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Preliminary communication

A NOVEL SYNTHETIC ROUTE TO SMALL-RING MONOSTANNACYCLOALKANES

E.J. BULTEN and H.A. BUDDING
Institute for Organic Chemistry TNO, Utrecht (The Netherlands)
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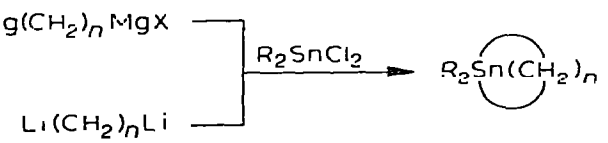
Summary

A novel synthetic route to small-ring monostannacycloalkanes, involving the intramolecular disproportionation of α,ω-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.



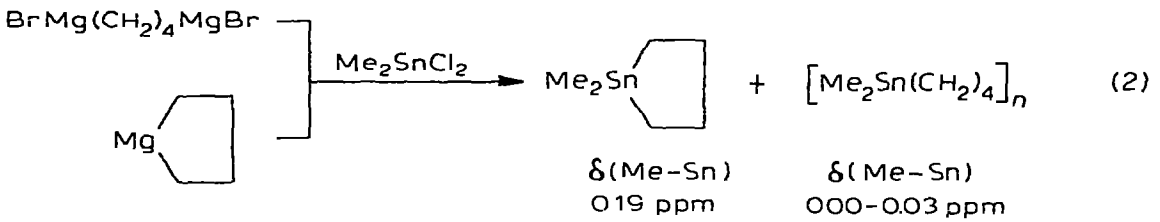
(1)

$n = 4$; R = Bu, neopentyl [3]

$n = 5$; R = Me, Et [1]; R = Bu, neopentyl [3], R = Ph [3,4]; R_2 = $-(CH_2)_5-$ [4]

$n = 6$, R = 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 Me_2SnCl_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 magnesiacyclopentane [5] did not improve significantly the cyclic compound/polymers



ratio. Treatment of 1,4-dibromobutane either with Me_2SnNa_2 in liquid ammonia or with Me_2SnLi_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 α,ω-bis(trialkylstannyl)alkanes, as represented in eqn. 3. As can be seen from the results in Table 1, reaction 3 (n = 4, R = Me) proceeds rapidly at 250-280°C.

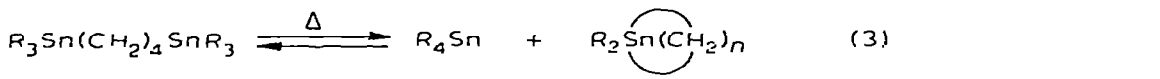


TABLE 1

$Me_3Sn(CH_2)_4SnMe_3 \xrightarrow{c} Me_4Sn + Me_2Sn(CH_2)_4$

(I) (II) (III)

Catalyst (mole %)	Time (min)	Temp. (°C)	Conversion of I (%)	Products (%)[b]	
				II	III
-	15	256	44	90	75
-	90	285	55	95	75
$ZnCl_2$ (20)	15	256	97	99	47
$ZnCl_2$ (20)	90	285	95	95	12
$AlCl_3$ (20)	30	200	100	96	0
$ZnCl_2$ (20)[c]	30	270	90	100	90

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

The reaction rate is markedly enhanced by $ZnCl_2$ catalysis. However, ring-opening to give polymeric species is also enhanced by this catalyst. This effect is even more pronounced with $AlCl_3$ 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 dialkylstannacyclo-pentanes and -hexanes in high yields (Table 2). 1,1-Dimethylstannacycloheptane is formed only when the reaction is carried out in great dilution (α-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[a]	B.p. (°C/mm Hg)	n_D^{20}	PMR data[b]	
					δ(Me—Sn) (ppm)	J(^{117}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[c]	6	40	82-84/15	1.5077	0.06	49

[a]Determined by GLC and PMR analysis; yields after distillation about 20 % lower. [b]In CCl_4 solution. [c]Cf. ref. 3.

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