

## Preliminary communication

# A NOVEL SYNTHETIC ROUTE TO SMALL-RING MONOSTANNACYCLOALKANES

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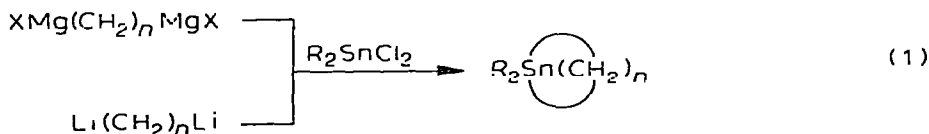
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## Summary

A novel synthetic route to small-ring monostannacycloalkanes, involving the intramolecular disproportionation of  $\alpha, \omega$ -bis(trialkylstannyl)alkanes, is reported.

Although the first examples of cycloalkanes containing heterocyclic tin were reported over half a century ago [1], the chemistry of monostannacycloalkanes has remained largely unexplored [2]. The few known tetraorganotins which incorporate a monostannacycloalkane ring were synthesized in rather poor yields (10-30 %) by means of Grignard or organolithium reagents, as in eqn. 1.



$n = 4$ ;  $R = \text{Bu, neopentyl}$  [3]

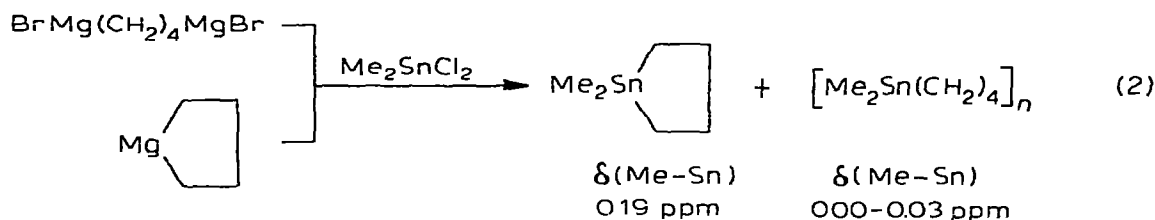
$n = 5$ ;  $R = \text{Me, Et}$  [1];  $P = \text{Bu, neopentyl}$  [3],

$R = \text{Ph}$  [3,4];  $R_2 = \text{---CH}_2\text{---}_5$  [4]

$n = 6$ ,  $R = \text{Me, Et, neopentyl, Ph}$  [3]

We now report preliminary results of studies of the synthesis of monostannacycloalkanes. A PMR study of the reaction of the bis-Grignard reagent of 1,4-dibromobutane with  $\text{Me}_2\text{SnCl}_2$  (eqn. 2) demonstrated that even under optimal conditions, such as low temperature and great dilution, the value of the stannacyclopentane/polymers ratio is always about one. Application of magnesia-cyclopentane [5] did not improve significantly the cyclic compound/polymers





ratio. Treatment of 1,4-dibromobutane either with  $\text{Me}_2\text{SnNa}_2$  in liquid ammonia or with  $\text{Me}_2\text{SnLi}_2$  in THF or HMPT gave only a trace of ring compound.

A new approach which appears to be very satisfactory involves the intramolecular disproportionation reaction of  $\alpha, \omega$ -bis(trialkylstannyl)alkanes, as represented in eqn. 3. As can be seen from the results in Table 1, reaction 3 ( $n = 4$ ,  $\text{R} = \text{Me}$ ) proceeds rapidly at 250-280°C.

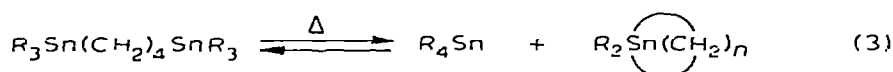
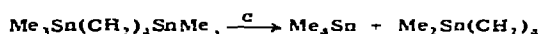


TABLE 1



(I)		(II)	(III)	Products (%) <sup>b</sup>	
Catalyst (mole %)	Time (min)	Temp. (°C)	Conversion of I (%)	II	III
-	15	256	44	90	75
-	90	285	55	95	75
$\text{ZnCl}_2$ (20)	15	256	97	99	47
$\text{ZnCl}_2$ (20)	90	285	95	95	12
$\text{AlCl}_3$ (20)	30	200	100	96	0
$\text{ZnCl}_2$ (20) <sup>c</sup>	30	270	90	100	90

<sup>a</sup>Experiments in a glass vessel fitted with a condenser. <sup>b</sup>Based on the amount of I converted; determined by PMR and GLC. <sup>c</sup>Experiment in a distillation apparatus; pot temperature 270°C, column temperature 170-180°C.

The reaction rate is markedly enhanced by  $\text{ZnCl}_2$  catalysis. However, ring-opening to give polymeric species is also enhanced by this catalyst. This effect is even more pronounced with  $\text{AlCl}_3$  as the catalyst. Optimal results are obtained when the reaction is carried out in a distillation apparatus with a pot temperature of 270-290°C and a column temperature well above the boiling points of II and III. By rapid and continuous removal of the reaction products from the reaction zone polymerization is kept at a minimum and the equilibrium is shifted to the right. That an equilibrium is indeed involved was demonstrated by the formation of I on heating II and III at 270°C in a sealed tube.

The reaction was found to be generally applicable for the synthesis of dialkylstannacyclopentanes and -hexanes in high yields (Table 2). 1,1-Dimethylstannacycloheptane is formed only when the reaction is carried out in great dilution ( $\alpha$ -bromonaphthalene as the solvent; ~40% yield), whereas only a trace of ring compound could be detected in the case of the corresponding stannacyclooctane.



Further studies on the scope and the mechanism of this new synthesis are in progress.

TABLE 2

MONOSTANNACYCLOALKANES PREPARED ACCORDING TO EQUATION 3

R	n	Yield <sup>a</sup>	B.p. (°C/mm Hg)	n <sub>D</sub> <sup>20</sup>	PMR data <sup>b</sup>	
					$\delta$ (Me—Sn) (ppm)	$J(^{117}\text{Sn—Me})$ (Hz)
Me	4	94	41-42/20	1.5050	0.19	52
Et	4	80	39-41/0.2	1.5095		
Me	5	90	76-79/15	1.5027	0.10	51
Me <sup>c</sup>	6	40	82-84/15	1.5077	0.06	49

<sup>a</sup>Determined by GLC and PMR analysis; yields after distillation about 20 % lower. <sup>b</sup>In CCl<sub>4</sub> solution.

<sup>c</sup>Cf. ref. 3.

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