Tetrahedron Letters No. 25, pp 2205 - 2208, 1977. Pergamon Press. Printed in Great Britain.

NEW WAYS FOR GENERATION OF REACTIVE STANNYLENES R_2Sn, R = Me, Et

Christian Grugel, Wilhelm P. Neumann *, and Peter Seifert
Lehrstuhl für Organische Chemie I der Universität, Otto-Hahn-Str.,D46 Dortmund 50

(Received in UK 15 April 1977; accepted for publication 16 May 1977)

Since the beginning of organotin chemistry attempts have been made to find the tin analogues of the carbenes, the stannylenes R_2Sn. However, for long only the polymers $(R_2Sn)_n$ were known.[1,2] Recently we described both insertion and addition reactions of the short-lived stannylene Bu_2Sn, generated thermally (60-130°C) from $XBu_2Sn-SnBu_2X$ (X = OAc, Cl, Br, I)[3] or photolytically at room temperature from $(Bu_2Sn)_6$.[4] Now we report a considerable widening of stannylene precursors, and reactions of Et_2Sn and Me_2Sn.

Bromopentaethyldistannane $Et_3Sn-SnEt_2Br$[5] decomposes at 100°C forming Et_3SnBr and a red, nonuniform polymer of general formula $(Et_2Sn)_n$.
If an alkyl halide is present, however, (ratio Sn : R-Hal = 1 : 10, without solvent) intermediate short lived stannylenes Et_2Sn can be trapped by insertion:

$$Et_3Sn{-}SnEt_2Br \xrightarrow[18h,k_1]{100^{o}C} Et_3SnBr + \left[Et_2Sn\right] \qquad (1)$$

$$\begin{tikzcd}[column sep=large] & {}^{1}/_{n}\ (Et_2Sn)_n & \\ \left[Et_2Sn\right] \arrow[ur, "k_2"] \arrow[r, "R-Hal"', "k_3" below] & Et_2(R)SnHal \arrow[r, "EtMgBr"] & Et_3SnR \end{tikzcd}$$

Because Br and Hal are exchanged subsequently, the yields were determinded after alkylation with EtMgBr, R-Hal = PrI (> 70%), iPrI (~ 30%), BuBr (16%). The other Et_2Sn residues polymerized (k_2). As can be seen, k_3 is decreased by more bulky residues R, and by replacement of iodides by bromides.

The decomposition temperature of the distannane is not influenced markedly by the presence of the alkyl halide: The mixture with PrBr remains unchanged at 70°C, and at 100°C the rate is similar for all compounds R-Hal investigated sofar. We conclude that no attack of the latter or of R$^\cdot$ on the distannane occurs, and that k_1 is rate-determining. The reactions proceed in the dark and equally in diffuse daylight. No CIDNP signals, which would follow from the presence of R$^{\bullet}$, could be observed with iPrI or tBuBr. In the presence of tBuO-N=N-OtBu, however, even at 35°C rapid radical reactions occur, probably involving the chain carriers $Et_3Sn^{\bullet}$ and $Et_2SnBr^{\bullet}$. They give higher yields of $Et_2(R)SnHal$, e.g. with BuBr 60-70%. Thus, one can distinguish between the stannylene and the free-radical reaction.

Insertions into Sn-Sn and C-Sn bonds also occur. With Me_6Sn_2 as solvent for the reaction (1), Me_nSn-containing (n = 1,2,3) polymers are obtained; with Et_6Sn_2 also the intermediate Et_8Sn_3 (15%, GC) could be observed, and with Et_4Sn as solvent some Et_6Sn_2 and Et_8Sn_3. Thus, the polymerization of Et_2Sn (k_2) is in fact mainly an insertion reaction of Et_2Sn into Sn-Sn and C-Sn bonds.

Surprisingly the corresponding methyl derivative decomposes (k_1) much faster, beginning at -30°C. Polymerization (k_2) is complete in benzene at room temperature, but is fully prevented in the presence of alkyl iodides (k_3):

$$Me_3Sn\text{-}SnMe_2Br \xrightarrow[1{,}5h,k_1]{20^{\circ}C} Me_3SnBr + \left[Me_2Sn\right] \qquad (2)$$

$$\left[Me_2Sn\right] \xrightarrow{k_2} 1/_n(Me_2Sn)_n$$

$$\left[Me_2Sn\right] \xrightarrow[k_3]{R\text{-}Hal} Me_2(R)SnHal \xrightarrow{EtMgBr} Me_2(Et)SnR$$

Yields: R-Hal = MeI, EtI, PrI (all quant.), EtBr(40%), PrBr(0%), the rest being the polymer $(Me_2Sn)_n$ (k_2), again a branched product of insertions into Sn-Sn and C-Sn bonds.

The striking difference between the Me and the other alkyl derivatives led us to investigate $ClMe_2Sn\text{-}SnMe_2Cl$.[7] This decomposed at much lower temperatures[8] than the corresponding Bu derivative[3] and gave smooth reactions at 50°C and even at room temperature without solvent. All are consistent with the assumption of the generation of a stannylene Me_2Sn, which inserts into a variety of bonds:

$$ClMe_2Sn\text{-}SnMe_2Cl \xrightarrow[3\ h]{37^{\circ}C} Me_2SnCl_2 + \left[Me_2Sn\right] \qquad (3)$$

$$\left[Me_2Sn\right] + RI \longrightarrow Me_2(R)SnI \quad 85\text{-}95\% \quad (R = Me,Et,Pr,Bu)$$

$$+ \ iPrI \longrightarrow Me_2(iPr)SnI \quad 50\%$$

$$+ \ EtBr \longrightarrow Me_2(Et)SnBr \quad 40\%$$

$$+ \ PhSSPh \longrightarrow Me_2Sn(SPh)_2 \quad (\text{quant., in benzene})$$

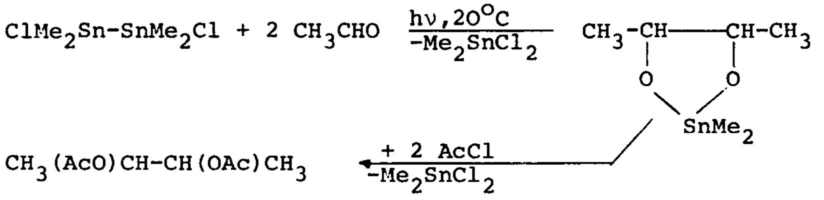
$$+ \ PhCOO\text{-}OCOPh \longrightarrow Me_2Sn(OCOPh)_2 \quad (\text{quant., in benzene})$$

Only $(Me_2Sn)_n$ was observed with tBuOOtBu and tBuSStBu. Sometimes ligands are exchanged afterwards with the Me_2SnCl_2:

$$Me_2Sn(OCOPh)_2 + Me_2SnCl_2 \longrightarrow 2\ Me_2Sn(Cl)OCOPh$$

PhI did not react. This proves that no stannyl radicals are involved, and that a clean distinction can be made between reactions of thermally generated stannylenes and those of stannyl radicals.

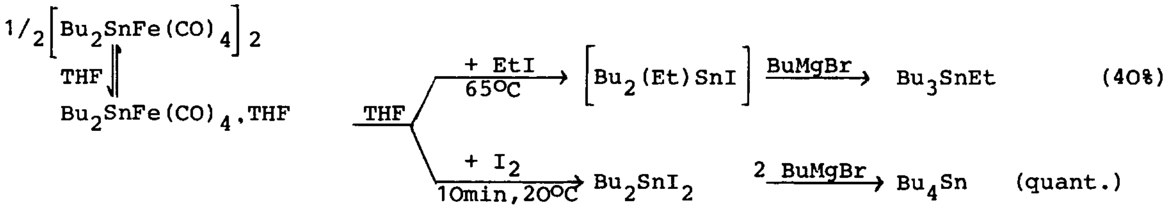
Addition to acetaldehyde could not be effected thermally, but on irradiation the addition product is formed without the appearance of CIDNP signals. Treatment with AcCl proved the presence of the meso and D,L forms in a 1 : 1 ratio (GC):



70%, colourless solid, perhaps polymer

It seems that two forms of a stannylene R_2Sn may exist, a less reactive one produced by thermal reactions, e.g. (1)-(3), giving only insertion reactions, and a more reactive one, generated photolytically, giving also addition reactions. This is in agreement with our earlier findings.[3,4] Perhaps one of these may be the singlet, the other the triplet form, or one is a free stanylene, the other a complexed one.

Complexes of transition metals with R_2Sn moieties, e.g. $[R_2SnFe(CO)_4]_2$, R = Me, Bu, tBu [9], give also stannylene reactions by gentle warming or at room temperature:



With EtI, 50% of the starting material had reacted after 36 hrs, and 6 % of Bu_2SnEt_2 are found as by-product. The rate and the yield of Bu_3SnEt are not lowered by galvinoxyl. Irradiation (daylight or high pressure mercury lamp) has no effect, except the known degradation of the complex as side reaction. Thus, free radicals are not important for the reactions of EtI and I_2 described above.

REFERENCES

1. For a review see W.P. Neumann: The Organic Chemistry of Tin, J. Wiley, London 1970.
2. However, the monomers have been found in the case of the mesomeric cyclopentadienyl or the very bulky bis(trimethylsilyl)methyl residues. See, e.g. for CPD: H.-J. Albert and U. Schröer, J. Organometal. Chem. 60, C 6 (1973); K.D. Bos, E.J. Bulten, and J.G. Noltes, ibid. 67, C 13 (1974); for $(Me_3Si)_2CH$: P.J. Davidson, D.H. Harris, and M.F. Lappert, J.C.S. Dalton Trans. 1976, 2268. Further literature is cited there.
3. U. Schröer and W.P. Neumann, Angew. Chem. 87, 247 (1975); Angew. Chem. Internat. Edit. 14, 246 (1975).
4. W.P. Neumann and A. Schwarz, Angew. Chem. 87, 844 (1975); Angew. Chem. Internat. Edit. 14, 812 (1975).
5. Preparation from Et_5Sn_2H[6] and tBuBr at 5°C in benzene. Colourless oil, undistillable. Identified by IR, NMR, MS, titration with I_2 and Cl_2. A similar procedure was used for Me_5Sn_2Br.
6. H.M.J.C. Creemers, Dissertation, Univ. Utrecht, 1967.
7. Prepared following the general procedure given by R. Sommer, B. Schneider, and W.P. Neumann, Liebigs Ann. Chem. 692, 12 (1966); J. Pedain, Dissertation, Univ. of Giessen, 1965. A considerable improvement in the present case was made by B. Mathiasch, Inorg. Nucl. Chem. Letters 13, 13 (1977), in using only traces of pyridine instead of an excess.
8. The primary products, Me_2SnCl_2 + $(Me_2Sn)_n$, give consecutive reactions forming Me_3SnCl. A similar conversion of R_2SnHal_2 was observed by S. Kozima, K. Kobayashi, and M. Kawanisi, Bull. Chem. Soc. Japan, 49, 2837 (1976).
9. W. Hieber and R. Breu, Chem. Ber. 90, 1270 (1957); T.J. Marks and A.R. Newman, J. Am. Chem. Soc. 95, 769 (1973).