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Preliminary communication

A NOVEL SYNTHETIC ROUTE TO SMALL-RING MONOSTANNACYCLOALKANES

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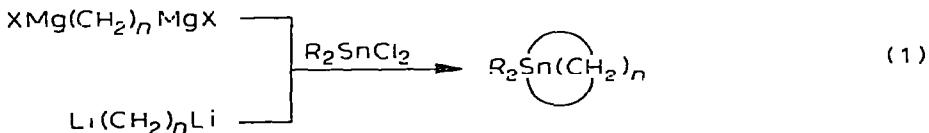
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Summary

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



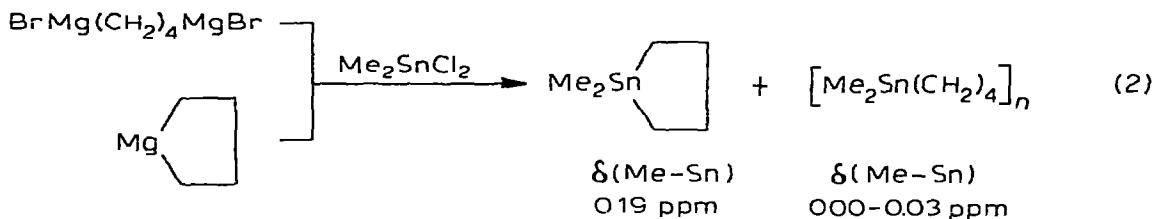
$$n = 4; R = Bu, neopentyl [3]$$

$$n = 5; R = Me, Et [1]; R = Bu, neopentyl [3],$$

$$R = Ph [3,4]; R_2 = -CH_2-\text{C}_5H_5 [4]$$

$$n = 6, R = Me, Et, neopentyl, Ph [3]$$

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 magnesiumcyclopentane [5] did not improve significantly the cyclic compound/polymers

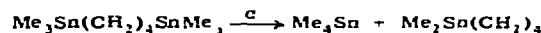


ratio. Treatment of 1,4-dibromobutane either with Me_2SnNa_2 in liquid ammonia or with Me_2SnLi_2 in THF or HMPT gave only a trace of ring compound.

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 I



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

^aExperiments in a glass vessel fitted with a condenser. ^bBased on the amount of I converted; determined by PMR and GLC. ^cExperiment 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-Dimethyl-stannacycloheptane 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)	$J(^{117}\text{Sn—Me})$ (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 ^c	6	40	82-84/15	1.5077	0.06	49

^aDetermined by GLC and PMR analysis; yields after distillation about 20 % lower. ^bIn CCl₄ solution.

^cCf. ref. 3.

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