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Synthesis of Allylsilanes by Reductive Lithiation of Thioethers

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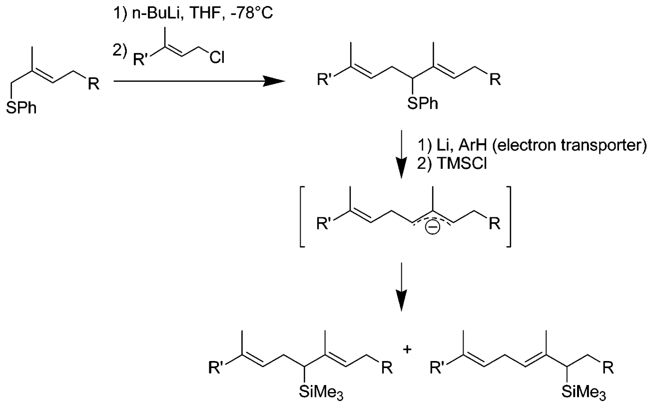
Received May 5, 2004

Although much work in reductive lithiation has been done, the utilization of allylthioethers bearing various substituents to prepare allylsilanes has not been explored. The main reason clearly stems from the anticipated lack of regioselectivity. We describe herein the first study on the regioselectivity of the reductive silylation involving dissymmetric allylthioethers. We surveyed a broad spectrum of parameters and showed that this process displays a great dependence of the reaction conditions. We also discovered that an electron transporter, DBB or naphthalene, can cleave THF at room temperature by sonication, to generate a strong base, 4-lithiobutoxide. This feature was successfully exploited to the straightforward synthesis of bis-silanes in one pot. Examples are provided for maximizing both the chemical yield and the regioselectivity of the reductive silylation through the tuning of the reaction conditions. By changing these conditions, several allylsilanes can be selectively synthesized from one thioether.

Introduction

The biological importance of polyprenoids has led to numerous methods for their preparation.[1] During the course of our synthesis of tricyclopolyprenols, we needed to develop a convenient method to introduce regiospecifically a trimethylsilyl group in the middle of a polyprenyl chain. Toward this end, we modified Biellmann and Ducep's method to construct the polyprenyl chain and to transform the allylthioether intermediate into a silane.[2] This approach involves the deprotonation and subsequent alkylation of allylic thioethers (Scheme 1). The thioether removal originally described by Biellmann and Ducep was performed with lithium in ethylamine.[2] Thus, this procedure is not suitable for the introduction of a silyl group, since both the intermediate carbanion and the chlorosilane would react with the solvent. In 1978, Screttas et al. have shown that the use of naphthalene (Np) allows this lithiation to be run in THF.[3] Generating organolithium from phenylthioethers has found many useful applications. The laboratories of Cohen, Yus, and others have clearly established this approach as one of the most general and versatile methods of organolithium production (Scheme 1).[4] Arenes other than naphthalene have been developed as electron transporters, such as 4,4′-di-*tert*-butyldiphenyl (DBB) and 1-(dimethylamino)naphthalene (DMAN).[5] A major improvement was the demonstration that a catalytic amount of electron transporter was sufficient to perform the reductive lithiation of phenylthioethers.[6] The reaction of allyllithiums, generated by this method, with carbonyl electrophiles can be stereocontrolled by the use of titanium isopropoxide or cerium chloride.[7] Unfortunately, this approach is limited to reactions with aldehydes and ketones. Thus, although much work in reductive lithiation has been done, the utilization of allylthioethers bearing various substituents to prepare allylsilanes has not been explored deeply: most of the described reductive silylations concerned symmetrically substituted allylthioethers, to avoid getting a mixture of regioisomers.[4,8]

SCHEME 1. Synthesis of Silylated Terpenes



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‡ These two authors contributed equally to this work.

[1] For some recent reviews, see: (a) Hanson, J. R. *Nat. Prod. Rep.* **2003**, 70−78. (b) Connolly, J. D.; Hill, R. A. *Nat. Prod. Rep.* **2003**, 640−659. (c) Fraga, B. M. *Nat. Prod. Rep.* **2003**, 392−413 and previous articles of these series.

[2] (a) Biellmann, J. F.; Ducep, J. B. *Tetrahedron Lett.* **1969**, *10*, 3707−3710. (b) Altman, L. J.; Ash, L.; Kowerski, R. C.; Epstein, W. W.; Larsen, B. R.; Rilling, H. C.; Muscio, F.; Gregonis, D. E. *J. Am. Chem. Soc.* **1972**, *94*, 3257−3259. (c) Altman, L. J.; Ash, L.; Marson, S. *Synthesis* **1974**, 129−135.

[3] Screttas, C. G.; Micha-Screttas, M. *J. Org. Chem.* **1978**, *43*, 1064−1071.

[4] For some reviews, see: (a) Cohen, T.; Bhupathy, M. *Acc. Chem. Res.* **1989**, *22*, 152−161. (b) Ramon, D. J.; Yus, M. *Eur. J. Org. Chem.* **2000**, 225−237.

[5] (a) Cohen, T.; Matz, J. R. *Synth. Commun.* **1980**, *10*, 311−317. (b) Freeman, P. K.; Hutchinson, L. L. *J. Org. Chem.* **1980**, *22*, 1924−1930.

[6] Yus, M.; Ramon, D. *J. Chem. Soc., Chem. Commun.* **1991**, 398−400.

10.1021/jo049237u CCC: $27.50

SCHEME 2. Reductive Silylation of Thioether 1

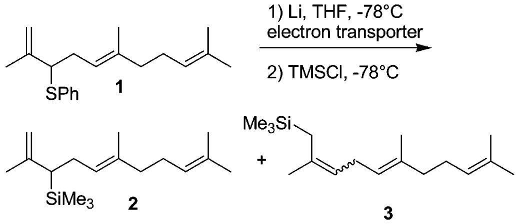


TABLE 1. Two-Step Reductive Silylation of Thioether 1 According to Scheme 2[a]

entry	electron transporter (equiv)	isolated yield, %	ratio 2:3
1	DMAN (1)	82	8:92
2	DMAN (0.1)	76	12:88
3	DMAN (0.5)	81	10:90
4	DBB (1)	87	14:86
5	DBB (0.1)	76	8:92
6	DBB (0.2)	79	15:85
7	DBB (0.5)	84	11:89
8	Np (0.05)	74	17:83

[a] All reactions were performed in THF at −78 °C.

Our need to develop a straightforward access to synthons substituted by a TMS in the middle of a polyprenyl chain prompted us to explore the potential of the reductive silylation. *We describe herein the first study on the regioselectivity of the reductive silylation involving dissymmetric allylthioethers.* We surveyed a broad spectrum of parameters such as the nature of the allylthioether, the nature and the quantity of the electron transporter, the temperature, and the time of reactions. The goal of this study was to establish procedures to control the selectivity of the reductive silylation.

Results and Discussion

Synthesis of Allylsilanes and Dual Function of DBB. First, we choose thioether **1** as a substrate to examine the effects of several parameters on the yield and the regioselectivity of the reaction depicted in Scheme 2.

When the mixture of allythioether **1**, lithium, and an electron transporter (DMAN, DBB, or naphthalene) recovered its original dark-green color, indicating that the lithiation was completed, it was quenched with TMSCl. The corresponding allylsilanes **2** and **3** were obtained in fairly good yields in a roughly 10:90 ratio (Table 1).The trimethylsilyl group was introduced at the least congested position. Neither the nature of the electron shuttle nor its concentration affected dramatically the outcome of this reaction. A quantity of electron transporter as low as 0.05 equiv was sufficient to efficiently catalyze the reductive lithiation (entry 8).

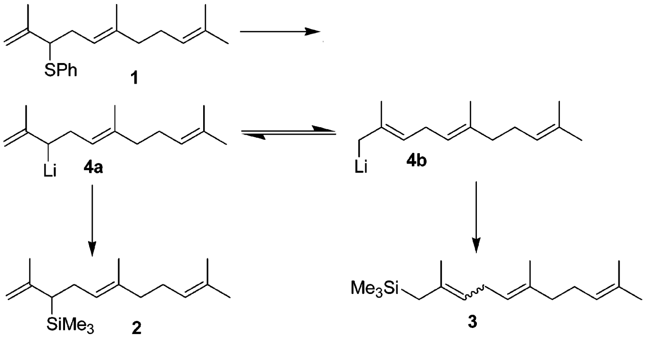
Next, we performed this reductive lithiation under Barbier-type conditions (i.e., performing this reduction in the presence of the chlorosilane) (Table 2). Just as before the nature of the electron transporter did not have any major impact on the yield or the regioselectivity of the reaction. Interestingly, the yields remained similar, while the regioselectivity changed: **2** became the major product. This reaction took more time to be completed than the corresponding two-step process. In analogy with a hypothesis proposed by Yus and colleagues for a similar case, an equilibration of intermediate **4a** to **4b** that would be too slow to occur under Barbier-type conditions could be invoked to account for our observation (Scheme 3).[9] Another explanation could involve a different aggregation state (probably dimeric) of the lithiated intermediates.[10]

TABLE 2. Reductive Silylation According to Barbier-Type Conditions of Thioether 1[a]

entry	electron transporter (equiv)	reaction time, h	yield, %	ratio 2:3
1	DMAN (1)	1.5	81	59:41
2	DMAN (0.1)	12	84	66:34
3	DMAN (0.5)	5	78	56:44
4	DBB (1)	1.5	79	58:42
5	DBB (0.1)	12	65	59:41

[a] All reactions were performed in THF at −78 °C.

SCHEME 3. Putative Equilibrium of Lithiated Intermediates



As experience was gained with the previous example, we applied the silylation reaction to **5** (Scheme 4). Surprisingly, the products changed dramatically according to reaction conditions (Table 3). At −78 °C, when TMSCl was added after the reduction by LiDBB, the adduct **6** was formed as a sole product in 71% yield (entry 1). Only the *Z* isomer of **6** was produced. In that case, this thioether had not been reduced, but deprotonated. *Although the reductive lithiation of phenylthioethers had been known for over 20 years, this observation was in apparent contradiction with previous reports.*[4,11]

Raising the temperature to −42 °C gave only the expected adduct **7** as a 85:15 mixture of *E*:*Z* isomers in 78% yield (entry 2). We did not detect any trace of the isomeric allylsilane **10**. Increasing the temperature to −11 °C changed dramatically the outcome of the reaction: only the product of rearrangement **8** was obtained with a good *E*:*Z* selectivity (entry 3). However, the yield was considerably lowered, probably due to degradation and polymerization of the radical intermediates at that temperature, as evidenced by the formation of some tarr. The regioisomer **9** was not detected. The same regioselectivity with another hard nucleophile (*tert*-butyl bro-

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(7) (a) Guo, B. S.; Doubleday, W.; Cohen, T. *J. Am. Chem. Soc.* **1987**, *109*, 4710−4711. (b) Abraham, W. D.; Cohen, T. *J. Am. Chem. Soc.* **1991**, *113*, 2313−2314. (c) McCullough, D. W.; Bhupathy, M.; Piccolino, E.; Cohen, T. *Tetrahedron* **1991**, *47*, 9727−9736.

(8) Regio- and stereoselective reductive silylation by a siloxy or hydroxyl group has been reported: Marumoto, S.; Kuwajima, I. *J. Am. Chem. Soc.* **1993**, *115*, 9021−9024.

(9) Guijarro, D.; Yus, M. *J. Organomet. Chem.* **2001**, *624*, 53−57.

(10) Clayden, J. *Organolithiums: Selectivity for Synthesis*; Pergamon Press: New York, 2002; Chapter 1, pp 1−8.

SCHEME 4. Reductive Silylation of Thioether 5 According to Conditions Displayed in Table 3

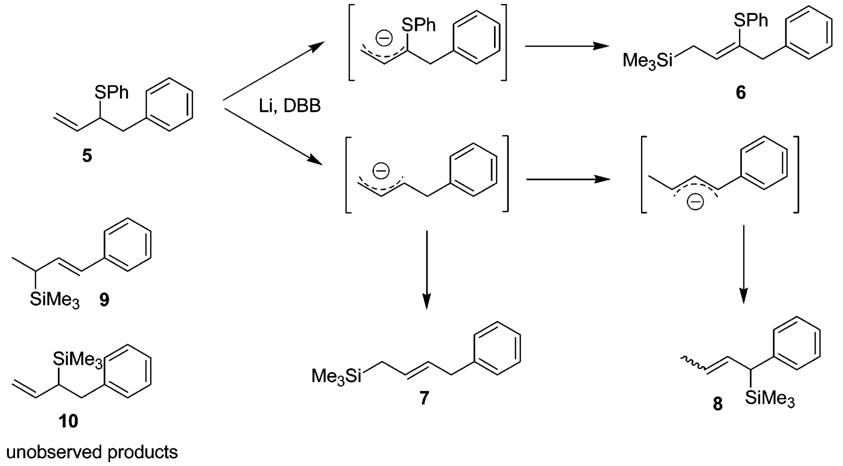
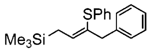
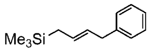


TABLE 3. Reductive Silylation of Thioether 5

Entry	Barbier-type Conditions	T(°C)	Yield [a] (%)	Ratio [a]  6	 7	 8
1	no	-78	71	100	-	-
2	no	-42	78	-	100 (E/Z: 85/15)	-
3	no	-11	47	-	-	100 (E/Z: 95/5)
4	yes	-78	67	-	100 (E/Z: 79/21)	-
5	yes	-42	81	-	100 (E/Z: 81/19)	-
6	yes	-11	38	-	-	100 (E/Z: 59/41)

[a] Isolated products.

mide) has been reported by Nojima and colleagues.[12] Running this silylation under Barbier-type conditions at −78 or −42 °C produced the expected adduct **7** as a sole product (entries 4 and 5). At −11 °C, the Barbier-type conditions diminished the stereoselectivity, since the product of rearrangement **8** was formed with a lower *E*:*Z* selectivity (compare entries 6 and 3). *This study is the first one to establish that by tuning the reaction conditions, three different allylsilanes (**6**, **7**, and **8**) can be obtained from the very same substrate with a high selectivity*.

To gain more information on the reactivity of trisubstituted thioethers, we studied the behavior of **11**, which carries two methyls at the extremity of the olefin (Table 4, Scheme 5).

TABLE 4. Reductive Silylation of Thioether 11 According to Scheme 5

entry	Barbier-type conditions	*T*, °C	yield,[a] %	ratio 12	13	14	16
1	no	−78	77	31	5	64	
2	no	−42	81	28		72	
3	no	−11	21				100
4	yes	−78	72	12		88	
5	yes	−42	84	8		92	
6	yes	−11	11				100

[a] Isolated products.

At −78 °C, when TMSCl was added after the reduction by LiDBB, the expected allylsilanes **12** and **14** were the major products, in a 31:64 ratio (Table 4, entry 1). Traces of bis-silylated adduct **13** were isolated. This compound

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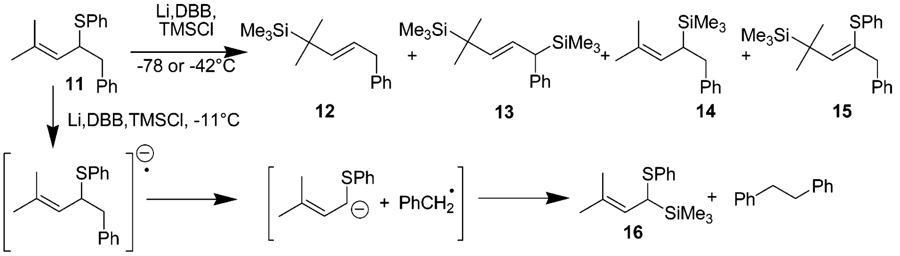
(11) For a preliminary communication of the results describing THF cleavage, see: Streiff, S.; Ribeiro, N.; Désaubry, L. *Chem. Commun.* **2004**, 346−347.

(12) Tanaka, J.; Nojima, M.; Kusabayashi, S. *J. Am. Chem. Soc.* **1987**, *109*, 3391−3397.

SCHEME 5. Reductive Silylation of Thioether 11



probably comes from the anomalous deprotonation of **12**.[13] For comparison, the same reaction conditions performed on thioether **5** led exclusively to an adduct substituted by both a thioether and a TMS moiety, indicating that the introduction of the methyl groups decreases dramatically the anomalous deprotonation of allylthioethers.

As previously, increasing the temperature to −42 °C totally suppressed this deprotonation: the expected allylsilanes **12** and **14** were the sole ones to be observed (entry 2). At −11 °C, the overall yield was again diminished (to 21%) (entry 3). Only the silyl thioether **16** and some bibenzyl were isolated, suggesting a homolytic cleavage of the radical anion as outlined in Scheme 5.

Under Barbier-type conditions at −78 and −42 °C, we observed uniquely the formation of the expected allylsilanes **12** and **14**, with, in particular, an improved regioselectivity at −42 °C (compare entries 4 and 5 to entries 1 and 2). In this latter case (entry 5), a 84% yield of a 8:92 ratio of regioisomers **12** and **14** was observed. At −11 °C, we isolated again only the debenzylated adduct **16**. These examples provide a second demonstration of the possibility to orientate selectively the reductive silylation to different major products (**14** and **16**) depending on reaction conditions.

Comparing the regioselectivity of the reductive silylation of **1**, **5**, and **11**, we can conclude that the structure of the substrate, the temperature, and the presence or the absence of chlorosilane during the reductive lithiation step are three critical factors that cannot be considered independently from one another, probably because each of these three factors will affect the aggregation state of the lithiated intermediates and its reactivity. Another effect that may intervene is the intramolecular π-complexation of the lithium cation to an alcene moiety. Such an interaction has been reported by Rölle and Hoffmann.[14]

The main common point that came out of this study is that Barbier-type conditions at −42 °C prevent the anomalous deprotonation and give the best yield and selectivity. We settled therefore on this condition to examine the reactivity of several allylthioethers (Table 5). We observed that the trimethylsilyl group was preferentially introduced at the least substituted position with a regioselectivity ranging from 100:0 (in the case of **26**, entry 4) to 56:44 (in the case of **23**, entry 3). The low selectivity of this latter case is due to a similar level of substitution of allylsilanes **24** and **25**. As expected, the benzyl group of compound **23** was removed during the course of this reaction.

Effective Activation Method and Specificity of DBB as an Electron Transporter. Next, we studied a parameter that had not been examined yet: the conditions of formation of the reducing agent LiDBB (Table 6). To prepare this reagent, an excess of lithium and a catalytic amount of DBB were sonicated for less than 5 min at room temperature to afford a dark-green solution. This was then immediately cooled to the desired temperature (conditions A). In the second procedure (conditions B) the time of LiDBB preparation was extended to 1 h. In conditions C, the medium was sonicated for 5 min and stirred at room temperature for 1 h. When LiDBB was prepared within 5 min (conditions A), the silyl thioether **32** was never formed (entries 1−4 and 10). On the other hand, when it was prepared according to conditions B, we observed a substantial amount of adduct **32** at −42 °C in non-Barbier-type conditions (entry 7). This reaction was exclusive at −78 °C (entry 6).

One possible reason for these observations which came to mind is that THF might be cleaved into 4-lithiobutoxide, which would deprotonate the thioethers. Such a reductive cleavage of THF has been reported, albeit under more drastic conditions. Eisch was the first to note that THF could be cleaved by lithium in the presence of an arene.[15] This author showed that refluxing a mixture of biphenyl and lithium in THF affords some butanol after hydrolysis of the reaction system. At that temperature, 4-lithiobutoxide decomposed, and its formation was not quantified. Later, Cohen showed that, in the presence of boron trifluoride etherate, LiDBB cleaves THF instantaneously at a temperature as low as −78 °C.[16] This reactivity stems from the complexation of the oxygen atom by this strong Lewis acid. More recently, Yus and colleagues reported that the dilithium naphthalene dianion reacts slowly with THF at room temperature for 24 h, affording after hydrolysis small amounts of butanol as well as products of condensation of naphthalene with THF.[17]

When we analyzed a solution of LiDBB prepared according to conditions B, we were pleased to notice the

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[13] Similar deprotonation by strong bases has been reported, see for example: (a) Marr, F.; Fröhlich, R.; Hoppe, D. *Tetrahedron: Asymmetry* **2000**, *13*, 2587−2592. (b) Schlosser, M.; Zellner, A.; Leroux, F. *Synthesis* **2001**, 1830−1836.

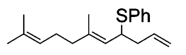
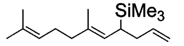
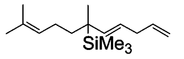
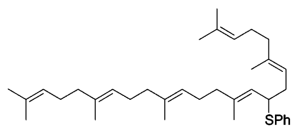
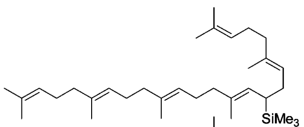
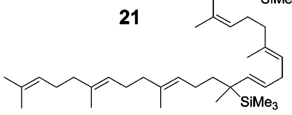
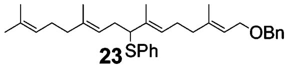
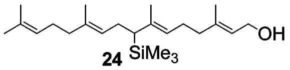
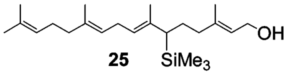
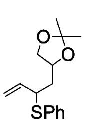
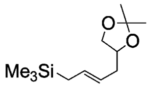
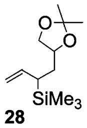
[14] Rölle, T.; Hoffmann, R. W. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1953−1954.

[15] Eisch, J. J. *J. Org. Chem.* **1963**, *28*, 707−710.

[16] (a) Mudryk, B.; Cohen, T. *J. Am. Chem. Soc.* **1991**, *113*, 1866−1867. THF cleavage can also be achieved with a catalytic amount of DBB or naphthalene, see: (b) Ramon, D. J.; Yus, M. *Tetrahedron* **1992**, *48*, 3585−3588. For other synthetic applications of THF cleavage, see: (c) Oikawa, M.; Oikawa, H.; Ichihara, A. *Tetrahedron* **1995**, *51*, 11457−11464. (d) Dvorak, C. A.; Rawal, V. H. *J. Chem. Soc., Chem. Commun.* **1997**, 2381−2382.

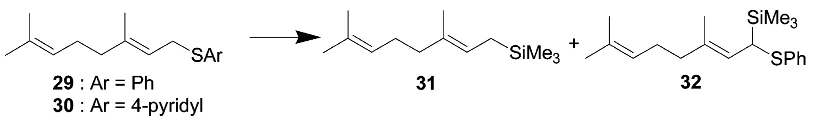
[17] Yus, M.; Herrera, R. P.; Guijarro, A. *Chem. Eur. J.* **2002**, *8*, 2574−2584.

TABLE 5. Reductive Silylation of Thioethers under Barbier-Type Conditions[a]

Entry	Substrates	Products	Isolated yield (%)	ratios
1	 **17**	 **18**  **19**	83	18:19 93:7
2	 **20**	 **21**  **22**	92	21:22 81:19
3	 **23**	 **24**  **25**	51	24:25 56:44
4	 **26**	 **27**  **28**	63	27:28 100:0

[a] Reactions performed with 0.1 equiv of DBB, 50 equiv of Li, and 1.5 equiv of TMSCl with 0.5 M substrate in THF at −42 °C.

TABLE 6. Conditions of Formation of the Reducing Agent "LiDBB": Effects on the Reductive Silylation of Thioethers 29 and 30



entry	thioether	conditions[a]	Barbier-type conditions[a]	*T*, °C	yield, %	**31**:**32**
1	**29**	A	no	−78	71	100:0
2	**29**	A	no	−42	72	100:0
3	**29**	A	yes	−78	83	100:0
4	**29**	A	yes	−42	86	100:0
6	**29**	B	no	−78	69	0:100
7	**29**	B	no	−42	59	88:12
8	**29**	B	yes	−78	71	100:0
9	**29**	B	yes	−42	83	100:0
10	**30**	A	no	−78	88	100:0
11	**30**	B	no	−78	92	100:0
12	**30**	B	yes	−78	79	100:0
13	**29**	C	no	−78	54	77:33

[a] Conditions A: a mixture of Li and DBB in THF was sonicated for less than 5 min at rt. Conditions B: sonication for 1 h at rt. Conditions C: a mixture of Li and DBB in THF was sonicated for less than 5 min and stirred at rt for 1 h. **29** or **30** was then added at the indicated temperature. For Barbier-type conditions TMSCl was added at the same time as **29** or **30**, otherwise it was added when the medium recovered its dark-green color.

formation of a substantial amount of *n*-butanol (0.27 M). We quantitatively monitored, after hydrolysis, the formation of *n*-butanol by GC (Figure 1). The efficiency of this process accounts well for the deprotonation of **29**, as depicted in Scheme 6. Naphthalene is also able to cleave THF in the same conditions with a slightly lower efficacy. Surprisingly biphenyl, whose reduction potential is intermediate between that of DBB and naphthalene, could not cleave THF significantly.[18]

Whatever the reaction conditions, the reductive lithiation of pyridylthioether **30** is much faster than its de-

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[18] (a) Evans, A. G.; Jerome, B.; Rees, N. H. *J. Chem. Soc., Perkin Trans. 2* **1973**, 447−453. (b) Curtis, M. E.; Allred, A. L. *J. Am. Chem. Soc.* **1965**, *87*, 2554−2563.

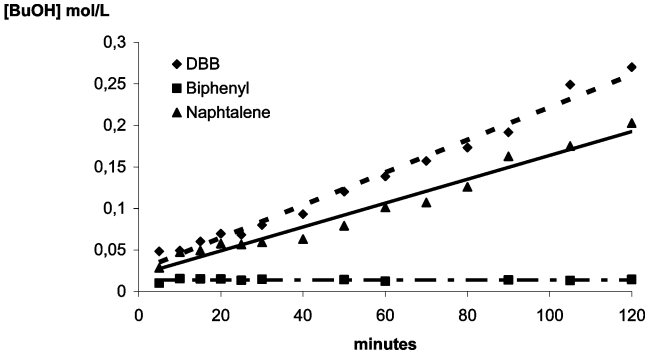
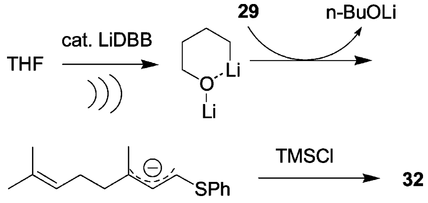
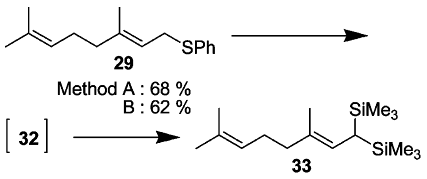


FIGURE 1. Formation of *n*-butanol after hydrolysis of 0.1 M solutions of electron transporter sonicated at room temperature.

SCHEME 6. THF Cleavage and in Situ Deprotonation of Thioeher 29



SCHEME 7. Synthesis of Bis-silane 33[a]



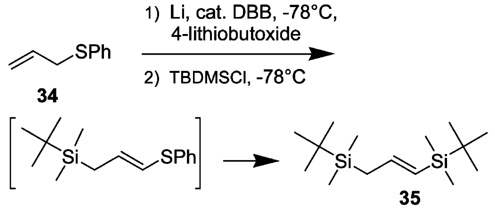
[a] Method A: (1) Li, cat. DBB, −78 °C, 4-lithiobutoxide, 30 min; (2) TMSCl (1 equiv), −78 °C; (3) 12 h, −78 °C; (4) TMSCl, −78 °C. Method B: (1) Li, cat. DBB, −78 °C, 4-lithiobutoxide, 30 min; (2) TMSCl (5 equiv), −78 °C, 4 h.

protonation by 4-lithiobutoxide: only allysilane **31** was observed (entries 10−12 of Table 6). Regarding phenylthioether **29**, deprotonation is faster than reduction at −78 °C (entry 6). At −42 °C, it is the opposite (entry 7). Interestingly, entry 13 (conditions C) shows that DBB can induce some THF cleavage at room temperature without sonication over 1 h (compare entry 13 with 6).

With few exceptions DDB-catalyzed lithiations do not involve extended sonication at room temperature, which may be why our observation has not been reported.[19]

Synthesis of Functionalized Allylsilanes. We took advantage of the property of DBB to catalyze the reductive lithiation of both THF and thioethers to synthesize the bis-silane **33** (Scheme 7).[11] Thioether **29** was first treated as in entry 6 in Table 6, to afford the intermediary adduct **32**, which underwent a subsequent reductive lithiation overnight before it was quenched by TMSCl. The bis-silane **33** was obtained in 68% yield. This procedure is particularly convenient. Compared to other methods, it does not require any preliminary titration and manipulation of a sensitive reagent. The reappearance of the original dark-green color indicates that the deprotonation of the thioether is completed and the chlorosilane may be added. When this color reappears again, the reductive lithiation is completed and the second portion of TMSCl is added.

SCHEME 8. Synthesis of Bis-silane 35



We also synthesized **33** in 61% under Barbier-type conditions using an excess of TMSCl (5 equiv) (method B).

Gratifyingly, we were able to apply the same strategy to allylthioether **34** (Scheme 8). TMSCl was replaced by TBDMSCl to get a less volatile product. The bis-silylated adduct **35** was obtained in 67% yield. This synthesis represents therefore an improvement of the published procedures that involved two steps.[20] This class of dinucleophilic reagents is useful in organic synthesis.[21]

Conclusion

The reductive lithiation enables the synthesis of allylsilanes from readily available starting materials in one operation. This process displays a great dependence of the reaction course not only from the reaction conditions, but also from the structure of the allylthioether. However, we demonstrated that it is possible to tune the reaction conditions to synthesize various allylsilanes selectively from the same thioether. We also provided the first evidence that an electron transporter can cleave THF at room temperature by sonication. This feature was successfully exploited to the straightforward synthesis of bis-silanes. Due to their usefulness in organic synthesis, the reductive lithiation reactions are still the subject of intensive development. These reactions are performed in THF. The only alternative solvent that has been used successfully is dimethyl ether.[22] Therefore, our finding that THF can be cleaved in mild conditions should be taken into account in the design of new reductive lithiations.

Experimental Section

Procedures for the Reductive Silylation of Thioether 1: Non-Barbier-Type Condition (Reaction Corresponding to Entry 5 of Table 1). To a two-necked round-bottom flask equipped with an argon inlet were added THF (1.4 mL) and DBB (18 mg, 0.07 mmol, 0.1 equiv). Small lithium pieces (233 mg, 33.5 mmol, 50 equiv) were prepared as previously and quickly added to the solution of DBB while the flask was

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[19] THF derivatives substituted by a vinyl moiety undergo a smooth reductive lithiation under mild condition, see ref 12a. For reviews on the reductive cleavage of small ring heterocycles, see ref 4b, and: Yus, M.; Foubelo, F. *Rev. Heteroatom Chem.* **1997**, *17*, 73−107.

[20] (a) Morita, T.; Okamoto, Y.; Sakurai, H. *Tetrahedron Lett.* **1980**, *21*, 835−838; (b) Hithcok, P. B.; Lappert, M. F.; Leung, W. P.; Liu, D. S.; Mak, T. C. W.; Wang, Z. X. *J. Chem. Soc., Dalton Trans.* **1999**, 1257−1262.

[21] (a) House, H. O.; Gaa, P. C.; VanDerveer, D. *J. Org. Chem.* **1983**, *48*, 1661−1670; (b) Narjes, F.; Bolte, O.; Icheln, D.; Konig, W. A.; Schaumann, E. *J. Org. Chem.* **1993**, *58*, 626−632. (c) Tubul, A.; Santelli, M. *Tetrahedron* **1988**, *44*, 3975−3982.

[22] Cohen, T.; Kreethadumrongdat, T.; Liu, X.; Kulkarni, V. *J. Am. Chem. Soc.* **2001**, *123*, 3478−3483.

rapidly being purged with argon. The mixture was sonicated for 5 min, then cooled to −78 °C. A solution of allylthioether **1** (200 mg, 0.67 mmol, 1 equiv) in THF (1 mL) was added to the preformed solution of LiDBB under argon and the mixture was stirred until the original dark-green color reappeared, then TMSCl (146 mg, 1.34 mmol, 2 equiv) was added. The reaction was maintained at −78 °C for an additional 5 min and the resulting solution was filtered to remove the lithium excess. The mixture was extracted three times with Et_2O. The combined organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated to dryness. Purification of the resulting yellow oily residue by chromatography (hexane) yielded 135 mg (76%) of a mixture of **2** and **3** in a 8:92 ratio as a colorless oil: R_f 0.78 (hexane).

Barbier-Type Condition (Reaction Corresponding to Entry 5 of Table 2). Lithium 4,4′-di-*tert*-butylbiphenyl was prepared as follows. To a two-necked round-bottom flask equipped with an argon inlet were added THF (1.4 mL) and DBB (18 mg, 0.07 mmol, 0.1 equiv). Small lithium pieces (233 mg, 33.5 mmol, 50 equiv) were prepared as previously and quickly added to the solution of DBB while the flask was rapidly being purged with argon. The mixture was sonicated for 5 min, then cooled to −78 °C. A solution of allylthioether **1** (200 mg, 0.67 mmol, 1 equiv) in THF (1 mL) and TMSCl (109 mg, 1.0 mmol, 1.5 equiv) were added to the preformed solution of LiDBB under argon and the mixture was stirred until the original dark-green color reappeared. The resulting solution was filtered to remove the lithium excess. The mixture was extracted three times with Et_2O. The combined organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated to dryness. Purification of the resulting yellow oily residue by chromatography (hexane) yielded 115 mg (65%) of a mixture of **2** and **3** in a 59:41 ratio as a colorless oil.

Trimethyl[(*E*)-2,6,10-trimethylundeca-1,5,9-triene-3-yl]silane (2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.00 (s, 9H), 1.46 (d, $J = 9.9$ Hz, 1H), 1.60 (s, 3H), 1.62 (s, 6H), 1.68 (s, 3H), 1.97−2.16 (m, 6H), 4.87−5.02 (m, 2H), 5.07−5.13 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.6, 16.7, 19.3, 23.2, 27.4, 27.7, 27.8, 30.5, 38.5, 110.4, 124.1, 125.9, 131.0, 136.7, 146.3.

Trimethyl[(2ξ,5*E*)-2,6,10-trimethylundeca-2,5,9-trienyl]silane (3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.04 (s, 9H), 1,25 (s, 2H), 1.54 (m, 3H), 1.60 (s, 6H), 1.61 (s, 3H), 1.67 (s, 4H), 1.93−2.14 (m, 2H), 4.87−5.02 (m, 1H), 5.07−5.13 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.0, 16.6, 18.3, 23.8, 26.4, 26.9, 27.3, 27.8, 40.4, 121.6, 124.2, 131.9, 133.8, 136.4.

Compounds **2** and **3** could not be separated. The following data concern the mixture of these two isomers: IR (KBr) 2960 (s), 2925 (s), 2855 (s), 1653 (w), 1444 (m), 1376 (m), 1248 (s), 1161 (m), 1108 (w), 933 (w), 910 (m), 854 (s), 736 (m), 694 (m) cm^{-1}. MS (IE, 70 eV) 264 (M$^+$, 27), 195 (4), 181 (4), 122 (4), 107 (7), 93 (5), 73,1 (100), 59 (4). Anal. Calcd for $C_{17}H_{32}Si$: C, 77.19; H, 12.19. Found: C, 77.31; H, 12.21.

Acknowledgment. We are indebted to Prof. Y. Nakatani and G. Ourisson for their invaluable support. We are also grateful to Prof. D. Uguen for having suggested to us that opening of THF may account for our observations. S.S. and N.R. have been funded by a doctoral fellowship from the Ministry of Research and Technology (MRT, France).

Supporting Information Available: Synthesis and characterization of thioethers and allysilanes. This material is available free of charge via the Internet at http://pubs.acs.org.

JO049237U