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ADDITIONS OF A STABLE STANNYLENE R_2Sn TO VINYL CARBONYL COMPOUNDS AND 1,2-DIKETONES

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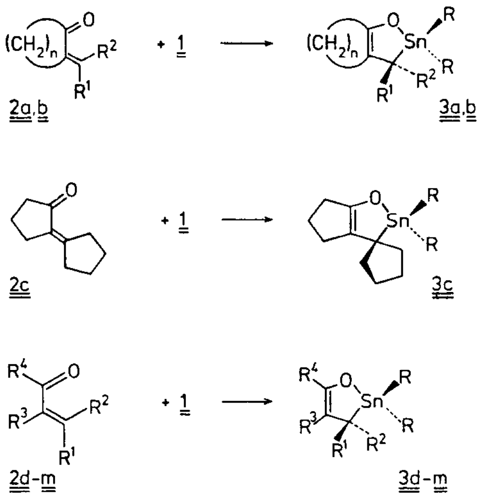
Summary: The stable stannylene R_2Sn **1**, R = bis(trimethylsilyl)methyl reacts with cyclic s-cis fixed and open-chained vinyl ketones and aldehydes **2** or 1,2-diketones **4**, apparently via an 1,4-addition, to give the corresponding 1-oxa-2-stannacyclopent-4-enes **3** or, resp., 1,3-dioxa-2-stannacyclopent-4-enes **5** at room temperature. Effects influencing the reactivity of the 4π-partners are investigated by competition reactions, and the structure-mechanism relationships are discussed.

The stable singlet stannylene **1**[1)] has been used in this laboratory as a good dienophile in cheletropic [4+2]-cycloadditions to conjugated 1,3-dienes[2)]. So we looked for the reactivity of **1** towards other conjugated 4π-systems such as vinyl ketones and aldehydes **2a** - **m** in the 1,4-cycloaddition[3)].

Both cyclic s-cis fixed vinyl carbonyl compounds **2a** - **c** as well as open-chained ones **2d** - **j** react smoothly with **1** in benzene at room temperature to give quantitatively, 30% with **2k** - **m**, the five-membered cycloadducts **3a** - **m** (R = bis(trimethylsilyl)methyl):



	R^1	R^2	R^3	R^4
2a, **3a**	Me	H	$-(CH_2)_4-$	
2b, **3b**	Ph	H	$-(CH_2)_4-$	
2d, **3c**	H	H	H	Me
2e, **3e**	Me	H	H	H
2f, **3f**	Me	Me	H	Me
2g, **3g**	Ph	H	H	H
2h, **3h**	Ph	H	H	Me
2i, **3i**	Ph	H	Me	Me
2j, **3j**	Ph	H	H	CH=CHPh
2k, **3k**	H	H	H	OMe
2l, **3l**	Me	H	H	OMe
2m, **3m**	Ph	H	H	OMe

All products were characterized by ^{1}H-NMR spectroscopy, typical ones also by MS and elemental analysis. In the NMR spectra of the adducts **3g** - **j**, **m** the free rotation of the Me_3Si-groups of the bulky substituents R is hindered by the 3-phenyl substituents so that four Me_3Si signals arise.

^{1}H-NMR Data of the 1-Oxa-2-stannacyclopent-4-enes **3a** - **m**

3a: (C_6H_6): 0.18 (s, 18H, SiMe); 0.30 (s, 18H, SiMe); 1.1-2.6 (m, 12H, CH, CH_2, CH_3)

3b: ($CDCl_3$): -0.07 (s, 6H, SiMe); 0.01 (s, 6H, SiMe); 0.20 (s, 12H, SiMe); 0.22 (s, 12H, SiMe); 1.0-2.9 (m, 8H, CH_2); 3.50 (m, 1H, CH); 7.33(s, 5H, Ph).
MS: M^+ = 624

3c: (C_6H_6): 0.25 (s, 18H, SiMe); 0.33 (s, 18H, SiMe); 1.0-2.6 (m, 14H, CH_2).
MS: M+ = 588

3d: (C_6H_6): 0.13 (s, 18H, SiMe); 0.28 (s, 18H, SiMe); 1.55 (s, 2H, CH_2); 1.92 (s, 3H, Me); 4.9 (m, 1H, =CH)

3e: ($CDCl_3$): 0.17 (s, 18H, SiMe); 0.27 (s, 18H, SiMe); 1.50 (d, 3H, Me); 2.4 (m, 1H, CH); 4.77 (dd, 1H, =CH); 6.93 (dd, 1H, =CH)

3f: (C_6H_6): 0.20 (s, 18H, SiMe); 0.27 (s, 18H, SiMe); 1.45 (s, 6H, Me); 1.83 (d, 3H, Me); 4.37 (s, 1H, =CH)

3g: (CCl_4): -0.15 (s, 6H, SiMe); -0.03 (s, 6H, SiMe); 0.17 (s, 12H, SiMe); 0.22 (s, 12H, SiMe); 3.77 (dd, 1H, CH); 4.82 (dd, 1H, =CH), 7.1 (m, 6H, Ph, =CH)

3h: (CCl_4): -0.15 (s, 6H, SiMe); -0.02 (s, 6H, SiMe); 0.18 (s, 12H, SiMe); 0.22 (s, 12H, SiMe); 1.88 (d, 3H, Me); 3.85 (dd, 1H, CH); 4.68 (d, 1H, =CH); 7.13 (s, 5H, Ph)

3i: (CCl_4): -0.08 (s, 6H, SiMe); 0.00 (s, 6H, SiMe); 0.18 (s, 12H, SiMe); 0.23 (s, 12H, SiMe); 1.62 (s, 3H, Me); 1.92 (s, 3H, Me); 3.53 (s, 1H, CH); 7.37 (s, 5H, Ph)

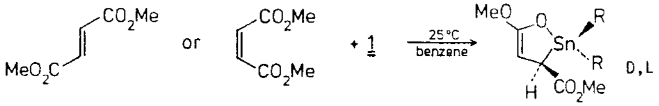
3j: (CCl_4): -0.18 (s, 9H, SiMe); -0.02 (s, 9H, SiMe); 0.18 (s, 9H, SiMe); 0.22 (s, 9H, SiMe); 3.93 (d, 1H, CH); 5.07 (d, 1H, =CH); 7.0 (m, 12H, Ph, =CH)

3k: (C_6H_6): 0.14 (s, 18H, SiMe); 0.30 (s, 18H, SiMe); 2.15 (d, 2H, CH_2); 3.47 (s, 3H, Me); 4.17 (t, 1H, =CH)

3l: (C_6D_6): 0.15 (s, 18H, SiMe); 0.18 (s, 18H, SiMe); 1.53 (d, 3H, Me); 3.45 (s, 3H, Me); 3.80 (d, 1H, CH); 4.03 (d, 1H, =CH)

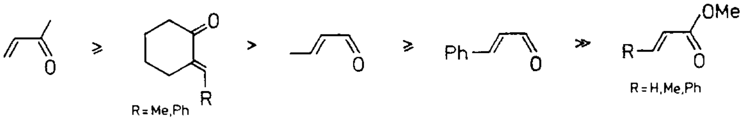
3m: (C_6D_6): 0.00 (s, 9H, SiMe); 0.12 (s, 9H, SiMe); 0.27 (s, 9H, SiMe); 0.37 (s, 9H, SiMe); 3.20 (d, 1H, CH); 3.52 (s, 3H, Me); 7.1 (m, Ph, =CH).

We were surprised by the reaction of **1** with α,β-unsaturated esters like **2k** - **m** because of the very little enolization (≤ 0.01%)[4] of the latter. Also the cycloadditions of **1** with fumaric and maleic acid dimethylester belong to this series (yield 60%):



This might be due to the acceptor group in 4-position of the heterodiene system which favours an inverse cheletropic 1,4-cycloaddition as found with the germylene Me$_2$Ge5) and **1**2).

In competition reactions the effects influencing this cycloaddition meaning steric, conformation, and substituents' effects were proved. A sequence of the heterodienes used here can be derived, and be compared with that for the cycloaddition of **1** with dienes2,6):



The results are the following:

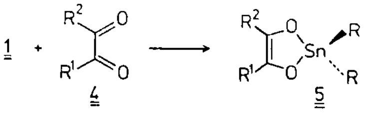
a) Cyclic s-cis fixed derivatives react faster than open-chained ones.

b) Aldehydes and ketones react faster than comparable α,β-unsaturated esters.

c) Substitution in the 4-position of the vinyl carbonyl compound lowers the rate, but different substituents (Me, Ph) have no measurably different influence on the rate (^{1}H-NMR).

It remains open whether a concerted [4+2]pericyclic 1,4-reaction occurs, or an 1,2-addition of **1** across the C=O- or the vinyl group of the heterodiene with subsequent rearrangement to the cycloadducts **3**. No intermediates could be observed (^{1}H-NMR), however. From these facts one may suppose, therefore, that the 1,4-cycloaddition of **1** with vinyl carbonyl compounds is a concerted one because of the dependence on the concentration of s-cis conformer and the nature of the substituent in 4-position of the 1,3-heterodiene system showed by the different yields in the reactions with α, β-unsaturated esters. Conclusive evidence for a synchroneous cheletropic cycloaddition, however, is not obtainable because no stereospecifity can be expected here in contrast to 1,3-dienes2,6).

In the same manner **1** reacts with 1,2-diketones **4**, in benzene at room temperature giving the corresponding 1-stannadioxolenes **5a** - **h** 3):



4: **a**: 3,5-di-*t*butyl-1,2-benzoquinone,
b: 1,2-naphthoquinone,
c: 9,10-phenanthroquinone,
d: benzil,
e: butane-2,3-dione,
f: 2,2,5,5-tetramethylhexane-3,4-dione,
g: 3,3,6,6-tetramethyl-1-thiacycloheptane--4,5-dione,
h: norbornane-2,3-dione.

1H-NMR Data of the 1,3-Dioxy-2-stannacyclopent-4-enes 5a - h

5a: (C_6H_6): 0.18 (s, 36H, SiMe); 1.35 (s, 9H, Me); 1.73 (s, 9H, Me)

5b: (CCl_4): 0.15 (s, 36H, SiMe); 7.2 (m, 6H, Ph)

5c: (C_6D_6): 0.13 (s, 36H, SiMe); 7.2-7.8 (m, 4H, Ph); 8.3-8.8 (m, 4H, Ph)

5d: (CCl_4): 0.30 (s, 36H, SiMe); 7.2 (m, 10H, Ph)

5e: (C_6H_6): 0.25 (s, 36H, SiMe); 2.02 (s, 6H, Me)

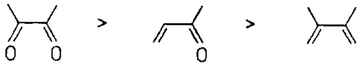
5f: (C_6H_6): 0.22 (s, 36H, SiMe); 1.50 (s, 18H, Me)

5g: (CCl_4): 0.20 (s, 36H, SiMe); 1.35 (s, 12H, Me); 1.35 (s, 12H, Me); 2.83 (s, 4H, CH_2)

5h: (C_6H_6): 0.30 (s, 18H, SiMe); 0.35 (s, 18H, SiMe); 1.1-2.5 (m, 8H, CH, CH_2)

All products were identified by ^{1}H-NMR spectroscopy and elemental analysis. No dimers of the cycloadducts 5 were observed as found with thermally generated Me_2Si[7].

The different reactivity of 1 towards the 1,3-dienes, vinyl carbonyl compounds, and 1,2-diketones has been shown by competition reactions of comparable derivatives:



In conclusion it can be noticed that, in general, stannylenes react with many conjugated organic compounds in a formal 1,4-cycloaddition, if the stannylenes are stabilized against polymerization, otherwise there is polymerization of the reactive species, as shown with Me_2Sn[2].

In a typical procedure 0.5 g (1.14 mmol) of 1 are stirred with an equimolar amount of the vinyl carbonyl compound or the 1,2-diketone in 8 ml of benzene for 1 h. The ester derivatives are stirred overnight. Evaporation of the solvent in vacuo yields colourless or pale yellow oils, slowly crystallizing in part.

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References:

1) J. D. Cotton, P. J. Davidson, and M. F. Lappert, J. Chem. Soc. Dalton Trans. 1976, 2268, 2275.
2) R. Marx, W. P. Neumann, and K. Hillner, Tetrahedron Lett. 25, 625 (1984).
3) For Me_2Ge see: E. Michels and W. P. Neumann, Tetrahedron Lett. 27, 2455 (1986).
4) A. Gero, J. Org. Chem. 19, 1960 (1954).
5) J. Köcher and W. P. Neumann, J. Am. Chem. Soc. 106, 3861 (1984).
6) K. Hillner and W. P. Neumann, in preparation.
7) H. Appler and W. P. Neumann, in preparation.

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