Journal of Organometallic Chemistry, 474 (1994) C8–C10

Preliminary Communication

The formation of distannanes from tin hydrides

Alwyn G. Davies and Daniel K. Osei-Kissi

Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ (UK)

(Received December 20, 1993)

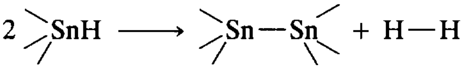
Abstract

The disproportionation of a dialkyltin hydride R_2SnXH (X = halide or carboxylate) to give H_2 and XR_2SnSnR_2X follows a radical chain mechanism, which may involve homolytic displacement by a tin radical of a hydrogen atom from a tin centre.

Key words: Tin; Hydride; Free radicals; Hydrostannation; Hydrostannolysis

Organotin hydrides, particularly tributyltin hydride, are used in a number of important organic synthetic methods [1,2], but some aspects of the chemistry of these compounds remains obscure. Greater understanding of these properties should make it possible to design better synthetic procedures.

One basic reaction which has received little attention is the decomposition of a hydride to give dihydrogen and a product containing an Sn–Sn bond [3,4].


(1)

These reactions are catalysed by amines, and are used as routes to distannanes from trialkyltin hydrides [5], and oligostannanes from dialkyltin dihydrides [6]. The mechanism does not appear to have been studied, but is usually assumed to be a polar process proceeding through a derivative R_3SnX (or R_2SnXH) (Eqns. (2) and (3)) which may be formed adventitiously, perhaps by autoxidation or hydrolysis [3,4].

$$R_3SnX + R_3SnH \longrightarrow R_3SnSnR_3 + HX \qquad (2)$$

$$R_3SnH + HX \longrightarrow R_3SnX + H_2 \qquad (3)$$

We report here a study of the formation of dihydrogen and distannane from some dialkyltin hydrides R_2SnXH, where X is an electronegative substituent such as halide or carboxylate.

Monitoring by ^1H NMR spectroscopy shows that dibutyltin dihydride (δ_H SnH 4.58) reacts with dibutyltin dichoride in ethanol, benzene, or toluene during about 20 min at room temperature to give an equilibrium mixture containing *ca.* 97% of the chloride hydride, and 3% of the dihydride [7]. If $CDCl_3$ is used as the solvent, the spectrum of $CHDCl_2$ rapidly becomes apparent.

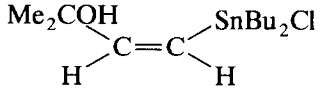
$$Bu_2SnH_2 + Bu_2SnCl_2 \rightleftharpoons 2Bu_2SnClH \qquad (4)$$

If pyridine is added to a solution of the chloride hydride in deuterobenzene, dihydrogen is seen to be evolved and dichlorotetrabutyldistannane is formed, but if a trace of 2,6-di-t-butyl-4-methylphenol is added to the decomposing solution the evolution of hydrogen is quenched and the chloride hydride is stabilised.

$$2Bu_2SnClH \xrightarrow{py} ClBu_2SnSnBu_2Cl + HH \qquad (5)$$

If 2-methyl-3-butyne-2-ol is added to a solution of the decomposing hydride the evolution of hydrogen is again quenched, but the decomposition continues, and the *Z*-vinyl adduct of the hydride with the alkyne is formed.

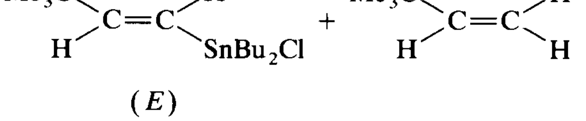
$Bu_2SnClH + Me_2C(OH)C{\equiv}CH \longrightarrow$


(6)

(*Z*)

A similar reaction with 3,3-dimethylbut-1-yne gives principally the *E*-adduct, but also about 10% of 3,3-dimethylbut-1-ene and the dichlorotetra-butyldistannane.

$Bu_2SnClH + Me_3CC{\equiv}CH \longrightarrow$


(*E*)

$+ ClBu_2SnSnBu_2Cl \qquad (7)$

The carboxylate hydrides are less stable than the chloride hydride [8]. For example, if solution of dibutyltin dihydride and dibutyltin diacetate are mixed at 25°C the 1H NMR signal of the acetate hydride can be observed at δ7.6, but decomposition starts immedi-

---

Correspondence to: Professor A.G. Davies.

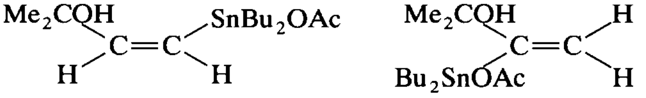
0022-328X/94/$7.00
SSDI 0022-328X(94)24464-T

ately with evolution of dihydrogen and the formation of the diacetoxytetrabutyldistannane.

$$Bu_2SnH_2 + Bu_2Sn(OAc)_2 \rightleftharpoons 2Bu_2Sn(OAc)H \rightleftharpoons AcOBu_2SnSnBu_2OAc + H_2 \quad (8)$$

Again, the reaction is stopped by a small amount of phenolic inhibitor, but the evolution of hydrogen recommences after a few minutes, the period of inhibition being roughly proportional to the amount of the inhibitor added. 2-Methyl-3-butyne-2-ol quenches the evolution of hydrogen, to give in 1.5–2 h a mixture of the *Z*- and *α*-adducts in the ratio of *ca.* 2:1 if the reaction is carried out at 25°C, or *ca.* 1:1 at 0°C.

$$Bu_2Sn(OAc)H + Me_2C(OH)C{\equiv}CH \longrightarrow$$



(*Z*) (*α*)

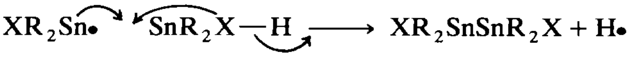
(9)

3,3-Dimethylbut-1-yne again quenched the evolution of hydrogen but gave only the diacetoxytetrabutyldistannane, and presumably the butene, rather than any adduct.

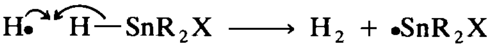
The inhibition of the decomposition of the hydrides R_2SnXH by small amounts of phenols establishes that the decomposition to give dihydrogen and distannane proceeds by a radical chain mechanism which is spontaneously initiated at room temperature or below. The observed reduction of deuteriochloroform and hydrostannation of alkynes that are observed shows that the tin-centred radicals which are generated in this decomposition can be diverted into familiar radical chain reactions.

Two interesting and important questions arise. What is the mechanism of the formation of dihydrogen and distannane? What is the mechanism of the spontaneous generation of radicals at room temperature?

We are not aware of any established mechanism by which a metal hydride MH decomposes to give MM and HH. The most reasonable component of a radical chain which could form the Sn–Sn bond appears to be the S_H2 reaction of the tin radical at tin to displace a hydrogen atom. This would then be expected to abstract H from the Sn–H bond to give dihydrogen, as is observed.



$$XR_2Sn\bullet \; SnR_2X{-}H \longrightarrow XR_2SnSnR_2X + H\bullet \quad (10)$$



$$H\bullet \; H{-}SnR_2X \longrightarrow H_2 + \bullet SnR_2X \quad (11)$$

There appears to be no close precedent for reaction (10). No bond dissociation energies are available for compounds XR_2SnSnR_2X or R_2SnXH, but data for related species suggest that the reaction is thermodynamically not unreasonable, and electronegative substituents are known to enhance the S_H2 reactivity (of alkoxyl radicals) at a tin centre [9]. The fact that some alkynes undergo dihydrogenation rather than hydrostannation provides some support for the formation of atomic hydrogen. Attack of the tin radical at hydrogen to displace a tin radical could, of course, also occur [10], but this would be a symmetrical reaction with no chemical consequences in the present context.

The decomposition, hydrostannolysis, and hydrostannation reactions proceed in the dark in the absence of air; photolysis or autoxidation appear to ruled out as the source of radicals. The most likely initiation process appears to be an electron transfer. This could involve the hydrides R_2SnXH, but more likely the pair R_2SnH_2 and R_2SnX_2, which are in equilibrium with R_2SnXH, and which would be expected to have a lower ionisation energy, and higher electron affinity, respectively. The organotin radical cation and/or anion which are formed could then dissociate to give a stannyl radical, *e.g.*:

$$R_2SnX_2 + R_2SnH_2 \longrightarrow R_2SnX_2^{\bullet -} + R_2SnH_2^{\bullet +} \quad (12)$$

$$R_2SnX_2^{\bullet -} \longrightarrow R_2SnX^{\bullet} + X^- \quad (13)$$

This availability of a wide range of tin hydrides R_2SnXH, and their ability to take part in homolytic hydrostannolysis and hydrostannation reactions at room temperature or below, with a different chemo-, regio-, and stereo-selectivity from that of the conventional trialkyltin hydrides may make them useful reagents in organic synthesis.

Acknowledgment

We acknowledge the award to D.K.O.K. of an SERC CASE Studentship in association with the International Tin Research Association.

References

1 W.P. Neumann, *Synthesis*, (1987) 665.
2 M. Pereyre, J.P. Quintard and A. Rahm, *Tin in Organic Synthesis*, Butterworths, London, 1987.
3 R.C. Poller, *The Chemistry of Organotin Compounds*, Logos, London, 1970.
4 W.P. Neumann, *The Organic Chemistry of Tin*, Wiley, London, 1970.
5 H. Puff, B. Bruer, G. Gehrke-Brinkmann, P. Kind, H. Reuter, W.

Schuh, W. Wald and G. Weidenbrück, *J. Organomet. Chem., 363* (1989) 265.
6 H.G. Kuivila, A.K. Sawyer and A.G. Armour, *J. Org. Chem., 26* (1961), 1426.
7 A.K. Sawyer, J.E. Brown and E.L. Hanson, *J. Organomet. Chem., 3* (1965) 464.
8 A.K. Sawyer and H.G. Kuivila, *Chem. Ind. (London)*, (1961) 260.
9 A.G. Davies, in J.J. Zuckerman (ed.) *Organotin Compounds: New Chemistry and Applications*, American Chemical Society, 1976, p. 26.
10 M. Lehnig and K. Dören, *J. Organomet. Chem., 210* (1981) 331.