600. *The Cleavage of Unsymmetrical Organolead Compounds by Silver Ions.*

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The reactions between silver ions and a series of unsymmetrical organolead compounds of the type Et_3PbR involves cleavage of the R group. Except in those cases (methallyl, benzyl) in which the radical R is resonance-stabilised, there is evidence for unstable organosilver, AgR, compounds which subsequently decompose to silver and the organic free radical.

The behaviour of several symmetrical tetra-alkyl and -aryl derivatives of lead towards silver ions has been reported.[1,2] The primary products are thermally unstable organosilver compounds apparently resulting from cleavage of one organic radical by a single electron-transfer reaction: $R_4Pb + Ag^+ \longrightarrow R_3Pb^+ + RAg$. Even at low temperatures, sometimes at −60°, these coloured organosilver compounds decompose to silver and organic products which could only result from the dimerisation and hydrogen-abstraction reactions of organic free radicals. For example, tetramethyl-lead yields ethane, tetraethyl-lead a mixture of ethane, ethylene, and butane,[1,2] and tetraphenyl-lead gives diphenyl in 74% yield.[3]

Only one unsymmetrical lead alkyl has been studied in this connection,[4] namely, triethylisobut-1-enyl-lead, which undergoes cleavage exclusively of the isobut-1-enyl group on reaction with silver ions in ethanol solution, with formation of isobut-1-enylsilver: $Et_3Pb\cdot CH{:}CMe_2 + Ag^+ \longrightarrow Et_3Pb^+ + Me_2C{:}CHAg$. Subsequent decomposition

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[1] Semmerano, Riccoboni, *et al.*, *Ber.*, 1941, **74**, 1089, 1297.

[2] Bawn and Whitby, *Discuss. Faraday Soc.*, 1947, **2**, 228.

[3] Gilman and Woods, *J. Amer. Chem. Soc.*, 1943, **65**, 435.

[4] Glockling, *J.*, 1955, 716; 1956, 3640.

of isobut-1-enylsilver affords silver and organic products derived from the isobut-1-enyl radical: $Me_2C{:}CHAg \longrightarrow Me_2C{:}CH\cdot \longrightarrow (Me_2C{:}CH-)_2 + Me_2C{:}CH_2$.

We now describe the reaction of silver nitrate with further organolead compounds Et_3PbR, the nature of the radical R having been varied with the object of investigating (*a*) the factors which influence the stability of the organosilver primary product R·Ag, and (*b*) the reason for the cleavage of the R–Pb bond rather than the Et–Pb bond. The following compounds, most of which are new, were studied: Triethyl-2-methylprop-2-enyl-lead, $Et_3Pb\cdot CH_2\cdot C(CH_3){:}CH_2$ (I); Benzyltriethyl-lead, $Et_3Pb\cdot CH_2Ph$ (II); Triethyl-*p*-trifluoromethylphenyl-lead, $Et_3Pb\cdot C_6H_4\cdot CF_3(p)$ (III); *p*-Dimethylaminophenyltriethyl-lead, $Et_3Pb\cdot C_6H_4\cdot NMe_2(p)$ (IV); Triethyl-α-styryl-lead, $Et_3Pb\cdot CH{:}CHPh$ (V).

For each compound reaction with an equivalent or excess of silver nitrate in ethanol resulted in exclusive cleavage of the unsymmetrical group, since in no case were C_2 or C_4 hydrocarbons formed. For the fluoro-compound (III) and the methiodide of the amine (IV) this result was rather surprising since the primary reaction was considered to involve attack by an Ag^+ ion on the most negative carbon atom, in these two cases presumed to be one of the ethyl groups. However, the high polarisability of the lead atom would probably result in the removal of any positive charge from an adjacent carbon atom and the course of the reaction might then be governed by steric factors. (In general, electrophilic substitution reactions occur far more readily at an aromatic than an aliphatic centre.)

Some idea of the relation between the stability of an organosilver compound and the nature of the organic group has emerged from the behaviour of the five compounds. The simple alkyls of silver decompose rapidly at —50°, but isobut-1-enylsilver was stable for several days below —30°. The propenyl compound (I), which should give the isomeric resonance-stabilised isobut-2-enyl (methallyl) radical on decomposition with silver ions, showed no indication of an intermediate organosilver compound. At all temperatures above —100° formation of silver was immediate and 2,5-dimethylhexa-1,5-diene was isolated in 96% yield, presumably being formed by the dimerisation of methallyl radicals: $[2CH_2{:}CMe\cdot CH\cdot_2 \longrightarrow (CH_2{:}CMe\cdot CH_2-)_2]$. In the case of benzyltriethyl-lead (II) the same general result was observed, *viz.*, no intermediate formation of benzylsilver, but dibenzyl was isolated in high yield, evidently having been formed by dimerisation of the resonance-stablised benzyl radicals. All other cases investigated showed at least signs of the intermediate formation of coloured organosilver compounds. In general it appears that the greater the stability of the radical R, the lower is the stability of the organosilver compound, and in the two extreme cases of methallyl and benzyl, no silver compounds are formed, at least under the conditions of these experiments.

The abnormally high thermal stability of isobut-1-enylsilver is probably connected not only with the low stability of the isobut-1-enyl radical, but also with the presence of a double bond adjacent to the silver atom. It was therefore expected that styrylsilver would show this enhanced thermal stability to a greater extent. Treatment of triethyl-α-styryl-lead (V) with silver nitrate in ethanol results in the formation of a deep red precipitate of styrylsilver which is stable for several hours in air at room temperature. Complete decomposition to silver requires several days at room temperature or several hours at the boiling point of the solvent. The fate of the styryl group was not satisfactorily resolved; 1,4-diphenylbutadiene was not formed, and only traces of styrene were isolated. Most of the styryl groups formed highly insoluble polymeric material.

EXPERIMENTAL

Identification and isolation of triethyl-lead nitrate and of gaseous and volatile products from reactions between silver nitrate and the various organolead compounds followed closely the earlier procedure.[4] Each reaction between an organolead compound and silver nitrate was shown to polymerise styrene.

Triethyl-2-methylprop-2-enyl-lead (I).—A solution of sodium (9·5 g., 0·413 mole) in liquid ammonia (600 c.c.) was added during 2 min. to a solution of tetraethyl-lead (44 c.c., 0·226 mole) in dry ether (250 c.c.) at −80° to −100° in a silvered vacuum flask. Ethane was rapidly evolved leaving a yellow solution containing sodiotriethyl-lead.[5] After 1 min., 3-chloro-2-methylpropene (30 c.c., 0·2 mole) in ether (100 c.c.) was added rapidly (1—2 min.) with vigorous stirring. The residue after evaporation of ammonia was extracted with ether and water. Distillation of the dried ether extract gave *triethyl-2-methylprop-2-enyl-lead* (30 g., 43%) as a colourless liquid, b. p. 45—50°/0·1 mm. (Found: C, 33·6; H, 6·5; Pb, 58·6. $C_{10}H_{22}Pb$ requires C, 34·4; H, 6·3; Pb, 59·3%). This material gave ethane, ethylene, and butane on reaction with excess of silver nitrate, corresponding to 4·7% of tetraethyl-lead. Two further vacuum distillations reduced this impurity to 0·6%. Bromination in carbon tetrachloride gave 1,2,3-tribromo-2-methylpropane, b. p. 95°/6 mm. (Found: C, 15·8; H, 2·4; Br, 81·4. Calc. for $C_4H_7Br_3$: C, 16·3; H, 2·4; Br, 81·3%). This alkyl decomposes rapidly in sunlight with the formation of a lead mirror. With solid silver nitrate the reaction is almost explosive.

Benzyltriethyl-lead (II).—Previous preparations have resulted in very poor yield. The following procedure gave a 67% yield. Triethyl-lead chloride (83 g., 0·25 mole) was added to a filtered solution of benzylmagnesium chloride prepared from benzyl chloride (50·6 g.; 0·4 mole) and magnesium (11 g.) in ether (200 c.c.), and the mixture heated under reflux with stirring (nitrogen atmosphere) for 1 hr. Distillation of the ether-extract after hydrolysis gave benzyltriethyl-lead (65 g.) as a pale yellow liquid, b. p. 80°/0·05 mm. (Found: C, 40·6; H, 5·8. Calc. for $C_{13}H_{22}Pb$: C, 40·5; H, 5·8%).

Triethyl-p-*trifluoromethylphenyl-lead* (III).—This was prepared from *p*-bromobenzotrifluoride (22·5 g.; 0·1 mole), tetraethyl-lead (39·0 g.; 0·12 mole), and sodium (5·5 g., 0·24 mole) in liquid ammonia. Vacuum distillation of the *product*, b. p. 80°/0·06 mm. (yield 14 g., 32%), was always accompanied by slight decomposition to lead (Found: C, 34·5; H, 4·6; F, 12·0; Pb, 47·8. $C_{13}H_{19}F_3Pb$ requires C, 35·5; H, 4·4; F, 13·0; Pb, 47·1%). *p*-Chlorbenzotrifluoride did not react with sodiotriethyl-lead under these conditions.

p-*Dimethylaminophenyltriethyl-lead* (IV).—This was prepared by the liquid-ammonia method described above from *p*-bromo-*NN*-dimethylaniline (40 g., 0·2 mole), tetraethyl-lead (71 g., 0·22 mole), and sodium (10·5 g., 0·46 mole) as a yellow oil (43·0 g., 52%), b. p. 150°/0·06 mm. (Found: C, 40·7; H, 6·4; Pb, 50·4. $C_{14}H_{25}NPb$ requires C, 40·7; H, 6·1; Pb, 50·0%). Although thermally stable to at least 180°, the *compound* slowly decomposed in air at room temperature. Excess of methyl iodide in ether solution gave a *methiodide*, m. p. 131—132° (Found: C, 31·3; H, 4·8. $C_{15}H_{28}NIPb$ requires C, 32·4; H, 5·1%).

Triethyl-α-styryl-lead (V).—This was prepared in 40% yield from 2-bromostyrene (37 g., 0·2 mole), tetraethyl-lead (87·5 g., 0·27 mole), and sodium (13 g., 0·56 mole) in liquid ammonia. Distillation gave *triethyl-α-styryl-lead*, b. p. 94°/10^{-2} mm., as a viscous yellow liquid (Found: C, 41·4; H, 5·6; Pb, 51·2. $C_{14}H_{22}Pb$ requires C, 42·3; H, 5·6; Pb, 52·1%). Decomposition takes place even at −78° with separation of a white solid. For reactions with silver nitrate it was used immediately after distillation. Bromination in carbon tetrachloride led to the isolation of 1,2,2-tribromo-1-phenylethane, b. p. 106—110°/0·1 mm. (Found: C, 28·4; H, 2·2; Br, 69·3. Calc. for $C_8H_7Br_3$: C, 28·2; H, 2·1; Br, 69·7%).

Reactions of Et_3PbR *with Silver Nitrate.*—(a) *Triethyl-2-methylprop-2-enyl-lead.* The lead alkyl (5·3 g.) in ethanol (20 c.c.) was treated with silver nitrate (4·0 g.) in methanol (150 c.c.) at −78°. A black precipitate of silver (91% based on lead alkyl) formed immediately. The reaction mixture, filtered off from silver, was shaken with water and ether. The ether extract was concentrated by fractional distillation and the residual ether separated by fractional condensation in a vacuum apparatus through a trap cooled to −70°. The residue, condensed on excess of 1-naphthyl isocyanate to remove ethanol, gave finally 2,5-dimethylhexa-1,5-diene, b. p. 112°/760 mm., (0·80 g.; 96%) (Found: C, 86·9; H, 12·8. Calc. for C_8H_{14}: C, 87·2; H, 12·8%).

(b) *Benzyltriethyl-lead.* The lead alkyl (2·33 g.) in ethanol (20 c.c.) was added to silver nitrate (1·4 g.) in ethanol (70 c.c.) at −78°. Silver (98·5% based on the lead compound) was formed slowly at this temperature and rapidly when the mixture had warmed to −60°. No volatile hydrocarbons could be detected after 20 hr. at room temperature. Ether-extraction gave dibenzyl (0·49 g., 89%), m. p. and mixed m. p. 52·5°.

(c) *Triethyl*-p-*trifluoromethylphenyl-lead.* The lead compound (1·0 g.) and silver nitrate (0·4 g.) in ethanol (30 c.c.) showed no sign of reaction at −78°, but on warming to room temperature silver was precipitated (90% recovery) with the formation of a transitory red colour. No volatile hydrocarbons were formed, but a small amount of yellow polymer was isolated.

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[5] Gilman and Bindschadler, *J. Org. Chem.*, 1953, **18**, 1675.

(d) p-*Dimethylaminophenyltriethyl-lead.* The lead compound (8·5 g.) and silver nitrate (4·0 g.) in ethanol (200 c.c.) at −78° gave a brown solid which slowly decomposed at room temperature with deposition of silver (110% based on the lead compound). No volatile hydrocarbons were produced, and the solution yielded mainly tars and dimethylaniline (0·25 g., 10%), characterised as the *p*-nitroso-derivative.

The methiodide of *p*-dimethylaminophenyltriethyl-lead (0·61 g.) in ethanol (20 c.c.) was treated with ethanolic silver nitrate (0·372 g.; 2 mol.) at −70°. Silver iodide was immediately precipitated, followed by slow formation of silver. As with the parent compound, no volatile hydrocarbons were formed, and extensive tar formation resulted.

(e) Triethyl-α-styryl-lead (20·0 g.) was added slowly to a solution of silver nitrate (9·0 g.) in ethanol (800 c.c.) at −78°. A deep red precipitate formed and was separated by centrifuging. This material, after being twice washed with cold ethanol, was shown to contain silver as the only metal, and to be free from nitrate (Found: Ag, 56. Calc. for $Ag{\cdot}CH{:}CHPh$: Ag, 51%). Decomposition of the crude styrylsilver by boiling it overnight in ethanol gave silver contaminated with insoluble and evidently polymeric material (10·0 g.). Styrene (0·05 g.) was also isolated as the dibromide.

In separate experiments triethyl-α-styryl-lead was shown to form no volatile hydrocarbons on reaction with silver nitrate; deliberate addition of a small amount of tetraethyl-lead resulted in the formation of ethane, ethylene, and butane.

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