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[8] In the course of this ET step G must be oxidized to a radical cation that is known to undergo a fast deprotonation step yielding a very unreactive delocalized G radical. Since we cannot detect any damage at G sites, we assume that the G radical is repaired by hydrogen atom abstraction under anaerobic conditions. For structure, reactivity, and repair of deoxyguanosine radical cations, see: a) S. Steenken, *Chem. Rev.* **1989**, *89*, 503; b) L. P. Candeias, S. Steenken, *J. Am. Chem. Soc.* **1989**, *111*, 1094; c) S. V. Jovanovic, M. G. Simic, *Biochim. Biophys. Acta* **1989**, *1008*, 39.

[9] G triple units were chosen for the experiments on the distance dependence because they are the most potent electron donating sites in DNA (see ref. [6]). We suppose that the closest G is the initially oxidized base. This assumption is permitted since the change from a single G to a triple G unit in 3′- as well as in 5′-direction has nearly the same ET-acceleration effect of 2.5 and 1.8, respectively (Table 1, entries 8, 11, and 9, 12).

[10] For the determination of the distance Δr, the corresponding DNA duplex sequences were constructed in the B-form with the nucleic acid building tool in the program MacroModel V4.5. In order to mimic the planar enol ether radical cation **3**, the deoxyribose enol ether **5** was modeled into the DNA structure using the AMBER* force field implemented in MacroModel V4.5. Distances Δr were taken between the radical center C3′ of the radical cation and the G carbon atom 5 which has the highest electron density of the HOMO.

[11] Independent experiments with glutathione diethyl ester as a trap for radical **6** demonstrated that, in G-free DNA strands, the addition of water to radical cation **3** (**3** → **6**) occurs in about 70 % yield.

[12] We determined the ratio $k_{\mathrm{ET}}/k_{\mathrm{trap}}$ from the HPLC areas (corrected by the extinction coefficients) of 5′-phosphate **4** (A_4), whose concentration is equal to the overall yield of radical cation **3** (Scheme 1) and enol ether **5** (A_5). The ratio $A_5/(A_4 - A_5)$ is equal to $k_{\mathrm{ET}}/k_{\mathrm{trap}}$. Because these ratios turned out to be independent of the conversion, the reactions follow first- or pseudo first-order kinetics.

[13] We used one-electron donors like methionine, selenomethionine, KI, and $K_4[Fe(CN)_6]$ to reduce the radical cation **3** by intermolecular ET in competition to water addition. KI is the fastest ET quencher. Under the assumption that this ET proceeds in a nearly diffusion controlled way, we could determine a rate coefficient of $10^6\,\mathrm{M}^{-1}\mathrm{s}^{-1}$ by pseudo first-order kinetic experiments with different concentrations of KI.

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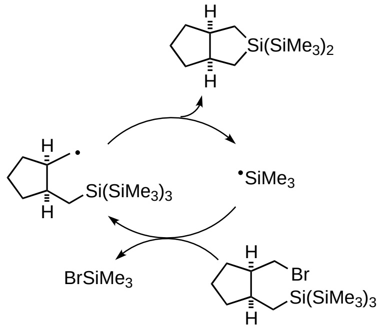
S_Hi Reactions at Silicon as Unimolecular Chain Transfer Steps in the Formation of Cyclic Alkoxysilanes[**]

Armido Studer[*]

Intermolecular transfer of bromine, iodine, phenylselenide, and aryltelluride groups between carbon-centered radicals is a well-established procedure for the synthesis of complex organic molecules.[1] In contrast (other than one example[2]), intramolecular transfer involving migration of selenium, tellurium or a halogen has not yet been observed. For the chalcogen group, only a single report describes the 1,4-transfer of a phenylsulfanyl group.[3] However, several reports on the intramolecular migration of stannyl or silyl groups have appeared.[4] The reasons for the facile intramolecular homolytic substitution (S_Hi) reaction at silicon or tin are not well understood.[5]

These S_Hi reactions can be used for the formation of silicon- or tin-containing heterocycles. Giese et al.[6] and Utimoto et al.[7] independently reported intramolecular homolytic substitutions at tris(trimethylsilyl)-substituted Si atoms by C-centered radicals. It was concluded that the trimethylsilyl radical generated during the intramolecular substitution acts as the chain carrier (Scheme 1). According to Curran's terminology,[8] this is an example of a unimolecular chain transfer (UMCT) reaction in which the key chain transfer step is a unimolecular process. After consideration of the results of Giese's and Utimoto's groups, we initiated further exploration of intramolecular homolytic substitutions at silicon. It was envisaged that this transformation would be a suitable UMCT step in bimolecular radical addition reactions, where either a silyl or a stannyl radical acts as the chain carrier. In addition, the cyclic silanes formed in these UMCT steps could be transformed into the corresponding alcohol derivatives by Tamao–Fleming oxidation.[9]



Scheme 1. S_Hi reaction at tris(trimethylsilyl)-substituted silanes.

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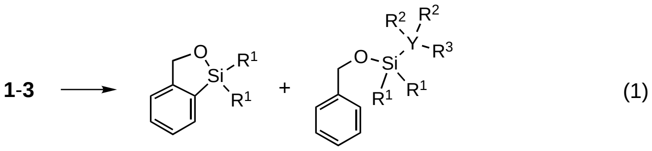
Initially, the $\mathrm{S_Hi}$ reaction of aryl radicals at differently substituted silanes was studied [Eq. (1)]. The required 2-halo-substituted benzyl silyl ethers **1**–**3** were synthesized from the



4 (R^1 = Ph)
6 (R^1 = $SiMe_3$)
5,**7**,**8**

(1)

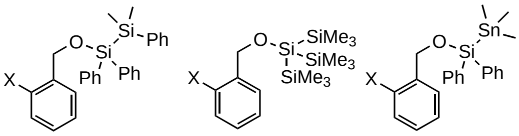
corresponding alcohols.[10] Reaction of disilane **1** with sub-stoichiometric amounts of Bu_3SnH (0.2 equiv) did not provide the desired alkoxysilane **4**. With 1.2 equivalents of $(TMS)_3SiH$ as initiator, 5 % of **4** and 43 % of the reduction product **5** were formed along with several unidentified side products. The reduction product was isolated in 38 % yield (Table 1, entry 1).

Table 1. $\mathrm{S_Hi}$ reactions of aryl radicals at substituted silanes.[a]

Entry	Starting material	Conditions	Unchanged material [%]	Yield [%] (product)	Yield [%] (side product)
1	**1**	1.2 equiv $(TMS)_3SiH$ benzene, 0.04 M, AIBN reflux	–	5 (**4**)	43[b] (**5**)
2	**2**	0.2 equiv Bu_3SnH benzene, 0.04 M, AIBN (10 %) reflux, syringe pump[c]	42	58 (**6**)	–
3	**2**	0.5 equiv Bu_3SnH benzene, 0.04 M, AIBN reflux	–	91 (**6**)	4 (**7**)
4	**2**	0.5 equiv $(TMS)_3SiH$ benzene, 0.04 M, AIBN (25 %) reflux, syringe pump[d]	60	30 (**6**)	–
5	**2**	$Bu_3SnSnBu_3$ (10 %) benzene, 0.1 M, acetone *hν*, 72 h	91	9 (**6**)	–
6	**2**	$Bu_3SnSnBu_3$ (10 %) hexane, 0.1 M, acetone *hν*, 45 h	89	11 (**6**)	–
7	**3**	0.2 equiv Bu_3SnH benzene, 0.02 M, AIBN reflux	–	80[e] (**4**)	–

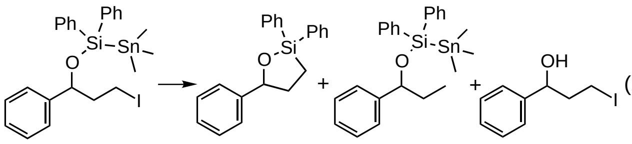
[a] Yields determined by ^1H NMR spectroscopy. AIBN = azoisobutyronitrile. [b] 38 % yield of isolated product. [c] Bu_3SnH (0.08 M) and AIBN were dissolved in benzene and added over 7 h. [d] $(TMS)_3SiH$ (0.13 M) and AIBN were dissolved in benzene and added over 8 h. [e] 68 % yield of isolated product.

Slow addition of $(TMS)_3SiH$ did not provide better results. Presumably, the Si–Si bond in **1** is too strong to be efficiently cleaved by an aryl radical.[13] Addition of Bu_3SnH (0.2 equiv) by syringe pump to **2** in benzene (0.04 M) afforded alkoxysilane **6** and starting material **2** in a ratio of 58:42 (entry 2). No other side product derived from **2** could be observed. This clearly showed that the UMCT was occurring. However, even after careful optimization, it was still necessary to use up to 0.5 equivalents of initiator for complete reaction. For example, addition of Bu_3SnH (0.5 equiv) to a solution of **2** in benzene (0.04 M) afforded **6** in 91 % yield alongside the direct reduction product **7** (4 % as determined by ^1H NMR analysis; entry 3). With $(TMS)_3SiH$ (0.5 equiv) as initiator, only 30 % of cyclization product was formed (entry 4). Irradiation (300 W sun lamp, 72 hours) of a benzene solution of **2** containing hexabutylditin (0.1 equiv) and acetone as a sensitizer[14] afforded **6** (9 %), along with 91 % unchanged starting material (entry 5). A slightly faster reaction was observed in this case if benzene was replaced by hexane (entry 6). This is probably due to the fact that silyl radicals add to benzene and are thus prevented from propagating the chain.[15] With silyl ether **3** (0.02 M, benzene), quantitative consumption of the starting material was observed with only 0.2 equivalents of Bu_3SnH, added in two portions; alkoxysilane **4** formed in 80 % yield as determined by ^1H NMR analysis (entry 7). No reduction product **8** was observed. Purification by reversed phase (RP) chromatography (RP-18 Nucleosil, Macherey-Nagel particle size 7, acetonitrile) afforded **4** in 68 % yield. Apparently, due to the weaker bond energy,[16] the Si–Sn bond is superior to the Si–Si bond for applications to intramolecular homolytic substitutions at silicon.



1 (X = Br) **2** (X = Br) **3** (X = I)
5 (X = H) **7** (X = H) **8** (X = H)

To elaborate this UMCT process further, the cyclization of alkyl radicals was studied. To this end, iodide **9** was prepared (62 %) from the corresponding iodoalcohol.[12] The UMCT reaction was studied under different conditions [Eq.(2)]. Under "atom transfer" conditions[17] on irradiation (300W sun lamp) of a benzene solution of **9** (0.1 M) containing hexabutylditin (0.1 equiv) lead to complete consumption of **9** after 16 hours (Table 2, entry 1). Besides alkoxysilane **10** (87 %, 66 % after chromatography), the reduced silyl ether **11** (13 %) was observed in the crude product.[18] Without addition of the ditin, under otherwise similar conditions, the reaction was much slower and iodoalcohol **12** (arising from desilylation of **9**) was formed as a side product (entry 2). Similar results were obtained if the reaction was conducted under atom transfer conditions with either hexaphenylditin (entry 3) or tetrakis (trimethylsilyl)silane[8b] (entry 4) as additives. The best result was obtained with Bu_3SnH as the initiator of the UMCT reaction. With 0.15 equivalents of



9 **10** **11** **12**

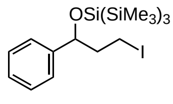
(2)

Table 2. Unimolecular chain transfer reaction of **9**.[a]

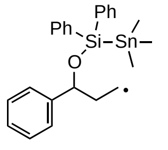
Entry	Conditions	**10**[%]	**11**[%]	**12**[%]
1	$Bu_3SnSnBu_3$ (10%), benzene 0.06 M, *hν*, 16 h	87	13	–
2	benzene, 0.1 M, *hν*, 36 h[b]	30	–	16
3	$Ph_3SnSnPh_3$ (10%), benzene 0.1 M, *hν*, 24 h	45	–	21
4	$(TMS)_4Si$ (10%), benzene 0.1 M, *hν*, 24 h	41	–	23
5	Bu_3SnH (15%), AIBN, benzene	89	4	–
6	Bu_3SnH (5%), AIBN, benzene	84	2	–

[a] Yields determined by ^1H NMR spectroscopy. [b] The reaction was stopped after 36 h; 16% of the starting material was detected.

Bu_3SnH (added in three portions) the cyclic alkoxysilane **10** was formed in 89% yield with only 4% of the reduction product **11** (entry 5). As little as 0.05 equivalents of Bu_3SnH could be used for complete consumption of the starting material; however, a slight decrease of the yield (84%) was observed (entry 6). The desilylation product **12** was not seen in these tin hydride experiments. By competition experiments with $(TMS)_3SiH$,[6] a rate constant of $1.2 \times 10^6 s^{-1}$ at 80° was estimated for the cyclization of radical **14** leading to **10**. In the case of iodide **13**, obtained by silylation ($(TMS)_3SiI$) of 3-chloro-1-phenylpropan-1-ol followed by Finkelstein reaction (32% overall), no UMCT reaction could be observed under atom transfer conditions with $Bu_3SnSnBu_3$ (0.1 equiv) as the additive. Starting material **13** could be identified as the main component in the NMR spectrum of the crude product (65% recovered after chromatography). The reduction product (also independently synthesized) was formed in 5% yield.[19] As with some of the reactions described earlier, the Si–Si bond is not suitable for UMCT reactions based on S_Hi reactions at silicon.

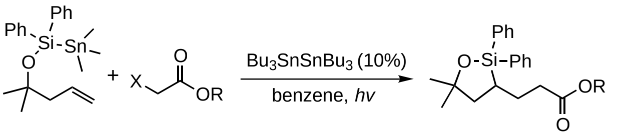


13



14

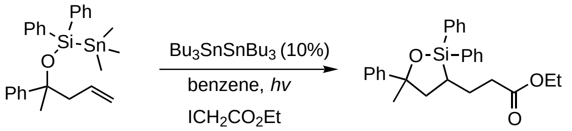
In order to demonstrate the preparative value of S_Hi reactions, bimolecular radical addition reactions with a subsequent S_Hi reaction were also studied. Radical acceptor **15** was prepared as previously described[12] from the corresponding tertiary alcohol (72%). Reaction of phenyl bromoacetate (1.2 equiv) with olefin **15** (0.3 M, benzene) under atom transfer conditions provided **16** [Eq. (3)]. Neither starting material nor side products derived from **15** could be identified in the NMR spectrum of the crude product.[20] Purification by chromatography (SiO_2) afforded **16** in 68% yield. Under similar conditions, ethyl ester **17** was isolated in 56% yield starting from ethyl iodoacetate and **15**.[21] If the bimolecular reaction of **15** with phenyl bromoacetate was conducted with tin hydride (1 equiv Bu_3SnH, syringe pump, 0.2 M in benzene) only 26% of **16**, besides unchanged **15** (70%), was observed.



(3)

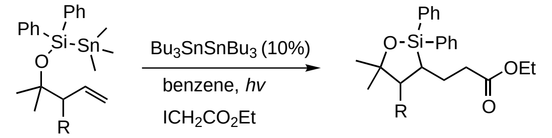
15 (X = Br, R = Ph) (X = I, R = Et) **16** (68%, R = Ph) **17** (56%, R = Et)

We also studied the cyclization reaction of chiral silyl ethers. The chiral olefins **18** and **19a,b** containing a stereogenic center either *β* or *α* to the double bond were synthesized as described above. UMCT reaction of **18** with ethyl iodoacetate under atom transfer conditions[17] provided alkoxysilane **20** as a 1.5:1 mixture of diastereoisomers in 67% yield [Eq. (4)].[22] Excellent selectivities were obtained for the cyclization of the secondary radical formed after addition of the ethyl iodoacetate derived radical to **19a,b** [Eq. (5)]. With radical acceptor **19a** only the *trans* product **21** was observed (87% isolated yield).[23] With **19b** a somewhat lower (but still good) selectivity was obtained for the UMCT reaction with ethyl iodoacetate. The two isomers, *trans*-**22** and *cis*-**22** (22:1) were isolated as an inseparable mixture in 76% yield. To our knowledge, these are the first examples of such high stereocontrol in these types of homolytic substitution reactions.[4,24]



(4)

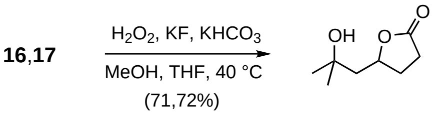
18 **20** (67%, *dr* = 1.5:1)



(5)

19a (R = Ph) **21** (R = Ph, 87%, only *trans*)
19b (R = Me) **22** (R = Me, 76%, *trans*:*cis* = 22:1)

As the final step of the reaction sequence, Tamao–Fleming oxidation was performed on alkoxysilanes **16** and **17** according to known procedures [Eq. (6)].[11] Acidification after standard workup provided lactone **23**, which was isolated in good yields (71, 72%).



(6)

23

In summary, it has been shown that S_Hi reactions at silicon by C-centered radicals in *γ*-position of stannylated silyl ethers are efficient UMCT reactions providing cyclic alkoxysilanes, which can easily be converted into the corresponding diol derivatives. In addition, excellent 1,2 stereoinduction was obtained in the cyclization reaction of chiral silyl ethers.

Experimental Section

All irradiation experiments were carried out in sealed tubes with a 300W sun lamp (OSRAM 300W standard lamp, clear). Radical addition reaction:

Silyl ether **19a** (150 mg, 0.28 mmol), ethyl iodoacetate (0.042 mL, 0.35 mmol), and $Bu_3SnSnBu_3$ (0.017 mL, 0.028 mmol) were dissolved under argon in benzene (1.1 mL). Irradiation for 16 hours and removal of the solvent afforded the crude product, which was purified by flash column chromatography (SiO_2, Et_2O/pentane 1/20) to give **21** (110 mg, 87%) as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 0.86$ (t, $J = 7.1$, 3H, CH_3), 1.06 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 1.59–1.67 (m, 1H), 1.77–1.83 (m, 1H), 2.19 (t, $J = 7.4$, 2H), 2.49–2.54 (m, 1H, SiCH), 3.03 (d, $J = 13.3$, 1H, PhCH), 3.78–3.89 (m, 2H, CH_2O), 7.06–7.10 (m, 1H, aromat.), 7.11–7.28 (m. 10H, aromat.), 7.81–7.84 (m, 2H, aromat.), 7.91–7.94 (m, 2H, aromat.); ^{13}C NMR (125 MHz, $CDCl_3$): 14.19 (CH_3), 24.75 (CH_2), 25.53 (CH_3), 28.74 (CH), 30.08 (CH_3), 35.09 (CH_2), 59.99 (CH_2), 62.66 (CH), 82.14 (C), 127.10 (CH), 127.94 (CH), 128.29 (CH), 128,39 (CH), 128.42 (CH), 130.47 (CH), 130.53 (CH), 134.03 (C), 135.24 (CH), 135.66 (CH), 135.93 (C), 140.47 (C), 172.46 (C). EI-MS: m/z (%): 444.2 (3, M^+), 388.2 (9), 386.2 (100), 295.1 (12), 227.1 (81), 199.1 (63), 183.1 (53). C,H analysis calcd for $C_{28}H_{32}O_3Si$ (444.6): C 75.64, H 7.25, O 10.79, Si 6.32; found: C 75.41, H 7.34.

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Keywords: radical reactions · silicon · silyl ethers · tin

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[10] Silyl ether **1** was prepared according to known procedures[11] from 2-bromobenzyl alcohol and 1-chloro-2,2-dimethyl-1,1,2-triphenyldisilane (78% yield). Compound **2** was obtained from the corresponding chlorosilane (imidazole, DMF, 87%). Stannylated silyl ether **3** was synthesized from (diphenylsilyl)trimethyl tin chloride[12] and 2-iodobenzyl alcohol (85%).

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[18] So far the origin of the reduction product is not clear. When the UMCT reaction was conducted under higher dilution (0.01 M) no reduction product **11** was observed; however, unidentified side products were formed.

[19] Since no authentic sample of the desired cyclization product was available, it was not possible to determine by NMR analyis whether the UMCT product was formed in small quantities. Initiation of the UMCT reaction with Bu_3SnH did not provide better results.

[20] Interestingly, the presence of the reduction product in analogy to the formation of **11** could not be observed.

[21] The mediocre yield is due to partial decomposition of the products during chromatography.

[22] The diastereoisomers could not be separated. We could not determine which isomer was formed in excess.

[23] The relative configuration was assigned by NOE experiments.

[24] L. J. Benja min, C. H. Schiesser, K. Sutej, *Tetrahedron* **1993**, *49*, 2557; D. Colombani, B. Maillard, *ibid.* **1996**, *52*, 14855. Other stereoselective UMCT reactions: D. P. Curran, J. Xu, *Synlett* **1997**, 1102.

The Weak-Link Approach to the Synthesis of Inorganic Macrocycles[**]

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Inorganic and organometallic macrocycles have been topics of intense study with implications for host–guest chemistry, modeling of biological systems, catalysis, and even molecular electronics.[1] These structures can vary in size, shape (rings, squares, rectangles, and cylinders), and the number of metal centers that comprise the macrocycle.[2] One of the most popular synthetic strategies for macrocycles is the "molecular box, square, or rectangle strategy", which was pioneered by Fujita et al.[3] and has now been utilized by many;[4] this strategy uses conformationally rigid ligands bound to metal centers in a *cis* fashion to form tetranuclear complexes in exceptionally high yields. Although this strategy works well for rigid ligands, it will undoubtedly fail with flexible ones because of competing oligimerization and polymerization reactions.

Herein we report a new, general, high-yield (>95%) strategy for synthesizing homobimetallic macrocycles with chemically tailorable cavity properties from flexible ligands (Scheme 1). We refer to this strategy as the "weak-link approach" to the synthesis of inorganic macrocycles. In 1996 Steel and co-workers showed that the reaction between Ag^I and an aromatic ligand with multiple ligating sites resulted in the formation of dimetallocyclophanes.[5] These solid-state structures, which do not remain intact in solution, have ether

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