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VINYLLEAD COMPOUNDS
I. CLEAVAGE OF VINYL GROUPS FROM TETRAVINYLLEAD

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Studies of reactions involving cleavage of unsymmetrical tetraorganotin compounds $R_2Sn(CH=CH_2)_2$ (R = alkyl or phenyl) have indicated an ease of cleavage order phenyl > vinyl > alkyl[1], although other studies[2] using tetravinyltin in absence of solvent suggest that ease of *complete* cleavage by carboxylic acids follows the order vinyl > phenyl > alkyl. Ease of cleavage studies on unsymmetrical organolead compounds containing vinyl groups have not been reported, but cleavage of tetravinyllead by alkali metals[3] and by chlorine and acids[4] suggest greater ease of cleavage than for tetraalkyl- or tetraphenyl-lead compounds. We report here studies of further cleavage reactions, carried out with the object of obtaining substituted compounds of type $(CH_2=CH)_{4-x}PbX_x$; the results are compared with those for tetraalkyllead and tetravinyltin, where these are available.

Juenge and Cook[4] have shown that reaction of tetravinyllead with chlorine in acetic acid at room temperature gives only the dichlorodivinyllead, and the monochloro derivative is not obtained with chlorine. It seemed possible, therefore, that reaction with halogen might offer a means of complete devinylation, and since bromine has been used to obtain lead(II) bromide from alkyllead compounds[5], the reaction of tetravinyllead with bromine was investigated. Excess bromine at room temperature, with no solvent, gave lead(II) bromide and 1,1,2-tribromoethane quantitatively according to the equation

$$Pb(CH=CH_2)_4 + 7\,Br_2 \rightarrow 4\,CHBr_2CH_2Br + PbBr_2$$

This reaction is therefore of use for the analysis of vinyllead compounds. Use of excess tetravinyllead in the reaction produced no identified (bromovinyl)lead derivatives, but formation of vinyl bromide suggested that cleavage of the lead–carbon bonds preceded bromination of vinyl groups. The easy fission of vinyl groups from organolead compounds by bromine may be compared with the reaction of divinyldi-n-butyltin with bromine at 15°, where only one vinyl group is cleaved[6]; the greater polarity of the lead–carbon bond may facilitate its readier cleavage.

Reaction of tetravinyllead with hydrogen chloride in n-hexane at room temperature has been shown to give a mixture of chlorotrivinyllead and dichlorodivinyllead, which were separated by sublimation[4]. We have found that pure dichlorodivinyllead is readily obtained by prolonged passage of hydrogen chloride through the n-hexane solution at room temperature, even though the primary product, the monochloro compound, is insoluble. The pure monochlorotrivinyllead is obtained by reaction in hexane at −78° using a twofold excess of tetravinyllead and removing the unreacted compound by washing with hexane. Here also, cleavage of vinyl groups is more readily achieved than with tetraalkyl- or tetraaryl-lead compounds where good yields of the monochloro derivatives require reaction with hydrogen chloride at elevated temperatures. Only one vinyl group is removed[7] from divinyldi-n-butyltin by hydrogen chloride in chloroform at 60°.

We have found that the reactions of tetravinyllead with the carboxylic acids RCO_2H ($R = CH_3, C_2H_5, CF_3$) at 100–120° followed the equation

$$(CH_2{=}CH)_4Pb + 3\ RCO_2H \rightarrow 3\ C_2H_4 + Pb(O_2CR)_2 + RCO_2CH{=}CH_2$$

Recovery of ethylene was quantitative, but the C_2H_4/Pb ratio never exceeded 3.0 even after prolonged heating. No volatile lead compounds were recovered, all lead being in the +2 oxidation state; recovery of vinyl ester was usually less than 50% theoretical because of polymerization, but no reactive vinyl groups remained in the residue. These reactions may be contrasted with the corresponding reactions with tetravinyltin where, with $R = CH_3, C_2H_5$, complete cleavage to give the tetracarboxylate $Sn(O_2CR)_4$ and ethylene occurs[2]. It is reasonable to assume that after cleavage of three vinyl groups, the vinyl tricarboxylate $CH_2{=}CHPb(O_2CR)_3$ breaks down to give the lead(II) carboxylate and the vinyl ester; an assumption of this kind has been made to explain the general instability of compounds $RPbX_3$ (R = alkyl) and has been verified for reactions of R_4Pb with carboxylic acid[8].

Reaction of tetravinyllead with an equimolar amount of carboxylic acid RCO_2H ($R = CH_3, CCl_3$) at room temperature in presence of silica gel yields the trivinyllead carboxylate[4]; we have verified this observation for $R = CH_3$ and we have prepared the propionate $(CH_2{=}CH)_3PbO_2CC_2H_5$ by the same method. In the infra-red spectra of the acetate and propionate, shifts in the carbonyl frequencies were observed when the solids were dissolved in carbon tetrachloride ($R = CH_3$: 1546 to 1623, 1418 to 1314 cm^{-1}; $R = C_2H_5$: 1524 to 1604, 1418 to *ca.* 1300 cm^{-1}). These are closely comparable with the shifts similarly observed for trihexyllead acetate (1560 to 1623 and 1406 to 1311 cm^{-1})[9] and are attributed to breakdown of the co-ordinated, acylate-bridged solid structure to ester-like monomers in solution.

Reactions of tetraorganolead compounds R_4Pb with silver nitrate in ethanol have been used to obtain unstable organosilver compounds RAg and thence study behaviour of the free radical R[10]. Reaction of tetravinyllead with ethanolic silver nitrate at −78° yielded a black solid but no volatile material; on warming to room temperature butadiene and a small amount of ethylene were evolved and silver was deposited, sometimes as a mirror. The total vinyl groups recovered as gaseous hydrocarbon, and the amount of lead rendered involatile, both slightly exceeded the amount of silver nitrate required by the equation

$$(CH_2{=}CH)_4Pb + AgNO_3 \rightarrow CH_2{=}CHAg + (CH_2{=}CH)_3PbNO_3$$

Hence in addition to the main decomposition reaction

$$CH_2{=}CHAg \rightarrow CH_2{=}CH^{\cdot} + Ag;\ 2\ CH_2{=}CH^{\cdot} \rightarrow CH_2{=}CHCH{=}CH_2$$

the chain propagation reactions

$$CH_2{=}CH^{\cdot} + EtOH \rightarrow CH_2{=}CH_2 + EtO^{\cdot}$$
$$EtO^{\cdot} + (CH_2{=}CH)_4Pb \rightarrow (CH_2{=}CH)_3PbOEt + CH_2{=}CH^{\cdot}$$

probably occurred also. Silver was recovered quantitatively in all reactions; vinylsilver appeared to be stable below about −33° (*cf.*[10] alkylsilver compounds, decomposing rapidly at −50°, and isobutenylsilver, at −20°). If the reactants were mixed at room temperature the organosilver compound appeared transiently as a blue precipitate before decomposing to silver. However, reaction under these conditions, and using excess tetravinyllead, provided a means of preparing trivinyllead nitrate, isolated as a cream-coloured solid which was not hydrolysed by water but which decomposed vigorously in air at *ca.* 80° forming metallic lead. In the infra-red spectrum, peaks at 1470, 1290 and 1034 cm^{-1} were assigned to the ν_4, ν_1 and ν_2 vibrational modes for the covalently bonded O–NO_2 group (C_{2v}). These values indicate a degree of covalency, as measured[11] by $\nu_4-\nu_1$, similar to that found in trimethyltin nitrate, where $\nu_4-\nu_1 = 220$ cm^{-1}.

EXPERIMENTAL

Tetravinyllead was prepared by reaction of lead(II) chloride with vinylmagnesium bromide in tetrahydrofuran; the product was extracted with n-hexane and the latter removed by fractionation. After drying over calcium hydride and fractionation the product gave n_D^{20} 1.5470 and an infra-red spectrum identical with that of authentic tetravinyllead (n_D^{20} 1.5462). Unless otherwise stated, reactions were carried out on a millimole scale and volatile products separated *in vacuo*. Typical results are as follows:

Tetravinyllead (0.50 mmole) on reaction with excess bromine gave 1.81 mmole 1,1,2-tribromoethane (Found: C, 9.6; H, 1.03; Br, 91.3. $C_2H_3Br_3$ calcd.: C, 9.0; H, 1.1; Br, 89.8%.) and 0.47 mmole lead(II) bromide. Tetravinyllead (0.93 mmole) and 0.72 mmole bromine gave 0.29 mmole vinyl bromide (identified by infra-red spectrum), 0.21 mmole 1,1,2-tribromoethane, with recovery of 0.43 mmole tetravinyllead. Tetravinyllead (1.61 mmole) and 1.40 mmole hydrogen chloride in hexane gave after 2 days at −78° 1.41 mmole ethylene, 0.20 mmol recovered tetravinyllead and a white solid product, m.p. 120°, Cl 11.0% [$(CH_2{=}CH)_3PbCl$ has m.p. 119–121°, Cl 11.30%].

Use of excess hydrogen chloride at 20° gave a white solid, m.p. >300°, Cl 21.2% [$(CH_2{=}CH)_2PbCl_2$ has m.p. >300°, Cl 21.4%].

Tetravinyllead (1.39 mmole) and excess acetic acid gave, after 7 days at 105°, 4.29 mmole ethylene and 0.51 mmole of volatile product with mol.wt. 85, and an infrared spectrum identical with that of vinylacetate (mol.wt. 86). The involatile residue gave no ethylene on reaction with sodium in liquid ammonia; acid hydrolysis gave 2.91 mmole acetic acid and 1.36 mmole lead(II) (as sulphate). Tetravinyllead (0.71 mmole) and 0.73 mmole propionic acid gave, after 8 h at 20°, 0.71 mmole ethylene, no other volatile products, and a residue of colourless needle-shaped crystals, m.p. 132, which gave on hydrolysis $Pb/EtCO_2H = 1/1$.

Tetravinyllead (2.66 mmole) and 1.07 mmole silver nitrate in ethanol gave, on warming to 20°, 0.50 mmole butadiene and 0.29 mmole ethylene, with recovery of 1.47 mmole tetravinyllead; the residue gave 1.01 mmole silver as metal. After addition of a 0.2 *M* solution of silver nitrate in ethanol (containing 40 mmole) to 65 mmole tetravinyllead in hexane/ethanol and filtration of precipitated silver, evaporation gave a cream-coloured solid, $(CH_2{=}CH)_3PbNO_3$, which was washed free of unreacted tetravinyllead and re-crystallised from ethanol. [Found: Pb, 58.5; $CH_2{=}CH$, 20.6, NO_3 (as ammonia) 18.7. $C_6H_9NO_3Pb$ calcd.: Pb, 59.1; $CH_2{=}CH$, 23.2; NO_3, 17.7%.]

SUMMARY

Trivinyllead compounds $(CH_2{=}CH)_3PbX$ have been obtained by controlled cleavage of tetravinyllead by hydrogen chloride (X = Cl), carboxylic acids ($X = O_2CR$) and silver nitrate ($X = NO_3$); the properties of some of these compounds are briefly described. More drastic cleavage by bromine gave lead(II) bromide and 1,1,2-tribromoethane quantitatively; carboxylic acids gave the lead(II), not lead(IV), carboxylates.

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