The S_Hi Reaction at Silicon—A New Entry into Cyclic Alkoxysilanes

Armido Studer* and Hanno Steen[a]

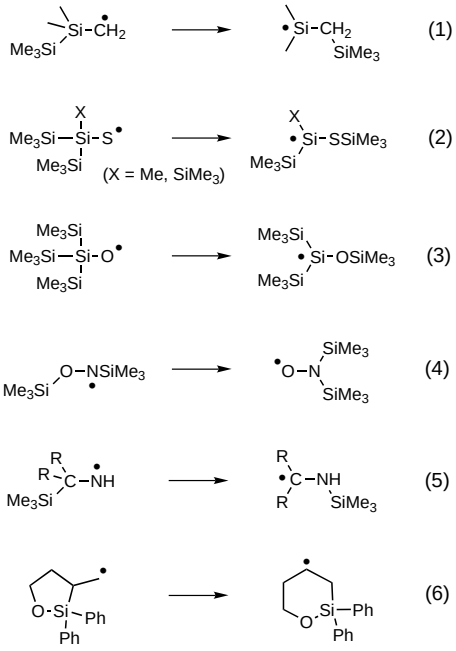
Abstract: A new mild radical method for the preparation of cyclic five-membered alkoxysilanes is reported. This method comprises an intramolecular homolytic substitution reaction at silicon (S_Hi). Various leaving groups ($SiMe_3$, $GeMe_3$, $SnMe_3$) were tested in the homolytic substitution reaction. We found that high yields were only obtained for silanes bearing a trimethylstannyl functionality as leaving group in the S_Hi reaction. Rate constants for the cyclization reaction were estimated by conducting standard competition experiments. Based on the kinetic data, more elaborate reaction sequences such as radical addition reactions with a subsequent S_Hi step were carried out. Stereoselective cyclization reactions were also investigated. Excellent 1,2 diastereoselectivities were observed. The products of the S_Hi reaction, cyclic alkoxysilanes, can easily be converted to the corresponding diol derivatives by Tamao–Fleming oxidation as demonstrated for several examples.

Keywords: homolytic substitution reactions · radical reactions · silicon · stereoselective reactions · tin

Introduction

Forty years ago, Kumada et al. reported the first intramolecular homolytic substitution at silicon.[1] They observed a 1,2 silyl migration from silicon to carbon at 600 °C in the gas phase (Scheme 1, [Eq. (1)]). Ten years later, Pitt and Fowler described the first 1,2 silyl shift in solution.[2] Thiyl radicals were shown to easily undergo an intramolecular homolytic substitution at silicon to form the corresponding silyl radicals [Eq. (2)]. A new radical allylation reagent based on this silyl migration (Si → S) was recently introduced.[3] The silyl migration from silicon to oxygen was reported to be a fast process [Eq. (3)].[4] Similar 1,2-silyl shifts from oxygen to nitrogen [Eq. (4)],[5] from carbon to nitrogen [Eq. (5)],[6] and from carbon to oxygen (radical Brook rearrangement)[7] were observed in solution. Very recently, Matsuda et al. suggested a radical ring-enlargement reaction based on a 1,2 silyl shift from carbon to carbon [Eq. (6)].[8]

Besides the 1,2 silyl shifts mentioned above, 1,3- (Scheme 2, [Eq. (7)]),[9] 1,4-,[10] and 1,5- ([Eq. (8)])[11] radical silyl migrations have also been observed. Even an intramolecular homolytic substitution has been reported.[12] Triplet-sensitized benzophenone was shown to react with hexamethyldisilane to form the corresponding ketyl radical [Eq. (9)]. Giese [Eq. (10)][13] and Utimoto[14] reported intramolecular homolytic substitution (S_Hi) reactions at tris(trimethylsilyl)-substituted Si atoms by C-centered radicals. Despite the various examples mentioned above, the homolytic substitution at silicon is still not well understood.[15]

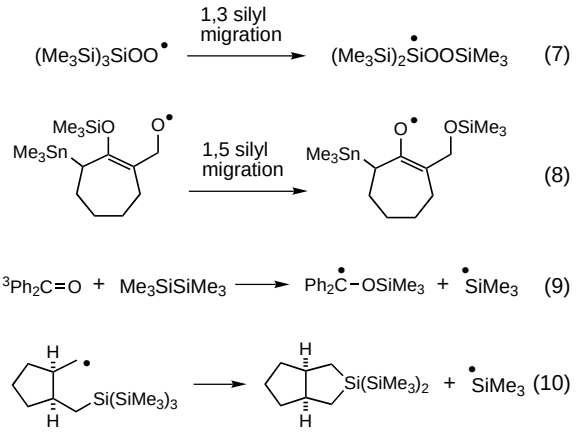


Scheme 1. Radical 1,2 silyl migrations.

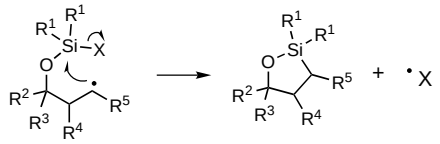
In a preliminary communication, we have recently introduced the S_Hi reaction at silicon using C-centered radicals in the γ position to diphenyl(trimethylstannyl)silyl ethers as an alternative method for the preparation of cyclic alkoxysilanes.[16] We have shown that the S_Hi reaction at silicon works best if a trimethylstannyl group is used as the leaving group ($X = SnMe_3$ in Scheme 3). Since the tin radical liberated is

[a] Dr. A. Studer, Dipl.-Chem. H. Steen
Laboratorium für Organische Chemie der
Eidgenössischen Technischen Hochschule, ETH-Zentrum
Universitätstrasse 16, CH-8092 Zürich (Switzerland)
Fax: (+41) 1-632-1144
E-mail: studer@org.chem.ethz.ch

  0947-6539/99/0502-0759 $ 17.50+.50/0



Scheme 2. Various homolytic substitution reactions at silicon.



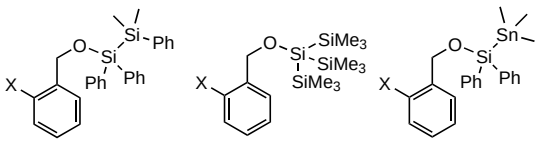
Scheme 3. S_Hi reaction at silicon: a general scheme.

able to propagate the chain by halogen abstraction we can consider this homolytic substitution at silicon as a unimolecular chain-transfer reaction (UMCT reaction).[17]

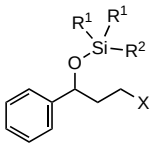
Herein we report in full detail[16] the scope and limitations of the S_Hi reaction at silicon to form cyclic five-membered alkoxysilanes. The effect of the substituents at silicon (R^1 and X in Scheme 3) and at the carbon backbone (R^2–R^5) on the cyclization reaction will be discussed. In addition, some stereoselective S_Hi reactions will also be reported.

Results and Discussion

We decided to first study the effect of the substituents at silicon (R^1 and X in Scheme 3) on the outcome of the S_Hi reaction. To this end, simple model compounds like *o*-halo-substituted benzylsilyl ethers **1**, **3**, and **5**, and their congeners **7**, **9**, **11**, and **13**–**15** were chosen. These model compounds and

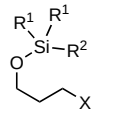


1 (X = Br) **3** (X = Br) **5** (X = I)
2 (X = H) **4** (X = H) **6** (X = H)



7-**13**

7 (X = I, R^1 = Ph, R^2 = $SnMe_3$)
8 (X = H, R^1 = Ph, R^2 = $SnMe_3$)
9 (X = I, R^1 = Ph, R^2 = $GeMe_3$)
10 (X = H, R^1 = Ph, R^2 = $GeMe_3$)
11 (X = I, R^1 = Ph, R^2 = $SiMe_3$)
12 (X = H, R^1 = Ph, R^2 = $SiMe_3$)
13 (X = I, R^1 = Me, R^2 = $SnMe_3$)



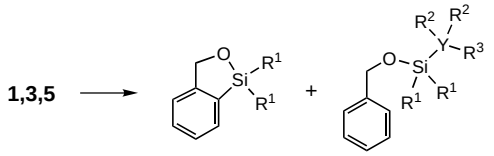
14,**15**

14 (X = I, R^1 = Ph, R^2 = $SnMe_3$)
15 (X = Br, R^1 = $SiMe_3$, R^2 = $SnMe_3$)

also their derived S_Hi products are of little preparative value; however, these initial experiments do allow us to gain information about the intrinsic reactivity of silicon in homolytic substitution reactions.

The silyl ether **1** was prepared, following known procedures,[18] from 1-chloro-2,2-dimethyl-1,1,2-triphenyldisilane and 2-bromobenzyl alcohol. Bromide **3** was obtained from chloro tris(trimethylsilyl)silane and 2-bromobenzyl alcohol (DMF, imidazole). Stannylated silyl ether **5** was synthesized from (chloro(diphenyl)silyl)trimethylstannane[19] and 2-iodobenzyl alcohol. The halides **7**, **9**, **11**, and **13**–**15** were prepared from 1-phenyl-3-iodo-1-propanol, 3-iodo-1-propanol, or 3-bromo-1-propanol and the corresponding silyl chlorides ($ClSiPh_2SnMe_3$,[19] $ClSiPh_2SiMe_3$,[20] $ClSiPh_2GeMe_3$,[21] $ClSiMe_2SnMe_3$,[22] and $ClSi(SiMe_3)_2SnMe_3$[23]) from standard procedures (see Experimental Section).

We first studied the S_Hi reaction of the aryl radicals derived from **1**, **3**, and **5** under various conditions (Scheme 4, Table 1). The reaction of **1** with 1.2 equivalents of $(Me_3Si)_3SiH$ afforded the reduction product **2** (43%) and only 5% of the desired cyclic silyl ether **16** (Table 1, entry 1). The Si–Si bond in **1** is probably too strong to be cleaved by aryl radicals.[24] With the tris(trimethylsilyl)-substituted silyl ether **3** slightly better results were obtained (entries 2 and 3). Slow addition of



16 (R^1 = Ph)
17 (R^1 = $SiMe_3$)

2,**4**,**6**

Scheme 4. S_Hi reaction with aryl radicals.

Abstract in German: *Einen neuen radikalchemischen Zugang zu cyclischen Silylethern bietet die intramolekulare homolytische Substitution (S_Hi Reaktion) an einem Siliciumzentrum. Verschiedene Abgangsgruppen wie $SiMe_3$, $GeMe_3$ und $SnMe_3$ wurden in der S_Hi Reaktion getestet, wobei mit der Stannylgruppe die besten Resultate erzielt wurden. Bei verschiedenen Systemen wurde die Geschwindigkeitskonstante der Cyclisierungsreaktion abgeschätzt. Basierend auf den Ergebnissen dieser Kinetikexperimente wurden komplexere Reaktionssequenzen, die eine Additionsreaktion mit anschliessender S_Hi Reaktion beinhalten, untersucht. Es wurde auch gezeigt, dass die Cyclisierung stereoselektiv abläuft. Die Produkte der S_Hi Reaktion konnten mittels Tamao–Fleming Oxidation in die entsprechenden Diol-Derivate umgesetzt werden.*

0947-6539/99/0502-0760 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 2

Table 1. S_Hi reaction of aryl radicals at silicon bearing different substituents under various conditions.

	Starting material	Conditions	Unreacted material [%][a]	Yield [%] (product)[a]	Yield [%] (side product)[a]
1	**1**	1.2 equiv $(TMS)_3SiH$, PhH 0.04 M AIBN, reflux	–	5 (**16**)	43 (**2**)
2	**3**	0.2 equiv Bu_3SnH, PhH 0.04 M, AIBN reflux, syring pump[b]	42	58 (**17**)	–
3	**3**	0.2 equiv Bu_3SnH, PhH 0.04 M, AIBN, reflux	–	91 (**17**)	4 (**4**)
4	**3**	0.2 equiv $(TMS)_3SiH$, PhH 0.04 M AIBN (25 %), reflux, syringe pump[c]	60	30 (**17**)	–
5	**3**	$Bu_3SnSnBu_3$ (10 %), PhH 0.1 M, acetone, *hν*, 72 hours	91	9 (**17**)	–
6	**3**	$Bu_3SnSnBu_3$ (10 %), PhH 0.1 M hexane, acetone, *hν*, 45 hours	89	11 (**17**)	
7	**5**	0.2 equiv Bu_3SnH, PhH 0.04 M AIBN, reflux		80 (68), (**16**)	

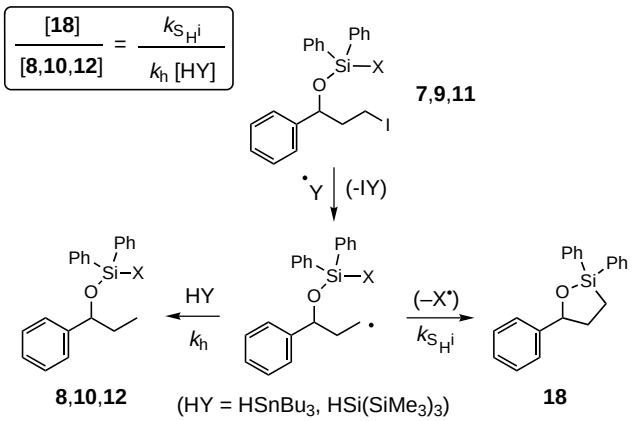
[a] Yields were determined by ^1H NMR analysis. Yield in brackets (entry 7) refers to isolated yield. [b] Tin hydride was added as a benzene solution (0.08 M) containing AIBN over 7 hours. [c] $(TMS)_3SiH$ was added as a benzene solution (0.13 M) containing AIBN over 8 hours.

Bu_3SnH (0.2 equiv) to a solution of **3** in benzene (0.04 M) afforded the S_Hi product **17** and starting material **3** in a ratio of 58:42. No other side product was detected. This clearly showed that the UMCT was occurring. However, in order to get quantitative consumption of the starting material it was necessary to use up to 0.5 equivalents of initiator. As side product, the reduced (dehalogenated) silyl ether **4** was formed in 4 % yield. Even worse results were obtained by use of other initiation methods (entries 4–6). We also found that the reaction works better if benzene is replaced by hexane as the solvent (compare entries 5 and 6). This is probably due to the fact that silyl radicals add to benzene and are thus prevented from propagating the chain.[25]

With the stannylated silyl ether **5**, addition of only 0.2 equivalents of initiator (Bu_3SnH) lead to quantitative conversion. No reduction product **6** was observed and the alkoxysilane was isolated in 68 % yield (entry 7). From these studies we concluded that the Si–Sn bond is superior to the Si–Si bond for conducting homolytic substitutions at silicon.[26] We have also shown that if the silicon atom is suitably substituted (additional Me_3Si groups) the homolytic substitution becomes feasible with disilanes (see also the results of Giese[13] and Utimoto[14]). In order to quantify the substitution effect at silicon on the cyclization reaction we next estimated some rate constants.

The various rate constants were estimated by conducting standard-competition kinetic studies,[27] with the appropriately calibrated hydrogen donor as exemplified in Scheme 5 for the compounds **7**, **9**, and **11** (variation of the leaving group). All reactions were conducted at $80 \pm 3\,^{\circ}C$ at different concentrations in benzene[28] in sealed tubes, generally under pseudo-first-order conditions (large excess of hydrogen donor). The ratio of the cyclized product **18** to the corresponding reduced product **8**, **10**, or **12** (authentic samples were also prepared) was determined by ^1H NMR integration of the H resonances of the benzylic hydrogen atoms, which are well separated (about 0.2 ppm) for the two products.[29] In Table 2, two sets of experiments are presented as examples. All the other rate constants discussed in the present paper were estimated in a similar way (see Experimental Section). In cases where the cyclization reaction is slow, the kinetic experiments were conducted under second order conditions. In these experiments the average hydrogen donor concentration was estimated as its concentration at 50 % conversion. Therefore those rate constants should be considered as estimates. For the germylated derivative **9** (second order conditions) we also calculated the rate constant with the more elaborate iterative process proposed by Newcomb.[27] However, it turned out that similar rates were obtained with this more accurate procedure showing that the error introduced by simplifying the analysis is not very significant.

As expected from the results described above (aryl radicals), the S_Hi reaction works best for trimethylstannylated silyl ethers. Thus, for the primary radical derived from **7** a rate contstant



Scheme 5. Representative competition experiments.

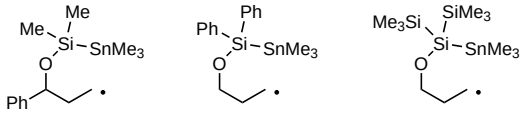
Table 2. Determination of the rate constant for the S_Hi reaction of the radicals derived from **7** and **9**.

X	YH	[**7**,**9**]	[YH]	[**18**]/[**8**,**10**]	k_{S_Hi} [s^{-1}]
$SnMe_3$	$(Me_3Si)_3SiH$	0.054	0.586	1.73	1.2×10^6
$SnMe_3$	$(Me_3Si)_3SiH$	0.047	0.560	1.81	1.2×10^6
$SnMe_3$	$(Me_3Si)_3SiH$	0.047	0.464	2.18	1.2×10^6
$GeMe_3$	Bu_3SnH	0.049	0.027	0.08	1.4×10^4
$GeMe_3$	Bu_3SnH	0.047	0.032	0.11	2.3×10^4
$GeMe_3$	Bu_3SnH	0.040	0.026	0.06	1.0×10^4

k_{S_Hi} of $1 \times 10^6\ s^{-1}$ was estimated for the cyclization reaction. With the trimethylgermyl radical as the leaving group (from **9**) a decrease of the rate by two orders of magnitude was observed ($k_{S_Hi} = 2 \times 10^4\ s^{-1}$). For the disilane **11** an even smaller rate was estimated ($k_{S_Hi} \approx 10^3 - 10^4\ s^{-1}$). So far, we do not fully understand the large increase of the rate for the S_Hi reaction in going from the disilane and the germylated silane to the stannylated derivative. A possible explanation could be a correlation of the bond dissociation energy (BDE) of the Si–X bond with the rate of the homolytic substitution reaction at silicon. However, since no accurate BDEs of silicon with

heavier Group 4 elements are reported in the literature, this correlation remains to be proven.

We then studied the effect on the rate of the cyclization reaction of those substituents at silicon that are not directly involved in the S_Hi reaction (R^1 in Scheme 3). As already mentioned above, the radical generated from **7** cyclizes at 80 °C with a rate constant of $1 \times 10^6\ s^{-1}$ (see Table 2). By replacing the two phenyls at silicon with two methyl groups a decrease of the rate was observed. Thus, a rate of $1 \times 10^5\ s^{-1}$ was estimated for the cyclization of radical **19** derived from **13**. Unfortunately, we were not able to prepare a radical

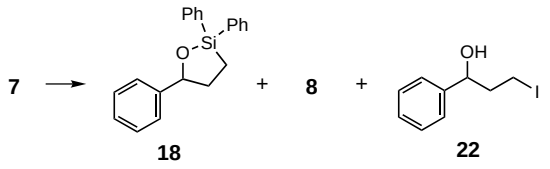


19 (from **13**) k_{S_Hi} 1 x $10^5\ s^{-1}$ **20** (from **14**) k_{S_Hi} 2 x $10^5\ s^{-1}$ **21** (from **15**) k_{S_Hi} 2 x $10^6\ s^{-1}$

precursor analoguous to **7** in which the silicon bears two additional trimethylsilyl groups instead of the phenyl substituents. The corresponding iodide as well as the bromide turned out to be too unstable for conducting kinetic experiments. We therefore switched to the more stable[30] silyl ethers derived from primary alcohols. For radical **20** derived from **14** a rate of $2 \times 10^5\ s^{-1}$ was estimated for the S_Hi reaction. As expected from the reactions with the aryl radicals (see above) the replacement of the phenyl groups at silicon with trimethylsilyl groups leads to an increase of the rate constant for the cyclization reaction. Radical **21** generated from **15** cyclizes about one order of magnitude faster ($2 \times 10^6\ s^{-1}$) than **20**.

Interestingly, similar substitution effects on the rate constant for the bimolecular reaction of various radicals with silicon hydrides have already been observed.[31] Furthermore, replacement of alkyl groups at silicon with phenyl groups causes a small increase of the rate constant for the hydrogen transfer (reduction). The tris(trimethylsilyl)-substituted silicon hydride ($(Me_3Si)_3SiH$) was shown to be an even better hydrogen donor. In fact, it is now often used as a substitute for the toxic tin hydride in radical chain reactions.[32] The reasons for the observed rate enhancement of the S_Hi reaction by replacing alkyl substituents at silicon with silyl groups are not entirely understood. We believe that as for the silicon hydrides, in which a decrease of the BDE of the Si–H bond was observed upon replacing alkyl by silyl groups, a decrease of the BDE of the Si–Sn bond may lead to the rate enhancement of the S_Hi reaction.

Based on these kinetic measurements we decided to use the relatively easily available diphenyl(trimethylstannylated)silyl ethers for our further studies on the S_Hi reaction at silicon.[33] In order to optimize the reaction conditions for preparative UMCT chemistry the reaction with the primary iodide **7** was studied using different initiation methods (Scheme 6, Table 3). Under atom-transfer conditions,[34] irradiation (300 W sun lamp) of a benzene solution of **7** (0.1 M) containing hexabutylditin (0.1 equiv) lead to complete consumption of the starting material after sixteen hours (Table 3, entry 1).



Scheme 6. UMCT reaction with the primary iodide **7**.

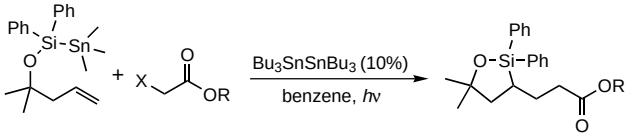
Table 3. UMCT reaction of **7** under different conditions.

	Conditions	Yield of **18** [%][a]	Yield of **8** [%][a]	Yield of **22** [%][a]
1	$Bu_3SnSnBu_3$ (10%), PhH, 0.06 M, *hν*, 16 hours	87	13	–
2	PhH, 0.1 M, *hν*, 36 hours	30[b]	–	16
3	$Ph_3SnSnPh_3$ (10%), PhH, 0.1 M, *hν*, 24 hours	45	–	21
4	$(TMS)_4Si$ (10%), PhH, 0.1 M, *hν*, 24 hours	41	–	23
5	Bu_3SnH (15%), AIBN, PhH	89	4	–
6	Bu_3SnH (5%), AIBN, PhH	84	2	–

[a] Yields were determined by ^1H NMR analysis. [b] Reaction was stopped after 36 hours, 16% of remaining starting material was observed.

Besides alkoxysilane **18** (87%, 66% after chromatography), the reduced silyl ether **8** (13%) was observed in the crude product. Hexabutylditin probably acts as the hydrogen source in the formation of **8**. Therefore, the reaction was conducted without addition of the ditin compound under otherwise similar conditions. Indeed, reduction product **8** could no longer be observed (entry 2). However, the reaction was much slower and the desilylated alcohol **22** was formed as a side product. Similar results were obtained when the reaction was conducted under atom-transfer conditions with either hexaphenylditin (entry 3) or tetrakis(trimethylsilyl)silane[17b] (entry 4) as additives. The best results were obtained with Bu_3SnH as the initiator of the reaction (entries 5 and 6).

Since the UMCT reactions can be conducted in the absence of good hydrogen donors (atom-transfer conditions), this chemistry should be specially suited for studying slow bimolecular addition reactions. To this end, the radical acceptor **23** was prepared as described above from the corresponding homoallylic alcohol. Irradiation of a solution of olefin **23** in benzene (0.3 M) in the presence of $Bu_3SnSnBu_3$ (0.1 equiv) and phenyl bromoacetate (1.2 equiv) for sixteen hours afforded cyclic silyl ether **24** in a very clean reaction (Scheme 7). In the crude reaction mixture, neither starting material nor side products derived from **23** could be identified. Partial product decomposition was observed during purification (chromatography, SiO_2). Similar results were obtained for the reaction with ethyl iodoacetate. If the



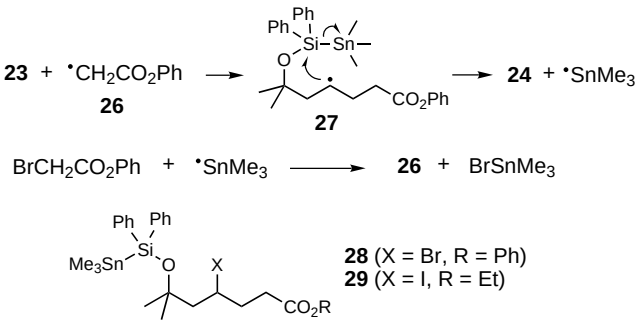
23 (X = Br, R = Ph) (X = I, R = Et) **24** (68%, R = Ph) **25** (56%, R = Et)

Scheme 7. Slow bimolecular addition reactions with a subsequent UMCT step.

0947-6539/99/0502-0762 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 2

reaction (with $BrCH_2CO_2Ph$) was conducted under tin hydride conditions (1 equiv Bu_3SnH, syringe pump 6 hours, benzene 0.2 M) only 26% of **24** was formed. The main component in the reaction mixture (70%) was unreacted olefin **23**. Thus, the photochemical initiation is superior to the tin hydride initiation for conducting slow bimolecular reactions.

In Scheme 8, the suggested mechanism for the reaction of phenyl bromoacetate with **23** is shown. Irradiation (sun lamp

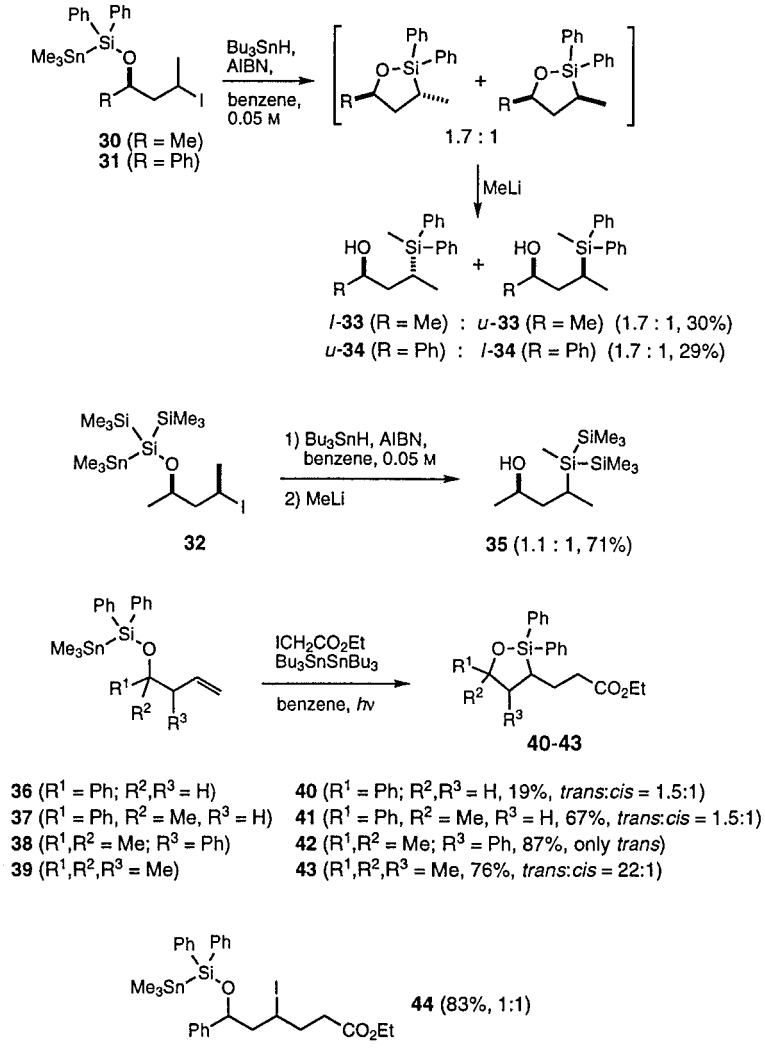


Scheme 8. Suggested mechanism for the reaction of phenyl bromoacetate with **23**.

300 W) of the bromide generates radical **26**, which reacts with acceptor **23** to form the secondary radical **27**. The intermediate **27** then undergoes fast intramolecular S_Hi reaction to afford **24** and the chain-carrying stannyl radical. In the reaction of ethyl iodoacetate, however, analysis of an aliquot of the reaction mixture taken after 90 minutes indicated the formation of iodine-transfer product **29**, together with **25** and starting iodide. Further irradiation of **29** eventually leads to the cyclic alkoxysilane **25**. In a control experiment, the reaction was stopped after three hours. The iodine-transfer product **29** was isolated in 63% yield. In the reaction with phenyl bromoacetate, the corresponding atom-transfer product **28** was not observed at any point of the reaction. In these reactions, in contrast to bromine transfer, iodine transfer is faster than the S_Hi reaction at silicon.[35] The ditin compound is added to scavenge the halogen atom generated during the initial bond homolysis.[34]

Stereoselective S_Hi reactions at silicon were studied next. The racemic silyl ethers **30**–**32** with an additional chirality center and racemic **36**–**39** were prepared from the corresponding alcohols as described in the Experimental Section.[36] We found that the photochemical initiation is very inefficient for slow-cyclizing systems. The secondary iodides **30** and **31** could not be transformed to the cyclic alkoxysilanes under atom-transfer conditions. Starting material was recovered after prolonged irradiation. However, slow addition of Bu_3SnH to a solution of **30** (mixture of diastereoisomers *l*:*u* = 7:3) in benzene (0.1 M) afforded the desired S_Hi product (*trans*:*cis* = 1.7:1) in moderate yield. Due to the instability of the cyclic alkoxysilane, we directly treated the S_Hi product with methyl lithium (MeLi) to afford the secondary alcohol **33**, which could be isolated in 30% yield as a 1.7:1 (*l*:*u*) mixture of diastereoisomers (Scheme 9).[37]

The size of the substituent at the stereogenic center has no significant effect on the selectivity. With the phenyl-substituted silyl ether **31** the same selectivity was observed. The ring-opened product **34** was isolated in 29% yield (*u*:*l* = 1.7:1). From the kinetic experiments discussed above we knew that upon replacing the two phenyl substituents at silicon with trimethylsilyl groups the rate of the S_Hi reaction increases.



Scheme 9. Stereoselective cyclization reactions.

Indeed, treatment of trisilane **32** (*like* isomer) under identical conditions provided, after MeLi treatment, alcohol **35** in 71% yield, but with no stereoselectively (1.1:1).

We also studied radical addition reactions with a subsequent stereoselective UMCT step. Reaction of homoallylic silyl ether **36** with ethyl iodoacetate ($Bu_3SnSnBu_3$, 50–60 °C, benzene, *hv*, 16 hours) did not lead to the desired S_Hi product. The iodine-transfer product **44** was isolated in 83% yield as a 1:1 mixture of diastereoisomers. At higher temperatures (>100 °C),[38] iodide **44** was slowly converted to the cyclic alkoxysilane **40**. Under these conditions, however, the formation of unidentified side products was observed. The S_Hi product **40** was isolated in only 19% yield as a 1.5:1 mixture of isomers (*trans*:*cis*).

With silyl ether **37**, derived from a tertiary alcohol, the analoguous reaction occurred smoothly at lower temperatures (50–60 °C). Alkoxysilane **41** was obtained with low selectivity (*trans*:*cis* = 1.5:1) in 67% isolated yield. The diastereoisomers could be separated by preparative HPLC. The relative configuration of the minor isomer was assigned by NOE experiments, whereas for the major isomer an X-ray crystal structure could be determined.[39] We also tried to increase the selectivity by lowering the reaction temperature. Irradiation of **37** and ethyl iodoacetate in CH_2Cl_2 (0.25 M) in the presence of $Bu_3SnSnBu_3$ (0.1 equiv) for 72 hours at −13 °C afforded **41** in 14% yield with a slightly higher selectivity (2.7:1). The main product observed, however, was the corresponding iodine-transfer product (no selectivity, 61% yield).

Excellent selectivities were obtained for the reaction of silyl ether **38** with ethyl iodoacetate. The S_Hi product **42** was isolated in 87% yield as a single isomer. In the cyclization reaction only the *trans* product was formed, the relative configuration of which was assigned by NOE experiments. Interestingly, the iodine-transfer product, an intermediate in this radical sequence analoguous to **44**, was formed with no selectivity. With **39** lower, but still good, selectivity (*trans*:*cis* = 22:1) was observed (76% yield).

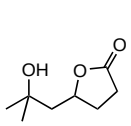
To summarize the outcome of the stereoselectivity studies we can state that generally low 1,3 diastereoselectivities are observed (→**33**–**35**, **40**, **41**), whereas high 1,2 steroselectivities (→**42**, **43**) are easily obtained. To our knowledge, these are the first examples of such high stereocontrol in these types of homolytic substitution reactions. It is also important to note that in going from silyl ethers derived from tertiary alcohols to the corresponding ethers derived from secondary ones, a decrease in the S_Hi reactivity was observed. In order to quantify that substitution effect some rate constants for the S_Hi reaction of radicals with different substitution patterns were estimated (variation of R^2–R^5 in Scheme 3).

The radical precursors **45**–**47** were prepared from the corresponding alcohols by standard procedures.[19] As already mentioned, the primary radical **20** derived from **14** cyclizes with a rate of $2 \times 10^5\ s^{-1}$. An increase of the rate by one order of magnitude was observed in going to the silyl ether **45** derived from a secondary alcohol (one additional methyl substituent: $k_{S_Hi} = 1 \times 10^6\ s^{-1}$). An even higher rate ($1 \times 10^7\ s^{-1}$) was estimated for the cyclization of the radical derived from **46**.

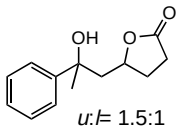
The acceleration of the cyclization reaction observed upon adding methyl substituents in the reacting molecule is a nice example of the so-called *gem*-dimethyl effect (Thorpe–Ingold), which has been previously observed in nonradical[40] as well as in radical chemistry.[41] A large decrease in the S_Hi reactivity was noticed upon switching from a primary to a secondary radical. The radical generated from **47** cyclizes about two orders of magnitude slower than its primary analogue ($9 \times 10^4\ s^{-1}$). The estimated rate constants are in full aggreement with the outcome of the stereoselectivity studies discussed above, in which high yields for the cyclization reactions have only been obtained for systems bearing two substituents next to the oxygen atom (Thorpe–Ingold, see **37**–**39**).

We also looked at the effect of different Lewis acids on the rate of the homolytic substitution. The silyl ether **14** was chosen as substrate in these investigations. With the bulky aluminum tris(2,6-diphenylphenoxide) [ATPH, 2 equiv, toluene, Bu_3SnH] as additive, which has been successfully used by Maruoka for increasing the rate of radical cyclization reactions,[42] no S_Hi reaction occurred. Only the reduction product was observed in the crude reaction mixture. The same result was obtained when trimethylaluminum (2 equiv) was added as Lewis acid. The addition of 2 equivalents of LiBr[43] lead to a small decrease of the rate constant for the cyclization of the primary radical derived from **14** (without LiBr: $2 \times 10^5\ s^{-1}$; with LiBr: $8 \times 10^4\ s^{-1}$). Thus, Lewis acids have a detrimental effect on the homolytic substitution reactions.

To further demonstrate the preparative value of the S_Hi reaction at silicon, the alkoxysilanes or their ring-opened products were transformed by Tamao–Fleming oxidation[44] to the corresponding diol derivatives. Cyclic silyl ethers **24** and **25** were oxidized following established procedures (H_2O_2, KF, $KHCO_3$, MeOH, THF, 40 °C).[18] Acidification after standard workup provided lactone **48**, which was isolated in good yields (71,72%). Oxidation of **41**–**43** under similar conditions

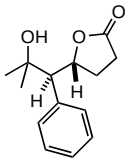


48
(71% from **24**)
(72% from **25**)

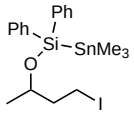


u:*l* = 1.5:1

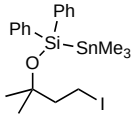
49
(83% from **41**)



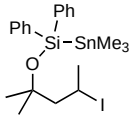
50
(97% from **42**)



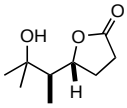
45
k_{S_Hi} = 1 x 10^6 s^{-1}



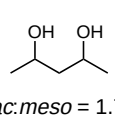
46
k_{S_Hi} = 1 x 10^7 s^{-1}



47
k_{S_Hi} = 9 x 10^4 s^{-1}



51
(57% from **43**)



rac:*meso* = 1.7:1

52
(50% from **33**)

0947-6539/99/0502-0764 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 2

provided the corresponding lactones **49**–**51**. Hydroxysilane **33** (1.7:1 diastereosiomeric mixture) was stereospecifically transformed in 50% overall yield to 3-hydroxy-2-pentanol (**52**, *rac*:*meso* = 1.7:1) from a procedure recently introduced.[45]

Conclusions

With the intramolecular homolytic substitution at silicon, a new, powerful, mild method for the formation of cyclic five-membered alkoxysilanes[46] has been uncovered. The results obtained from the study of various rate constants for different cyclization reactions (S_Hi reactions at silicon) allow us now to predict general reactivity trends of silicon towards homolytic substitution reactions. In general, good results are only obtained if stannylated silanes with weak easily cleavable Si–Sn bonds are used as substrates. Since a tin radical is liberated in these reactions, we can consider this process as a unimolecular chain-transfer reaction. In various examples, Curran has demonstrated the advantages of UMCT reactions over tin-hydride-mediated radical reactions.[17a–d] In the present paper we have pointed out the importance of this new principle for conducting slow radical reactions difficult to run under conventional tin hydride conditions. In addition, in contrast to the tin-hydride-conducted radical reactions in which the final radical is reduced, in the present method the final step is a carbon–heteroatom bond formation.

We have also shown that the substituents at silicon not directly involved in the cyclization reaction (R^1 in Scheme 3) influence the S_Hi reactivity. Analogous to the reactivity of silicon hydrides in hydrogen-transfer reactions, the best results were obtained when the reacting silicon atom bears additional trimethylsilyl groups. Another important issue is the so-called *gem*-dimethyl effect that also operates in the S_Hi reaction and which should be considered in synthetic planning.

During the last fifteen years, stereoselective radical reactions have become more and more important.[47] Here we have shown that in the S_Hi reaction, excellent 1,2 diastereoselectivity may be obtained. Finally, we must point out that the products obtained in the cyclization reaction are easily converted to the corresponding diol derivatives, a synthetically important class of compounds, by Tamao–Fleming oxidation.[44]

Experimental Section

General: TLC: Merck silica gel 60 F_{254} plates; detection with UV or dipping into a solution of $KMnO_4$ (1.5 g in 333 mL 1M NaOH) or a solution of $Ce(SO_4)_2 \cdot H_2O$ (10 g), phosphormolybdic acid hydrate (25 g), conc. H_2SO_4 (60 mL), and H_2O (940 mL), followed by heating. Flash chromatography (FC): Fluka silica gel 60 (40–63 μm); at c.a. 0.3 bar. Preparative HPLC: Knauer HPLC system (pump type 64, UV detector (variable-wavelength monitor)), Macherey-Nagel C_{18}-column (Nucleosil 7 C18, VP 250/21) or a Chiracel OD column (DAICEL CHEMICAL INDUSTRIES, 422-707-40513). Melting points: Büchi-510 apparatus; uncorrected. I.R. Spectra: Perkin–Elmer 782 spectrophotometer (s = strong, m = medium, w = weak). NMR Spectra: Bruker AMX 500 (^{1}H 500 MHz, ^{13}C 125 MHz), AMX 400 (^{1}H 400 MHz, ^{13}C 100 MHz), ARX 300 (^{1}H 300 MHz), Varian Gemini 300 (^{1}H 300 MHz, ^{13}C 75 MHz), or Gemini 200 (^{1}H 200 MHz, ^{13}C 50 MHz); chemical shifts (δ) in ppm relative to $SiMe_4$ ($\delta = 0$ ppm); Mass Spectra: VG Tribrid (EI) in *m*/*z* (% of basis peak). For tin-containing compounds, only the peaks of the ^{120}Sn isotope will be listed. In the case of the germanium compounds only the peaks of the ^{74}Ge isotope are presented. Elemental analyses were performed by the Microanalytical Laboratory of the Laboratorium für Organische Chemie, ETH-Zürich. All irradiation experiments were carried out in sealed tubes (pyrex glas) with a 300 W sun lamp (OSRAM 300 W standard lamp, clear, distance lamp to the sealed tube around 15 cm). Tetrahydrofuran (THF) and benzene (PhH) were freshly destilled from sodium/benzophenone.

2-Bromobenzyl-2,2-dimethyl-1,1,2-triphenyldisilyl ether (**1**): Chloro-2,2-dimethyl-1,1,2-triphenyldisilane[20] (0.53g, 1.50 mmol) was dissolved under Ar in DMF (2 mL). 2-Bromobenzyl alcohol (281 mg, 1.50 mmol) was added followed by imidazole (154 mg, 2.25 mmol). After stirring at RT for 45 min Et_2O was added and the solution was washed with saturated aqueous NH_4Cl and brine. The organic phase was dried ($MgSO_4$) and evaporated to yield the crude product. Purification by FC (Et_2O/pentane 1:60) yielded **1** (597 mg, 78%). IR ($CHCl_3$): $\tilde{\nu} = 3053$ (m), 3008 (m), 1427 (s), 1107 (s), 1086 (s), 1026 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.52-7.21$ (m, 18H; aromatic), 7.12–7.08 (m, 1H; aromatic), 4.76 (s, 2H; CH_2O), 0.47 (s, 6H; CH_3Si); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 139.84$ (C), 137.85 (C), 135.70 (C), 134.73 (CH), 134.30 (CH), 131.98 (CH), 129.72 (CH), 128.80 (CH), 128.21 (CH), 127.98 (CH), 127.83 (CH), 127.75 (CH), 127.29 (CH), 121.10 (C), 65.68 (CH_2), −2.92 (2CH_3); EI MS: *m*/*z* (%): 489.1 (3) [M^+(^{81}Br) − CH_3], 369.0 (32), 333.1 (100), 255.0 (83), 211.0 (23), 183.0 (27), 168.9 (26); $C_{27}H_{27}OSi_2Br$ (503.6): calcd C 64.49, H 5.40; found C 64.39, H 5.56.

2-Bromobenzyltris(trimethylsilyl)silyl ether (**3**): 2-Bromobenzyl alcohol (561 mg, 3.00 mmol) was dissolved under Ar in DMF (5 mL) and cooled to 0 °C. Slow addition of a solution $ClSi(SiMe_3)_3$ [3 mmol, prepared by stirring of $HSi(SiMe_3)_3$ (0.93 mL, 3.00 mmol) in CCl_4 (15 mL) for 12 hours] in DMF (3 mL) at 0 °C. After removal of the ice bath the reaction mixture was stirred at RT for 30 min. Workup as described above for **1** and purification by FC (Et_2O/pentane 1:60) yielded **3** (1.14 g, 87%). IR ($CHCl_3$): $\tilde{\nu} = 2950$ (m), 2893 (w), 1084 (m), 840 cm^{-1} (s); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 7.51–7.47 (m, 2H; aromatic), 7.37–7.30 (m, 1H; aromatic), 7.16–7.08 (m, 1H; aromatic), 4.61 (s, 2H; CH_2O), 0.23 (s, 6H; CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 140.82$ (C), 132.13 (CH), 128.34 (CH), 127.53 (CH), 127.42 (CH), 121.00 (C), 69.41 (CH_2), 24.70 (3CH_3); EI MS: *m*/*z* (%): 419.0 (1) [M^+(^{81}Br) − CH_3], 361.0 (3) [M^+(^{81}Br) − $Si(CH_3)_3$], 263.1 (100), 248.1 (25), 175.1 (93), 131.1 (42), 117.1 (38); $C_{16}H_{33}OSi_4Br$ (433.7): calcd C 44.31, H 7.67; found C 44.48, H 7.88.

General procedure 1 for the silylation of alcohols (**GP 1**): The chlorosilane was dissolved under Ar in Et_2O or THF. The solution was cooled to 0 °C and NEt_3 was added. A solution of the alcohol in Et_2O/THF was added over 3 min. DMAP was added and the suspension formed was stirred for the given time. Addition of hexane and filtration of the solid, after evaporation of the solvent, gave the crude product, which was purified either by distillation or flash chromatography (SiO_2).

[(2-Iodobenzyloxy)diphenylsilyl]trimethylstannane (**5**): Compound **5** was prepared by the use of GP 1 with (chlorodiphenylsilyl)trimethylstannane[19] (762 mg, 2.00 mmol), Et_2O (8 mL + 4 mL), 2-iodobenzyl alcohol (514 mg, 2.20 mmol), and NEt_3 (0.32 mL, 2.30 mmol), and a reaction time of 45 min at 0 °C (without DMAP). Purification by distillation (bulb to bulb, 150–160 °C, 0.07 Torr): 484 mg (78%). M.p. 48–48.5 °C; IR ($CHCl_3$): $\tilde{\nu} = 3008$ (m), 2909 (w), 1428 (s), 1110 (s), 1083 (s), 1013 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.78$ (dd, $J_1 = 7.9$ Hz, $J_2 = 1.2$ Hz, 1H; aromatic), 7.60–7.52 (m, 5H; aromatic), 7.44–7.31 (m, 7H; aromatic), 6.99–6.94 (m, 1H; aromatic), 4.76 (s, 2H; CH_2O), 0.19 (s, 9H; $J_{SnH} = 47.2$ Hz, 49.3 Hz, $Sn(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 142.06$ (C), 138.78 (CH), 136.92 (C), 134.25 (CH), 129.90 (CH), 128.79 (CH), 128.22 (CH), 128.18 (CH), 127.65 (CH), 95.99 (C), 71.16 (CH_2); −10.38 (3 CH_3); EI MS: *m*/*z* (%): 565.0 (2) [$M^+ - CH_3$], 415.0 (100) [$M^+ - Sn(CH_3)_3$], 217.0 (21), 211.1 (23); $C_{22}H_{25}OSiSnI$ (579.1): calcd C 45.63, H 4.35; found C 45.87, H 4.23.

[(3-Iodo-1-phenylpropan-1-oxy)diphenylsilyl]trimethylstannane (**7**): This compound was prepared by the use of GP 1 with (chlorodiphenylsilyl)-trimethylstannane[19] (571 mg, 1.50 mmol), Et_2O (5 mL + 2 mL), 3-iodo-1-phenyl-1-propanol (445 mg, 1.70 mmol), NEt_3 (0.25 mL, 1.79 mmol), and DMAP (36 mg), and a reaction time of 45 min at 0 °C. Purification by FC (Et_2O/pentane 1:200): 820 mg (62%). IR ($CHCl_3$): $\tilde{\nu} = 3069$ (m), 3007 (m),

1428 (s), 1107 (s), 1084 (s), 1067 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.66 – 7.19 (m, 15H; aromatic), 4.78 (dd, $J_1 = 7.1$ Hz, $J_2 = 5.0$ Hz, 1H; HCO), 3.47 – 3.06 (m, 1H), 3.03 – 2.97 (m, 1H), 2.36 – 2.26 (m, 1H), 2.19 – 2,11 (m, 1H), – 0.02 (s, 9H; $J_{SnH} = 47.0$ Hz, 49.2 Hz, $Sn(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 142.78$ (C), 137.27 (C), 137.18 (C), 134.76 (CH), 134.23 (CH), 129.99 (CH), 129.62 (CH), 128.46 (CH), 128.17 (CH), 127.95 (CH), 127.75 (CH), 126.18 (CH), 76.74 (CH), 44.44 (CH_2), 2.00 (CH_2), – 10.40 (3 CH_3); EI MS: *m/z* (%): 593.0 (7) [$M^+ - CH_3$], 443.1 (86) [$M^+ - Sn(CH_3)_3$], 415.1 (100), 309.1 (87), 167.1 (57); $C_{24}H_{29}OSiSnI$ (607.2): calcd C 47.47, H 4.81; found C 47.57, H 4.76.

[(1-Phenylpropan-1-oxy)diphenylsilyl]trimethylstannane (**8**): This compound was prepared by the use of GP 1 with (chlorodiphenylsilyl)trimethylstannane[19] (191 mg, 0.50 mmol), Et_2O (2 mL + 1 mL), 1-phenyl-1-propanol (0.1 mL, 0.7 mmol), NEt_3 (0.1 mL, 0.7 mmol), and DMAP (15 mg), and a reaction time of 60 min at RT. Purification by FC (Et_2O/pentane 1:100): 194 mg (81%). IR ($CHCl_3$): $\tilde{\nu} = 3068$ (m), 3007 (m), 2976 (m), 1428 (s), 1103 (s), 1053 (s), 1010 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.54 – 7.17 (m, 15H; aromatic), 4.65 (t, $J = 6.1$ Hz, 1H; HCO), 1.87 – 1.77 (m, 1H), 1.76 – 1.67 (m, 1H), 0.79 (t, $J = 7.4$ Hz, 3H; CH_3), 0.00 (s, 9H; $J_{SnH} = 46.7$ Hz, 48.8 Hz, $Sn(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 144.13 (C), 137.74 (C), 137.70 (C), 134.62 (CH), 134.23 (CH), 129.73 (CH), 129.46 (CH), 128.10 (CH), 128.00 (CH), 127.86 (CH), 127.16 (CH), 126.30 (CH), 78.22 (CH), 33.32 (CH_2), 9.73 (CH_3), – 10.44 (3 CH_3); EI MS: *m/z* (%): 467.2 (2) [$M^+ - CH_3$], 317.2 (6) [$M^+ - Sn(CH_3)_3$], 199.1 (100), 119.1 (13); $C_{24}H_{30}OSiSn$ (481.3): calcd C 59.89, H 6.28; found C 60.05, H 6.32.

(Chlorodiphenylsilyl)trimethylgermane: *N,N*-Diethylaminochlorodiphenylsilane[20] (8.63 g, 30.0 mmol) was added to lithium wire (833 mg, 120 mmol) in THF (30 mL) as described in ref. [20]. The resulting lithium silanide was slowly added to a solution of bromotrimethylgermane (3.85 g, 30.0 mmol) in THF (30 mL) at 0 °C. The solution was stirred at 0 °C for 2.5 h. After evaporation of the solvent under reduced pressure the residue was treated under Ar with dry hexane and was filtered. Removal of the solvents and purification by distillation (0.02 Torr, 115 °C) yielded the germylated aminosilane (7.8 g, 70%). The aminosilane (7.8 g, 21.0 mmol) was dissolved under Ar in CH_2Cl_2 (23 mL) at 0 °C and was treated with acetyl chloride (1.82 mL, 25.6 mmol). After stirring for 1 h the solvent was removed and the residue distilled (0.02 Torr, 109 – 110 °C) to afford the (chlorodiphenylsilyl)trimethylgermane (5.9 g, 59%). IR ($CHCl_3$): $\tilde{\nu} = 3067$ (m), 2974 (m), 2903 (m), 1482 (m), 1431 (s), 1107 (s), 831 cm^{-1} (s); ^1H NMR (400 MHz): $\delta =$ 7.59 – 7.57 (m, 4H; aromatic), 7.45 – 7.39 (m, 6H; aromatic), 0.36 (s, 9H; $Ge(CH_3)_3$); ^{13}C NMR (100 MHz): $\delta = 134.63$ (C), 134.27 (C), 130.24 (CH), 128.21 (CH), – 2.56 (CH_3); EI MS: *m/z* (%): 336.0 (4) [M^+], 321.0 (3) [$M^+ - CH_3$], 217.0 (28), 197.0 (100), 181.0 (13), 249.0 (56), 119.0 (15); $C_{15}H_{19}SiGeCl$ (335.5): calcd C 53.71, H 5.71; found C 53.86, H 5.50.

[(3-Iodo-1-phenylpropan-1-oxy)diphenylsilyl]trimethylgermane (**9**): This compound was prepared by the use of GP 1 with (chlorodiphenylsilyl)-trimethylgermane (600 mg, 1.80 mmol), THF (8 mL + 2 mL), 3-iodo-1-phenyl-1-propanol (576 mg, 2.20 mmol), NEt_3 (0.32 mL, 2.30 mmol), and DMAP (30 mg), and a reaction time of 12 h at RT. Purification by FC (Et_2O/pentane 1:100): 953 mg (94%). IR ($CHCl_3$): $\tilde{\nu} = 3068$ (m), 3007 (s), 2903 (m), 1492 (m), 1428 (s), 1364 (m), 1109 (s), 1083 (s), 934 (m), 828 cm^{-1} (s); ^1H NMR (400 MHz): $\delta =$ 7.51 – 7.48 (m, 4H; aromatic), 7.43 – 7.20 (m, 11H; aromatic), 4.79 (dd, $J_1 = 6.7$ Hz, $J_2 = 5.3$ Hz, 1H; HCO), 3.09 – 3.03 (m, 1H; HCI), 2.98 – 2.92 (m, 1H; HCI), 2.35 – 2.27 (m, 1H; CH_2), 2.20 – 2.15 (m, 1H; CH_2), 0.12 (s, 9H; $Ge(CH_3)_3$); ^{13}C NMR (100 MHz): $\delta =$ 143.04 (C), 136.15 (C), 136.07 (C), 134.90 (CH), 134.51 (CH), 129.87 (CH), 129.60 (CH), 128.31 (CH), 128.00 (CH), 127.84 (CH), 127.60 (CH), 126.13 (CH), 76.20 (CH), 44.46 (CH_2), 1.83 (CH_3), – 1.84 (CH_3); EI MS: *m/z* (%): 561.0 (< 1) [M^+], 547.0 (2) [$M^+ - CH_3$], 444.0 (30), 443.0 (100), 415.0 (88), 308.9 (83), 288.1 (32), 199.0 (81), 197.1 (76), 167.1 (91), 117.1 (97), 91.0 (32); $C_{24}H_{29}OSiGeI$ (561.1): calcd C 51.38, H 5.21; found C 51.44, H 5.22.

[(1-Phenylpropan-1-oxy)diphenylsilyl]trimethylgermane (**10**): This compound was prepared by the use of GP 1 with (chlorodiphenylsilyl)trimethylgermane (607 mg, 1.81 mmol), THF (9 mL + 2 mL), 1-phenyl-1-propanol (0.27 mL, 2.00 mmol), NEt_3 (0.27 mL, 1.94 mmol), and DMAP (30 mg), and a reaction time of 12 h at RT. Purification by FC (Et_2O/pentane 1:100): 691 mg (88%). IR ($CHCl_3$): $\tilde{\nu} = 3068$ (m), 3008 (s), 2972 (s), 1428 (s), 1105 (s), 1079 (s), 1054 (s), 1011 (s), 828 cm^{-1} (s); ^1H NMR (400 MHz): $\delta =$ 7.53 – 7.48 (m, 4H; aromatic), 7.41 – 7.16 (m, 11H; aromatic), 4.66 (t, $J = 6.1$ Hz, 1H; HCO), 1.84 – 1.64 (m, 2H; CH_2), 0.75 (t, $J = 7.4$ Hz, 3H; CH_3), 0.14 (s, 9H; $Ge(CH_3)_3$); ^{13}C NMR (100 MHz): $\delta = 144.41$ (C), 136.66 (C), 136.62 (C), 134.81 (CH), 134.53 (CH), 129.61 (CH), 129.42 (CH), 127.94 (CH), 127.83 (CH), 127.73 (CH), 126.99 (CH), 126.27 (CH), 77.56 (CH), 33.27 (CH_2), 9.54 (CH_3), – 1.82 (CH_3); EI MS: *m/z* (%): 436.2 (< 1) [M^+], 421.1 (2) [$M^+ - CH_3$], 317.1 (36), 199.1 (100); $C_{24}H_{30}OSiGe$ (435.2): calcd C 66.24, H 6.95; found C 66.39, H 6.88.

[(3-Iodo-1-phenylpropan-1-oxy)diphenylsilyl]trimethylsilane (**11**): This compound was prepared by the use of GP 1 with (chlorodiphenylsilyl)-trimethylsilane[20] (560 mg, 1.93 mmol), THF (8 mL + 2 mL), 3-iodo-1-phenyl-1-propanol (576 mg, 2.20 mmol), NEt_3 (0.32 mL, 2.30 mmol), and DMAP (30 mg), and a reaction time of 12 h at RT. Purification by FC (Et_2O/pentane 1:100): 921 mg (84%). IR ($CHCl_3$): $\tilde{\nu} = 3068$ (s), 3007 (s), 2953 (s), 1492 (m), 1428 (s), 1364 (m), 1108 (s), 1087 (s), 933 (m), 838 cm^{-1} (s); ^1H NMR (400 MHz): $\delta =$ 7.53 – 7.46 (m, 4H; aromatic), 7.40 – 7.20 (m, 11H; aromatic), 4.77 (dd, $J_1 = 6.6$ Hz, $J_2 = 5.4$ Hz, 1H; HCO), 3.07 – 3.01 (m, 1H; HCI), 2.96 – 2.89 (m, 1H; HCI), 2.36 – 2.25 (m, 1H; CH_2), 2.18 – 2.09 (m, 1H; CH_2), 0.04 (s, 9H; $Si(CH_3)_3$); ^{13}C NMR (100 MHz): $\delta = 143.30$ (C), 136.56 (C), 136.41 (C), 135.05 (CH), 134.73 (CH), 129.63 (CH), 129.43 (CH), 128.26 (CH), 127.89 (CH), 127.80 (CH), 127.52 (CH), 126.16 (CH), 76.00 (CH), 44.52 (CH_2), 1.84 (CH_2), – 1.46 (CH_3); EI MS: *m/z* (%): 501.1 (< 1) [$M^+ - CH_3$], 443.1 (26) [$M^+ - Si(CH_3)_3$], 415.0 (43), 309.0 (70), 271.1 (100), 239.1 (23), 199.1 (59), 193.1 (44); $C_{24}H_{29}OSi_2I$ (516.6): calcd C 55.80, H 5.66; found C 55.86, H 5.67.

[(1-Phenylpropan-1-oxy)diphenylsilyl]trimethylsilane (**12**): This compound was prepared by the use of GP 1 with (chlorodiphenylsilyl)trimethylsilane[20] (523 mg, 1.80 mmol), THF (8 mL + 2 mL), 1-phenyl-1-propanol (0.31 mL, 2.30 mmol), NEt_3 (0.32 mL, 2.30 mmol), and DMAP (30 mg), and a reaction time of 12 h at RT. Purification by FC (Et_2O/pentane 1:150): 268 mg (40%). IR ($CHCl_3$): $\tilde{\nu} = 3068$ (m), 3008 (s), 2962 (s), 1428 (s), 1105 (s), 1054 (s), 1010 (s), 837 cm^{-1} (s); ^1H NMR (400 MHz): $\delta =$ 7.56 – 7.49 (m, 4H; aromatic), 7.41 – 7.20 (m, 11H; aromatic), 4.66 (t, $J =$ 6.1 Hz, 1H; HCO), 1.82 – 1.64 (m, 2H; CH_2), 0.75 (t, $J = 7.4$ Hz, 3H; CH_3), 0.07 (s, 9H; $Si(CH_3)_3$); ^{13}C NMR (100 MHz): $\delta = 144.70$ (C), 137.10 (C), 136.97 (C), 134.98 (CH), 134.74 (CH), 129.38 (CH), 129.24 (CH), 127.90 (CH), 127.73 (CH), 127.68 (CH), 126.90 (CH), 126.30 (CH), 77.28 (CH), 33.28 (CH_2), 9.48 (CH_3), – 1.43 (CH_3); EI MS: *m/z* (%): 317.3 (2) [$M^+ - Si(CH_3)_3$], 271.2 (62), 199.2 (100), 84.0 (90); $C_{24}H_{30}OSi_2$ (390.7): calcd C 73.79, H 7.74; found C 73.75, H 7.78.

[(3-Iodo-1-phenylpropan-1-oxy)dimethylsilyl]trimethylstannane (**13**): Preparation of the chlorosilane: A solution of *N,N*-diethylaminochlorodimethylsilane[20] (6.6 g, 40 mmol) in THF (24 mL) at 0 °C was treated (slow addition) with a THF solution of $LiSnMe_3$ (prepared from lithium powder (1.9 g, 270 mmol) in THF (50 mL) and Me_3SnCl (9 g, 45 mmol) at 0 °C for 2 h). The solution was stirred at 0 °C for 2 h. After evaporation of the solvent under reduced pressure, the residue was treated under Ar with dry hexane and filtered. Removal of the solvents and purification by distillation (18 Torr, 80 – 100 °C) yielded the stannylated aminosilane (7.19 g). The aminosilane (7.1 g) was dissolved under Ar in CH_2Cl_2 (16 mL) at 0 °C and was treated with lauroyl chloride (6.0 mL, 25.3 mmol). After stirring for 1 h the solvent was removed and the residue distilled (18 Torr, 80 – 100 °C) to afford the (chlorodimethylsilyl)trimethylstannane (≈ 60% purity according to ^1H NMR). The chlorosilane was used without further purification for silylation.

Preparation of **13**: This compound was prepared by the use of GP 1 with (chlorodimethylsilyl)trimethylstannane (≈ 1.5 mmol), Et_2O (5 mL + 2 mL), 3-iodo-1-phenyl-1-propanol (445 mg, 1.70 mmol), NEt_3 (0.25 mL, 1.79 mmol), and DMAP (36 mg), and a reaction time of 1 h at 0 °C. Purification by FC (Et_2O/pentane 1:100): 365 mg (≈ 50%). IR ($CHCl_3$): $\tilde{\nu} = 3004$ (m), 2958 (s), 2908 (s), 1492 (m), 1452 (m), 1361 (m), 1089 (s), 934 (s), 834 cm^{-1} (s); ^1H NMR (400 MHz): $\delta =$ 7.38 – 7.22 (m, 5H; aromatic), 4.70 (dd, $J_1 = 8.0$ Hz, $J_2 = 4.3$ Hz, 1H; HCO), 3.75 – 3.31 (m, 1H; HCI), 3.27 – 3.10 (m, 1H; HCI), 2.28 – 2.05 (m, 2H; CH_2), 0.37 (s, 3H; $SiCH_3$, $J_{SnH} = 22.8$ Hz), 0.29 (s, 3H; $SiCH_3$, $J_{SnH} = 22.8$ Hz), – 0.04 (s, 9H; $J_{SnH} =$ 47.7 Hz, 45.8 Hz, $Sn(CH_3)_3$); ^{13}C NMR (100 MHz): $\delta = 143.52$ (C), 128.43 (CH), 127.61 (CH), 125.90 (CH), 74.14 (CH), 44.02 (CH_2), 3.18 (2 CH_3), 3.12 (CH_2), – 11.50 (CH_3); EI MS: *m/z* (%): 469.0 (5) [$M^+ - CH_3$], 319.1 (47) [$M^+ - Sn(CH_3)_3$], 291.0 (100), 245.0 (20), 149.1 (26), 117.1 (98); $C_{14}H_{25}OSiSnI$ (483.1): calcd C 34.81, H 5.22; found C 34.97, H 5.06.

[(3-Iodopropan-1-oxy)diphenylsilyl]trimethylstannane (**14**): (Chlorodiphenylsilyl)trimethylstannane[19] (575 mg, 1.51 mmol) was dissolved under Ar in THF (5 mL) and cooled to – 18 °C. After addition of NEt_3 (0.25 mL,

0947-6539/99/0502-0766 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 2

1.79 mmol), a solution of 3-iodo-1-propanol (294 mg, 1.58 mmol) in THF (2 mL) was slowly added. After stirring at −18 °C for 4 h and workup according to GP 1, purification by FC (Et_2O/pentane 1:400) yielded **14** as a colorless oil (431 mg, 54 %). IR ($CHCl_3$): $\tilde{\nu}$ = 3069 (m), 3008 (m), 2910 (m), 1710 (m), 1428 (s), 1104 (s), 1047 (m), 925 cm^{-1} (w); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.49 (m, 4H; aromatic), 7.41–7.36 (m, 6H; aromatic), 3.77 (t, J = 5.7 Hz, 2H; CH_2O), 3.30 (t, J = 6.8 Hz, 2H; CH_2I), 2.07 (m, 2H; CH_2), 0.21 (s, J_{SnH} = 47 Hz, J_{SnH} = 49 Hz, 9H; $Sn(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.04 (C), 134.23 (CH), 129.84 (CH), 128.13 (CH), 64.41 (CH_2), 35.97 (CH_2), 3.09 (CH_2), −10.39 (CH_3); EI MS: m/z (%): 516.9 (4) [$M^+ - CH_3$], 367.0 (75), 309.0 (100), 197.1 (31); HRMS calcd for $C_{15}H_{16}SiOI$ [$M^+ - SnMe_3$] 367.0010; found 367.0017.

[(3-Bromopropan-1-oxy)bis(trimethylsilyl)silyl]trimethylstannane (**15**): Preparation of the chlorosilane: $(Me_3Si)_3SiH$ (12.3 mL, 40.2 mmol) was dissolved under Ar in THF (80 mL) and cooled to 0 °C. Methyl lithium (1.58 M solution in hexane, 26.7 mL, 42.2 mmol) was slowly added. After stirring at 0 °C for 12 h, the Li-silanide solution was slowly added to a solution of Me_3SnCl (7.0 g, 35.2 mmol) in THF (20 mL) at 0 °C, and stirring was continued for 2 h. After evaporation of the solvent under reduced pressure, the residue was treated under Ar with dry hexane and filtered. Removal of the solvents and purification by distillation (0.5 Torr, 70–76 °C) yielded the stannylated silane $HSi(SiMe_3)_2SnMe_3$ (7.1 g, purity ≈ 80 %). IR ($CHCl_3$): $\tilde{\nu}$ = 2952 (s), 2842 (s), 2047 (s), 1400 (m), 846 (s), 830 (s), 610 cm^{-1} (s); ^1H NMR (300 MHz, $CDCl_3$): δ = 2.45 (s, 1H; HSi), 0.23 (s, 18H; 2 $Si(CH_3)_3$), 0.21 (s, 9H; $Sn(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 1.89 (6 CH_3), 1.55 (3 CH_3); EI MS: m/z (%): 339.1 (4) [M^+], 325.1 (12) [$M^+ - CH_3$], 276.2 (11), 251.1 (20), 202.2 (62), 131.2 (100).

Preparation of **15**: $HSi(SiMe_3)_2SnMe_3$ (0.6 g, ≈1.76 mmol) was dissolved under Ar in CCl_4 (5 mL) and was stirred at RT for 14 h. After removal of the solvent the residue was treated with THF (8 mL) and the solution cooled to −18 °C. After addition of NEt_3 (0.25 mL, 1.79 mmol), 3-bromo-1-propanol (0.17 mL, 1.80 mmol) and DMAP (cat.), the resulting suspension was stirred for 45 min. Workup as described in GP 1 and purification by FC (Et_2O/pentane 1:150) yielded **15** (500 mg, 60 %) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.54 (t, J = 5.7 Hz, 2H; CH_2O), 3.46 (t, J = 6.6 Hz, 2H; CH_2I), 1.20 (tt, J_1 = 6.6 Hz, J_2 = 5.7 Hz, 2H; CH_2), 0.203 (s, 18H; 2 $SiMe_3$), 0.197 (s, J_{SnH} = 46.8 Hz, J_{SnH} = 44.7 Hz, 9H; $Sn(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 66.03 (CH_2), 35.54 (CH_2), 30.41 (CH_2), 0.06 (CH_3), −9.17 (CH_3); EI MS: m/z (%): 461.1 (<1) [$M^+ - CH_3$], 403.0 (<1) [$M^+ - Si(CH_3)_3$], 313.1 (21) [$M^+ - Sn(CH_3)_3$], 255.0 (37), 131.1 (52), 84.0 (93), 73.0 (100).

1,1-Diphenyl-2-oxa-1-silaindan (**16**): Silyl ether **5** (100 mg, 0.17 mmol) was dissolved under Ar in benzene (8.5 mL). After addition of 0.08 mL of a solution of Bu_3SnH (36 μL, 0.13 mmol) and AIBN (6.4 mg) in benzene (0.80 mL), the mixture was stirred under reflux for 90 min. Then, tin hydride solution (0.12 mL) was added and stirring was continued for 2 h. After removal of the solvent, the residue was purified by reversed phase HPLC (C_{18} column) with acetonitrile as eluent. To completely remove the tin residues the product was recrystallized from Et_2O to yield **16** (34 mg, 68 %). M.p. 84–85 °C; IR ($CHCl_3$): $\tilde{\nu}$ = 3071 (w), 3008 (m), 1590 (w), 1444 (m), 1429 (s), 1120 (s), 1042 (s), 1020 (s), 820 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.75–7.73 (m, 1H; aromatic), 7.66–7.63 (m, 4H; aromatic), 7.46–7.30 (m, 9H; aromatic), 5.35 (s, 2H; CH_2O); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.66 (C), 134.94 (CH), 134.03 (C), 132.25 (CH), 131.95 (C), 130.52 (CH), 130.13 (CH), 128.00 (CH), 127.25 (CH), 121.87 (CH), 72.11 (CH_2); EI MS: m/z (%): 288.2 (35) [M^+], 211.1 (94) [M^+ – phenyl], 210.1 (100), 165.1 (27); $C_{19}H_{16}OSi$ (288.4): calcd C 79.12, H 5.59; found C 78.95, H 5.71.

1,1-Bis(trimethylsilyl)-2-oxa-1-silaindan (**17**): Silyl ether **3** (173 mg, 0.40 mmol) was dissolved under Ar in benzene (10 mL) and was heated to reflux. A solution of Bu_3SnH (22 μL, 0.08 mmol) and AIBN (7.2 mg) in benzene (1 mL) was added over 7 h through a syringe pump. After removal of the solvent, the product mixture was analyzed by ^1H NMR spectroscopy. No side products could be observed; **17** was formed in 58 % yield besides unreacted starting material. For analytical purposes a sample was purified by preparative TLC (SiO_2, Et_2O/pentane 1:20). Compound **17** turned out to be very unstable. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.46 (m, 1H; aromatic), 7.40–7.20 (m, 3H; aromatic), 5.20 (s, 2H; CH_2O), 0.14 (s, 18H; $Si(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.30 (C), 131.19 (C), 130.93 (CH), 128.39 (CH), 126.80 (CH), 121.17 (CH), 74.58 (CH_2), −1.20 (CH_3); EI MS: m/z (%): 281.1 (29) [M^++H], 265.1 (22) [$M^+ - CH_3$], 207.0 (100) [$M^+ - Si(CH_3)_3$], 179.0 (37).

2,2,5-Triphenyl-1-oxa-2-silacyclopentane (**18**): Silyl ether **7** (87 mg, 0.14 mmol) was dissolved under Ar in benzene (1.4 mL; pyrex glass). $Bu_3SnSnBu_3$ (8 μL, 0.01 mmol) was added and the sealed tube was irradiated with the sun lamp for 16 h. Removal of the solvent and evaporation yielded **18** in 87 % yield, determined by NMR spectroscopy. Purification by reversed phase HPLC (C_{18} column) with acetonitrile as eluent yielded 30 mg (66 %) of **18**. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.69–7.67 (m, 4H; aromatic), 7.50–7.30 (m, 11H; aromatic), 5.14 (dd, J_1 = 9.9 Hz, J_2 = 4.6 Hz, 1H; HCO), 2.56–2.49 (m, 1H), 1.96–1.85 (m, 1H), 1.48–1.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.18 (C), 134.86 (C), 134.65 (CH), 134.60 (CH), 134.18 (C), 130.24 (CH), 128.34 (CH), 128.29 (CH), 128.00 (CH), 127.80 (CH), 127.14 (CH), 125.44 (CH), 80.79 (CH), 35.15 (CH_2), 10.81 (CH_2); EI MS: m/z (%): 316.2 (23) [M^+], 288.2 (100), 238.1 (43), 210.1 (79), 181.1 (47). Since the compound was too unstable to be fully characterized, in an additional experiment the crude reaction mixture was treated after irradiation with a large excess (10 equiv) of MeLi. The resulting compound was purified after aqueous workup by FC (Et_2O/pentane 1:3) to yield the corresponding alcohol, 3-(methyldiphenylsilanyl)-1-phenylpropan-1-ol, in 55 % yield. IR ($CHCl_3$): $\tilde{\nu}$ = 3603 (s), 3428 (br.m), 3069 (s), 3008 (s), 1428 (s), 1253 (s), 1112 (s), 998 (m), 834 cm^{-1} (m); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.40 (m, 4H; aromatic), 7.40–7.20 (m, 11H; aromatic), 4.61–4.57 (m, 1H; HCO), 1.88–1.73 (m, 3H; CH_2, OH), 1.26–1.14 (m, 1H; CH), 1.00–0.89 (m, 1H; CH), 0.53 (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.34 (C), 136.92 (C), 134.47 (CH), 129.22 (CH), 128.45 (CH), 127.87 (CH), 127.57 (CH), 126.11 (CH), 76.74 (CH), 33.15 (CH_2), 9.91 (CH_2), −4.50 (CH_3); EI MS: m/z (%): 333.2 (<1) [M^++H], 255.1 (16) [M^+ – phenyl], 197.1 (100), 137.1 (17); $C_{22}H_{24}OSi$ (332.5): calcd C 79.47, H 7.27; found C 79.54, H 7.09.

General procedure (GP 2) for conducting kinetic experiments: The silyl ether (0.04–0.09 mmol) and the appropriate reducing agent (Bu_3SnH, $(Me_3Si)_3SiH$, or Ph_3SnH) and AIBN were dissolved in benzene (or C_6D_6). In a sealed tube the mixture was stirred for (2–3h) at 80 ± 3 °C. (For volatile compounds in which the experiments were conducted in C_6D_6, anisole was directly added as internal standard and the mixture was then analyzed by ^1H NMR spectroscopy.) After complete reaction the solvent was evaporated and the crude reaction mixture (anisol was used as internal standard) was analyzed by ^1H NMR spectroscopy. From the ratio of the cyclized to the reduced product, the rate was calculated according to the equation specified in Scheme 5. For some slow-cyclizing systems the rate was calculated according to the equation suggested by Newcomb[27] for experiments performed under second-order conditions. Mass balances were good (>80 %). Normally, the experiments were repeated two times. (Rate for the reduction of a primary radical with Ph_3SnH at 80 °C: $2.5 \times 10^7\ M^{-1}s^{-1}$.[48]) The results of the kinetic experiments for **7** and **9** are presented in Table 2.

Estimation of the rate constant for the cyclization of the radical derived from 11: The calculated rates for **11** are given in Table 4. Since only small amounts of cyclization product were observed, larger errors may be obtained during integration, we therefore suggest for k_{S_Hi} a value between 10^3 and $10^4\ s^{-1}$.

Table 4. Determination of the rate constant for the cyclization of the radical derived from **11**.

[**11**]	[Bu_3SnH]	[**18**]/[**12**]	k_{S_Hi} [s^{-1}]
0.049	0.055	0.02	7.0×10^3
0.041	0.052	0.03	9.9×10^3

Estimation of the rate constant for the cyclization of the radical derived from 13: $k_{S_Hi} = 1 \times 10^5\ s^{-1}$ (see Table 5). Since the cyclization product derived from **13** was too unstable to be characterized, in a separate experiment we irradiated the silyl ether **13** (100 mg, 0.21 mmol) and $Bu_3SnSnBu_3$ (12 μL, 0.02 mmol) in benzene (2 mL) for 24 h. The reaction mixture was then treated with MeLi (solution in hexane, 1.22 mL, 2.07 mmol) for 12 h. Purification after aqueous workup by FC (Et_2O/pentane 1:6) yielded the known alcohol 3-(trimethylsilanyl)-1-phenylpropan-1-ol (23 mg, 53 %).

Table 5. Determination of the rate constant for the cyclization of the radical derived from **13**.

[**13**]	[$(Me_3Si)_3SiH$]	[cycl.]/[red]	$k_{S_{HI}}$ [s^{-1}]
0.075	0.158	0.67	1.3×10^5
0.068	0.162	0.38	7.4×10^4
0.065	0.170	0.65	1.3×10^5

Estimation of the rate constant for the cyclization of the radical derived from 14: $k_{S_{HI}} = 2 \times 10^5\ s^{-1}$ (see Table 6). Since the cyclization product derived from **14** was too unstable to be characterized, in a separate experiment silyl ether **14** (83 mg, 0.16 mmol) was dissolved in benzene (3 mL) and heated to reflux. With a syringe pump a solution of Bu_3SnH (41 μL, 0.16 mmol) and AIBN (2 mg) in benzene (0.5 mL) was added over

Table 6. Determination of the rate constant for the cyclization of the radical derived from **14**.

[**14**]	[$(Me_3Si)_3SiH$]	[cycl.]/[red]	$k_{S_{HI}}$ [s^{-1}]
0.044	0.36	0.38	1.6×10^5
0.050	0.35	0.31	1.3×10^5
0.043	0.43	0.23	1.4×10^5
0.044	0.34	0.42	1.7×10^5

6 h. Stirring was continued for additional 30 min. The reaction mixture was then allowed to cool to RT and MeLi (1.5 M in hexane, 1.5 mL, 2.25 mmol) was added and the resulting solution was stirred for 12 h at RT. Water was carefully added to destroy the excess of MeLi. After addition of Et_2O the solution was washed with saturated aqueous NH_4Cl and brine. The organic phase was dried ($MgSO_4$) and evaporated to yield the crude product. Purification by FC (Et_2O/pentane 1:3) gave the known alcohol 3-(methyldiphenylsilanyl)-propan-1-ol (17 mg, 42 %). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.53-7.49$ (m, 4H; aromatic), 7.39–7.32 (m, 6H; aromatic), 3.60 (t, $J =$ 6.7 Hz, 2H; CH_2OH), 1.67–1.59 (m, 2H; CH_2), 1.31 (s, 1H; OH), 1.10–1.05 (m, 2H; CH_2Si), 0.56 (s, 3H; $SiCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 136.95 (C), 134.45 (CH), 129.23 (CH), 127.87 (CH), 65.60 (CH_2), 27.14 (CH_2), 9.98 (CH_2), −4,49 (CH_3); EI MS: *m/z* (%): 241.1 (3, $[M - CH_3]^+$), 199.1 (65), 197.1 (100), 179.1 (41), 137.1 (41). An authentic sample of the reduction product was also prepared: [(1-propoxy)diphenylsilyl]trimethylstannane: IR ($CHCl_3$): $\tilde{\nu} = 3067$ (w), 2964 (s), 1468 (w), 1428 (m), 1365 (m), 1172 (m), 1102 (s), 1023 (s), 902 (w); ^1H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.54–7.49 (m, 4H; aromatic), 7.38–7.32 (m, 6H; aromatic), 1.50–1.36 (m, 4H; CH_2CH_2), 1.23 (s, 6H; $C(CH_3)_2$), 0.87 (t, $J = 7.1$ Hz, 3H; CH_2CH_3), 0.16 (s, $J_{SnH} = 45.4$ Hz, $J_{SnH} = 47.4$ Hz, 9H; $Sn(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): 139.63 (C), 134.30 (CH), 129.28 (CH), 127.83 (CH), 75.60 (C), 47.25 (CH_2), 29.88 (CH_3), 17.73 (CH_2), 14.60 (CH_3), −10.07 (CH_3); EI MS: *m/z* (%): 448.0 (< 1) $[M^+]$, 433.0 (1), 363.0 (1), 332.9.0 (3), 283.1 (9), 199.1 (100); $C_{21}H_{32}OSiSn$ (447.3): calcd C 56.39, H 7.21; found C 56.49, H 7.10.

Estimation of the rate constant for the cyclization of the radical derived from 15: $k_{S_{HI}} = 2 \times 10^6\ s^{-1}$ (see Table 7). Since the cyclization product derived from **15** was too unstable to be characterized, in a separate experiment silyl ether **15** (120 mg, 0.25 mmol) was dissolved in benzene (5 mL) and heated to reflux. With a syringe pump a solution of Bu_3SnH (74 μL, 0.27 mmol) and AIBN (5 mg) in benzene (0.5 mL) was added over 6 h. Stirring was continued for additional 30 min. The reaction mixture was then allowed to cool to RT and MeLi (1.55 M in hexane, 1.6 mL, 2.5 mmol) was added, and the resulting solution was stirred for 45 min at RT. Water was carefully added to destroy the excess of MeLi. After addition of Et_2O the solution was washed with saturated aqueous NH_4Cl and brine. The organic phase was dried ($MgSO_4$) and evaporated to yield the crude product. Purification by FC (Et_2O/pentane 1:6) gave 3-[methylbis(trimethylsilyl)silanyl]-propan-1-ol (31 mg, 49 %). IR ($CHCl_3$): $\tilde{\nu} = 3624$ (s), 3448 (br. m)., 2950 (s), 2891 (s), 1396 (m), 836 (s), 621 cm^{-1} (s); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.60$ (t, $J = 6.6$ Hz, 2H; CH_2O), 1.65–1.57 (m, 2H; CH_2), 0.71–0.65 (m, 2H; $SiCH_2$), 0.10 (s, 18H; $Si(CH_3)_3$), 0.07 (s, 3H; $SiCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 65.97$ (CH_2), 29.63 (CH_2), 7.27 (CH_2), −0.88 (CH_3), −9.02 (CH_3); EI MS: *m/z* (%): 249.0 (2) $[M^+ + H]$, 233.1 (3) $[M^+ - CH_3]$, 175.1 (33), 133.1 (81), 73.1 (100); $C_{10}H_{28}OSi_3$ (248.6): calcd C 48.32, H 11.35; found C 48.31, H 11.27.

[(4-Methyl-1-penten-4-oxy)diphenylsilyl]trimethylstannane (**23**): This compound was prepared by the use of GP 1 with (chlorodiphenylsilyl)-trimethylstannane[19] (572 mg, 1.50 mmol), Et_2O (5 mL + 2 mL), 2-methylpent-4-en-2-ol (170 mg, 1.7 mmol), NEt_3 (0.25 mL, 1.79 mmol), and DMAP (36 mg), and a reaction time of 3 h at RT. Purification by distillation (bulb to bulb, 0.07 Torr, 100–110 °C): 479 mg (72 %). IR ($CHCl_3$): $\tilde{\nu} = 3068$ (m), 3007 (m), 2976 (s), 1428 (s), 1144 (m), 1102 (s), 1035 (s), 1024 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.56-7.49$ (m, 4H; aromatic), 7.39–7.31 (m, 6H; aromatic), 5.94–5.84 (m, 1H; vinylic), 5.07–4.99 (m, 2H; vinylic), 2.28 (d, $J = 7.3$ Hz, 2H), 1.23 (s, 6H; CH_3), 0.16 (s, 9H; $J_{SnH} = 45.5$ Hz, 47.6 Hz, $Sn(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 139.42$ (C), 134.96 (CH), 134.31 (CH), 129.35 (CH), 127.86 (CH), 117.43 (CH_2), 75.21 (C), 49.40 (CH_2), 29.69 (CH_3), −10.09 (3 CH_3); EI MS: *m/z* (%): 431.1 (0.4) $[M^+ - CH_3]$, 281.2 (75) $[M^+ - Sn(CH_3)_3]$, 223.1 (100), 199.1 (55); $C_{21}H_{30}OSiSn$ (445.3): calcd C 56.65, H 6.79; found C 56.81, H 6.70.

General procedure (GP 3) for slow bimolecular addition reactions with a subsequent UMCT step: The silyl ether and the α-halo acetic acid ester were dissolved under Ar in benzene. $Bu_3SnSnBu_3$ was added and the solution was irradiated in a sealed tube (pyrex glass) for the given time with a sun lamp. (The lamp was placed at a distance of about 15 cm, reaction temperature: 50–60 °C). After removal of the solvent the crude product was purified by FC (SiO_2).

3-[2-(Phenoxycarbonyl)ethyl]-5,5-dimethyl-2,2-diphenyl-1,2-oxasilolane (**24**): This compound was prepared by the use of GP 3 with silyl ether **23** (100 mg, 0.23 mmol), phenyl bromoacetate (59 mg, 0.28 mmol), and $Bu_3SnSnBu_3$ (14 μL, 0.02 mmol) in benzene (0.88 mL), and a reaction time of 16 hours. Purification by FC (Et_2O/pentane 1:13) yielded **24**: 64 mg (68 %). IR ($CHCl_3$): $\tilde{\nu} = 3071$ (m), 3004 (m), 2970 (s), 2927 (m), 1753 (s), 1493 (s), 1428 (s), 1261 (s), 1118 (s), 969 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.71-7.68$ (m, 2H; aromatic), 7.60–7.58 (m, 2H; aromatic), 7.47–7.33 (m, 2H; aromatic), 7.23–7.18 (m, 1H; aromatic), 7.02–6.99 (m, 2H; aromatic), 2.63–2.49 (m, 2H), 2.26 (dd, $J_1 = 12.7$ Hz, $J_2 = 7.4$ Hz, 1H), 2.04–1.89 (m, 2H), 1.81–1.71 (m, 1H), 1.66 (t, $J = 12.5$ Hz, 1H), 1.54 (s, 3H; CH_3), 1.30 (s, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 171.79$ (C), 150.66 (C), 135.01 (CH), 134.74 (C), 134.61 (CH), 133.03 (C), 130.27 (CH), 130.18 (CH), 129.40 (CH), 128.70 (CH), 127.92 (CH), 125.76 (CH), 121.50 (CH), 79.74 (C), 45.38 (CH_2), 35.12 (CH_2), 31.24 (CH_3), 29.34 (CH_3), 25.74 (CH_2), 24.13 (CH); EI MS: *m/z* (%): 416.2 (2) $[M^+]$, 401.2 (1) $[M^+ - CH_3]$, 323.2 (44), 223.2 (56), 199.1 (100); $C_{26}H_{28}O_3Si$ (416.6): calcd C 74.96, H 6.77; found C 75.04, H 6.72.

3-[2-(Ethoxycarbonyl)ethyl]-5,5-dimethyl-2,2-diphenyl-1,2-oxasilolane (**25**): This compound was prepared by the use of GP 3 with silyl ether **23** (300 mg, 0.68 mmol), ethyl iodoacetate (97 μL, 0.81 mmol), and $Bu_3SnSnBu_3$ (41 μL, 0.07 mmol) in benzene (2.65 mL), and a reaction time of 16 hours. Purification by FC (Et_2O/pentane 1:13) yielded **25**: 138 mg (56 %). IR ($CHCl_3$): $\tilde{\nu} = 3071$ (w), 3002 (m), 2972 (s), 2928 (m), 1724 (s), 1428 (s), 1370 (s), 1118 (s), 968 (s), 938 (s), 918 (s), 828 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.67-7.65$ (m, 2H; aromatic), 7.57–7.55 (m, 2H; aromatic), 7.46–7.35 (m, 6H; aromatic), 4.08 (q, $J = 7.2$ Hz, 2H; CH_2O), 2.36–2.17 (m, 3H), 1.92–1.77 (m, 2H), 1.67–1.58 (m, 2H), 1.52 (s, 3H; CH_3), 1.28 (s, 3H; CH_3), 1.21 (t, $J = 7.1$ Hz, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 173.36$ (C), 135.00 (CH), 134.89 (C), 134.60 (CH), 133.14 (C), 130.18 (CH), 130.09 (CH), 127.99 (CH), 127.86 (CH), 79.69 (C), 60.23 (CH_2), 45.39 (CH_2), 35.17 (CH_2), 31.23 (CH_3), 29.30 (CH_3), 25.75 (CH_2), 24.21 (CH_3), 14.22 (CH); EI MS: *m/z* (%): 368.3 (13) $[M^+]$, 353.2 (4) $[M^+ - CH_3]$, 287.2 (39), 199.1 (100), 181.1 (31); $C_{22}H_{28}O_3Si$ (368.6): calcd C 71.70, H 7.66; found C 71.79, H 7.48.

[(1-Ethoxycarbonyl-3-iodo-5-methylhexan-5-oxy)diphenylsilyl]trimethylstannane (**29**): This compound was prepared by the use of GP 3 with silyl ether **23** (50 mg, 0.11 mmol), ethyl iodoacetate (17 μL, 0.14 mmol), and $Bu_3SnSnBu_3$ (7 μL, 0.01 mmol) in benzene (0.5 mL), and a reaction time of 3 hours. Purification by FC (Et_2O/pentane 1:12) yielded **29**: 56 mg (63 %).

0947-6539/99/0502-0768 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 2

IR ($CHCl_3$): $\tilde{\nu}$ = 3068 (w), 2976 (s), 2910 (m), 1727 (s), 1428 (s), 1103 (s), 1021 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.48 (m, 4H; aromatic), 7.40–7.34 (m, 6H; aromatic), 4.43–4.12 (m, 1H), 4.08 (q, J = 7.2 Hz, 2H; CH_2O), 2.56–2.47 (m, 1H), 2.44–2.30 (m, 1H), 2.27 (dd, J_1 = 15.1 Hz, J_2 = 6.9 Hz, 1H), 2.20–2.11 (m, 1H), 2.05–1.96 (m, 1H), 1.34 (s, 3H; CH_3), 1.26 (s, 3H; CH_3), 1.21 (t, J = 7.2 Hz, 3H; CH_3), 0.17 (s, 9H; J_{SnH} = 47.8 Hz, 45.8 Hz, $Sn(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.52 (C), 138.87 (C), 138.83 (C), 134.41 (CH), 134.36 (CH), 129.56 (CH), 129.52 (CH), 127.98 (CH), 127.97 (CH), 76.22 (C), 60.42 (CH_2), 55.88 (CH_2), 37.06 (CH_2), 35.01 (CH_2), 31.29 (CH_3), 30.75 (CH), 29.14 (CH_3), 14.20 (CH_3), –10.07 (CH_3); EI MS: m/z (%): 645.0 (<1) [$M^+ - CH_3$], 495.1 (44) [$M^+ - Sn(CH_3)_3$], 309.0 (60), 281.1 (30), 199.1 (100), 169.1 (77); $C_{25}H_{37}O_3SiSnI$ (659.3): calcd C 45.55, H 5.66; found C 45.66, H 5.67.

[(4-Iodopentan-2-oxy)diphenylsilyl]trimethylstannane (**30**): This compound was prepared by the use of GP 1 with (chlorodiphenylsilyl)trimethylstannane[19] (1.44 g, 3.67 mmol), THF (13 mL), *l*-4-iodopentan-2-ol (700 mg, 3.72 mmol), NEt_3 (0.54 mL, 3.76 mmol), and DMAP (cat.), and a reaction time of 12 h at RT. Purification by FC (Et_2O/pentane 1:200) afforded **30**: 1.27 g (69%). During silylation epimerization (30%) occurred. IR ($CHCl_3$): $\tilde{\nu}$ = 3068 (s), 2973 (s), 2914 (s), 1428 (s), 1377 (s), 1142 (s), 1105 (s), 1052 (s), 996 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): *l* compound: δ = 7.60–7.50 (m, 4H; aromatic), 7.45–7.30 (m, 6H; aromatic), 4.33–4.25 (m, 1H), 4.15–4.05 (m, 1H), 2.00–1.85 (m, 1H; CH_2), 1.91 (d, J = 6.9 Hz, 3H; CH_3), 1.73–1.66 (m, 1H; CH_2), 1.20 (d, J = 6.1 Hz, 3H; CH_3), 0.22 (s, 9H; $Sn(CH_3)_3$); *u* compound: 7.60–7.50 (m, 4H; aromatic), 7.45–7.30 (m, 6H; aromatic), 4.15–4.07 (m, 1H), 4.07–3.99 (m, 1H), 2.32–2.24 (m, 1H; CH_2), 1.80 (d, J = 6.8 Hz, 3H; CH_3), 1.80–1.70 (m, 1H; CH_2), 1.16 (d, J = 6.1 Hz, 3H; CH_3), 0.21 (s, 9H; $Sn(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): *l* compound: δ = 137.99 (C), 137.83 (C), 134.50 (CH), 134.45 (CH), 129.68 (CH), 129.64 (CH), 128.00 (CH), 127.96 (CH), 71.91 (CH), 52.41 (CH_2), 29.52 (CH_3), 27.75 (CH), 23.93 (CH_3), –9.94 (CH_3); *u* compound: 137.67 (2C), 134.36 (CH), 134.32 (CH), 129.76 (CH), 129.72 (CH), 128.07 (CH), 128.04 (CH), 71.27 (CH), 52.21 (CH_2), 28.64 (CH_3), 24.26 (CH), 22.82 (CH_3), –10.27 (CH_3); EI MS: m/z (%): 545.0 (<1) [$M^+ - CH_3$], 395.0 (30) [$M^+ - Sn(CH_3)_3$], 353.0 (100), 309.0 (89), 267.1 (21), 249.0 (56), 199.1 (47), 197.1 (87), 69.1 (25); HRMS calcd for $C_{17}H_{20}SiOI$ [$M^+ - SnMe_3$] 395.0322, found 395.0325.

[(3-Iodo-1-phenylbutan-1-oxy)diphenylsilyl]trimethylstannane (**31**): This compound was prepared by the use of GP 1 with (chlorodiphenylsilyl)-trimethylstannane[19] (275 mg, 0.72 mmol), THF (4 mL + 1 mL), 3-iodo-1-phenylbutan-1-ol (200 mg, 0.72 mmol), NEt_3 (0.11 mL, 0.72 mmol), and DMAP (cat.), and a reaction time of 12 h at RT. Purification by FC (Et_2O/pentane 1:100) afforded **31**: 284 mg (63%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.30 (m, 15H; aromatic), 4.90 (dd, J_1 = 2.8 Hz, J_2 = 9.2 Hz, 1H; HCO), 4.31–4.21 (m, 1H; HCI), 2.10 (ddd, J_1 = 2.9 Hz, J_2 = 10.5 Hz, J_3 = 15.0 Hz, 1H), 1.99 (ddd, J_1 = 3.4 Hz, J_2 = 9.1 Hz, J_3 = 15.0 Hz, 1H), 1.90 (d, J = 6.9 Hz, 3H; CH_3), –0.02 (s, 9H; J_{SnH} = 47.0 Hz, 49.1 Hz, $Sn(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.57 (C), 137.43 (C), 137.24 (C), 135.03 (CH), 134.35 (CH), 129.93 (CH), 129.52 (CH), 128.44 (CH), 128.10 (CH), 127.86 (CH), 127.67 (CH), 126.21 (CH), 77.29 (C), 54.31 (CH_2), 29.42 (CH_3), 27.27 (CH), –10.23 (CH_3); EI MS: m/z (%): 607.2 (<1) [$M^+ - CH_3$], 457.2 (8) [$M^+ - Sn(CH_3)_3$], 415.2 (71), 309.1 (69), 197.2 (100), 167.2 (28).

***l*-[(4-Iodopentan-2-oxy)bis(trimethylsilyl)silyl]trimethylstannane** (**32**): This compound was prepared by the use of GP 1 with [chlorobis(trimethylsilyl)silyl]trimethylstannane (1.8 mmol, for the preparation of this chlorosilane see the synthesis of **15**), THF (8 mL), *l*-4-iodopentan-2-ol (428 mg, 2.0 mmol), NEt_3 (0.28 mL, 2.00 mmol), and DMAP (cat.), and a reaction time of 12 h at RT. Purification by FC (Et_2O/pentane 1:150) yielded **32**: 529 mg (48%). IR ($CHCl_3$): $\tilde{\nu}$ = 2962 (s), 2893 (s), 1444 (w), 1372 (w), 1141 (s), 1045 (s), 836 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 4.27–4.19 (m, 1H; HCI), 3.63–3.57 (m, 1H; HCO), 1.91 (d, J = 6.9 Hz, 3H; CH_3), 1.83 (ddd, J_1 = 2.6 Hz, J_2 = 10.8 Hz, J_3 = 14.8 Hz, 1H), 1.47 (ddd, J_1 = 3.1 Hz, J_2 = 9.2 Hz, J_3 = 14.8 Hz, 1H), 1.12 (d, J = 6.1 Hz, 3H; CH_3), 0.21 (s, 9H; $Si(CH_3)_3$), 0.19 (s, J_{SnH} = 44.2 Hz, 46.3 Hz, 9H; $Sn(CH_3)_3$), 0.19 (s, 9H; $Si(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 73.25 (CH), 52.76 (CH_2), 29.60 (CH_3), 27.76 (CH), 22.89 (CH_3), 0.28 (CH_3), 0.15 (CH_3), –8.73 (CH_3); EI MS: m/z (%): 387.1 (1) [$M^+ - Sn(CH_3)_3$], 301.1 (7), 86.0 (60), 84 (100), 49.0 (90); $C_{14}H_{37}OSi_3SnI$ (551.3): calcd C 30.50, H 6.76; found C 30.59, H 6.59.

4-(Methyldiphenylsilanyl)pentan-2-ol (**33**): The silyl ether **30** (300 mg, 0.54 mmol) was dissolved under Ar in benzene (12 mL) and heated to reflux. With a syringe pump a solution of Bu_3SnH (212 μL, 0.78 mmol) and AIBN (10 mg) in benzene (0.5 mL) was added over 6 h. Stirring was continued for additional 30 min. The reaction mixture was then allowed to cool to RT, and MeLi (1.3 M in hexane, 7.5 mL, 9.7 mmol) was added and the resulting solution was stirred for 12 h at RT. Water was carefully added to destroy the excess of MeLi. After addition of Et_2O the solution was washed with saturated aqueous NH_4Cl and brine. The organic phase was dried ($MgSO_4$) and evaporated to yield the crude product. Purification by FC (Et_2O/pentane 1:5) gave 77 mg of an inseparable mixture of **33** (30%, 1.7:1 mixture of diastereoisomers) and 4-phenyl-2-pentanol (35%).[37] The diastereoselectivity was determined after transformation of the alcohol into the corresponding trifluoroacetylated compound with subsequent GC analysis (Chirasil-Val, Macherey-Nagel, 25 m × 4 mm, temperature programme: 70 °C for 5 min then heating with a rate of 4 °C min^{-1}). Since **33** could not be separated from the side product we oxidized it by Tamao–Fleming oxidation to the known diol (see preparation of **52**).

3-(Methyldiphenylsilanyl)-1-phenylbutan-1-ol (**34**): The silyl ether **31** (150 mg, 0.24 mmol) was dissolved under Ar in benzene (5 mL) and heated to reflux. With a syringe pump a solution of Bu_3SnH (79 μL, 0.29 mmol) and AIBN (5 mg) in benzene (0.5 mL) was added over 6 h. Stirring was continued for additional 30 min. The reaction mixture was then allowed to cool to RT, and MeLi (1.3 M in hexane, 2.7 mL, 3.6 mmol) was added and the resulting solution was stirred for 12 h at RT. Water was carefully added to destroy the excess of MeLi. After addition of Et_2O the solution was washed with saturated aqueous NH_4Cl and brine. The organic phase was dried ($MgSO_4$) and evaporated to yield the crude product. Purification by FC (Et_2O/pentane 1:5) gave 55 mg of an inseparable mixture of **34** (29%, 1.7:1 mixture of diastereoisomers, ^1H NMR spectroscopy), 1,3-diphenyl-1-butanol (38%) and 1-phenyl-1-butanol (28%) as determined by ^1H NMR spectroscopy. For proof of identity and to assign the relative configuration of the major isomer of **34**, the mixture containing **34** was oxidized according to the procedure of Knölker et al.[45] to afford the known alcohol, 1-phenyl-1,3-butandiol as 1.7:1 (*u*:*l*) mixture of diastereoisomers (in analogy to the preparation of **52**).

4-[Methylbis(trimethylsilyl)silanyl]pentan-2-ol (**35**): The silyl ether **32** (300 mg, 0.24 mmol) was dissolved under Ar in benzene (10.8 mL) and heated to reflux. With a syringe pump a solution of Bu_3SnH (147 μL, 0.29 mmol) and AIBN (10 mg) in benzene (0.5 mL) was added over 6 h. Stirring was continued for additional 30 min. The reaction mixture was then allowed to cool to RT, and MeLi (solution in hexane, 3.6 mL, 5.4 mmol) was added and the resulting solution was stirred for 45 min at RT. Water was carefully added to destroy the excess of MeLi. After addition of Et_2O the solution was washed with saturated aqueous NH_4Cl and brine. The organic phase was dried ($MgSO_4$) and evaporated to yield the crude product. Purification by FC (Et_2O/pentane 1:6) gave 55 mg (37%) of the first eluted isomer of **35** and 50 mg (34%) of the second isomer. IR ($CHCl_3$, second isomer): $\tilde{\nu}$ = 3608 (w), 3449 (br. w.), 2949 (s), 2893 (s), 835 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$, first eluted isomer): δ = 3.97–3.90 (m, 1H; HCO), 1.60–1.50 (m, 1H), 1.34–1.20 (m, 1H), 1.19 (d, J = 6.1 Hz, CH_3), 1.05 (d, J = 6.9 Hz, CH_3), 0.13 (s, 18H; $Si(CH_3)_3$), 0.07 (s, 3H; $SiCH_3$); ^1H NMR (400 MHz, $CDCl_3$, second isomer): δ = 3.98–3.89 (m, 1H; HCO), 1.61–1.51 (m, 1H), 1.28 (d, J = 4.5 Hz, OH), 1.17 (d, J = 6.1 Hz, CH_3), 1.07–0.98 (m, 4H), 0.13 (s, 18H; $Si(CH_3)_3$), 0.07 (s, 3H; $SiCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, first eluted isomer): δ = 64.69 (CH), 43.81 (CH_2), 24.28 (CH_3), 16.31 (CH_3), 13.92 (CH), –0.06 (CH_3), –0.14 (CH_3), –9.48 (CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, second isomer): δ = 67.44 (CH), 44.28 (CH_2), 22.57 (CH_3), 17.09 (CH_3), 15.61 (CH), –0.12 (CH_3), –0.16 (CH_3), –9.33 (CH_3); EI MS (second isomer): 203.2 (6) [$M^+ - Si(CH_3)_3$], 133.1 (100), 117.1 (10), 73.1 (43); $C_{12}H_{32}OSi_3$ (276.6): calcd C 52.10, H 11.66; found C 52.17, H 11.79.

[(1-Phenyl-3-buten-1-oxy)diphenylsilyl]trimethylstannane (**36**): This compound was prepared by the use of GP 1 with (chlorodiphenylsilyl)trimethylstannane[19] (762 mg, 2.0 mmol), Et_2O (6 mL + 2.5 mL), 1-phenylbut-3-en-1-ol (333 mg, 2.25 mmol), NEt_3 (0.33 mL, 2.25 mmol), and DMAP (47 mg), and a reaction time of 3 h at RT. Purification by distillation (bulb to bulb, 0.07 Torr, 160–170 °C): 675 mg (69%). IR ($CHCl_3$): $\tilde{\nu}$ = 3068 (s), 3008 (s), 2909 (s), 1640 (m), 1428 (s), 1105 (s), 1081 (s), 1063 (s), 919 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.15 (m, 15H; aromatic), 5.71–5.61 (m, 1H; vinylic), 4.97–4.91 (m, 2H; vinylic), 4.73 (t, J = 6.2 Hz, 1H; HCO), 2.59–2.51 (m, 1H), 2.47–2.40 (m, 1H), 0.00 (s, 9H; J_{SnH} = 48.9 Hz, 46.8 Hz, $Sn(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.70 (C), 137.59

(C), 137.49 (C), 134.66 (CH), 134.53 (CH), 134.27 (CH), 129.78 (CH), 129.51 (CH), 128.15 (CH), 127.99 (CH), 127.86 (CH), 127.34 (CH), 126.28 (CH), 117.32 (CH_2), 76.83 (C), 45.05 (CH_2), −10.41 (3 CH_3); EI MS: *m/z* (%): 479.1 (5) [$M^+ - CH_3$], 329.2 (100) [$M^+ - Sn(CH_3)_3$], 199.1 (79), 131.1 (19), 84.0 (38); $C_{25}H_{30}OSiSn$ (493.3): calcd C 60.87, H 6.13; found C 61.05, H 6.23.

[(4-Phenyl-1-penten-4-oxy)diphenylsilyl]trimethylstannane (**37**): This compound was prepared by the use of GP 1 with (chlorodiphenylsilyl)-trimethylstannane[19] (550 mg, 1.44 mmol), Et_2O (5 mL + 1.5 mL), 4-phenylpent-1-en-4-ol (280 mg, 1.73 mmol), NEt_3 (0.25 mL, 1.73 mmol), and DMAP (34 mg), and a reaction time of 2 h at RT. Purification by distillation (bulb to bulb, 0.07 Torr, 185–195 °C): 353 mg (48 %). IR ($CHCl_3$): $\tilde{\nu}$ = 3068 (s), 3007 (s), 2980 (s), 2911 (s), 1428 (s), 1103 (s), 1071 (s), 996 (s), 918 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.54 (m, 4H; aromatic), 7.49–7.16 (m, 11H; aromatic), 5.71–5.61 (m, 1H; vinylic), 4.99–4.91 (m, 2H; vinylic), 2.61 (dd, J_1 = 13.8 Hz, J_2 = 6.6 Hz, 1H), 2.53 (dd, J_1 = 13.8 Hz, J_2 = 7.1 Hz, 1H), 1.60 (s, 3H; CH_3), 0.02 (s, 9H; J_{SnH} = 48.2 Hz, 46.2 Hz, $Sn(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.31 (C), 139.42 (C), 138.90 (C), 134.53 (CH), 134.30 (CH), 134.26 (CH), 129.60 (CH), 129.32 (CH), 128.05 (CH), 128.01 (CH), 127.90 (CH), 127.87 (CH), 126.71 (CH), 125.47 (CH), 117.70 (CH_2), 78.51 (C), 50.85 (CH_2), 28.56 (CH_3), −9,98 (3 CH_3); EI MS: *m/z* (%): 493.1 (<1) [$M^+ - CH_3$], 343.2 (11) [$M^+ - Sn(CH_3)_3$], 199.1 (18), 84.0 (100); $C_{26}H_{32}OSiSn$ (507.3): calcd C 61.55, H 6.36; found C 61.39, H 6.30.

[(4-Methyl-3-phenyl-1-penten-4-oxy)diphenylsilyl]trimethylstannane (**38**): This compound was prepared by the use of GP 1 with (chlorodiphenylsilyl)trimethylstannane[19] (892 mg, 2.33 mmol), THF (5 mL + 2 mL), 4-methyl-3-phenylpent-1-en-4-ol (445 mg, 2.50 mmol), NEt_3 (0.36 mL, 2.50 mmol), and DMAP (40 mg), and a reaction time of 4 h at 0 °C. Purification by distillation (bulb to bulb, 0.05 Torr, 150–160 °C): 743 mg (61 %). IR ($CHCl_3$): $\tilde{\nu}$ = 3068 (s), 3007 (s), 2978 (s), 2913 (m), 1428 (s), 1148 (s), 1103 (s), 1021 (s), 920 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.43 (m, 4H; aromatic), 7.43–7.19 (m, 11H; aromatic), 6.43–6.34 (m, 1H; vinylic), 5.13–5.02 (m, 2H; vinylic), 3.21 (d, J = 9.2 Hz, 1H), 1.22 (s, 3H; CH_3), 1.13 (s, 3H; CH_3), 0.12 (s, 9H; J_{SnH} = 47.7 Hz, 45.7 Hz, $Sn(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.81 (C), 139.16 (C), 139.11 (C), 138.73 (CH), 134.53 (CH), 134.48 (CH), 129.65 (CH), 129.38 (CH), 129.33 (CH), 127.87 (CH), 127.82 (CH), 127.78 (CH), 126.31 (CH), 116.77 (CH_2), 77.07 (C), 62.69 (CH), 29.09 (CH_3), 29.02 (CH_3), −10.08 (3 CH_3); EI MS: *m/z* (%): 507.2 (2) [$M^+ - CH_3$], 357.3 (27) [$M^+ - Sn(CH_3)_3$], 299.2 (100), 199.2 (33), 197.2 (42), 84.0 (36); $C_{27}H_{34}OSiSn$ (521.4): calcd C 62.20, H 6.57; found C 61.97, H 6.55.

[(3,4-Dimethyl-1-penten-4-oxy)diphenylsilyl]trimethylstannane (**39**): This compound was prepared by the use of GP 1 with (chlorodiphenylsilyl)-trimethylstannane[19] (870 mg, 2.27 mmol), THF (5 mL + 2 mL), 3,4-dimethylpent-1-en-4-ol (285 mg, 2.50 mmol), NEt_3 (0.36 mL, 2.50 mmol), and DMAP (30 mg), and a reaction time of 4 h at 0 °C. Purification by FC (Et_2O/pentane 1:200): 376 mg (36 %). IR ($CHCl_3$): $\tilde{\nu}$ = 3068 (s), 2978 (s), 2910 (m), 1428 (s), 1136 (s), 1103 (s), 1021 (s), 919 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.51 (m, 4H; aromatic), 7.39–7.32 (m, 6H; aromatic), 5.92–5.83 (m, 1H; vinylic), 5.02–4.97 (m, 2H; vinylic), 2.23 (m, 1H), 1.18 (s, 3H; CH_3), 1.17 (s, 3H; CH_3), 1.07 (d, J = 6.9 Hz, 3H; CH_3), 0.16 (s, 9H; J_{SnH} = 47.5 Hz, 45.5 Hz, $Sn(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.20 (CH), 139.52 (C), 139.49 (C), 134.41 (CH), 134.39 (CH), 129.34 (CH), 127.84 (CH), 114.80 (CH_2), 49.97 (CH), 29.64 (CH_3), 27.22 (CH_3), 14.95 (CH_3), −10.06 (3 CH_3); EI MS: *m/z* (%): 445.1 (<1) [$M^+ - CH_3$], 295.1 (51) [$M^+ - Sn(CH_3)_3$], 237.1 (53), 199.0 (23), 83.9 (100); $C_{22}H_{32}OSiSn$ (459.3): calcd C 57.53, H 7.02; found C 57.59, H 6.80.

3-[2-(Ethoxycarbonyl)ethyl]-2,2,5-triphenyl-1,2-oxasilolane (**40**): This compound was prepared by the use of GP 3 with silyl ether **36** (50 mg, 0.1 mmol), ethyl iodoacetate (15 µL, 0.12 mmol), and $Bu_3SnSnBu_3$ (6 µL, 0.01 mmol) in benzene (1 mL), and a reaction time of 20 hours with the sun lamp close to the reaction vessel (T > 100 °C). Purification by reversed phase HPLC (C_{18} column) with acetonitrile/H_2O (10:1) as eluent yielded 8 mg (19 %) of **40** as a 1.5:1 (*trans*:*cis*) mixture of diastereoisomers as determined by ^1H NMR spectroscopy. ^1H NMR (300 MHz, $CDCl_3$, mixture of the isomers): δ = 7.8–7.6 (m, 4H; aromatic), 7.55–7.10 (m, 11H; aromatic), 5.46 (dd, J_1 = J_2 = 6.3 Hz, 1H; *trans* isomer, HCO), 5.09 (dd, J_1 = 11.1 Hz, J_2 = 3,9 Hz, 1H; *cis* isomer, HCO), 4.09 (q, J = 7.2 Hz, 2H; *cis* isomer, CH_2O), 4.06 (q, J = 7.2 Hz, 2H; *trans* isomer, CH_2O), 2.70–1.60 (m, 7H; both isomers), 1.29–1.17 (m, 3H; CH_3 of both isomers); EI MS: *m/z* (%): 416.2 (33) [M^+], 328.1 (61), 287.1 (52), 250.1 (58), 199.1 (100), 181.1 (53), 130.1 (40); $C_{26}H_{28}O_3Si$ (416.6): calcd C 74.96, H 6.77; found C 74.73, H 6.72.

3-[2-(Ethoxycarbonyl)ethyl]-5-methyl-2,2,5-triphenyl-1,2-oxasilolane (**41**): This compound was prepared by the use of GP 3 with silyl ether **37** (145 mg, 0.28 mmol), ethyl iodoacetate (40 µL, 0.34 mmol), and $Bu_3SnSnBu_3$ (16 µL, 0.03 mmol) in benzene (1.1 mL), and a reaction time of 24 hours. Purification by FC (Et_2O/pentane 1:15) yielded **41** (82 mg, 67 %) as a 1.5:1 mixture of its *trans* and *cis* isomer. For analytical purposes and for assigning the relative configuration, the diastereosiomers were separated by prep HPLC (Chiracel OD column) with hexane/*i*PrOH (99:1) as eluent. The relative configuration of the minor isomer (*cis*) was assigned by NOE experiments. For the major isomer an X-ray structure[39] could be obtained proving the relative *trans* configuration. IR ($CHCl_3$, mixture of isomers): $\tilde{\nu}$ = 3071 (w), 3008 (m), 2980 (m), 2927 (w), 1725 (s), 1428 (s), 1373 (s), 1118 (s), 950 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$, *trans* isomer): δ = 7.66–7.63 (m, 2H; aromatic), 7.51–7.40 (m, 6H; aromatic), 7.36–7.32 (m, 4H; aromatic), 7.24–7.15 (m, 3H; aromatic), 4.01 (m, 2H; CH_2O), 2.75 (dd, J_1 = 13.0 Hz, J_2 = 6.6 Hz, 1H; H−C4), 2.30–2.16 (m, 2H; CH_2CO), 1.91 (dd, J_1 = J_2 = 12.9 Hz, 1H; H′−C4), 1.76 (s, 3H; CH_3), 1.80–1.70 (m, 1H), 1.68–1.50 (m, 3H), 1.14 (t, J = 5.7 Hz, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, *trans* isomer): δ = 173.24 (C), 147.57 (C), 135.33 (CH), 135.17 (CH), 133.58 (C), 132.82 (C), 130.43 (CH), 130.23 (CH), 127.92 (CH), 127.89 (CH), 127.83 (CH), 126.42 (CH), 125.08 (CH), 83.37 (C), 60.20 (CH_2), 45.67 (CH_2), 35.07 (CH_2), 33.04 (CH_3), 25.00 (CH_2), 23.01 (CH_3), 14.13 (CH); ^1H NMR (400 MHz, $CDCl_3$, *cis* isomer): δ = 7.78–7.75 (m, 2H; aromatic), 7.61–7.58 (m, 2H; aromatic), 7.55–7.20 (m, 11H; aromatic), 4.08 (q, J = 7.2 Hz, 2H; CH_2O), 2.68 (dd, J_1 = 12.5 Hz, J_2 = 7.3 Hz, 1H; H(*trans*)−C4), 2.37–2.24 (m, 2H; CH_2CO), 2.06–1.97 (m, 1H; H−C3), 1.87 (dd, J_1 = J_2 = 12.6 Hz, 1H; H(*cis*)−C4), 1.83–1.79 (m, 1H; H−C1′), 1.70–1.55 (m, 1H; H−C1′), 1.54 (s, 3H; CH_3−C5), 1.21 (t, J = 7.1 Hz, 3H; CH_3). NOE: Irradiation at δ = 2.68 (dd, J_1 = 12.5 Hz, J_2 = 7.3 Hz, 1H; H(*trans*)−C4) led to weak NOEs for δ = 2.06–1.97 (m, 1H; H−C3) and 1.54 (s, 3H; CH_3−C5); irradiation at δ = 1.54 (s, 3H; CH_3−C5) led to NOEs for δ = 2.06–1.97 (m, 1H; H−C3) and 2.68 (dd, J_1 = 12.5 Hz, J_2 = 7.3 Hz, 1H; H(*trans*)−C4); irradiation at δ = 2.06–1.97 (m, 1H; H−C3) led to an NOE for δ = 1.54 (s, 3H; CH_3−C5); ^{13}C NMR (100 MHz, $CDCl_3$, *cis* isomer): δ = 173.37 (C), 149.68 (C), 135.16 (CH), 134.71 (C), 134.67 (CH), 132.91 (C), 130.31 (CH), 130.19 (CH), 128.17 (CH), 128.09 (CH), 127.89 (CH), 126.42 (CH), 124.27 (CH), 82.71 (C), 60.29 (CH_2), 45.87 (CH_2), 35.06 (CH_2), 30.92 (CH_3), 25.62 (CH_2), 23.98 (CH), 14.22 (CH_3); EI MS (mixture): 430.3 (9) [M^+], 310.2 (30), 302.2 (100), 287.1 (39), 281.1 (33), 199.1 (86), 181.1 (26); $C_{27}H_{30}O_3Si$ (430.6): calcd C 75.31, H 7.02; found C 75.42, H 7.17.

***trans*-3-[2-(Ethoxycarbonyl)ethyl]-5,5-dimethyl-2,2,4-triphenyl-1,2-oxasilolane** (**42**): This compound was prepared by the use of GP 3 with silyl ether **38** (150 mg, 0.28 mmol), ethyl iodoacetate (42 µL, 0.35 mmol), and $Bu_3SnSnBu_3$ (17 µL, 0.03 mmol) in benzene (1.1 mL), and a reaction time of 16 hours. Purification by FC (Et_2O/pentane 1:20) yielded **42** (110 mg, 87 %) as a diastereoisomerically pure compound. The relative *trans* configuration was assigned by NOE experiments. IR ($CHCl_3$): $\tilde{\nu}$ = 3008 (m), 2974 (m), 2930 (w), 1725 (s), 1428 (s), 1370 (s), 1110 (s), 968 cm^{-1} (s); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.91–7.94 (m, 2H; aromatic), 7.81–7.84 (m, 2H; aromatic), 7.11–7.28 (m, 10H; aromatic), 7.06–7.10 (m, 1H; aromatic), 3.78–3.89 (m, 2H; CH_2O), 3.03 (d, J = 13.3 Hz, 1H; PhCH), 2.49–2.54 (m, 1H; SiCH), 2.19 (t, J = 7.4 Hz, 2H), 1.77–1.83 (m, 1H), 1.59–1.67 (m, 1H), 1.47 (s, 3H; CH_3), 1.06 (s, 3H; CH_3), 0.86 (t, J = 7.1 Hz, 3H; CH_3). NOE: Irradiation at δ = 1.06 (s, 3H; CH_3) led to an NOE for δ = 2.49–2.54 (m, 1H; SiCH); irradiation at δ = 3.03 (d, J = 13.3 Hz, 1H; PhCH) led to an NOE for δ = 1.47 (s, 3H; CH_3); irradiation at δ = 2.49–2.54 (m, 1H; SiCH) led to an NOE for δ = 1.06 (s, 3H; CH_3); irradiation at δ = 1.47 (s, 3H; CH_3) led to an NOE for δ = 3.03 (d, J = 13.3 Hz, 1H; PhCH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.46 (C), 140.47 (C), 135.93 (C), 135.66 (CH), 135.24 (CH), 134.03 (C), 130.53 (CH), 130.47 (CH), 128.42 (CH), 128,39 (CH), 128.29 (CH), 127.94 (CH), 127.10 (CH), 82.14 (C), 62.66 (CH), 59.99 (CH_2), 35.09 (CH_2), 30.08 (CH_3), 28.74 (CH), 25.53 (CH_3), 24.75 (CH_2), 14.19 (CH_3); EI MS: *m/z* (%): 444.2 (3) [M^+], 388.2 (9), 386.2 (100), 295.1 (12), 227.1 (81), 183.1 (53), 199.1 (63); $C_{28}H_{32}O_3Si$ (444.6): calcd C 75.64, H 7.25; found C 75.41, H 7.34.

***trans*-3-[2-(Ethoxycarbonyl)ethyl]-4,5,5-trimethyl-2,2-diphenyl-1,2-oxasilolane** (**43**): This compound was prepared by the use of GP 3 with silyl ether **39** (190 mg, 0.42 mmol), ethyl iodoacetate (59 µL, 0.50 mmol), and

0947-6539/99/0502-0770 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 2

$Bu_3SnSnBu_3$ (25 μL, 0.04 mmol) in benzene (1.7 mL), and a reaction time of 22 hours. Purification by FC (Et_2O/pentane 1:14) yielded **43** (121 mg, 76%) as a diastereoisomeric mixture *trans*:*cis* = 22:1 as determined by ^1H NMR spectroscopy. (The relative *trans* configuration was assigned in analogy to **42**). *trans*-**43**: IR ($CHCl_3$): $\tilde{\nu}$ = 3071 (w), 2972 (s), 2931 (w), 1726 (s), 1428 (s), 1370 (s), 1116 (s), 961 (s), 911 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.68–7.66 (m, 2H; aromatic), 7.57–7.54 (m, 2H; aromatic), 7.46–7.34 (m. 6H; aromatic), 4.06 (q, J = 7.1 Hz, 2H; CH_2O), 2.34–2.22 (m, 2H), 1.99–1.92 (m, 1H), 1.86–1.77 (m, 1H), 1.47 (s, 3H; CH_3), 1.45–1.34 (m, 2H), 1.19 (t, J = 7.2 Hz, 3H; CH_3), 1.11 (s, 3H; CH_3), 1.07 (d, J = 6.7 Hz, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.19 (C), 135.18 (CH), 134.96 (C), 134.79 (CH), 133.20 (C), 130.15 (CH), 127.97 (CH), 127.86 (CH), 82.45 (C), 60.23 (CH_2), 49.38 (CH), 35.26 (CH_2), 31.11 (CH), 29.45 (CH_3), 24.13 (CH_2), 24.10 (CH_3), 15.60 (CH_3), 14.20 (CH_3); EI MS: *m*/*z* (%): 382.3 (9) [M^+], 287.2 (61), 227.2 (25), 199.1 (100), 181.1 (42), 105.1 (16); $C_{23}H_{30}O_3Si$ (382.6): calcd C 72.21, H 7.90; found C 72.11, H 8.06.

[(5-Ethoxycarbonyl-3-iodo-1-phenyl-1-pentan-1-oxy)diphenylsilyl]trimethylstannane (**44**): This compound was prepared by the use of GP 3 with silyl ether **36** (126 mg, 0.25 mmol), ethyl iodoacetate (36 μL, 0.30 mmol), and $Bu_3SnSnBu_3$ (15 μL, 0.03 mmol) in benzene (0.9 mL), and a reaction time of 14 hours (T = 50–60 °C). Purification by FC (Et_2O/pentane 1:15) yielded **44** (150 mg, 83%) as a 1:1 diastereoisomeric mixture (inseparable). IR ($CHCl_3$): $\tilde{\nu}$ = 3068 (w), 3008 (s), 2907 (w), 1728 (s), 1428 (s), 1376 (s), 1103 (s), 917 cm^{-1} (w); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.6–7.2 (m, 15H; aromatic), 4.98–4.91 (m, 1H; HCO of both isomers), 4.22–4.17 (m, 1H; HCI), 4.10 (q, J = 7.1 Hz, 2H; CH_2O), 4.05 (q, J = 7.1 Hz, 2H; CH_2O), 3.63–3.56 (m, 1H; HCI), 2.6–2.3 (m, 2H; both isomers), 2.2–1.7 (m, 4H; both isomers), 1.22 (t, J = 7.1 Hz, CH_3), 1.19 (t, J = 7.1 Hz, CH_3), 0.00 (s, 9H; J_{SnH} = 49.2 Hz, 47.2 Hz, $Sn(CH_3)_3$), −0.03 (s, 9H; J_{SnH} = 49.2 Hz, 47.1 Hz, $Sn(CH_3)_3$); EI MS: *m*/*z* (%): 693.0 (<1) [$M^+ - CH_3$], 543.1 (100) [$M^+ - Sn(CH_3)_3$], 415.0 (55), 308.9 (54), 199.0 (41), 197.1 (71), 129.1 (32); $C_{29}H_{37}O_3SiSnI$ (707.3): calcd C 49.25, H 5.27; found C 49.30, H 5.08.

[(1-Iodobutan-3-oxy)diphenylsilyl]trimethylstannane (**45**): This compound was prepared by the use of GP 1 with (chlorodiphenylsilyl)trimethylstannane[19] (471 mg, 1.23 mmol), THF (4 mL + 2 mL), 4-iodo-butan-2-ol (308 mg, 1.54 mmol), NEt_3 (0.2 mL, 1.5 mmol), and DMAP (cat.), and a reaction time of 4 h at 0 °C. Purification by FC (Et_2O/pentane 1:200): 438 mg (67%). IR ($CHCl_3$): $\tilde{\nu}$ = 3068 (w), 3007 (m), 2972 (m), 1428 (s), 1378 (w), 1103 (s), 1057 (s), 963 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.49 (m, 4H; aromatic), 7.39–7.34 (m, 6H; aromatic), 4.03–3.96 (m, 1H; HCO), 3.22–3.12 (m, 2H; CH_2I), 2.10–2.01 (m, 1H; C*H*H), 1.99–1.90 (m, 1H; C*H*H), 1.17 (d, J = 6.2 Hz, 3H; CH_3), 0.20 (s, J_{SnH} = 45.8 Hz, J_{SnH} = 47.8 Hz, 9H; $Sn(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.77 (C), 137.67 (C), 134.40 (CH), 134.35 (CH), 129.77 (CH), 129.71 (CH), 128.07 (CH), 128.03 (CH), 71.40 (CH), 43.07 (CH_2), 23.19 (CH_3), 2.59 (CH_2), −10.17 (CH_3); EI MS: *m*/*z* (%): 531.0 (3) [$M^+ - CH_3$], 381 (74), 309.1 (100), 199.2 (21); $C_{19}H_{27}OSiSnI$ (545.1): calcd C 41.86, H 4.99; found C 42.36, H 4.98.

[(1-Iodo-3-methylbutan-3-oxy)diphenylsilyl]trimethylstannane (**46**): This compound was prepared by the use of GP 1 with (chlorodiphenylsilyl)-trimethylstannane[19] (564 mg, 1.48 mmol), THF (5 mL + 2 mL), 4-iodo-2-methylbutan-2-ol (380 mg, 1.78 mmol), NEt_3 (0.25 mL, 1.78 mmol), and DMAP (cat.), and a reaction time of 4 h at 0 °C. Purification by FC (Et_2O/pentane 1:200): 277 mg (33%). IR ($CHCl_3$): $\tilde{\nu}$ = 3068 (w), 3007 (m), 2974 (s), 1710 (m), 1428 (s), 1367 (m), 1178 (s), 1103 (s), 1022 (s), 996 (m), 904 cm^{-1} (w); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.49 (m, 4H; aromatic), 7.39–7.34 (m, 6H; aromatic), 3.27–3.23 (m, 2H; CH_2I), 2.16–2.12 (m, 2H; CH_2), 1.23 (s, 6H; $C(CH_3)_2$), 0.17 (s, J_{SnH} = 45.8 Hz, J_{SnH} = 47.8 Hz, 9H; $Sn(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.90 (C), 134.26 (CH), 129.57 (CH), 128.02 (CH), 76.47 (C), 49.79 (CH_2), 29.52 (CH_3), −0.19 (CH_2), −10.12 (CH_3); EI MS: *m*/*z* (%): 545.1 (1) [$M^+ - CH_3$], 395.0 (50), 309.0 (36), 199.1 (100); HRMS calcd for $C_{17}H_{20}SiOI$ [$M^+ - SnMe_3$] 395.0322; found 395.0318.

[(4-Iodo-2-methylpentan-2-oxy)diphenylsilyl]trimethylstannane (**47**): This compound was prepared by the use of GP 1 with (chlorodiphenylsilyl)-trimethylstannane[19] (631 mg, 1.65 mmol), THF (6 mL + 3 mL), 4-iodo-2-methylpentan-2-ol (416 mg, 1.82 mmol), NEt_3 (0.25 mL, 1.78 mmol), and DMAP (cat.), and a reaction time of 4 h at 0 °C. Purification by FC (Et_2O/pentane 1:200): 520 mg (55%). IR ($CHCl_3$): $\tilde{\nu}$ = 3068 (w), 2875 (m), 2914 (w), 1428 (m), 1384 (w), 1166 (s), 1103 (s), 1021 (s), 939 cm^{-1} (w); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.49 (m, 4H; aromatic), 7.38–7.32 (m, 6H; aromatic), 4.53–4.45 (m, 1H; CH), 2.42 (dd, J_1 = 5.1 Hz, J_2 = 14.9 Hz, 1H; C*H*H), 2.16 (dd, J_1 = 7.4 Hz, J_2 = 14.9 Hz, 1H; C*H*H), 1.99 (d, J = 6.9 Hz, 3H; CHICH_3), 1.31 (s, 3H; CH_3), 1.24 (s, 3H; CH_3), 0.17 (s, J_{SnH} = 45.8 Hz, J_{SnH} = 47.8 Hz, 9H; $Sn(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.93 (C), 138.91 (C), 134.44 (CH), 134.39 (CH), 129.54 (CH), 129.50 (CH), 127.96 (CH), 76.23 (C), 57.62 (CH_2), 31.43 (CH_3), 31.30 (CH_3), 29.19 (CH_3), 22.92 (CH), −10.08 (CH_3); EI MS: *m*/*z* (%): 559.0 (0.1) [$M^+ - CH_3$], 459.0 (3), 409.1 (15), 367.1 (71), 309.0 (73), 199 (100); $C_{21}H_{31}OSiSnI$ (573.2): calcd C 44.01, H 5.45; found C 44.29, H 5.34.

Estimation of the rate constant for the cyclization of the radical derived from 45: $k_{S_{Hi}} = 1 \times 10^6\ s^{-1}$ (see Table 8). Experiments were conducted by following GP 2 (described above). Since the cyclization product derived from **45** was too unstable to be characterized, in a separate experiment silyl ether **45** (174 mg, 0.32 mmol) and $Bu_3SnSnBu_3$ (17 μL, 0.03 mmol) were dissolved in benzene (3.2 mL) and irradiated as described in GP 3. The reaction mixture was then allowed to cool to RT, and MeLi (1.65 M in hexane, 2.9 mL, 4.8 mmol) was added and the resulting solution was stirred for 12 h at RT. Water was carefully added to destroy the excess of MeLi. After addition of Et_2O the solution was washed with saturated aqueous NH_4Cl and brine. The organic phase was dried ($MgSO_4$) and evaporated to yield the crude product. Purification by FC (Et_2O/pentane 1:5) gave 1-(methyldiphenylsilanyl)butan-3-ol (44 mg). IR ($CHCl_3$): $\tilde{\nu}$ = 3607 (w), 3446 (w), 3008 (s), 2968 (m), 2927 (m), 1428 (s), 1377 (w), 1112 (s), 1015 (w), 888 (m), 834 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.49 (m, 4H; aromatic), 7.39–7.32 (m, 6H; aromatic), 3.76–3.68 (m, 1H; C*H*OH), 1.55–1.45 (m, 2H; CH_2), 1.37 (s, 1H; OH), 1.22–1.14 (m, 2H; C*H*H), 1.16 (d, J = 6.2 Hz, 3H; CHCH_3), 1.05–0.97 (m, 2H; C*H*H), 0.55 (s, 3H; $SiCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.96 (C), 134.45 (CH), 129.22 (CH), 127.87 (CH), 70.27 (CH), 33.31 (CH_2), 22.80 (CH_3), 9.89 (CH_2), −4,53 (CH_3); EI MS: *m*/*z* (%): 271.1 (<1) [M^++H], 214.1 (1), 197.1 (100), 137.0 (92); $C_{17}H_{22}OSi$ (270.45): calcd C 75.50, H 8.20; found C 75.40, H 8.16. An authentic sample of the reduced product was also prepared: [(Butan-2-oxy)diphenylsilyl]trimethylstannane. IR ($CHCl_3$): $\tilde{\nu}$ = 3068 (w), 2971 (m), 2927 (m), 1428 (s), 1377 (m), 1104 (s), 1043 (s), 1008 (s), 947 (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.51 (m, 4H; aromatic), 7.39–7.33 (m, 6H; aromatic), 3.88–3.81 (m, 1H; CHO), 1.62–1.43 (m, 2H; CH_2), 1.16 (d, J = 6.1 Hz, 3H; CH_3), 0.87 (t, J = 7.5 Hz, 3H; CH_2CH_3), 0.18 (s, J_{SnH} = 46.2 Hz, J_{SnH} = 48.3 Hz, 9H; $Sn(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.26 (C), 138.15 (C), 134.36 (CH), 134.31 (CH), 129.56 (CH), 129.53 (CH), 127.95 (CH), 127.94 (CH), 72.97 (CH), 32.20 (CH_2), 22.95 (CH_3), 9.96 (CH_3), −10.30 (CH_3); EI MS: *m*/*z* (%): 420.1 (<1) [M^+], 405.1 (19), 333.0 (6), 255.1 (79), 199.0 (100); $C_{19}H_{28}OSiSn$ (419.23): calcd C 54.44, H 6.73; found C 54.57, H 6.79.

Table 8. Determination of the rate constant for the cyclization of the radical derived from **45**.

[**45**]	[$(Me_3Si)_3SiH$]	[cycl.]/[red]	$k_{S_{Hi}}$ [s^{-1}]
0.049	0.98	0.9	1.1×10^6
0.050	1.10	0.8	1.0×10^6
0.050	1.25	0.7	1.1×10^6

Estimation of the rate constant for the cyclization of the radical derived from 46: $k_{S_{Hi}} = 1 \times 10^7\ s^{-1}$ (see Table 9). Experiments were conducted by following GP 2 (described above). Since the cyclization product derived from **46** was too unstable to be characterized, in a separate experiment silyl ether **46** (190 mg, 0.34 mmol) and $Bu_3SnSnBu_3$ (18 μL, 0.04 mmol) were dissolved in benzene (3.4 mL) and irradiated as described in GP 3. The reaction mixture was then allowed to cool to RT, and MeLi (1.3 M in hexane, 3.9 mL, 5.1 mmol) was added. The resulting solution was stirred for 12 h at

Table 9. Determination of the rate constant for the cyclization of the radical derived from **46**.

[**46**]	[Ph_3SiH]	[cycl.]/[red]	$k_{S_{Hi}}$ [s^{-1}]
0.046	0.36	1.2	1.1×10^7
0.046	0.33	1.0	0.8×10^7
0.047	0.28	1.6	1.1×10^7
0.049	0.64	0.7	1.1×10^7
0.046	0.36	1.6	1.4×10^7

RT. Water was carefully added to destroy the excess of MeLi. After addition of Et_2O, the solution was washed with saturated aqueous NH_4Cl and brine. The organic phase was dried ($MgSO_4$) and evaporated to yield the crude product. Purification by FC (Et_2O/pentane 1:3) gave 3-methyl-1-(methyldiphenylsilanyl)butan-3-ol (58 mg, 60 %). IR ($CHCl_3$): $\tilde{\nu}$ = 3602 (m), 3440 (w), 3070 (m), 3008 (s), 2971 (s), 2928 (m), 1466 (w), 1428 (s), 1112 (s), 998 (w), 955 (w), 898 (m), 878 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.53 – 7.49 (m, 4H; aromatic), 7.39 – 7.32 (m, 6H; aromatic), 1.53 – 1.48 (m, 2H; CH_2), 1.22 (s, 1H; OH), 1.19 (s, 6H; $C(CH_3)_2$), 1.12 – 1.08 (m, 2H; CH_2), 0.55 (s, 3H; $SiCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.97 (C), 134.46 (CH), 129.21 (CH), 127.88 (CH), 71.58 (C), 37.66 (CH_2), 22.80 ($C(CH_3)_2$), 8.22 (CH_2), – 4,61 (CH_3); EI MS: *m*/*z* (%): 284.2 (< 1) [M^+], 266.1 (6), 197.1 (100), 137.0 (40); $C_{18}H_{24}OSi$ (284.47): calcd C 76.00, H 8.50; found C 75.80, H 8.60. An authentic sample of the reduced product was also prepared as described in GP 1: [(2-Methylbutan-2-oxy)diphenylsilyl]trimethylstannane. IR ($CHCl_3$): $\tilde{\nu}$ = 3067 (w), 2973 (s), 2921 (m), 1462 (w), 1428 (m), 1172 (m), 1102 (s), 1067 (s), 1024 (s), 910 cm^{-1} (w); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.55 – 7.50 (m, 4H; aromatic), 7.37 – 7.31 (m, 6H; aromatic), 1.54 (q, *J* = 7.5 Hz, 2H; CH_2), 1.22 (s, 6H; $C(CH_3)_2$), 0.92 (t, *J* = 7.5 Hz, 3H; CH_2CH_3), 0.16 (s, J_{SnH} = 45.4 Hz, J_{SnH} = 47.4 Hz, 9H; $Sn(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.63 (C), 134.29 (CH), 129.28 (CH), 127.82 (CH), 75.77 (C), 37.27 (CH_2), 29.37 (CH_3), 8.87 (CH_3), – 10.10 (CH_3); EI MS: *m*/*z* (%): 419.0 (1) [$M^+ - CH_3$], 348.9 (2), 332.9 (1), 269.1 (6), 199.1 (100); $C_{20}H_{30}OSiSn$ (433.3): calcd C 55.45, H 6.98; found C 55.49, H 6.96.

Estimation of the rate constant for the cyclization of the radical derived from 47: $k_{SnH} = 9 \times 10^4\ s^{-1}$ (see Table 10). Experiments were conducted by following GP 2 (described above). Cyclized product: 5,5-Dimethyl-2,2-diphenyl-1,2-oxasilolane. IR ($CHCl_3$): $\tilde{\nu}$ = 3070 (w), 3002 (m), 2970 (s), 2868 (m), 1590 (w), 1460 (m), 1428 (s), 1368 (m), 1178 (m), 1117 (s), 969 (s), 932 (s), 879 (m), 825 (m), 635 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.67 – 7.63 (m, 2H; aromatic), 7.58 – 7.55 (m, 2H; aromatic), 7.45 – 7.35 (m, 6H; aromatic), 2.17 – 2.11 (m, 1H; C*H*H), 1.96 – 1.85 (m, 1H; C*H*Si), 1.62 – 1.56 (m, 1H; C*H*H), 1.50 (s, 3H; CH_3), 1.40 (s, 3H; CH_3), 1.06 (d, *J* = 7.3 Hz, 3H; $CHCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.28 (C), 134.95 (CH), 134.52 (CH), 133.49 (C), 130.05 (CH), 129.84 (CH), 127.93 (CH), 127.71 (CH), 79.67 (C), 47.92 (CH_2), 31.26 (CH_3), 29.41 (CH_3), 18.03 (CH), 14.56 (CH_3); EI MS: *m*/*z* (%): 282.1 (19) [M^+], 267.1 (53), 240.1 (41), 199.1 (100), 182.0 (51); $C_{18}H_{22}OSi$ (282.46): calcd C 76.54, H 7.85; found C 76.50, H 7.86. An authentic sample of the reduced product was also prepared as described in GP 1: [(2-Methylpentan-2-oxy)diphenylsilyl]trimethylstannane. IR ($CHCl_3$): $\tilde{\nu}$ = 3067 (w), 2964 (s), 1468 (w), 1428 (m), 1365 (m), 1172 (m), 1102 (s), 1023 (s), 902 (w); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.54 – 7.49 (m, 4H; aromatic), 7.38 – 7.32 (m, 6H; aromatic), 1.50 – 1.36 (m, 4H; CH_2CH_2), 1.23 (s, 6H; $C(CH_3)_2$), 0.87 (t, *J* = 7.1 Hz, 3H; CH_2CH_3), 0.16 (s, J_{SnH} = 45.4 Hz, J_{SnH} = 47.4 Hz, 9H; $Sn(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.63 (C), 134.30 (CH), 129.28 (CH), 127.83 (CH), 75.60 (C), 47.25 (CH_2), 29.88 (CH_3), 17.73 (CH_2), 14.60 (CH_3), – 10.07 (CH_3); EI MS: *m*/*z* (%): 448.0 (< 1) [M^+], 433.0 (1), 363.0 (1), 332.9.0 (3), 283.1 (9), 199.1 (100); $C_{21}H_{32}OSiSn$ (447.3): calcd C 56.39, H 7.21; found C 56.49, H 7.10.

Table 10. Determination of the rate constant for the cyclization of the radical derived from **47**.

[**47**]	[$(Me_3Si)_3SiH$]	[cycl.]/[red]	k_{SnH} [s^{-1}]
0.050	0.45	0.46	8.4×10^4
0.050	0.36	0.62	9.0×10^4
0.050	0.40	0.58	9.6×10^4
0.050	0.55	0.41	9.4×10^4
0.050	0.44	0.47	8.5×10^4

General procedure 4 (GP 4) for the oxidation of cyclic alkoxysilanes to the corresponding diol derivatives: The cyclic silyl ether was dissolved in THF/MeOH (1:1) at RT. KF (2 equiv), $KHCO_3$ (5 equiv), and H_2O_2 (30 %) were added. The resulting suspension was stirred at 50 – 60 °C for 5 hours. The reaction mixture was then allowed to cool to RT, and Et_2O was added. After careful addition of 1N HCl (until pH = 2), the biphasic mixture was stirred for 15 min. After removal of the organic phase the aqueous phase was additionally extracted twice with Et_2O. The combined organic phases were washed with brine, dried ($MgSO_4$), and evaporated to afford the crude lactone, which was purified by FC (SiO_2).

5-(2-Hydroxy-2-methylpropyl)tetrahydrofuran-2-one (**48**): This compound was prepared by the use of GP 4 with alkoxysilane **24** (52 mg, 0.13 mmol), THF (0.6 mL), MeOH (0.6 mL), KF (15 mg, 0.25 mmol), $KHCO_3$ (63 mg, 0.63 mmol), and H_2O_2 (0.13 mL). Purification by FC (Et_2O/MeOH 15:1) yielded **48**: 14 mg (71 %). IR ($CHCl_3$): $\tilde{\nu}$ = 3596 (m), 3460 (br.w.), 3007 (w), 2976 (m), 1772 (s), 1175 (s), 920 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 4.80 – 4.73 (m, 1H; HCO), 2.54 – 2.50 (m, 1H), 2.42 – 2.34 (m, 1H), 1.97 – 1.84 (m, 2H), 1.80 (dd, J_1 = 14.8 Hz, J_2 = 3.5 Hz, 1H), 1.32 (s, 3H; CH_3), 1.31 (s, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.96 (C), 78.15 (CH), 69.96 (C), 48.68 (CH_2), 30.18 (CH_3), 29.68 (CH_3), 29.44 (CH_2), 28.61 (CH_2); EI MS: *m*/*z* (%): 159.0 (3) [M^++H], 142.1 (31), 125.0 (42), 100.0 (94), 85.0 (100); $C_8H_{14}O_3$ (158.2): calcd C 60.74, H 8.92; found C 60.74, H 8.70.

5-(2-Hydroxy-2-phenylpropyl)tetrahydrofuran-2-one (**49**): This compound was prepared by the use of GP 4 with alkoxysilane **41** (260 mg, 0.60 mmol, 1.5:1 mixture of *trans*:*cis* isomers), THF (2.5 mL), MeOH (2.5 mL), KF (72 mg, 1.21 mmol), $KHCO_3$ (308 mg, 3.02 mmol), and H_2O_2 (0.65 mL). Purification by FC (Et_2O/pentane 10:1) yielded **49**: 110 mg (83 %) as a 1.5:1 mixture of *u*:*l* isomers as determined by ^1H NMR spectroscopy. IR ($CHCl_3$): $\tilde{\nu}$ = 3580 (s), 3007 (w), 1773 (s), 1177 (s), 912 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$, *u* isomer): δ = 7.47 – 7.42 (m, 2H; aromatic), 7.38 – 7.33 (m, 2H; aromatic), 7.29 – 7.23 (m, 1H; aromatic), 4.43 – 4.32 (m, 1H; HCO), 2.84 (s, OH), 2.51 – 2.07 (m, 5H), 1.82 – 1.72 (m, 1H), 1.59 (s, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, *u* isomer): δ = 176.41 (C), 147.02 (C), 128.46 (CH), 126.85 (CH), 124.65 (CH), 78.33 (CH), 74.11 (C), 49.05 (CH_2), 31.27 (CH_3), 28.99 (CH_2), 28.28 (CH_2); ^1H NMR (400 MHz, $CDCl_3$, *l* isomer): δ = 7.47 – 7.42 (m, 2H; aromatic), 7.38 – 7.33 (m, 2H; aromatic), 7.29 – 7.23 (m, 1H; aromatic), 4.43 – 4.32 (m, 1H; HCO), 2.84 (s, OH), 2.51 – 2.07 (m, 5H), 1.97 – 1.89 (m, 1H), 1.67 (s, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, *l* isomer): δ = 176.81 (C), 146.81 (C), 128.41 (CH), 127.07 (CH), 124.72 (CH), 78.29 (CH), 73.63 (C), 49.39 (CH_2), 30.29 (CH_3), 29.38 (CH_2), 28.64 (CH_2); EI MS: *m*/*z* (%): 220.2 (28) [M^+], 203.1 (100), 121.1 (85), 105.1 (55), 85.1 (41); $C_{13}H_{16}O_3$ (220.3): calcd C 70.89, H 7.32; found C 70.66, H 7.36.

***l*-5-(2-Hydroxy-2-methyl-1-phenylpropyl)tetrahydrofuran-2-one** (**50**): This compound was prepared by the use of GP 4 with alkoxysilane **42** (290 mg, 0.65 mmol), THF (3.3 mL), MeOH (3.3 mL), KF (78 mg, 1.31 mmol), $KHCO_3$ (334 mg, 3.27 mmol), and H_2O_2 (0.70 mL). Purification by FC (Et_2O/pentane 10:1) yielded **50**: 149 mg (97 %). IR ($CHCl_3$): $\tilde{\nu}$ = 3580 (m), 3007 (m), 1776 (s), 1174 (s), 1021 (s), 919 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35 – 7.27 (m, 3H; aromatic), 7.20 – 7.18 (m, 2H; aromatic), 5.11 – 5.04 (m, 1H; HCO), 2.87 (d, *J* = 10.3 Hz, HCPh), 2.61 (s, 1H; OH), 2.46 – 2.37 (m, 2H), 2.00 – 1.92 (m, 1H), 1.74 – 1.64 (m, 1H), 1.32 (s, 3H; CH_3), 1.15 (s, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.36 (C), 137.84 (C), 128.67 (2 CH), 127.54 (CH), 81.00 (CH), 72.82 (C), 61.77 (CH), 29.48 (CH_3), 28.59 (CH_2), 28.14 (CH_2), 27.15 (CH_3); EI MS: *m*/*z* (%): 252.2 (7) [M^++H_2O], 234.2 (7) [M^+], 217.2 (40), 176.2 (100), 117.2 (65); $C_{14}H_{18}O_3 \cdot 0.5\,H_2O$ (229.3): calcd C 69.11, H 7.87; found C 69.10, H 7.72.

***l*-5-(1,2-Dimethyl-2-hydroxypropyl)tetrahydrofuran-2-one** (**51**): This compound was prepared by the use of GP 4 with alkoxysilane **43** (245 mg, 0.64 mmol), THF (3.3 mL), MeOH (3.3 mL), KF (76 mg, 1.28 mmol), $KHCO_3$ (327 mg, 3.20 mmol), and H_2O_2 (0.70 mL). Purification by FC (Et_2O/pentane 10:1) yielded **51**: 63 mg (57 %). IR ($CHCl_3$): $\tilde{\nu}$ = 3582 (m), 2977 (s), 1778 (s), 1177 (s), 1126 (s), 1014 (s), 906 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 4.56 – 4.50 (m, 1H; HCO), 2.55 – 2.50 (m, 3H), 2.39 – 2.31 (m, 1H), 2.03 – 1.86 (m, 2H), 1.242 (s, 3H; CH_3), 1.239 (s, 3H; CH_3), 0.90 (d, *J* = 10.3 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.33 (C), 82.57 (CH), 72.69 (C), 48.26 (CH), 28.64 (CH_3), 28.55 (CH_2), 27.44 (CH_2), 25.53 (CH_3), 11.20 (CH_3); EI MS: *m*/*z* (%): 157.1 (7) [$M^+ - CH_3$], 139.1 (12), 114.1 (50), 85.1 (75), 59.1 (100); $C_9H_{16}O_3$ (172.2): calcd C 62.77, H 9.36; found C 62.75, H 9.23.

Pentan-1,3-diol (**52**): Silane **33** (0.16 mmol, see preparation of **33**) was dissolved in CH_2Cl_2 (0.5 mL) at RT and $BF_3 \cdot HOAc$ (0.11 mL, 0.80 mmol) was added. The resulting solution was stirred at RT for 7 hours. The reaction mixture was then poured into saturated aqueous $NaHCO_3$ solution and extracted twice with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and evaporated to yield the corresponding fluorosilane, which was dilluted with THF (3 mL) and MeOH (3 mL). KF (58 mg, 1.0 mmol), $NaHCO_3$ (42 mg, 0.5 mmol), and H_2O_2 (0.51 mL, 5.0 mmol) were added. The resulting suspension was stirred at 50 – 60 °C for 5 hours. The reaction mixture was then allowed to cool to RT, and Et_2O was added. After extraction with Et_2O, the organic phases were additionally washed with

0947-6539/99/0502-0772 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 2

brine, dried ($MgSO_4$), and evaporated. Purification by FC (Et_2O/pentane 6:1) gave **52** (4 mg, 50%) as a 1.7:1 mixture of the *rac* and *meso* pentan-1,3-diol.

Acknowledgements

We are grateful to Prof. D. Seebach for generous financial support and for helpful comments during the preparation of the manuscript. We also thank Prof. D. P. Curran for helpful discussions and Dr. J. L. Matthews and D. Christen for improvements to the English.

[1] K. Shiima, M. Kumada, *J. Org. Chem.* **1958**, *23*, 139; H. Sakurai, R. Koh, A. Hosomi, M. Kumada, *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2050.
[2] C. G. Pitt, M. S. Fowler, *J. Am. Chem. Soc.* **1968**, *90*, 1928.
[3] D. P. Curran, B. Yoo, *Tetrahedron Lett.* **1992**, *33*, 6931; see also: M. Ballestri, C. Chatgilialoglu, G. Seconi, *J. Organomet. Chem*. **1991**, *408*, C1.
[4] M. Ballestri, C. Chatgilialoglu, M. Lucarini, G. F. Pedulli, *J. Org. Chem.* **1992**, *57*, 948; M. Lucarini, E. Marchesi, G. F. Pedulli, C. Chatgilialoglu, *J. Org. Chem.* **1998**, *63*, 1687; C. Chatgilialoglu, A. Guerrini, M. Lucarini, G. F. Pedulli, P. Carrozza, G. Da Roit, V. Borzatta, V. Lucchini, *Organometallics* **1998**, *17*, 2169.
[5] R. West, P. Boudjouk, *J. Am. Chem. Soc.* **1973**, *95*, 3983.
[6] J. M. Harris, I. MacInnes, J. C. Walton, B. Maillard, *J. Organomet. Chem.* **1991**, *403*, C25; J. M. Harris, J. C. Walton, B. Maillard, S. Grelier, J. P. Picard, *J. Chem. Soc. Perkin Trans. 2* **1993**, 2119.
[7] Y.-M. Tsai, C.-D. Cherng, *Tetrahedron Lett.* **1991**, *32*, 3515; D. P. Curran, W.-T. Jiaang, M. Palovich, Y.-M. Tsai, *Synlett* **1993**, 403; Y.-M. Tsai, K.-H. Tang, W.-T. Jiaang, *Tetrahedron Lett.* **1996**, *37*, 7767; S.-Y. Chang, W.-T. Jiaang, C.-D. Cherng, K.-H. Tang, C.-H. Huang, Y.-M. Tsai, *J. Org. Chem.* **1997**, *62*, 9089.
[8] S. Shuto, M. Kanazaki, S. Ichikawa, M. Minakawa, A. Matsuda, *J. Org. Chem.* **1998**, *63*, 746. However, in a recent computational study Schiesser concluded the intramolecular 1,2 silyl migration from carbon to carbon to be unlikely: C. H. Schiesser, M. L. Styles, *J. Chem. Soc. Perkin Trans. 2* **1997**, 2335.
[9] C. Chatgilialoglu, A. Guarini, A. Guerrini, G. Seconi, *J. Org. Chem.* **1992**, *57*, 2207.
[10] A. I. Prokof'ev, T. I. Prokof'eva, I. S. Belostotskaya, N. N. Bubnov, S. P. Solodovnikov, V. V. Ershov, M. I. Kabachnik, *Tetrahedron* **1979**, *35*, 2471; A. Alberti, A. Hudson, *Chem. Phys. Lett.* **1977**, *48*, 331; A. Alberti, C. Chatgilialoglu, *Tetrahedron* **1990**, *46*, 3963.
[11] S. Kim, J. Y. Doo, K. M. Lim, *J. Chem. Soc. Perkin Trans. 1* **1994**, 2517.
[12] A. Alberti, S. Dellonte, C. Paradisi, S. Roffia, G. F. Pedulli, *J. Am. Chem. Soc.* **1990**, *112*, 1123.
[13] K. J. Kulicke, C. Chatgilialoglu, B. Kopping, B. Giese, *Helv. Chim. Acta* **1992**, *75*, 935.
[14] K. Miura, K. Oshima, K. Utimoto, *Chem. Lett.* **1992**, 2477; K. Miura, K. Oshima, K. Utimoto, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2348.
[15] C. H. Schiesser, L. M. Wild, *Tetrahedron* **1996**, *52*, 13265; C. H. Schiesser, M. L. Styles, L. M. Wild, *J. Chem. Soc. Perkin Trans. 2* **1996**, 2257.
[16] A. Studer, *Angew. Chem.* **1998**, *110*, 507; *Angew. Chem. Int. Ed.* **1998**, *37*, 462.
[17] a) D. P. Curran, J. Xu, E. Lazzarini, *J. Chem. Soc. Perkin Trans I* **1995**, 3049; b) D. P. Curran, J. Xu, *J. Chem. Soc. Perkin Trans I* **1995**, 3061; c) A. Martinez-Grau, D. P. Curran, *J. Org. Chem.* **1995**, *60*, 8332; D. P. Curran, J. Xu, E. Lazzarini, *J. Am. Chem. Soc.* **1995**, *117*, 6603; A. Martinez-Grau, D. P. Curran, *Tetrahedron* **1997**, *53*, 5679; d) D. P. Curran, J. Xu, *Synlett* **1997**, 1102. For other UMCT reactions see: G. E. Keck, E. J. Enholm, J. B. Yates, M. R. Wiley, *Tetrahedron* **1985**, *41*, 4079; S. Kim, J. S. Koh, *J. Chem. Soc. Chem. Commun.* **1992**, 1377; J. Boivin, J. Camara, S. Z. Zard, *J. Am. Chem. Soc.* **1992**, *114*, 7909.
[18] M. Murakami, M. Suginome, K. Fujimoto, H. Nakamura, P. G. Andersson, Y. Ito, *J. Am. Chem. Soc.* **1993**, *115*, 6487.
[19] A. Kawachi, N. Doi, K. Tamao, *J. Am. Chem. Soc.* **1997**, *119*, 233.
[20] K. Tamao, A. Kawachi, Y. Ito, *J. Am. Chem. Soc*. **1992**, *114*, 3989.
[21] Prepared in analogy to $ClSiPh_2SiMe_3$[20] with $BrGeMe_3$.
[22] Prepared from $ClSiMe_2(NEt_2)$ and $LiSnMe_3$ with subsequent chlorodeamination according to ref. [20]. The stannylated chlorosilane was isolated in 60% purity.
[23] Prepared from $(Me_3Si)_3SiH$ over three steps (see Experimental Section). The chlorosilane was not easily purified and was used in 60–80% purity for the subsequent silylation reaction.
[24] For a compilation of Si–Si bond energies see: R. Walsh, *Acc. Chem. Res.* **1981**, *14*, 246.
[25] S. J. Cole, J. N. Kirwan, B. P. Roberts, C. R. Willis, *J. Chem. Soc. Perkin Trans I* **1991**, 103. See also: C. Chatgilialoglu, K. U. Ingold, J. C. Scaiano, *J. Am. Chem. Soc.* **1983**, *105*, 3292.
[26] M. F. Lappert, J. B. Pedley, J. Simpson, T. R. Spalding, *J. Organomet. Chem.* **1971**, *29*, 195.
[27] M. Newcomb, *Tetrahedron* **1993**, *49*, 1151.
[28] For volatile compounds, the experiments were conducted in C_6D_6 and analysed prior to the removal of the solvent.
[29] For **9** and **11** small amounts of an arylated side product were observed; this was formed by a 1,5-phenyl transfer from silicon to carbon. With secondary radicals this aryl transfer is the main reaction: A. Studer, M. Bossart, H. Steen, *Tetrahedron Lett*. **1998**, *39*, 8829.
[30] Silyl ethers derived from primary alcohols cyclize much slower than their congeners derived from secondary or tertiary alcohols (see below). For the fast cyclizing systems it was difficult to isolate pure radical precursors, because traces of an initiator can start the UMCT reaction and thus lead to decomposition of the starting material.
[31] C. Chatgilialoglu, *Chem. Rev.* **1995**, *95*, 1229.
[32] C. Chatgilialoglu, *Acc. Chem. Res.* **1992**, *25*, 188.
[33] The bis(trimethylsilyl)trimethylstannylsilyl ethers analoguous to **15** despite being best suited for conducting S_Hi reactions at silicon are rather difficult to prepare. In fact, tertiary alcohols could not be silylated with the corresponding bulky iodo- and chlorosilanes $(ISi(SiMe_3)_2SnMe_3$, $ClSi(SiMe_3)_2SnMe_3)$.
[34] D. P. Curran, M.-H. Chen, D. Kim, *J. Am. Chem. Soc.* **1989**, *111*, 6265.
[35] D. P. Curran, A. A. Martin-Esker, S.-B. Ko, M. Newcomb, *J. Org. Chem.* **1993**, *58*, 4691.
[36] All the compounds were prepared as racemic mixtures.
[37] The relative configuration was assigned after transformation of **33** to the corresponding known diol derivative by Tamao–Fleming oxidation, see below. 3-Phenyl-2-pentanol (35%, $u{:}l = 10{:}1$) was formed as the main product. This product derives from a stereoselective 1,5 phenyl transfer from Si to C with subsequent desilylation: A. Studer, M. Bossart, H. Steen, ref. [21].
[38] The sun lamp was placed very close to the reaction vessel (sealed tube, $T > 100\,^{\circ}C$). The relative configuration was assigned in analogy.
[39] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102599 (*trans*-**41**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). The X-ray analysis was carried out by Dr. V. Gramlich (ETH Zürich).
[40] R. M. Beesley, C. K. Ingold, J. F. Thorpe, *J. Chem. Soc.* **1915**, *107*, 1080; M. E. Jung, J. Gervay, *J. Am. Chem. Soc.* **1991**, *113*, 224; A. L. Parrill, D. P. Dolata, *Tetrahedron Lett.* **1994**, *35*, 7319; M. E. Jung, M. Kiankarimi, *J. Org. Chem*. **1998**, *63*, 2968.
[41] S.-U. Park, T. R. Varick, M. Newcomb, *Tetrahedron Lett.* **1990**, *31*, 2975; M. E. Jung, R. Marquez, *Tetrahedron Lett.* **1997**, *38*, 6521.
[42] T. Ooi, Y. Hokke, K. Maruoka, *Angew. Chem.* **1997**, *109*, 1230; *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 1181.
[43] D. Seebach, A. K. Beck, A. Studer, in *Modern Synthetic Methods 1995* (Eds.:B. Ernst, C. Leumann), VHCA, Basel, **1995**.
[44] G. R. Jones, Y. Landais, *Tetrahedron* **1996**, *52*, 7599.
[45] H.-J. Knölker, G. Wanzl, *Synlett* **1995**, 378.
[46] M. Bols, T. Skrydstrup, *Chem. Rev.* **1995**, *95*, 1253; L. Fensterbank, M. Malacria, S. McN. Sieburth, *Synthesis* **1997**, 813.
[47] D. P. Curran, N. A. Porter, B. Giese, *Stereochemistry of Radical Reactions*, VCH, Weinheim, 1995.
[48] D. P. Curran, U. Diederichsen, M. Palovich, *J. Am. Chem. Soc.* **1998**, *119*, 4797.

Received: August 7, 1998 [F1289]