The Formation of iso*But*-1-*enyl Radicals from* iso*But*-1-*enylsilver. Part I.*

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*iso*But-1-enyltriethyl-lead, $\text{Et}_3\text{Pb}\cdot\text{CH}\dot{:}\text{CMe}_2$, with ethanolic silver nitrate at low temperature forms triethyl-lead nitrate and the orange, very unstable *iso*but-1-enylsilver. Evidence is presented that *iso*but-1-enylsilver decomposes into silver and *iso*but-1-enyl radicals $\text{Me}_2\text{C}\dot{:}\text{CH}\cdot$, most of which dehydrogenate the solvent forming *iso*butene. Ethyl deuteroxide, $\text{C}_2\text{H}_5\cdot\text{OD}$, affords $\text{Me}_2\text{C}\dot{:}\text{CHD}$. In the presence of excess of *iso*but-1-enyltriethyl-lead a chain reaction takes place whereby ethoxy-radicals attack the organo-lead compound giving further *iso*but-1-enyl radicals.

Detailed investigations of the decomposition of lead tetra-alkyls by silver nitrate, whereby free alkyl radicals are formed, have previously been confined to the saturated methyl, ethyl and *n*-propyl compounds. Semmerano, Riccoboni, and their co-workers (*Ber.*, 1941, **74**, 1089, 1297; *Z. physikal. Chem.*, 1941, **189**, 203; *Z. Elektrochem.*, 1941, **47**, 484) have shown that these lead alkyls react with alcoholic silver nitrate by an electron-transfer process, forming coloured unstable silver alkyls, RAg, and a trialkyl-lead nitrate :

$$\text{R}_4\text{Pb} + \text{AgNO}_3 = \text{RAg} + \text{R}_3\text{PbNO}_3$$

Methyl- and ethyl-silver, which are sparingly soluble in alcohol, decompose above —70° to silver and gaseous hydrocarbons. Ethane is formed exclusively from methylsilver, but ethane, ethylene, and *n*-butane from ethylsilver. These hydrocarbon products are consistent with decomposition of the intermediate alkylsilver into silver and alkyl radicals: $MeAg = Ag + Me\cdot$; $2Me\cdot = C_2H_6$. $EtAg = Ag + Et\cdot$; $2Et\cdot = n\text{-}C_4H_{10}$; $2Et\cdot = C_2H_4 + C_2H_6$. These reactions have been confirmed by quantitative kinetic studies (Bawn and Whitby, *Discuss. Faraday Soc.*, 1947, **1**, 228).

Since both the behaviour of unsaturated radicals and the preparation and properties of unsaturated organometallic compounds are of considerable interest, the preparation of *iso*but-1-enylsilver from *iso*but-1-enyltriethyl-lead and its decomposition were studied. *iso*But-1-enyltriethyl-lead, prepared from triethyl-lead chloride and *iso*but-1-enyl-lithium (Braude and Timmons, *J.*, 1950, 2007), is a colourless liquid, stable up to 140° in the absence of air, but slowly decomposed by air in daylight. Its constitution, $Et_3Pb{\cdot}CH{:}CMe_2$, was confirmed by its infra-red spectrum and by conversion by bromine to 1 : 1 : 2-tribromo-2-methylpropane and lead bromide.

Ethyl- or *iso*but-1-enyl-silver or both could result from reaction with silver nitrate, but the course of the reaction can be ascertained by analysis of the hydrocarbon products. *iso*But-1-enyl radicals from the decomposition of *iso*but-1-enylsilver might be expected to form *iso*butene (by extraction of hydrogen from the solvent) and 2 : 5-dimethylhexa-2 : 4-diene (by dimerisation of *iso*but-1-enyl radicals). In contrast to ethyl radicals they cannot react by simple disproportionation.

An orange precipitate, evidently *iso*but-1-enylsilver, is formed when alcoholic solutions of *iso*but-1-enyltriethyl-lead and silver nitrate (both at —78°) are mixed. There is no gas evolution. Gradual rise of temperature from —78° resulted in a slow change in colour of the precipitate from orange to pale blue-green, and above —20° silver was slowly deposited. The gaseous hydrocarbon produced contained 97—100% of *iso*butene (shown by combustion over copper oxide and bromine absorption). The composition of this gas was unchanged when the lead alkyl–silver nitrate ratio was varied from 1 : 1 to 140 : 1. It follows that silver nitrate removed exclusively the *iso*butenyl group under the conditions of the experiments. About 60—80% of the total *iso*butenyl present was recovered as *iso*butene; this shows that the *iso*but-1-enyl radicals, assumed to be intermediates, reacted mainly by abstraction of hydrogen from the solvent, *e.g.*, $CMe_2{:}CH\cdot + EtOH \longrightarrow Me_2C{:}CH_2 + EtO\cdot$.

Reactions carried out with excess of lead alkyl gave much more *iso*butene than corresponded with the amount of silver. This differs from the behaviour of tetramethyl-lead from which a mol. of ethane is formed for every two mols. of silver nitrate. Typical results obtained with *iso*butenyltriethyl-lead are shown in the Table. Much *iso*butene was formed with only catalytic quantities of silver nitrate, although the proportion of the total *iso*butenyl present recovered as *iso*butene was considerably reduced. These results indicate a chain reaction, and evidence for the following reaction sequence is discussed below:

$AgNO_3$ used (mmoles)	$Et_3Pb{\cdot}CH{:}CMe_2$ (mmoles)	$Me_2C{:}CH_2$ (mmoles)	Pb/Ag	C_4H_8/Ag
1·24	1·24	0·795	1·0	0·64
0·473	0·678	0·412	1·43	0·87
0·237	0·678	0·522	2·86	2·21
0·118	0·623	0·534	5·28	4·52
0·237	1·36	1·12	5·74	4·68
0·0947	0·678	0·43	7·16	4·53
0·00473	0·678	0·181	143·3	38·2

$$Et_3Pb{\cdot}CH{:}CMe_2 + AgNO_3 \longrightarrow Et_3Pb{\cdot}NO_3 + Me_2C{:}CHAg \quad . \quad . \quad . \quad . \tag*{(1)}$$

$$Me_2C{:}CHAg \longrightarrow Ag + Me_2C{:}CH\cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag*{(2)}$$

$$2Me_2C{:}CH\cdot \longrightarrow Me_2C{:}CH{\cdot}CH{:}CMe_2 \quad . \quad . \quad . \quad . \quad . \quad . \tag*{(3)}$$

$$Me_2C{:}CH\cdot + EtOH \longrightarrow Me_2C{:}CH_2 + EtO\cdot \quad . \quad . \quad . \quad . \quad . \quad . \tag*{(4) *}$$

$$Et_3Pb{\cdot}CH{:}CMe_2 + EtO\cdot \longrightarrow Et_3Pb{\cdot}OEt + Me_2C{:}CH\cdot \quad . \quad . \quad . \quad . \quad . \tag*{(5) *}$$

$$2EtO\cdot \longrightarrow EtOH + CH_3{\cdot}CHO \quad . \quad . \quad . \quad . \quad . \quad . \tag*{(6)}$$

* Chain propagation stages.

Reaction (1). Triethyl-lead nitrate (Löwig, *J. pr. Chem.*, 1853, **60**, 304) was with some difficulty isolated from the reaction in high yield. Previous workers have either assumed it to be formed or (Gilman and Woods, *J. Amer. Chem. Soc.*, 1943, **65**, 435) converted it into the readily isolated chloride. Conclusive analytical evidence that the orange precipitate initially formed was *iso*but-1-enylsilver was not obtained, but the presence of silver and the absence of lead and nitrate have been demonstrated by repeatedly centrifuging and washing the precipitate with ethanol at −78° : it afforded *iso*butene on decomposition in ethanol.

Reaction (2). Metallic silver was formed quantitatively in the overall reaction. In attempts to obtain direct evidence for the formation of *iso*butenyl radicals in solution, it was established that the yield of *iso*butene was hardly affected by the presence of oxygen or of 1 : 1-diphenyl-2-picrylhydrazyl. Failure to combine appreciably with the hydrazyl is remarkable since the activation energy for a radical–radical reaction should be less than for the hydrogen abstraction process (4).

Reaction (3). In the complete absence of ethanol or other solvent a high yield of 2 : 5-dimethylhexa-2 : 4-diene was obtained, and a silver mirror was deposited, in accord with the reaction sequence 1—3. In the presence of ethanol about 10% of the total *iso*butenyl was converted into the diene, which was estimated by its absorption at 242 mμ, and some diene was formed under all conditions investigated. The small amount of radical dimerisation observed in ethanol contrasts with the high yield of ethane obtained from tetramethyl-lead under similar conditions.

There was no evidence that *iso*butenyl radicals isomerise to the resonance-stabilised *iso*but-2-enyl radical, $\cdot CH_2\cdot CMe{:}CH_2 \rightleftharpoons CH_2{:}CMe\cdot CH_2\cdot$, and the absence of the dimer, $CH_2{:}CMe\cdot CH_2\cdot CH_2\cdot CMe{:}CH_2$, is evidence that such isomerisation did not occur.

Reaction (4). It is difficult to see how *iso*butene can be formed in this reaction other than by hydrogen abstraction by *iso*butenyl radicals. In the reactions carried out in solution, ethanol molecules are more numerous than any others and are the most likely source of hydrogen. On this reaction scheme the active product is either $C_2H_5\cdot O\cdot$ or $CH_3\cdot CH(OH)\cdot$. The relative ease of rupture of O–H and C–H bonds by *iso*butenyl radicals will depend on the bond energies and also on steric and polarisation factors. Phibbs and Derwent (*J. Chem. Phys.*, 1950, **18**, 495) have shown that high yields of ethylene glycol result from the mercury-photo-sensitised decomposition of methanol, indicating that the primary step is $CH_3\cdot OH \longrightarrow \cdot CH_2\cdot OH + H\cdot$. However, search for butane-2 : 3-diol by chemical and infra-red methods failed to reveal any. By adding a known quantity of this diol to the reaction mixture it was shown that if the reaction, $2CH_3\cdot CH(OH)\cdot \longrightarrow [CH_3\cdot CH(OH)]_2$, accounted for even 10% of the radicals formed from the alcohol the diol could have been detected by its infra-red spectrum after removal of alcohol and low-pressure distillation of the residue.

Evidence was obtained that at least a considerable proportion of *iso*butene was formed by abstraction of hydrogen from the hydroxy-group by using ethyl deuteroxide as solvent. The resulting [1-^{2}H]*iso*butene (possibly containing some *iso*butene) had a strong absorption band at 4·4 μ corresponding to the C–D stretching vibration. This contrasts with much other work involving attack by radicals on ethyl alcohol. For example, the peroxide- and light-induced addition of ethanol to olefins (Urry, Stacey, Huyser, and Juveland, *J. Amer. Chem. Soc.*, 1954, **76**, 450) was explicable only in terms of the formation of hydroxyethyl radicals : $Me_3C\cdot C\cdot + CH_3\cdot CH_2\cdot OH \longrightarrow Me_3C\cdot OH + CH_3\cdot CH(OH)\cdot$. It is possible that [1-^{2}H]*iso*butene could have resulted from an exchange reaction between *iso*butene and solvent, ·EtOD, though this is considered rather unlikely in the slightly alkaline medium. Further work designed to clarify this point is in progress.

Reaction (5). A chain reaction involving the *iso*butenyltriethyl-lead must take place, to account for the high yields of *iso*butene relative to the amount of silver nitrate used, particularly at high lead alkyl–silver nitrate ratios. Reaction (5) seems the only feasible process though no triethyl-lead ethoxide was isolated (Leeper, Summers, and Gilman, *Chem. Reviews*, 1954, **54**, 143, report its m. p. as 18° but give no other details). In reactions involving an excess of lead alkyl a small quantity of white crystalline sublimate, identified as triethyl-lead hydroxide was always formed on removal of volatile materials at the conclusion of a reaction. This could have resulted from the hydrolysis of the ethoxide by traces of water which might have been present, and, in fact, more triethyl-lead hydroxide was isolated when a little moist ethanol had been added to the residue from a reaction. This compound was never found in reactions between equimolar quantities of *iso*butenyltriethyl-lead and silver nitrate.

Reaction (6). Care was taken to use ethanol free from aldehyde and to exclude oxygen. After an experiment the solution gave a strong positive reaction for aldehydes. In addition to arising by reaction (6), acetaldehyde could result from the disproportionation of $CH_3{\cdot}CH(OH){\cdot}$ radicals.

As it was never possible to account for all the *iso*butenyl introduced in the form of the lead alkyl, it is likely that reactions other than those formulated above take place to a small extent, *e.g.*, the formation of a little *iso*butenyl ethyl ether, $Me_2C{:}CH{\cdot} + EtO{\cdot} \longrightarrow Me_2C{:}CH{\cdot}OEt$, and polymerisation involving *iso*butene and ethoxy- or *iso*butenyl radicals, $EtO{\cdot} + Me_2C{:}CH_2 \longrightarrow EtO{\cdot}CMe_2{\cdot}CH_2{\cdot} \longrightarrow$ etc. However it is difficult to account for the experimental observations on any basis other than the formation and subsequent reaction of *iso*butenyl radicals.

EXPERIMENTAL

The term N-c.c. refers to the volume a substance would occupy at N.T.P., *e.g.*, 1 mmole = 22·4 N-c.c. Analyses for lead were carried out by Saunders and Stacey's method (*J.*, 1949, 919).

iso*But-1-enyltriethyl-lead.*—*iso*Butenyl bromide (27·0 g.) (Braude and Timmons, *loc. cit.*), which had been refluxed over sodium and fractionated (b. p. 91·5°/768 mm.), was added dropwise to refluxing ether (100 c.c.) and freshly cut lithium (3·0 g.) under nitrogen. Triethyl-lead chloride (19·0 g.) (Heap and Saunders, *loc. cit.*), suspended in dry ether, was then added and the mixture stirred and refluxed for 3 hr. Unchanged lithium was removed by filtration and the solution treated with ice-water. The ether layer was washed several times with water, dried ($MgSO_4$), and fractionated, and gave iso*but-1-enyltriethyl-lead* (15·7 g.), b. p. 99—101°/12 mm. (Found: C, 34·9; H, 6·6; Pb, 59·0. $C_{10}H_{22}Pb$ requires C, 34·35; H, 6·35; Pb, 59·3%). Its vapour pressure (mm.) is given by $\log_{10} p = 8{\cdot}65 - 2863/T$, whence the extrapolated b. p. is 224°. The mean latent heat (70—140°) 13·1 kcal./mole.

The presence of an *iso*butenyl group was confirmed by (*a*) the strong absorption band at 12·32 μ (Thompson and Torkington, *Proc. Roy. Soc.*, 1945, *A*, **184**, 3) and (*b*) treatment with bromine in carbon tetrachloride, giving 1 : 1 : 2-tribromo-2-methylpropane, b. p. 83°/13 mm. (Found: C, 16·4; H, 2·5. Calc. for $C_4H_7Br_3$: C, 16·3; H, 2·4%).

Reactions between iso*Butenyltriethyl-lead and Silver Nitrate.*—(a) *In the absence of solvent.* An alcoholic solution of silver nitrate (0·476 mmole, 10·6 N-c.c.) was evaporated *in vacuo*, leaving silver nitrate finely dispersed over the surface of the vessel. A large excess of *iso*but-1-enyltriethyl-lead (~0·5 g.) was condensed on the silver nitrate and the mixture, which soon formed a silver mirror, was left at room temperature for 5 days. Fractional condensation of the volatile products in traps cooled to −20°, −65°, −78°, and −196° gave *iso*butene in the last (0·55 N-c.c.; completely absorbed by bromine in aqueous potassium bromide) and 2 : 5-dimethylhexa-2 : 4-diene (3·51 N-c.c.) from the trap at −65°. The diene formed transparent plates, m. p. 13·7°, b. p. (extrapolated) 133°, $\lambda_{\max.}$ 2420 Å (Harper, Reed, and Thompson, *J., Sci. Food Agr.*, 1951, **2**, 94, record $\lambda_{\max.}$ 2420 Å, ε 25,200).

(b) *In the presence of ethanol.* Stock solutions of silver nitrate and *iso*but-1-enyltriethyl-lead in ethanol (previously freed from acetaldehyde) were used. The former was kept in an amber, stoppered bottle, and the latter at 0°. In general, known volumes of each solution were introduced into two bulbs connected by a tube leading through an internally sealed joint about which part of the evacuated system could be rotated, and de-gassed by pumping at room temperature. The solutions were mixed at −78° and allowed to warm to ~ −30°; some of the ethanol was then back-distilled, thus allowing complete transfer of lead alkyl. Except where the concentration of silver nitrate was very low, an orange precipitate (considered to be *iso*but-1-enylsilver) was formed as soon as the two solutions were mixed at −78°. Above −50° the orange solid gradually became blue-green, while above −20° silver slowly separated from the solution both as a brownish-black sludge and as a mirror. Gas evolution became appreciable only above −10°.

Volatile products were separated after the mixture had been kept for 24 hr. at room temperature, and fractionally condensed with continuous pumping through two traps cooled to

$-78°$ [to remove ethanol, $(Me_2C{:}CH)_2$, and any traces of lead compound], one trap cooled to $-95°$ (to condense any acetaldehyde), and a liquid nitrogen trap (to condense *iso*butene). The condensation procedure was always repeated on the contents of the $-78°$ traps. *iso*Butene was transferred by Töpler pump from a $-95°$ bath to a gas burette and was characterised by combustion over cupric oxide at 500° and by bromine absorption. The combustion gave the amount of C_4 hydrocarbon in the range 97—100% and the latter 98—100% of unsaturated hydrocarbon.

Experiments illustrating the isolation of the various reaction products are as follows:

(i) Equimolar quantities (27·9 N-c.c.) of silver nitrate and *iso*but-1-enyltriethyl-lead were mixed at $-78°$ (volume of solution, 36 c.c.), and *iso*butene (20·27 N-c.c., 72·7%) was isolated as described above. The non-volatile residue (containing $Et_3Pb{\cdot}NO_3$ and silver) was extracted with cold ethanol to remove triethyl-lead nitrate, and the silver in the residue estimated by standard methods, the recovery being 98·5%. Triethyl-lead nitrate was isolated by removing the ethanol *in vacuo* and pumping until a viscous oil was obtained. This was dissolved in *dry* benzene and filtered, and the benzene removed by rapid pumping without the application of heat, giving triethyl-lead nitrate (0·36 g.) as an intensely hygroscopic white power (Found: C, 20·1; H, 4·6; N, 4·1; Pb, 57·5. Calc. for $C_6H_{15}O_3NPb$: C, 20·2; H, 4·2; N, 3·97; Pb, 58·0%). Triethyl-lead nitrate is very soluble in most solvents except light petroleum. The contents of the $-78°$ and $-95°$ ampoules [ethanol, and traces of $(Me_2C{:}CH)_2$ and acetaldehyde] were removed from the vacuum-apparatus. The mixture gave positive qualitative tests for aldehydes, and negative tests for peroxides. Estimation of the 2 : 5-dimethylhexa-2 : 4-diene in a Unicam Spectrophotometer, $\varepsilon_{max.}$ being taken as 25,200 (cf. Harper *et al.*, *loc. cit.*), gave 1·2 N-c.c. of the diene.

(ii) *Reaction with excess of* iso*but-*1*-enyltriethyl-lead.* Ethanolic solutions containing silver nitrate (5·3 N-c.c.) and *iso*but-1-enyltriethyl-lead (30·4 N-c.c.) were mixed (total volume, 15 c.c.) *in vacuo* and treated as described, giving *iso*butene (25·04 N-c.c.; 82·4%). The residue accounted for 99·6% of the silver used. Estimation of 2 : 5-dimethylhexa-2 : 4-diene (2 N-c.c.) was only possible by first distilling the ethanolic solution from a bath at $-20°$. In addition to the diene peak at 242 mμ there was an unidentified stronger maximum at 249 mμ. When the volatile components were removed from the reaction vessel, a small amount of crystalline sublimate, triethyl-lead hydroxide, was formed on warming. This was sublimed on to a cold finger and purified by further sublimation in high vacuum at 60° (Found: C, 23·24; H. 5·1. Calc. for $C_6H_{16}OPb$: C, 23·1; H, 5·2%). Its aqueous solution was strongly alkaline. It partly melted at 50° and decomposed to a brown solid between 120° and 130° with gas evolution. Triethyl-lead hydroxide prepared by Saunders and Stacey's method (*J.*, 1949, 919) behaved similarly.

Reaction in the Presence of Deuteroethanol.—Deuteroethanol was prepared in a vacuum-apparatus from deuterium oxide and sodium ethoxide. Infra-red examination of the product showed a weak O–H band at 2·96 μ and a very strong O–D band at 4·2 μ. Silver nitrate (0·01 g.) was dissolved in the deuteroethanol (4 c.c.) and *iso*but-1-enyltriethyl-lead condensed on the mixture. After 2 days at room temperature the C_4 hydrocarbon was isolated in the usual manner (5·2 N-c.c.). The gas which is essentially [1-^{2}H]*iso*butene was completely adsorbed by bromine water; its infra-red spectrum showed a strong sharp peak at 4·4 μ corresponding to the C–D vibration.

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