Reaction of Allylsilanes and Monothioacetals in the Presence of Lewis Acids: Regioselectivity in the Cleavage of the Acetals

Hisao Nishiyama, Shinzo Narimatsu, Koji Sakuta, and Kenji Itoh*

School of Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi 440, Japan

Trimethylallylsilane reacts with monothioacetals in the presence of tin(IV) chloride, titanium tetrachloride, or boron trifluoride–diethyl ether to give the homoallyl ethers and homoallyl sulphides.

Allylsilanes react with acetals in the presence of various common Lewis acids,[1] trimethylsilyl trifluoromethanesulphonate,[2] or trimethylsilyl iodide,[3] to give homoallyl ethers. We now show that the reaction of the allylsilanes (**1**), (**2**), and (**3**) with the monothioacetals (**4**) in the presence of several Lewis acids affords the corresponding homoallyl ethers (**5**) or homoallyl sulphides (**6**) (Table 1).

The *S*-methyl monothioacetals[4] (**4a**), (**4b**), and (**4c**) reacted with (**1**), (**2**), and (**3**) in dichloromethane for 30 min on treatment with tin(IV) chloride to give predominantly the homoallyl ethers (**5a**), (**5b**), (**5c**), (**5d**), (**5e**), and (**5f**), respectively, with generally regioselective cleavage of the C–S bond (Table 1; entries 1—9). This selective cleavage was interpreted as arising from the strong affinity of the tin atom for the sulphur atom in a soft acid–soft base interaction. In this respect, the contrast between C–S bond cleavage with $SnCl_4$ (entry 5) and C–O cleavage with $TiCl_4$ (entry 6) is interesting.

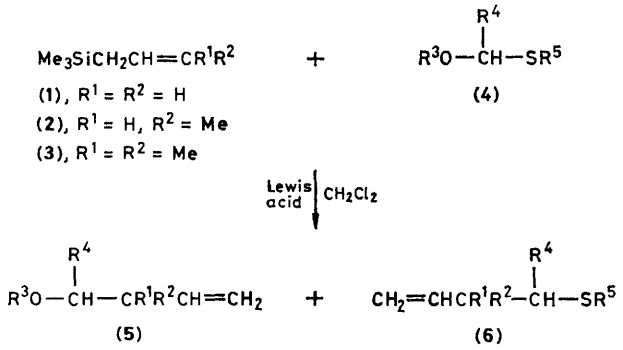
The *S*-phenyl thioacetals (**4d**) and (**4e**), in contrast, gave the homoallyl sulphides resulted from C–O bond fission which is preferred owing to the stabilisation of the thionium cation by the phenyl group (entries 10—12).

Treatment of the cyclic monothioacetals[5] (**4f**) and (**4g**) with

Table 1. Reactions of the monothioacetals (**4**) with the allylsilanes (**1**).

Entry	Mono-thioacetal	Allyl silane[a]	Lewis acid[b]	Products (% yield)[c]			
1	(**4a**)	(**1**)	A	(**5a**)	(70);	(**7**)	(38)
2	(**4a**)	(**2**)	A	(**5b**)	(40);	(**7**)	(28)
3	(**4b**)[d]	(**1**)	A	(**5c**)	(80);	(**8**)	(2)
4	(**4b**)	(**2**)	A	(**5d**)	(88);	(**8**)	(8)
5	(**4b**)	(**3**)	A	(**5e**)	(74);	(**8**)	(26)
6	(**4b**)	(**1**)	B	(**5c**)	(4);	(**8**)	(88)
7	(**4b**)	(**1**)	C	(**5c**)	(45);	(**8**)	(54)
8	(**4b**)	(**1**)	D	(**5c**)	(28);	(**8**)	(69)
9	(**4c**)	(**1**)	A	(**5f**)	(4);	(**9**)	(89)
10	(**4d**)	(**1**)	A	(**5a**)	(26);	(**6a**)	(43)
11	(**4e**)	(**1**)	A		(**6a**)	(63)	
12	(**4e**)	(**1**)	B		(**6a**)	(81)	
13	(**4f**)	(**1**)	A		(**5g**)	(86)	
14	(**4f**)	(**1**)	B	(**5g**)	(72);	(**6b**)	(13)
15	(**4g**)	(**1**)	A	(**5h**)	(90);	(**6c**)	(2)
16	(**4g**)	(**1**)	B	(**5h**)	(9);	(**6c**)	(71)

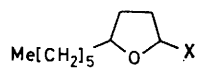
[a] 1.3—1.5 equiv. of the allylsilanes (**1**)—(**3**) with respect to the monothioacetals (**4**) were used. [b] Lewis acids (1.2—1.4 equiv.): A, $SnCl_4$; B, $TiCl_4$; C, BF_3–Et_2O; D, $AlCl_3$; solvent, CH_2Cl_2; time, 30 min; room temp. for A, C, and D, and −20 °C for B. [c] Products (**7**)—(**9**) resulted from C—O bond cleavage. [d] Compound (**4b**) was a mixture of *cis*- and *trans*-isomers in each case.



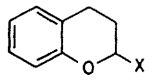
Scheme 1

Compounds (4)	R^3	R^4	R^5
a	$PhCH_2CH_2$	H	Me
b	4-t-butylcyclohexyl	H	Me
c	$CH_2[CH_2]_{10}CHEt-$	H	Me
d	$PhCH_2CH_2$	H	Ph
e	$Me[CH_2]_3CHEtCH_2-$	H	Ph

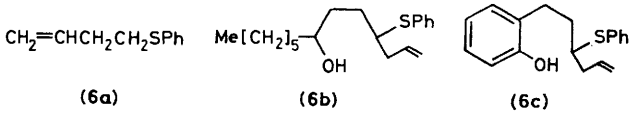
Compounds (5)	R^1	R^2	R^3	R^4
a	H	H	$PhCH_2CH_2$	H
b	H	Me	$PhCH_2CH_2$	H
c	H	H	4-t-butylcyclohexyl	H
d	H	Me	4-t-butylcyclohexyl	H
e	Me	Me	4-t-butylcyclohexyl	H
f	H	H	$CH_2[CH_2]_{10}CHEt-$	H



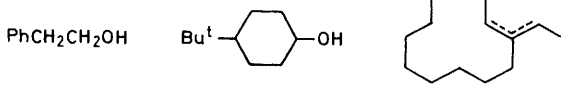
(4f); X = SPh
(5g); X = $CH_2CH{=}CH_2$



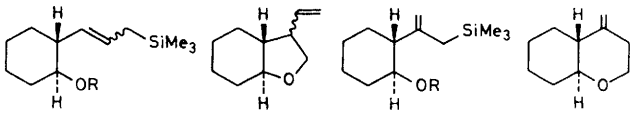
(4g); X = SPh
(5h); X = $CH_2CH{=}CH_2$



(6a) (6b) (6c)



(7) (8) (9)



(10) R = H (11) R = CH_2SMe (12) (13) R = H (14) R = CH_2SMe (15)

Scheme 2. (10) → (11), Me_2SO–Ac_2O, room temp., 1 day, 55%; (11) → (12), $SnCl_4$, room temp., 1 h, 78%; (13) → (14) Me_2SO–Ac_2O, room temp., 1 day, 69%; (14)→(15), $SnCl_4$, −30 °C, 1 h, 73%. Compounds (10) and (11) were prepared by reaction of cyclohexene oxide with the Grignard reagents of 3- and 2-bromoallyltrimethylsilane, respectively: see ref. 7.

tin(IV) chloride gave the ethers (**5g**) and (**5h**) in good yields (entries 13, 14, and 15) however. With titanium tetrachloride, (**4g**) gave mainly the sulphide (**6c**), in contrast with entry 15.

As a demonstration of the application of this cyclic etherification under selective conditions, the tetrahydrofuran derivative (**12**) and the tetrahydropyran derivative (**15**) were synthesized *via* regioselectively induced oxonium ion formation (Scheme 2).[6]

Received, 21st December 1981; Com. 1453

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