Tetrahedron Letters,Vol.23,No.45,pp 4655-4658,1982 0040-4039/82/454655-04$03.00/0
Printed in Great Britain

MATRIX ISOLATION AND IR SPECTROSCOPY OF STANNYLENES $(CH_3)_2Sn$ AND $(CD_3)_2Sn$

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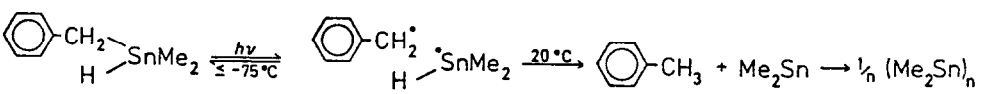
Summary: Free stannylenes Me_2Sn and $(CD_3)_2Sn$, generated thermally from the cyclic hexamers or by microwave discharge from Me_2SnH_2, are isolated by Argon matrix technique. All IR bands could be attributed to the important molecular vibrations by normal coordinate analysis. As shown by ab initio SCF calculations, Me_2Sn has a singlet ground state, the angle C-Sn-C is 95.3°, the C-Sn bond length is 2.203 Å.

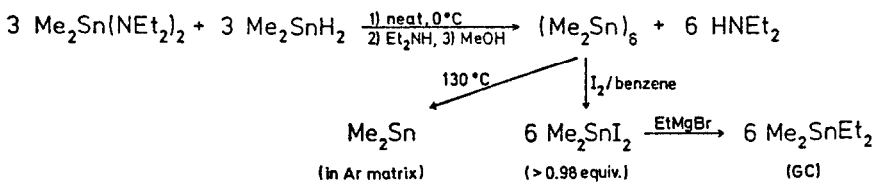
The concept of carbenes was - and still is - one of the most fruitful in organic chemistry. In recent years, it has given considerable impetus to the field of the heavy carbene analogues, R_2M, M = Si, Ge, Sn[1].

Now we wish to report the matrix isolation of Me_2Sn and its IR spectroscopy with complete identification of all relevant vibrations. For this purpose, an adequate Me_2Sn generation had to be found, giving no volatile interfering by-products. First, we photolysed dimethylbenzyltin hydride. In THF at 20°C we detected, as expected, toluene and a polymer $(Me_2Sn)_n$. But, in benzene matrix at -75°C, and in THF matrix at ca. -230°C the hydrogen abstraction no longer occurred, presumably prevented by its activation energy, ca. 4 kcal/mol[2]. Instead, only recombination could be observed needing no activation energy and therefore being preferred at low temperatures (an adamantane matrix at 20°C was found to be too soft in this case, allowing diffusion, since only polystannanes have been found):

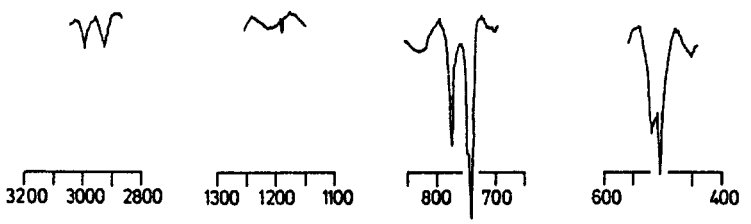


A promising source of free stannylenes Me_2Sn was the thermolysis of $(Me_2Sn)_6$ since this cyclostannane, formerly believed to be stable up to 150°C showed splitting off of $Me_2Sn^{\oplus}$ in the mass spectrometer above 70°C, and rapidly at 120°C. Ditin fragments, e.g. $Me_3Sn_2^{\oplus}$, appear only above 130°C. Also in solution $(Me_2Sn)_n$ depolymerises at 80°C[3].

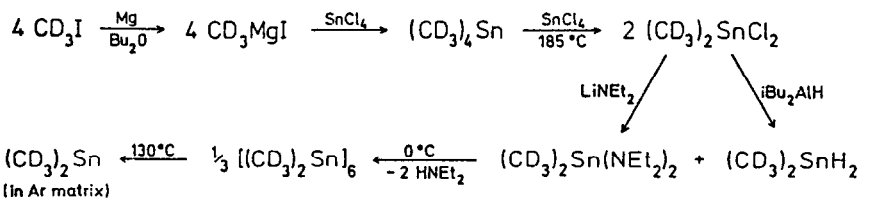
$(Me_2Sn)_6$ (^{1}H-NMR in benzene, δ = 0.53 ppm), very sensitive towards oxygen, is prepared best by condensation at 0°C. It contains small amounts of the heptamer (δ = 0.63 ppm) and is built up exclusively by Me_2Sn units as shown by degradation with iodine (Me_3Sn, MeSn units < 0.1%):



Using a special matrix technique and experience of other work[4] we recorded in an Argon matrix at 5 K well resolved IR spectra of good intensity. All bands could be attributed to a monomeric,strongly bent particle Me_2Sn, i.e. the free stannylene, see table.



The observed IR bands were assigned to molecular vibrations by means of a normal coordinate analysis[5]. To minimize difficulties of assignments of calculated frequencies to observed ones, we have measured and considered in our calculations, see table, also $(CD_3)_2Sn$. Satisfying IR spectra of the latter could be obtained by thermolysis of its hexamer and matrix technique:



There are 2 Sn-C stretching vibrations, as to be expected for Me_2Sn, at 518 and 504 cm^{-1}[6].

Ab initio SCF calculations for Me_2Sn using the pseudopotential method of Durand and Barthelat[7] yielded a singlet ground state with a C-Sn bond length of 2.203 Å, a C-Sn-C bond angle of 95.3°, and a dipole moment of 0.43 D. That the singlet is the ground state is deduced from CI calculations for SnH_2[8] resulting in a singlet-triplet separation of 22 kcal/mol.

Table: Observed and calculated IR frequencies (cm^{-1}) of the matrix-isolated molecules

Assignment X = D or H	$(CD_3)_2Sn$ Obs.[a]	Calc.	$(CH_3)_2Sn$ Obs.[a]	Calc.
ν_{as} (C-X)	2240	2231	2990	3008
ν_s (C-X)	2123	2114	2924	2923
δ_{as} (XCX)	1032	1038	--	1425
δ_s (XCX)	932	921	1187	1181
	927sh	916	1182sh[c]	1179
ρ (CX_3)	596	561[b]	774	755[b]
	569sh	560	745sh	752
	565	558	739	751
ν_{as} (SnC)	476	470	518	522
ν_s (SnC)	462	458	504	509

Notes:
Symmetry: C_{2v}
δ: deformation vibration
ρ: rocking vibration
a: average value of 12 measurements
b: deviation of this type of vibration is obs. in other compounds, too[9].
c: visible only by abscissa expansion

It has to be discussed whether the measured IR spectra are really those of Me_2Sn. In principle there might be a very rapid dimerization forming the distannene: 2 $Me_2Sn \longrightarrow Me_2Sn{=}SnMe_2$. Corresponding disilenes $R_2Si{=}SiR_2$ have been generated by dimerization of silylenes[10] and other ways[11]. We have tempered the Ar matrix up to 30 K, without any change of the IR spectra. When we heated the Me_2Sn source to above 130°C, new IR C-Sn bands in the matrix grew up at 518 and 531 cm^{-1} possibly belonging to the dimer, since at these temperatures ditins appear in the MS, see above. Therefore, it is unlikely that the values given in the table do not represent the stannylene. Moreover, we got identical results, especially strong bands at 518 and 505 cm^{-1}, with an independent stannylene source, using the technique of microwave activation of Argon[12], and again an Argon matrix at 10 K[4]. The occurence of H_2 is established by a decrease of the high vacuum:

$$Me_2SnH_2 + Ar^* \xrightarrow{-Ar} Me_2SnH_2^* \longrightarrow Me_2Sn + H_2$$

The number of encounters of two Me_2Sn particles in the gas phase under these conditions ($6 \cdot 10^{-6}$ Torr, 4 cm flight path) is certainly less than 1 and probably $\sim$ 0.01. Again, the occurrence of the dimer, Me_4Sn_2, is quite unlikely, and the IR spectra recorded can certainly be regarded as those of the free stannylene Me_2Sn.

Acknowledgement. - The work carried out at Dortmund has been supported by the Minister für Wissenschaft und Forschung, Düsseldorf. G.O. is obliged to Professor Ph. Durand for providing a copy of the pseudopotential integral program.

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(Received in Germany 26 July 1982)