

SYNTHESES AND STRUCTURAL STUDIES ON FOUR, FIVE AND SIX-COORDINATED UNSYMMETRICAL DIORGANOTIN HYDRIDES

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ABSTRACT

Four, five and six – coordinated unsymmetrical diorganotin hydrides have been synthesised and characterised on the basis of elemental analysis, FTIR, ^1H NMR, ^{13}C NMR and ^{119}Sn NMR studies.

Key words: Unsymmetrical diorganotin hydride, four, five and six-coordinated.

INTRODUCTION

Due to the unique reducing properties^{1,2} and their ability to add a cross multiple bond leading to the compounds which could not otherwise be easily obtained³, some symmetrical organotin hydrides have been synthesised. A literature survey revealed that no attempts have been made so far to prepare unsymmetrical organotin hydrides and keeping this view in mind, the present paper is concerned with the syntheses and characterisations of unsymmetrical organotin hydrides.

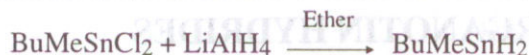
EXPERIMENTAL

All operations were carried out under dry nitrogen atmosphere on a vacuum line using Schlenk equilibrium. BuMeSnCl_2 , PhMeSnCl_2 , PhEtSnCl_2 and PhBuSnCl_2 were prepared by reported methods⁴⁻⁶. Tin and chloride were estimated by standard methods⁷. All the solvents were dried and distilled by conventional methods. IR spectra were recorded in the range of $4000\text{--}200\text{ cm}^{-1}$ using FTIR. ^1H NMR spectra were recorded on Perkin-Elmer R-32, 90 MHz spectrometer in CDCl_3 using TMS as internal reference. ^{13}C NMR and ^{119}Sn NMR spectra were recorded on Bruker 300, 300 MHz instrument using TMS and Me_4Sn as internal standards. Elemental analysis were carried out at RSIC, Chandigarh.

Synthesis of unsymmetrical butylmethyltin dihydrides

Lithium aluminium hydride and ether was added to butylmethyltin dichloride slowly over a long period and was stirred for 4–5 h and filtered. A viscous product was obtained. The product

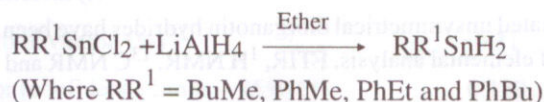
was susceptible to hydrolysis and soluble in benzene, carbon disulphide, carbon tetrachloride and chloroform. The reaction may be written as follows :



Similar procedure was adopted for other reactions of unsymmetrical organotin dichlorides with lithium aluminium hydride. The details of which are given in Table-1 along with their analytical data.

RESULTS AND DISCUSSION

The reaction of unsymmetrical organotin dichloride with lithium aluminium hydride in 1:2 molar ratio can be represented as follows :



All the compounds were creamish viscous, liquids, susceptible to hydrolysis and soluble in benzene, carbon disulphide, carbon tetrachloride and chloroform.

IR Spectra:

IR spectra of the hydrides exhibited two C-H stretching bands due to methyl group at $\sim 2960 \text{ cm}^{-1}$ and $\sim 2870 \text{ cm}^{-1}$. Bands at $\sim 2930 \text{ cm}^{-1}$ and $\sim 2850 \text{ cm}^{-1}$ were assigned to $-\text{CH}_2$ stretching frequencies. Bands assigned to $-\text{CH}$ deformation were observed at $\sim 1460 \text{ cm}^{-1}$ due to $-\text{CH}_3$ asymmetric and at $\sim 1370 \text{ cm}^{-1}$ in methyl group was due to symmetric vibrations. In the spectra of PhMeSnH_2 , PhEtSnH_2 and PhBuSnH_2 , the $-\text{CH}$ stretching band was observed at $\sim 3050 \text{ cm}^{-1}$ and C=C skeletal in plane vibrations were observed at $\sim 1640 \text{ cm}^{-1}$, 1580 cm^{-1} , $\sim 1500 \text{ cm}^{-1}$ and 1450 cm^{-1} . A sharp absorption band in the range $1880\text{--}1820 \text{ cm}^{-1}$ was due to $\nu (\text{Sn-H})_8$ (Table-2). The absence of $\nu (\text{Sn-Cl})$ band suggested the removal of Sn-Cl bond.

^1H NMR Spectra:

^1H NMR spectrum (Table-2) of BuMeSnH_2 exhibited a multiplet in the range $\delta 1.3\text{--}0.2$ due to intermixing of butyl and methyl protons. A signal observed at $\delta 4.3$ was due to hydrogen directly attached to Sn atom. ^1H NMR spectra of PhMeSnH_2 , PhEtSnH_2 and PhBuSnH_2 displayed a multiplet in range of $\delta 7.4\text{--}7.1$ due to phenyl ring protons. In the case of PhMeSnH_2 a signal was observed at $\delta 0.4$ due to methyl protons directly attached to tin $^2J (\text{Sn-H} = 4.5 \text{ Hz})$. A signal resonating at $\delta 5.0$ could be assigned to proton attached with tin $^3J (\text{HC-SnH} = 3 \text{ Hz})$. In case of PhEtSnH_2 , a signal centered at $\delta 1.1$ was due to the intermixing of methylene and methyl protons of ethyl group. A signal was found at $\delta 5.2$ that could be ascribed to protons attached to Sn atom. In case of PhBuSnH_2 , a multiplet was observed in the range of $\delta 1.6\text{--}0.8$

due to butyl protons attached to tin. A signal was observed at δ 5.8 that could be represented by hydrogen directly attached to tin.

Table 1.

Reactants g. (mmol)		Molar Ratio	Product	Analysis Found (Calcd)		
				C	H	Sn
BuMeSnCl ₂ 0.99(3.79)	LiAlH ₄ 0.29(7.59)	1:2	BuMeSnH ₂	30.7(31.2)	7.1(7.3)	61.0(61.6)
PhMeSnCl ₂ 0.91 (3.23)	LiAlH ₄ 0.24(6.45)	1:2	PhMeSnH ₂	39.0(39.5)	4.3(4.7)	55.3(55.8)
PhEtSnCl ₂ 1.46(4.94)	LiAlH ₄ 0.37(9.87)	1:2	PhEtSnH ₂	41.9(42.4)	5.1(5.3)	51.9(52.3)
PhBuSnCl ₂ 0.55(1.71)	LiAlH ₄ 0.13(3.41)	1:2	PhBuSnH ₂	46.8(47.1)	6.0(6.3)	46.0(46.6)

Table 2

Compound	IR Data	¹ H NMR Data			¹³ C NMR Data (₁ CH ₃ - ₂ CH ₂ - ₃ CH ₂ - ₄ CH ₂ -Sn)CH ₃ /CH ₂ -CH ₃			¹¹⁹ Sn NMR Data
		Sn-H	C ₆ H ₅	Bu/Me/Et	a	b		
BuMeSnH ₂	1840 s	4.3 s	—	1.3 – 0.2 m	26.4(C-1), 25.7(C-2) 24.4(C-3), 13.6(C-4)	6.9	—	2.1
PhMeSnH ₂	1865 s	5.0 s	7.4 – 7.1 m	0.4 t	—	7.2	—	-110.1, -349.2
PhEtSnH ₂	1880 s	5.2 s	7.4 – 7.2 m	1.1 m	—	—	12.3 ^a , 10.4 ^b	-0.01, -339.9
PhBuSnH ₂	1820 s	5.8 s	7.4 – 7.2 m	1.6 – 0.8 m	26.3(C-1), 25.4(C-2) 24.8(C-3), 13.7(C-4)	—	—	105.2

¹³C NMR Spectra:

¹³C NMR spectra (Table-2) of BuMeSnH₂ exhibited signals at δ 26.4, δ 25.7, δ 24.4 and δ 13.6 due to C-1, C-2, C-3 and C-4 carbon (₁CH₃-₂CH₂-₃CH₂-₄CH₂-Sn-₅CH₃) of the butyl group and a signal at δ 6.9 due to methyl carbon attached with tin⁹. ¹³C NMR spectra of PhMeSnH₂, PhEtSnH₂, and PhBuSnH₂ produced signals in the range δ 137.9–127.9 due to carbons of the phenyl ring. In case of PhMeSnH₂, the methyl carbon appeared at δ 7.2 while the methylene and methyl carbons in case of PhEtSnH₂ furnished signals at δ 12.3 and δ 10.4, respectively. In case of PhBuSnH₂, the signals due to butyl carbons appeared at δ 26.6, δ 25.4, δ 24.8 and δ 13.7.

¹¹⁹Sn NMR Spectra

¹¹⁹Sn NMR spectrum of BuMeSnH₂ exhibited signal at δ 2.1 due to tetra-coordinated Sn atom. PhMeSnH₂ gave signals at δ -110.1 and δ -349.2 due to penta and hexa-coordinated Sn atom. Two signals at δ - 0.01 and δ -339.90 were observed in the spectrum of PhBuSnH₂, which were due to penta and hexa-coordinated Sn atom. In case of PhBuSnH₂, a signal at δ 105.19 was exhibited due to tetra-coordinated Sn atom¹⁰.

ACKNOWLEDGEMENT

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