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

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*iso*But-1-enyl radicals formed by the heterogeneous decomposition of *iso*but-1-enylsilver are shown by isotope studies with $C_2H_5{\cdot}OD$ and $C_2D_5{\cdot}OH$ to attack the O–H (or O–D) bond of ethanol rather than the α-C–H (or C–D) bond. In contrast methyl radicals attack the α-C–H bond in agreement with previous observations.[1] Styrene is polymerised by decomposing *iso*but-1-enylsilver, while α-methylstyrene is unaffected. Qualitative experiments on the co-ordination properties of *iso*but-1-enylsilver are described.

In Part I * it was shown that *iso*but-1-enylsilver is produced from *iso*but-1-enyltriethyl-lead and silver nitrate in ethanol: $Et_3Pb{\cdot}CH{:}CMe_2 + AgNO_3 \longrightarrow Me_2C{:}CHAg + Et_3Pb{\cdot}NO_3$. Evidence was produced that *iso*but-1-enylsilver decomposes above −20°, forming silver and *iso*but-1-enyl radicals, $Me_2C{:}CH{\cdot}$, of which some 10% dimerise to $(Me_2C{:}CH)_2$. The main reaction product is *iso*butene and in order to account for the high yield of *iso*butene relative to *iso*but-1-enylsilver (the lead alkyl being present in excess) the following radical-chain reaction was postulated:

$$Me_2C{:}CH{\cdot} + EtOH \longrightarrow Me_2C{:}CH_2 + EtO{\cdot} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$Et_2PbCH{:}CMe_2 + EtO{\cdot} \longrightarrow Et_3PbOEt + Me_2C{:}CH{\cdot} \quad . \quad . \quad . \quad (2)$$

The main object of the present work has been to clarify reaction (1), which involves abstraction of the hydroxylic-hydrogen atom from ethanol, forming *iso*butene and an ethoxy-radical. It was shown in Part I that in the presence of ethyl deuteroxide, EtOD, the gaseous product was 1-deutero*iso*butene, indicating that the O–D rather than an α-C–H bond is attacked by the *iso*but-1-enyl radical. The same result has now been obtained with methyl deuteroxide as solvent. However, the reaction is heterogeneous, *iso*but-1-enylsilver being largely insoluble in the concentration range studied, and silver being formed as the reaction proceeds. It was therefore considered possible that isolation of 1-deutero*iso*butene had resulted from a hydrogen–deuterium exchange and that in fact the radical-transfer reaction involved the formation of hydroxyethyl radicals: $Me_2C{:}CH{\cdot} + EtOH \longrightarrow Me_2C{:}CH_2 + CH_3{\cdot}CH(OH){\cdot}$.

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* Part I, *J.*, 1955, 716.

[1] Kharasch, Rowe, and Urry, *J. Org. Chem.*, 1951, **16**, 905.

In order to resolve this problem it was first established that *iso*butene does not undergo hydrogen–deuterium exchange in the presence of ethyl deuteroxide and the solid reaction products (Ag, $Et_3Pb{\cdot}NO_3$, etc.) in one week at room temperature. More convincing proof that reaction (1) does involve the hydroxylic-hydrogen atom of ethanol was then obtained by using pentadeuteroethanol as solvent. This showed strong C–D and O–H absorption bands in the infrared spectrum, the C–H stretching frequency being only just detectable. *iso*Butene obtained from this reaction showed *no* C–D absorption in the infrared spectrum. This observation, combined with the fact that ethyl deuteroxide affords 1-deutero*iso*butene, can only be regarded as proof that reaction (1) does occur.

This result is unexpected, particularly in view of the closely related work of Kharasch and his co-workers [1] who studied the reactions of methyl radicals (from diacetyl peroxide) with propan-2-ol containing some 40 mole % of $Me_2CH{\cdot}OD$, and *tert.*-butyl alcohol containing 4 mole % of $Me_3C{\cdot}OD$. In each case the methane formed gave no deuterium oxide on combustion. These authors also refer to the reaction of methyl radicals in propan-2-ol enriched with 2-deuteropropan-2-ol and report that a mixture of methane and deuteromethane is formed. The earlier work of Gellison and Hermans [2] on the decomposition of benzoyl peroxide in *iso*butan-1-ol apparently led to products such as $Me_2CH{\cdot}CH_2{\cdot}O{\cdot}C_6H_4{\cdot}CO_2H$, indicating that the hydroxylic-hydrogen atom was attacked by radicals derived from the peroxide.

Kharasch's work is perhaps open to the criticism that only partly deuterated alcohols were used. However, in the present work it was found that in virtually 100% ethyl deuteroxide methyl radicals give methane free from deuterium, while reaction of methyl radicals with pentadeuteroethanol gave monodeuteromethane, thus confirming Kharasch's results for the behaviour of methyl radicals in isotopically mixed alcohols. It thus appears that it is *iso*but-1-enyl radicals which behave anomalously by attacking O–H or O–D rather than C–H or C–D bonds.

In view of this anomaly a demonstration that *iso*but-1-enylsilver decomposes with the formation of radicals rather than ions (which would naturally attack O–H bonds) was important. When the reaction is carried out in the presence of styrene, the yield of *iso*butene is approximately halved and polystyrene is produced. Infrared examination of a film of the polystyrene did not provide convincing evidence about the end-groups present, though there was a strong absorption at 4·3 μ, not normally found in polystyrene. α-Methylstyrene, which is not polymerised by free-radical initiators, did not affect the yield of *iso*butene, nor was any polymer isolated.

Attempts have been made to stabilise *iso*but-1-enylsilver by co-ordination. Thus, if a large excess of trimethylamine is added to the orange sparingly soluble *iso*but-1-enylsilver at —78° a clear colourless solution is formed which, at room temperature, slowly deposits metallic silver. Co-ordination is apparently quite weak since at —30° trimethylamine was readily lost *in vacuo* with reprecipitation of the alkenylsilver. 2 : 2′-Dipyridyl behaved similarly, though deposition of silver occurred much more slowly at room temperature. Triethylphosphine also gave a colourless solution at —78° from which silver separated at —40°.

EXPERIMENTAL

Pentadeuteroethanol, etc.—Dideuteroacetylene was converted into tetradeuteroethylene *via* 1 : 2-dibromotetradeuteroethane, essentially by the methods described by Leitch and Morse [3] except that purifications were effected by fractional condensation so that the deuterated intermediates were never removed from the vacuum-apparatus.

Pentadeuteroethyl bromide was obtained in essentially quantitative yield when tetradeuteroethylene (4·5 l. at N.T.P.) and deuterium bromide (4·5 l.) were mixed and irradiated overnight with a 150 w incandescent lamp. It was purified by condensation in a trap cooled to −95°.

This fully deuterated ethyl bromide (22 g.) was converted into the acetate pentadeuteroethyl acetate when shaken with silver acetate (38 g.) and acetic acid (45 c.c.) in a sealed bulb, equipped with a break-seal, for 3 days at 100°. Most of the acetic acid was separated from the deuterated ester by repeated evaporation from a bath at −40°. The crude acetate was

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[2] Gellison and Hermans, *Ber.*, 1925, **58**, 765.

[3] Leitch and Morse, *Canad. J. Chem.*, 1952, **30**, 924.

hydrolysed by shaking it in a sealed bulb at 100° for 6 hr. with sodium hydroxide (12 g.) and water (13 c.c.). Volatile materials were separated by pumping and dried, first, over anhydrous magnesium sulphate, then in a large bulb containing calcium turnings. The pentadeuteroethanol thus obtained was kept over fresh calcium until no increase in hydrogen pressure was observed during 4 hr. (yield, 7 g.) (traces of mercury appear to accelerate greatly the rate of reaction of the alcohol with calcium).

An infrared spectrum on this deuterated ethanol showed a weak C–H stretching frequency at 3·44 μ and very strong absorption bands at 3·04 and 4·5 μ corresponding to the O–H and C–D stretching frequencies respectively. Strong absorption also occurred at 4·78 μ, similar to that observed in 2-deuteropropan-2-ol.[4]

Decomposition of iso*But-*1*-enylsilver in Pentadeuteroethanol.*—Dry, finely powdered silver nitrate (0·02 g.) was dissolved in the deuterated alcohol (3 g.), and *iso*but-1-enyltriethyl-lead (0·35 g.) distilled on to the mixture. The orange *iso*but-1-enylsilver was allowed to decompose overnight, the volatile materials being separated. The condensable gas which passed through a trap cooled to −95° was collected (13·5-N-c.c.) and shown to have an infrared spectrum identical with that of *iso*butene.

Reactions of Methyl Radicals with Ethyldeuteroxide and Pentadeuteroethanol.—Diacetyl peroxide[5] (0·05 g.), which had been crystallised three times from carbon tetrachloride–pentane and freed from solvents by pumping at −10° for several hours, was treated with the alcohol, and the mixture heated at 60—70° for 8 hr. The non-condensable gas was separated and examined spectroscopically. From ethyl deuteroxide, methane was produced; the non-condensable gas from pentadeuteroethanol showed a strong C–D stretching frequency.

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[4] Amer. Pet. Inst. Spectrogram No. 1146.

[5] Edwards and Mayo, *J. Amer. Chem. Soc.*, 1950, **72**, 1265.