravinyllead at −78°; removal of the trivinylboron (volatile at this temperature) as formed assists its production. The other product is a white solid containing predominantly trivinyllead chloride, a small amount of divinyllead dichloride, and involatile boron residues which react violently with water to give butadiene, suggesting the presence of gem-vinyl groups on the boron atoms. Reaction of tetravinyllead and boron trichloride at ordinary temperatures, with or without a thermal diluent (n-octane), gave lead, butadiene, no volatile boron compounds, and spontaneously-inflammable boron-containing residues.

The reactions of vinyllead derivatives with compounds containing boron–hydrogen bonds are of interest, in that at least two possibilities exist. As in the tetramethyllead–diborane reaction[7] which proceeds by methyl–hydrogen exchange, vinyl–hydrogen exchange may occur in the corresponding tetravinyllead–diborane reaction, formation of trivinylplumbane being the first stage:

$$>B{-}H + (CH_2{=}CH)_4Pb \rightarrow >B{-}CH{=}CH_2 + (CH_2{=}CH)_3PbH$$

However, reaction of trimethylvinylsilane with trimethylamine-borane has been shown[8] to give derivatives containing $Me_3SiC_2H_4B<$ groups, *i.e.* the silicon-attached vinyl group is hydroborated. Hence the formation of $\geqslant PbC_2H_4B<$ units is a second possibility.

Although tetramethyllead and diborane do not react in absence of solvent, tetravinyllead and excess diborane reacted with explosive violence at room temperature, and control of the reaction was only achieved by reducing the temperature to −78°, when excess diborane could be removed without formation of lead or any volatile products other than a trace of ethyldiborane. The reaction ratio then obtained was $(CH_2{=}CH)_4Pb/B_2H_6 = 4$. On warming to room temperature, an exothermic decomposition occurred very rapidly and hydrogen and ethylene were evolved, in amounts such that $[C_2H_4 \text{ evolved}] + 2\,[H_2 \text{ evolved}] = [(CH_2{=}CH)_4Pb \text{ used}]$, with deposition of metallic lead. If $\geqslant PbC_2H_4B<$ units had been formed, the appearance of hydrogen and ethylene in stoichiometric amounts is difficult to explain. A more probable mechanism involves vinyl–hydrogen exchange, with an initial reaction

$$4\,(CH_2{=}CH)_4Pb + B_2H_6 \rightarrow 4\,(CH_2{=}CH)_3PbH + B_2H_2(CH{=}CH_2)_4$$

followed on warming by decomposition of the trivinylplumbane to give lead, tetravinyllead and hydrogen and ethylene:

$$4\,(CH_2{=}CH)_3PbH \rightarrow 2\,H_2 + 3\,(CH_2{=}CH)_4Pb + Pb \qquad (1)$$

$$2\,(CH_2{=}CH)_3PbH \rightarrow 2\,C_2H_4 + (CH_2{=}CH)_4Pb + Pb \qquad (2)$$

The lead deposited exceeded the amount expected by these equations, but the appearance of some butadiene with the ethylene and hydrogen suggests that the exothermic reaction may have produced some decomposition of the tetravinyllead, possibly by the mechanism

$$(CH_2{=}CH)_4Pb \rightarrow 2\,CH_2{=}CH{-}CH{=}CH_2 + Pb$$

Treatment of the volatile boron-containing reaction products with propionic acid gave hydrogen, ethylene and 1-butene from the smaller, more volatile fraction [indicating the presence of $>B{-}H$, $>BCH{=}CH_2$ and $>B(CH)_2CH{=}CH_2$ terminal groups] and hydrogen and ethane from the larger, less volatile fraction (indicating the presence of $>B{-}H$ and, probably, of bridging $>BC_2H_4B<$ groups, these being responsible for the low volatility). The persistence of $>B{-}H$ units in the presence of tetravinyllead is to be noted; this indicates that complete vinylation of the diborane is not achieved, a similar situation to that obtaining in the methylation of diborane with tetramethyllead[7]. The presence of $>BC_2H_4B<$ and $>B(CH_2)_2CH{=}CH_2$ units can be ascribed to hydroboration reactions, *e.g.*

$$>BCH{=}CH_2 + H{-}B< \rightarrow\ >B(CH_2)_2B<$$

$$CH_2{=}CH{-}CH{=}CH_2 + H{-}B< \rightarrow CH_2{=}CH(CH_2)_2B<$$

there being no evidence for hydroboration of lead-attached vinyl groups.

Further studies were now made in an attempt to obtain more evidence for the existence of trivinylplumbane and its mode of decomposition. The following reactions were studied: trivinyllead chloride–lithium hydride, in diethyl ether; trivinyllead chloride–potassium borohydride, in liquid ammonia; trivinyllead chloride–sodium borohydride, in 1,2-dimethoxyethane; and tetravinyllead–diborane, in 1,2-dimethoxyethane. Excess lithium hydride and trivinyllead chloride reacted slowly (because of the heterogeneous reaction conditions) at room temperature; the products were a small amount of ethylene, and hydrogen, tetravinyllead and lead, in amounts suggesting that the main reaction was the decomposition of trivinylplumbane by, predominantly, reaction (1), with reaction (2) occurring to a minor extent. A 1:1 mixture of trivinyllead chloride and potassium borohydride in liquid ammonia at −78° readily precipitated potassium chloride, and removal of solvent at this temperature then gave a white solid product $[KCl + (CH_2{=}CH)_3PbBH_4 \cdot x\,NH_3]$, $x \ngtr 2$; this slowly decomposed at $-65°$, and the appearance of lead, ethylene, hydrogen and 1 mole of ammonia indicated that the reaction

$$(CH_2{=}CH)_3PbBH_4 \cdot 2\,NH_3 \rightarrow (CH_2{=}CH)_3PbH + NH_3 + NH_3 \cdot BH_3$$

was followed by decomposition of trivinylplumbane according to equations (1) and (2) also. However, more lead, hydrogen and ethylene were formed than these equations would predict; vinyl–hydrogen exchange with the ammonia-borane must therefore be assumed, *i.e.*

$$NH_3 \cdot BH_3 + (CH_2{=}CH)_4Pb \rightarrow (CH_2{=}CH)_3PbH + NH_3 \cdot BH_2(CH{=}CH_2)$$

This assumption was verified experimentally; tetravinyllead and ammonia-borane reacted slowly in absence of solvent, and rapidly in 1,2-dimethoxyethane, to give lead, ethylene, a small amount of hydrogen and no ammonia. This reaction may be contrasted with the reaction (already mentioned), of trimethylvinylsilane with trimethylamine-borane in which $\geqslant SiC_2H_4B<$ units were formed[8]. In these reactions no volatile boron-containing compounds were formed, but again evidence for the presence of $>B{-}H$, $>B(CH_2)_2B<$ and $>B(CH_2)_2CH{=}CH_2$ units in the residues was obtained from degradation with propionic acid.

The reaction of trivinyllead chloride with sodium borohydride in 1,2-dimethoxyethane was expected to form trivinyllead borohydride, and this might then decompose to give trivinylplumbane and diborane:

$$2\,(CH_2{=}CH)_3PbBH_4 \rightarrow 2\,(CH_2{=}CH)_3PbH + B_2H_6$$

The further decomposition of trivinylplumbane to give tetravinyllead implied that the reaction products actually found would be those from the reaction of this tetravinyllead and the diborane. The study of this latter reaction in 1,2-dimethoxyethane (see below) did in fact give the same ultimate products as the trivinyllead chloride–sodium borohydride reaction, and the latter was therefore not further studied; a darkening of colour in the reaction mixture at $-78°$ indicated decomposition even at this temperature.

The reaction of tetravinyllead and diborane in 1,2-dimethoxyethane occurred readily at $-50°$, with a colour change to orange-brown and then rapid precipitation of lead. (Tetramethyllead reacts only slowly at room temperature[7].) The products were hydrogen, ethylene and lead, and recovery of lead as metal was *ca.* 90% even with a 2:1 excess of tetravinyllead; these data again imply vinyl–hydrogen exchange, but any stoichiometric relationship of hydrogen and ethylene to the tetravinyllead used and the lead obtained was obscured by hydroboration of some of the ethylene. The boron-containing products varied greatly in volatility and composition between experiments; in a typical reaction, as much as 70% of the boron added became involatile. However, where excess diborane was used, tetraethyldiborane was identified as one volatile product, and with excess tetravinyllead, triethylborane was obtained; both these presumably originated through hydroboration of ethylene. In absence of excess diborane, some butadiene appeared; this was absent when excess diborane was used, but here the appearance of n-butane from propionic acid degradation of both volatile and non-volatile boron fractions suggested dihydroboration of butadiene to give $>B(CH_2)_4B<$ units. With excess diborane, all the lead was converted to metal, and the ratio (B–H bonds reacted)/(tetravinyllead) varied between 6 and 6.8. This ratio can be explained by overall reaction schemes such as

$$6(>B{-}H)+(CH_2{=}CH)_4Pb \rightarrow Pb+2>BC_2H_5+2>BC_2H_4B<$$

$$8(>B{-}H)+(CH_2{=}CH)_4Pb \rightarrow Pb+2\,H_2+4>BC_2H_4B<$$

Although formation of trivinylplumbane in the above reactions seems to provide a probable explanation for the products found, its instability is such that isolation has not been possible. The decomposition of trivinylplumbane appears to be influenced by the other substances present; thus, in absence of solvent, decomposition at room temperature yielded mainly ethylene (tetravinyllead–diborane reaction), whereas in an ether solvent, decomposition at room temperature gave mainly hydrogen (trivinyllead chloride–lithium hydride reaction) and decomposition at lower temperatures gave both ethylene and hydrogen (trivinyllead chloride–borohydride reactions).

EXPERIMENTAL

Tetravinyllead, trivinyllead chloride, diborane and ammonia-borane were prepared and purified by published methods, and the reactions were studied as described previously[9]. Reactions were carried out on a mmole scale and quantities are in mmole unless otherwise stated; results are given for typical runs.

Tetravinyllead–boron trichloride

Boron trichloride, purified by fractionation (2.77) and tetravinyllead (9.23) gave trivinylborane (2.36) after 3 days at −78°. The product had mol.wt. 91.0 (vapour density) [$(CH_2{=}CH)_3B$ requires 91.9] and v.p. at 0° 34 mm, at 22° 80 mm; and 0.37 gave, with propionic acid at 120°, 1.13 ethylene and, after residual hydrolysis, 0.41 boric acid. The other reaction products were: unused tetravinyllead [3.25; hence ratio $(CH_2{=}CH)_4Pb/BCl_3 = 2.2$] and butadiene (1.42); hydrolysis at 100° of the involatile residue gave ethylene (1.64) and butadiene (0.31), with Pb (as chromate), 5.45.

Tetravinyllead–diborane

Diborane (2.66) and tetravinyllead (2.02) in absence of solvent at −78° gave only diborane (2.09) and ethyldiborane (infrared spectrum), 0.07. Warming to room temperature gave hydrogen (0.48), ethylene (1.00), butadiene (0.24) and lead; other material volatile at room temperature, after degradation with propionic acid gave hydrogen (0.20), ethylene (0.31) 1-butene (0.45) and boric acid (0.26), while the involatile material similarly gave hydrogen (1.00), ethane (0.10) and boric acid (1.00); recovery of lead was 1.32 as metal, 0.54 as lead(II). Using excess diborane (6.25) and tetravinyllead (4.27) in 8 ml 1,2-dimethoxyethane gave hydrogen (2.26), lead (4.16), no ethylene, and boron-containing fractions *A* (volatile with solvent at −33°), *B* (volatile at 20°) and *C* (involatile). Treatment with propionic acid gave, with *A*, hydrogen (0.70), ethane (1.45) and boric acid (0.69) indicating *A* to be essentially tetraethyldiborane; *B* gave n-butane (0.27) (identified by infrared spectrum, mol.wt. 56 and vapour pressure 11 mm at −78°) ethane (0.84) hydrogen (0.63) and boric acid (0.76): *C* gave n-butane (0.27), ethane (6.82), hydrogen (7.13) and boric acid (7.30), corresponding essentially to BC_2H_5. Recovery: boron, 70 %; lead 97 %; reaction ratio $(>B-H)/[(CH_2=CH)_4Pb] = 6.8$. Using excess tetravinyllead (5.01) and diborane (2.07) in 6 ml 1,2-dimethoxyethane gave butadiene (0.53), ethylene (1.79) and hydrogen (0.39) with residual lead, 4.62. Fractionation as before and propionic acid degradation gave: *A*: no hydrogen, ethane (0.13) and boric acid (0.05), suggesting triethylborane; *B*: no hydrogen, n-butane (0.18) and boric acid (0.05); *C*: no hydrogen, ethylene (0.17), ethane (1.82), 1-butene (1.52) (infrared spectrum, mol.wt. and vapour pressure) and boric acid (3.62). Recovery: boron, 92 %; lead, 92 %.

Trivinyllead chloride–lithium hydride

Trivinyllead chloride (1.99) and lithium hydride (7.92) in 25 ml hydride-dried diethyl ether gave, after 2 weeks at 20° with stirring, hydrogen (1.06), ethylene (0.1) and tetravinyllead (1.37); hydrolysis of the residue gave hydrogen (6.15), chloride (1.97) and lead metal (0.48).

Trivinyllead chloride–potassium borohydride

Trivinyllead chloride (1.83) and 1.83 potassium borohydride (re-crystallised from liquid ammonia) were mixed at −78° in 10 ml sodium-dried liquid ammonia. Removal of solvent was effected without loss of other volatile material at −78°, leaving $KCl + (CH_2=CH)_3PbBH_4 \cdot x\,NH_3$. Warming to −65° initiated decomposition, and at 20° gave ethylene (2.00), hydrogen (2.80), ammonia (1.62), tetravinyllead (~0.15), and lead (1.61); other involatile material gave, with propionic acid, hydrogen (0.76), ethylene (0.76), boric acid (1.77), ammonia (0.88) (as NH_4^+), and lead(II) (0.15).

Tetravinyllead–ammonia-borane

Tetravinyllead (3.01) and ammonia-borane (2.83) in 1,2-dimethoxyethane gave, after 24 h at 20°, hydrogen (0.55), ethylene (4.10), no ammonia and no volatile boron-containing products. Treatment of the residue with propionic acid gave hydrogen (0.08), 1-butene (0.60), ethane (2.38), ethylene (1.44), boric acid (1.88), ammonia (1.27) and lead metal (1.32). Recovery of B-H hydrogen, 97 %.

Tetravinyllead (1.11) and ammonia-borane (3.22) in absence of solvent gave, after 10 days at 33°, hydrogen (0.19), ethylene (0.88) and butadiene (0.07). Treatment of involatile residue with propionic acid gave hydrogen (6.53) (from remaining B–H bonds), 1-butene (0.41), ethane (0.46), ethylene (0.16), boric acid (2.57), ammonia (1.36), lead metal (0.65) and lead(II) (0.49). Recovery of B-H hydrogen, 89 %.

SUMMARY

The production of trivinylboron in high yield by reaction of boron trichloride with tetravinyllead illustrates the use of organolead compounds for the synthesis of organoboron compounds.

Reaction of tetravinyllead with diborane, violent at ambient temperatures, occurs by vinyl–hydrogen exchange giving the unstable trivinylplumbane, and vinylboron species which may be hydroborated to give polymers containing $>BC_2H_4B<$ units. The decomposition of trivinylplumbane, as shown by the reaction of trivinyllead chloride and lithium hydride in ether, gives predominantly hydrogen, lead and tetravinyllead; hence excess diborane finally reduces tetravinyllead quantitatively to lead.

The white solid $(CH_2{=}CH)_3PbBH_4 \cdot 2\,NH_3$, formed in liquid ammonia, decomposes to give trivinylplumbane and ammonia-borane; the latter also undergoes vinyl–hydrogen exchange with tetravinyllead, but here the lead-attached hydrogen appears predominantly as ethylene.

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