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[2+4] CHELETROPIC CYCLOADDITIONS OF STANNYLENES R_2Sn (R = ALKYL, AMINO, HALOGEN)

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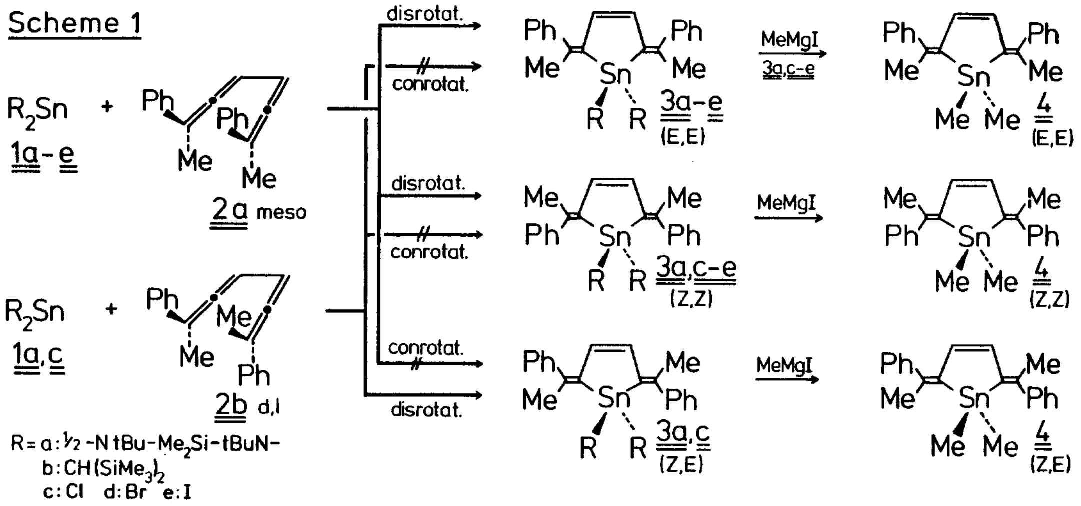
Summary: Free stannylenes $Me_2Si(tBuN)_2Sn$ 1a and $[(Me_3Si)_2CH]_2Sn$ 1b as well as $SnCl_2$, $SnBr_2$, and SnI_2 give 1,4-cycloadditions to different 1,3-dienes yielding 1-stannacyclopent-3-enes. A singlet heavy carbene analogue behaviour is shown with the two isomers of the diallene 2 : only those stereoisomers are found to be postulated for a [2+4] cheletropic addition. In the other cases, a similar mechanism is likely. 1b acts as a donor towards E,E-1,4-disubstituted 1,3-dienes, reacting faster with electron deficient ones.

The heavy carbene analogues R_2Si, R_2Ge, and R_2Sn attracted increasing attention during the last years with respect to synthetic, mechanistic, and theoretical considerations. Thus, short lived free germylenes Me_2Ge showed insertions as well as smooth synchroneous, pericyclic [2+4] cycloadditions to conjugated dienes, classifying them as a singlet reactive species[1]. Whereas with free dimethyl stannylene Me_2Sn insertions also could be effected[2], no additions to olefines or dienes have been possible insofar. This is probably due to their reduced reactivity compared with Me_2Ge, competing unsuccessfully with their very rapid polymerisation $n\ Me_2Sn \xrightarrow{k} (Me_2Sn)_n$. The latter occurs below 0°C, needs apparently no or nearly no activation energy and is only diffusion controlled, k may be assumed to be $10^8 - 10^9\ M^{-1}\ sec^{-1}$.

So, we looked for free stannylenes R_2Sn 1[3] more stable or even completely stable against polymerisation, and mixed them at room temperature in CH_2Cl_2 or benzene with the pure meso or the pure d,l isomer of the diallene 2 (meso or d,l 2,7-diphenylocta-2,3,5,6-tetraene). This rather sophisticated 1,3-diene has been taken because it offers a good chance to decide clearly whether there is a stepwise addition[4] or a synchroneous one, and more over to identify the structure of the products to be expected by ^{1}H-NMR.

We detected exclusively those of the stereoisomers 3[5] to be expected if only disrotatory ring closure takes place. Therefore, the stannylenes used here react via a concerted thermal [2+4] cycloaddition, a cheletropic reaction of the linear type allowed by the Woodward-Hoffmann rules[6], see Scheme 1 and Table 1. All reactions are completed at room temperature, no by-products could be detected, (^{1}H-NMR)[7].

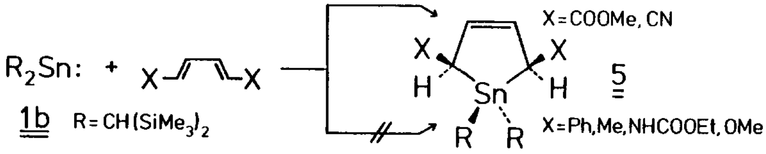
Scheme 1



The conclusions derived above have been established or supported by methylation of the 1-stannacyclopent-3-enes 3a, c-e with MeMgI/Et$_2$O in benzene, giving the corresponding 2,5-disubstituted 1-dimethylstannacyclopent-3-enes 4, see Scheme 1 and Table 1. In all cases, with the meso diallene 2a only the Z,Z and E,E isomers are found whereas 2b (d,l) gives only Z,E isomer as to be postulated.

It is of interest that neither the donating groups in the diamino stannylene 1a nor very bulky substituted methyl groups in 1b did prevent the cycloaddition. We were surprised by the smooth reaction of the suspensions of the tin dihalides 1c-e in CH$_2$Cl$_2$ showing that a reactive species is present - maybe in an equilibrium - behaving clearly as a singlet stannylene, providing a new and one-step access to complicated stanna heterocycles and their reactions from well available tin chemicals.

If in the transition state of the cheletropic reaction discussed, the HOMO of the dienophile, the stannylene 1, i.e. the lone pair of electrons, interacts with the LUMO of the diene, then electron deficient dienes should react faster. If the LUMO of 1b, i.e. the vacant p orbital, interacts with the HOMO of the diene, electron rich ones should be preferred. To clarify this important mechanistic detail, we selected the following E,E-1,4-disubstituted 1,3-dienes and looked for a reaction with 1b at room temperature in benzene:



Only the most electron deficient dienes gave the cycloadduct 5, see Table 1[8], the electron neutral or electron rich ones gave not, even at 80 or 110°C in toluene (only the syn isomers could be detected, pointing again to a cheletropic reaction). We conclude that the HOMO$_{stannylene}$ interacts with the LUMO$_{diene}$.

Table 1. ^1H-NMR (δ in ppm, CCl_4) of 1-stannacyclopent-3-enes 3 and 4 of Scheme 1, and of 5 and 6. 2a gives E,E- and Z,Z-3 about 1:1, the Z,E isomer is absent, 2b gives only Z,E-3[5].

	3a				3b			3c	
	vinyl	allyl	tBu	$SiMe_2$	vinyl	allyl	$SiMe_3$	vinyl	allyl
E,E	6.53[a]	2.49[b]	1.20[c]	0.32[b]	6.30[a]	2.30[b]	0.25[d]	6.61[a]	2.53[b]
Z,Z	7.04[a]	2.36[b]	0.82[c]	-0.17[b]	-[e]	-[e]	-[e]	7.04[a]	2.39[b]
Z,E	6.78[a]	2.30[f]	1.02[c]	0.28[f]	-	-	-	6.80[a]	2.36[f]
		2.48		0.38					2.46

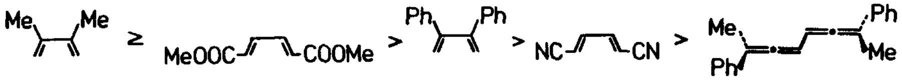
	3d		3e		4		
	vinyl	allyl	vinyl	allyl	vinyl	allyl	$SnMe_2$
E,E	6.52[a]	2.52[b]	6.39[a]	2.58[b]	6.38[a]	2.28[b]	0.58[b]
Z,Z	6.88[a]	2.38[b]	6.84[a]	2.42[b]	6.80[a]	2.28[b]	-0.25[b]
Z,E	-	-	-	-	6.62[a]	2.20[f]	0.17[b]
						2.25	

5, X = COOMe				6, X = Me		
vinyl	COOMe	allyl	$SiMe_3$	allyl	$SiMe_3$	
6.20[g]	3.60[b]	3.18[g]	0.07[c] 0.20[c]	1.73[h]	0.07[d]	
X = CN				X = Ph		
vinyl	allyl	$SiMe_3$		Ph	allyl	$SiMe_3$
6.18[g]	2.78[g]	0.18[c] 0.25[c]		6.78[i]	2.27[j]	0.17[d]

a) s, 2H. b) s, 6H. c) s, 18H. d) s, 36H. e) The very bulky 1b seems to attack 2a only from the less hindered Me-side. f) 2 s, 3H each. In addition, 7.2-7.5 ppm 10H, less characteristic H_{aryl}. g) d, 2H. h) s, 10H. i) m, 10H. j) s, 4H.

Mainly the frontier orbitals are supposed to influence the reactivity of dienes in pericyclic reactions, hence also in the present cheletropic ones, and these are governed by 1,4-substitutions much more than by 2,3-substitutions[6]. Thus, we were surprised to find a high reactivity of 2,3-substituted dienes, giving **6**, see Table 1 (on the other hand, E,E-1,2,3,4-Ph_4-butadiene did not react). The unexpected high reactivity of the 2,3-disubstituted dienes may be due to a higher extent of s-cis conformation:

By competition experiments using two dienes and **1b** in a 1:1:1 molar ratio we found at room temperature the following sequence of reactivity:



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2) L.-W. Gross, R. Moser, W.P. Neumann, and K.-H. Scherping, Tetrahedron Lett. 23, 635 (1982).

3) a: Preparation of **1a**: M. Veith, Angew. Chem. Internat. Edit. 14, 263 (1975).
   b: Preparation of **1b**: P.J. Davidson, D.H. Harris, and M.F. Lappert, J. Chem. Soc. Dalton Trans. 2268, 2275 (1976).

4) In this case, the 1,4-addition would have to pass an open-chain intermediate, presumably a biradical, in which the rotations around C-2 and C-7 already are finished because of the generation of the stable conjugated triene system, as discussed elsewhere[1]. Since these rotations can occur clockwise or anticlockwise, the meso and the d,l diallene both should give more or less the same mixture of products **3**, and not exclusively the isomers observed.

5) Within the accuracy of ^{1}H-NMR assessment.

6) See, e.g., I. Fleming, "Frontier Orbitals and Organic Chemical Reactions", Wiley, New York, 1976.

7) **1a** needs 5 min, **1b** 60 min, **1c** 4 h, **1d**,**e** 12 h. The products **3a** (Z,Z), **3b** (E,E), **3c**,**d** (Z,Z), **3e** (E,E + Z,Z mixture) have been isolated and identified by MS and elemental analysis, in addition.

8) Identified by ^{1}H- and ^{13}C-NMR. **5** with X = COOMe has been isolated and, in addition, identified by elemental, MS and IR analysis.

9) The addition of **1b** to 2,3-dimethylbutadiene is briefly mentioned[3b].

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