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Asymmetric Synthesis of 2,3-Dihydrofurans and of Unsaturated Bicyclic Tetrahydrofurans through α-Elimination and Migratory Cyclization of Silyloxy Alkenyl Aminosulfoxonium Salts. Generation and Intramolecular O,Si-Bond Insertion of Chiral Disubstituted β-Silyloxy Alkylidene Carbenes

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Abstract: Treatment of the bis(allylsulfoximine)titanium complexes derived from the β-methyl-substituted acyclic allylic sulfoximines **13a** and **13b** with aldehydes gave with high selectivities the corresponding sulfoximine-substituted homoallylic alcohols which were isolated as the silyl ethers **15a**−**h**. Methylation of sulfoximines **15a**−**h** afforded the aminosulfoxonium salts **5a**−**h** which upon treatment with LiN(H)*t*Bu gave in high yields the enantio- and diastereomerically pure silyl-substituted 2,3-dihydrofurans **4a**−**h**. Treatment of the titanium complexes derived from the cyclic allylic sulfoximines **17a**, **17b**, and *ent*-**17c** with *p*-$MeOC_6H_4$-CHO delivered with high selectivities the corresponding sulfoximine-substituted cyclic homoallylic alcohols which were isolated as the silyl ethers **18a**, **18b**, and *ent*-**18c**, respectively. Methylation of sulfoximines **18a**, **18b**, and *ent*-**18c** furnished the aminosulfoxonium salts **8a**, **8b**, and *ent*-**8c**, respectively, whose treatment with LiN(H)*t*-Bu gave the enantio- and diastereomerically pure fused bicyclic 2,3-dihydrofurans **6a**, **6b**, and *ent*-**6c**, respectively, in good yields. It is proposed that the 1-alkenyl aminosulfoxonium salts **5a**−**h**, **8a**, **8b**, and *ent*-**8c** react with the base under α-elimination and formation of the acyclic and cyclic β-silyloxy alkylidene carbenes **2a**−**h**, **7a**, **7b**, and *ent*-**7c**, respectively, which then undergo a 1,5-O,Si-bond insertion and 1,2-silyl migration. The cyclic aminosulfoxonium salts **8a**, **8b**, and *ent*-**8c** upon treatment with 1,8-diazabicyclo[5.4.0]-7-undecene did not undergo an α-elimination but suffered a novel migratory cyclization with formation of the enantio- and diastereomerically pure bicyclic tetrahydrofurans **9a**, **9b**, and *ent*-**9c**, respectively. It is proposed that the 1-alkenyl sulfoxonium salts **8a**, **8b**, and *ent*-**8c** are isomerized to the allylic aminosulfoxonium salts **10a**, **10b**, and *ent*-**10c**, respectively, which then suffer an intramolecular substitution of the (dimethylamino)sulfoxonium group by the silyloxy group followed by a desilylation. The syntheses of the 2,3-dihydrofurans **4a**−**h**, **6a**, and **6b** and of the tetrahydrofurans **9a** and **9b** are accompanied by the formation of sulfinamide **16** of ≥98% ee, which can be converted via sulfoxide **28** of ≥98% to the starting sulfoximine **11** of ≥98% ee.

Introduction

We recently described an asymmetric synthesis of the disubstituted homopropargylic alcohols **3**, a key step of which is an elimination of the alkylidene carbene aminosulfoxonium ylides **1**, $R^3 = H$, with formation of the alkylidene carbenes **2**, $R^3 = H$ (Figure 1).[1] During the course of these investigations we observed that the β-Me-substituted alkenyl sulfoxonium salt **1**, $R^1 = Ph$, $R^2 = i$-Pr, $R^3 = Me$, rather than giving the corresponding methyl-substituted alkyne afforded the 2,3-dihydrofuran **4a** in good yield. Apparently the intermediate methyl-substituted alkylidene carbene **2a**, $R^1 = Ph$, $R^2 = i$-Pr, $R^3 = Me$, had suffered an intramolecular 1,5-O,Si-bond insertion rather than a 1,2-Me shift. This type of O,Si-bond insertion of β-silyloxy alkylidene carbenes had been observed previously.[2−4] However, the few studies of silyloxy alkylidene carbenes reported thus far dealt only with achiral or racemic carbenes, and it has not yet been demonstrated whether the methods applied to their generation are suitable for the enantio- and diastereoselective synthesis of disubstituted alkylidene carbenes of type **2**.

Highly substituted 2,3-dihydrofurans of type **4** would make particularly interesting starting materials for the asymmetric synthesis of tetrahydrofurans, structural motifs which can be found in many important natural products including polyether antibiotics, lignans, and nucleosides.[5] Not only the activated double bond but also the vinylic silyl group of **4** should allow useful synthetic transformations,[6] including a replacement by a

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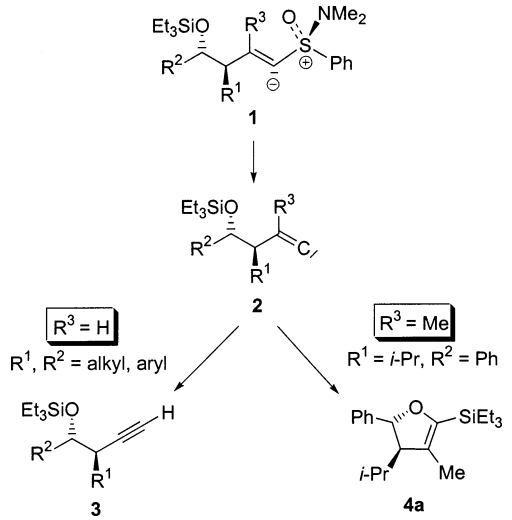

Figure 1. Generation and reactivity of silyloxy alkylidene carbenes.

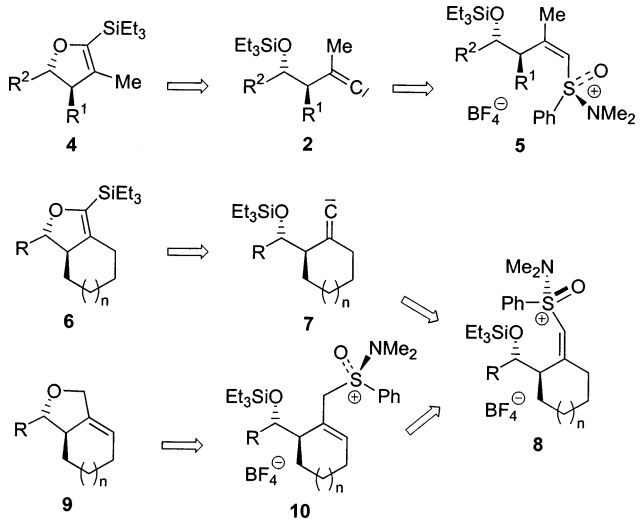

Figure 2. Retrosynthetic analysis of mono- and bicyclic 2,3-dihydrofurans and bicyclic tetrahydrofurans.

metal atom.[6c,d,f] Up to now the application of chiral 2,3-dihyrofurans in natural product synthesis has been hampered by the lack of general methods for their asymmetric synthesis.[7,8] The only more general route giving access to 2,3-dihydrofurans carrying, however, no substituent at the 2-position involves the reductive elimination of γ-butyrolactones,[9] several asymmetric syntheses of which have been described.[10] Since a number of tetrahydrofuranoide natural products contain a fused bicyclic ring skeleton,[5] the attainment of bicyclic 2,3-dihydrofurans of type **4** in which R^1 and R^2 are part of a ring system would also be highly desirable. These considerations led us to probe the generation of the silyloxy-substituted alkylidene and cycloalkylidene carbenes **2** and **7**, respectively, from the 1-alkenyl aminosulfoxonium salts **5** and **8**, respectively (Figure 2) and to study their propensity for 1,5-O,Si-bond insertion. We have already described an asymmetric synthesis of sulfoximine-substituted homoallylic alcohols of type **5** and **8** starting from the corresponding bis(allylsulfoximine)titanium complexes and aldehydes.[11,12] The methyl-substituted salts **5** were selected in anticipation of a O,Si-bond insertion of **2** being faster than a 1,2-methyl migration (vide supra). Very little was known, however, at the beginning of our investigations about the reactivity of alkylidene carbenes of type **2** with regard to the competition between O,Si-bond insertion, methyl migration, and 1,5-C,H-bond insertion[13] in dependence of the substituents R^1 and R^2. Since silyloxy-substituted cycloalkylidene carbenes of type **7** were unknown at the beginning of our investigations, it was particularly interesting to see whether 1,5-O,Si-bond insertion or ring enlargement with formation of the corresponding alkynes would predominate.[13,14]

Although the primary goal of our investigations was the development of an asymmetric synthesis of 2,3-dihydrofurans of types **4** and **6**, the prospect of 1-alkenyl aminosulfoxonium salts serving as a new source for chiral alkylidene carbenes was also of particular interest. Alkylidene carbenes have already received much attention in mechanistic and synthetic terms.[13] However, the development of a new entry to these reactive intermediates could open new possibilities for their application in organic synthesis.[15] The starting materials which have been used most frequently for their generation are diazoalkenes,[2,3,15a,d−i,16] alkenyl halides,[17] and alkenyliodonium

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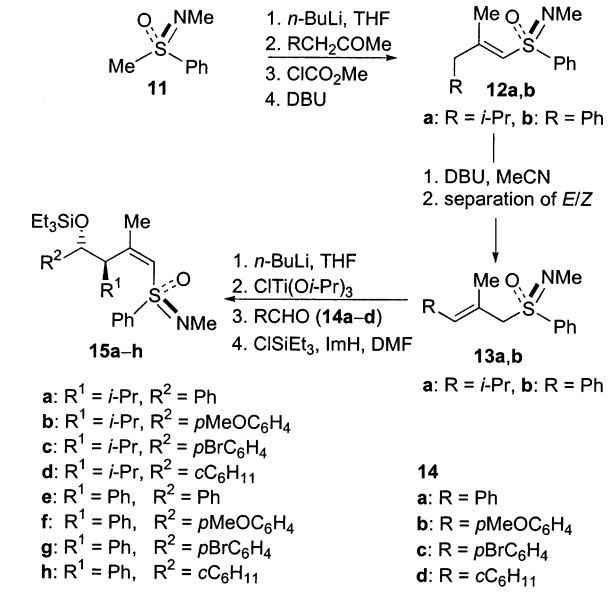
ylides,[4,15b,c,f,18] all containing, however, an achiral leaving group.[13] The interesting aspect of 1-alkenyl aminosulfoxonium salts as a potential alkylidene carbene source is the chiral leaving group which is readily generated through methylation of the corresponding sulfonimidoyl group. The latter has already found many applications as a chiral auxiliary in asymmetric synthesis.[19] Because of this the synthesis of a number of 1-alkenyl sulfoximine groups containing chiral compounds can be envisioned, which could perhaps serve for the generation of enantiopure alkylidene carbens including analogues of **2** and **7** which carry a sulfonylamino instead of a silyloxy group[20] and axially chiral cycloalkylidene carbenoids.[21,22]

In this paper we report about the generation of chiral alkylidene and cycloalkylidene carbenes of type **2** and **7** from **5** and **8**, respectively, and their utilization in the asymmetric synthesis of highly substituted mono- and bicyclic 2,3-dihydrofurans of types **4** and **6**, respectively. Furthermore we describe that by the suitable choice of a base a novel migratory cyclization of **8** can be induced, which also provides with the putative intermediate formation of the allylic aminosulfoxonium salts **10** an asymmetric synthesis of the unsaturated fused bicyclic tetrahydrofurans **9**.

Results and Discussion

Silyloxy Alkylidene Carbenes and Synthesis of 2,3-Dihydrofurans. (A) Monocyclic 2,3-Dihydrofurans. The acyclic allylic sulfoximines **13a** and **13b** were selected for the synthesis of the alkenyl aminosulfoxonium salts **5** in order to see whether various 2.3-dihydrofurans **4** can be obtained carrying aryl and sterically demanding alkyl groups at the 3-position. Sulfoximines **13a** and **13b**[11b,23] were prepared from sulfoximine **11**[24] and the corresponding methyl ketones following the addition−elimination−isomerization route[11,23] depicted in Scheme 1. The intermediate 1-alkenyl sulfoximines **12a** and **12b** were not isolated but treated with 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) in MeCN at elevated temperature to give mixtures of the *E* and *Z* configured allylic sulfoximines **13a** and **13b** in ratios of 70:30 and 79:21, respectively. The *E*/*Z*-mixtures were readily separated by preparative HPLC. Isomerization of the unwanted *Z* isomers with DBU in MeCN again gave mixtures of the *E* and *Z* isomers, which were separated. The *N*-methyl-*S*-phenyl sulfoximines **13a** and **13b** were selected because of the ease of the preparation of **11** (and *ent*-**11**) in enantiomerically pure form.[24]

Scheme 1. Asymmetric Synthesis of Sulfoximine-Substituted Acyclic Homoallylic Alcohols



The successive treatment of **13a** and **13b** with *n*-BuLi, ClTi(O*i*-Pr)$_3$, and 0.5 equiv of aldehydes **14a**−**d** and the subsequent silylation of the thus-formed homoallylic alcohols afforded the diastereomerically pure (anti,*Z*)-configured silyl ethers **15a**−**h** in good yields (Table 1). Hydroxyalkylation of the methyl-substituted titanium complexes derived from **13a** and **13b** with the aromatic and aliphatic aldehydes **14a**−**d** proceeded with high regio- and diastereoselectivities similar to those of the corresponding titanium complexes having only a disubstituted CC double bond.[11a] Conversion of **13a** and **13b** was approximately 50%, and the allylic sulfoximines were recovered in 38−44% yield. The incomplete conversion of **13a** and **13b** is due to the formation of bis(allyl)titanium complexes in the reaction of the lithiated allylic sulfoximines with equimolar amounts of ClTi(O*i*-Pr)$_3$, which are, however, only capable of transferring one allylic sulfoximine unit with high selectivities to the aldehyde.[11a]

Methylation of the alkenyl sulfoximines **15a**−**h** with Me_3OBF_4 in CH_2Cl_2 [1] afforded in practically quantitative yields the (dimethylamino)sulfoxonium salts **5a**−**h** which were generally not isolated (Scheme 2). Treatment of salts **5a**−**h** with 1.1 equiv of LiN(H)*t*-Bu in tetrahydrofuran (THF) first at −78 °C and then at room temperature cleanly gave the silyl-substituted 2,3-dihydrofurans **4a**−**h** in high overall yields, based on **15a**−**h**. These results show that this 2,3-dihydrofuran synthesis works equally well for derivatives carrying aliphatic and aromatic

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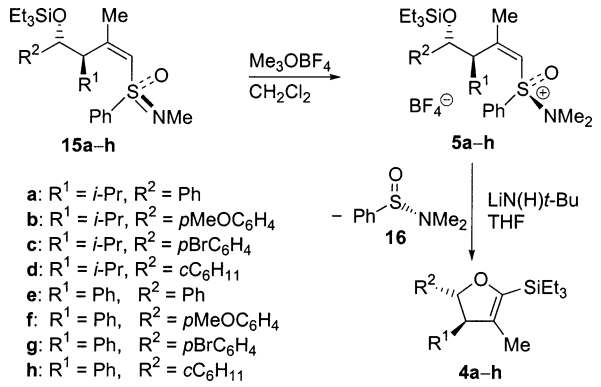
Table 1. Asymmetric Synthesis of 2,3-Dihydrofurans **4a**−**h**

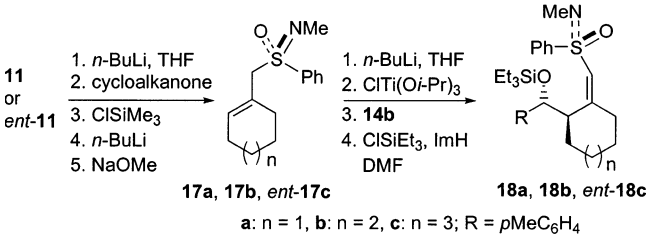
compd	R^1	R^2	R^3	**15** yield (%)[a,b]	**15** dr	**4** yield (%)	**16** yield (%)
a	*i*-Pr	CH_3	Ph	77 (96)	≥98:2	95	86
b	*i*-Pr	CH_3	$pMeOC_6H_4$	76 (95)	≥98:2	90	85
c	*i*-Pr	CH_3	$pBrC_6H_4$	76 (92)	≥98:2	92	85
d	*i*-Pr	CH_3	cC_6H_{11}	80 (95)	≥98:2	86	87
e	Ph	CH_3	Ph	71 (94)	≥98:2	96	89
f	Ph	CH_3	$pMeOC_6H_4$	81 (97)	≥98:2	92	85
g	Ph	CH_3	$pBrC_6H_4$	77 (95)	≥98:2	94	86
h	Ph	CH_3	cC_6H_{11}	79 (94)	≥98:2	92	90

[a] Yields are based on recovered allylic sulfoximine. [b] Values in parentheses are yields based on aldehyde.

Scheme 2. Asymmetric Synthesis of Monocyclic 2,3-Dihydrofurans



Scheme 3. Asymmetric Synthesis of Sulfoximine-Substituted Cyclic Homoallylic Alcohols



substituents, including sterically demanding ones. Besides the 2,3-dihydrofurans the sulfinamide **16** with ≥98% ee was isolated in all cases in high yields.

(B) Bicyclic 2,3-Dihydrofurans. Having developed a high-yield synthesis of the enantio- and diastereomerically pure monocyclic 2,3-dihydrofurans **4a**−**h** from the acyclic δ-silyloxy-substituted alkenyl sulfoximines **15a**−**h**, the synthesis of bicyclic 2,3-dihydrofurans of type **6** was investigated. The known cyclic allylic sulfoximines **17a** and **17b** were prepared in one synthetic operation without the isolation of intermediates from sulfoximine **11** and the corresponding cycloalkanones by the inverse Peterson-olefination and isomerization sequence described previously (Scheme 3).[11a,25] Similarly the new eight-membered cyclic allylic sulfoximine *ent*-**17c** was synthesized from sulfoximine *ent*-**11** and cyclooctanone in 79% yield, based on *ent*-**11**.

The successive treatment of **17a**, **17b**, and *ent*-**17c** with *n*-BuLi, $ClTi(Oi\text{-}Pr)_3$ and 0.5 equiv of aldehyde **14b**, and the subsequent silylation of the intermediate homoallylic alcohols afforded the silyl ethers **18a**, **18b**, and *ent*-**18c**, respectively, each as a single diastereomer in good yields (Table 2). Conversion of **17a**, **17b**, and *ent*-**17c** was approximately 50%,

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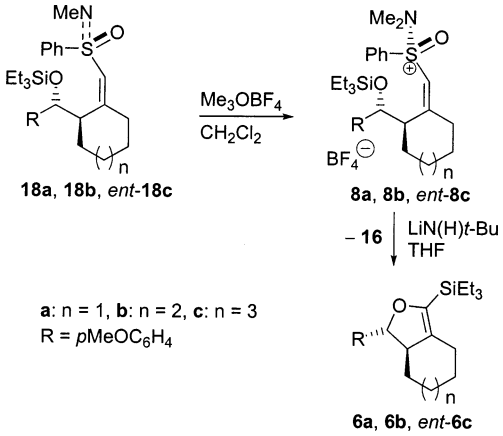
Table 2. Asymmetric Synthesis of Bicyclic 2,3-Dihydrofurans **6a**, **6b**, and *ent*-**6c**

		18/ent-**18**			
compd	n	yield (%)a,b	dr	**6**/ent-**6** yield (%)	**16**/ent-**16** yield (%)
a	1	78 (96)	≥98:2	89	86
b	2	79 (95)	≥98:2	91	90
c	3	77 (96)	≥98:2	90	88

[a] Yields are based on recovered allylic sulfoximine. [b] Values in parentheses are yields based on aldehyde.

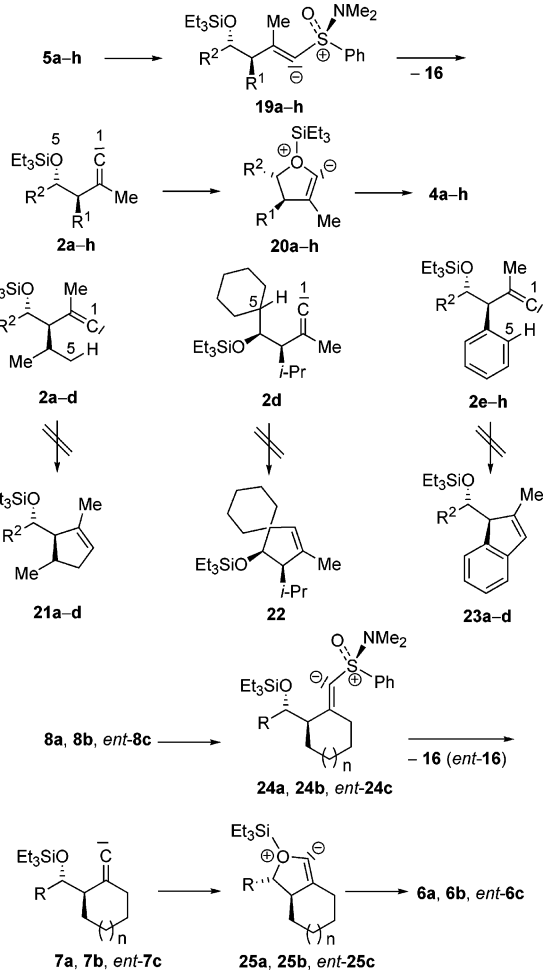
Scheme 4. Asymmetric Synthesis of Bicyclic 2,3-Dihydrofurans



and the allylic sulfoximines were recovered in 38−40% yield (vide supra). Methylation of sulfoximines **18a**, **18b** ,and *ent*-**18c** with Me_3OBF_4 proceeded readily and gave the cyclic (dimethylamino)sulfoxonium salts **8a**, **8b**, and *ent*-**8c**, respectively, in practically quantitative yields (Scheme 4). Salts **8a**, **8b**, and *ent*-**8c** cleanly delivered upon treatment with LiN(H)-*t*-Bu first at −78 °C and then at room temperature the enantio- and diastereomerically pure bicyclic 2,3-dihydrofurans **6a**, **6b**, and *ent*-**6c**, respectively, having a six-, seven-, and eight-membered carbocyclic ring, in high overall yields, based on **18a**, **18b**, and *ent*-**18c**, respectively.

Mechanistic Considerations. On the basis of the results obtained previously with the synthesis of ylides **1** (R^3 = H),[1] it is proposed that the reaction of the aminosulfoxonium salts **5a**−**h**, **8a**, **8b**, and *ent*-**8c** with the lithium amide at low temperatures affords the alkylidene carbene sulfoxonium ylides **19a**−**h**, **24a**, **24b**, and *ent*-**24c**, respectively (Scheme 5). These alkylidene carbenoids eliminate sulfinamides **16** and *ent*-**16**, respectively, at higher temperatures with formation of the δ-silyloxy alkylidene carbenes **2a**−**h**, **7a**, **7b**, and *ent*-**7c**, respectively. Subsequently, the alkylidene carbenes **2a**−**h**, **7a**, **7b**, and *ent*-**7c** preferentially undergo a 1,5-O,Si-bond insertion rather than a 1,2-Me(CH_2R)-shift to deliver the 2,3-dihydrofurans **4a**−**h**, **6a**, **6b**, and *ent*-**6c**, respectively. Thus the 1,5-O,Si-bond insertion

Scheme 5. Mechanistic Scheme for the Formation of Silyloxy Alkylidene Carbenes and 2,3-Dihydrofurans



competes favorably with the 1,2-Me shift and the ring enlargement irrespective of the substituents and the ring size. The O,-Si-bond insertion may occur either in a concerted or nonconcerted fashion. In the latter case the oxonium ylides **20a**−**h**, **25a**, **25b**, and *ent*-**25c** should be formed as intermediates, which then suffer a [1,2]-silyl migration. This scheme would be in accordance with the results of previous studies of acyclic siloxy alkylidene carbenes[2−4] and of alkylidene carbenes in general.[13] Because of the different conformations the alkylidene carbenes **2** can adopt in regard to the Csp^2-Csp^3 bond (cf. Scheme 5) and the high propensity alkylidene carbenes normally show for C,H-bond insertion, not only a 1,5-O,Si-bond but also a 1,5-C,H-bond insertion[13] could in principle occur in the case of **2a**−**h** with formation of the cyclopentene derivatives **21a**−**d**, **22**, and **23a**−**d**, respectively. This was, however, not observed within the limits of the yields obtained. Thus, carbenes **2** are characterized by the following reactivity orders: 1,2-H shift > O,Si-bond insertion, 1,5-C,H-bond insertion, and O,Si-bond insertion > 1,2-Me(CH_2R) shift, 1,5-C,H-bond insertion.

Synthesis of Unsaturated Bicyclic Tetrahydrofurans. It was recently observed that (sulfonylamino)alkyl-substituted 1-alkenyl aminosulfoxonium salts of type **I** suffer upon treatment with 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) a novel migratory cyclization leading, via allylic aminosulfoxonium salts of type **II**, to the formation of unsaturated fused bicyclic proline derivatives of type **III** (Figure 3).[26]

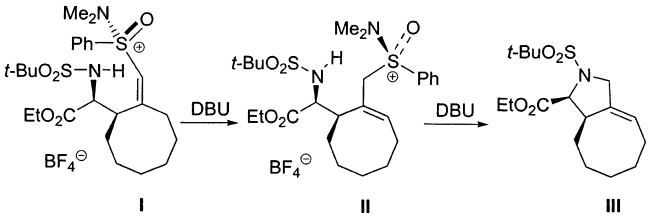
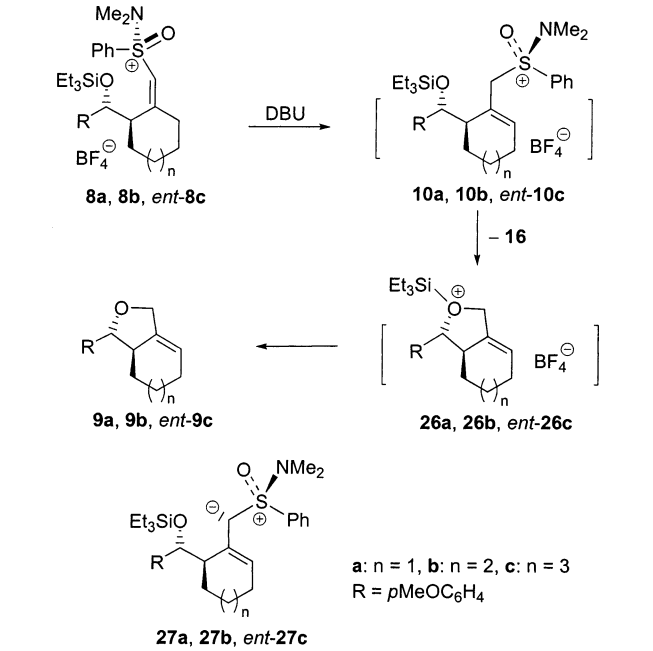


Figure 3. Migratory cyclization of (sulfonylamino)alkyl-substituted 1-alkenyl aminosulfoxonium salts.[26]

Scheme 6. Asymmetric Synthesis of Unsaturated Fused Bicyclic Tetrahydrofurans



This observation led us to study the reaction of the cyclic aminosulfoxonium salts **8a**, **8b**, and *ent*-**8c** with DBU in order to see whether an access to unsaturated fused bicyclic tetrahydrofurans **9a**, **9b**, and *ent*-**9c** (Scheme 6) could also be opened. Tetrahydrofurans **9** having the various ring size should be of particular synthetic interest because of the many natural products containing a bicyclic tetrahydrofuranoide skeleton or structural element.[5,27] The double bond should allow further synthetic transformations. An asymmetric synthesis of **9** has to the best of our knowledge not been described yet.[28] While the chances for a regioselective isomerization of **8** to the allylic aminosulfoxonium salts **10** seemed to be good, the prospects for a cyclization of the latter with formation of **9** were considered to be less promising because of the poor nucleophilicity of the silyloxy group. The DBU-assisted conversion of **II** to **III** is perhaps not representative because here the strongly nucleophilic deprotonated sulfonylamino group attacks the C-atom in the α-position to the aminosulfoxonium group.

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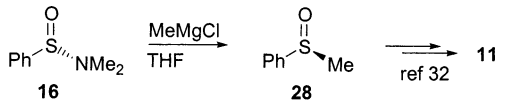
Table 3. Asymmetric Synthesis of Bicyclic Tetrahydrofurans **9a**, **9b**, and *ent*-**9c**

compd	*n*	**9**/ent-**9** yield (%)	**16**/ent-**16** yield (%)
a	1	69	84
b	2	72	87
c	3	74	88

Treatment of **8a**, **8b**, and *ent*-**8c** with DBU in CH_2Cl_2 at room temperature led to a highly regioselective migratory cyclization and gave the enantio- and diastereomerically pure bicyclic tetrahydrofurans **9a**, **9b**, and *ent*-**9c**, respectively, in 69−72% yield after aqueous workup and chromatography. Formation of **6a**, **6b**, and *ent*-**6c** under these conditions was not observed. The structures of the tetrahydrofurans **9b** and *ent*-**9c**, containing a seven- and eight-membered carbocyclic ring, were determined by X-ray crystal structure analysis (see Supporting Information). Besides **9a**, **9b**, and *ent*-**9c** the sulfinamides **16** and *ent*-**16**, respectively, were isolated in good yields (Table 3). It is proposed that the 1-alkenyl aminosulfoxonium salts **8a**, **8b**, and *ent*-**8c** also suffer a regioselective isomerization upon treatment with DBU with formation of the allylic aminosulfoxonium salts **10a**, **10b**, and *ent*-**10c**, respectively. Although the mechanism of the isomerization of **8a**, **8b**, and *ent*-**8c** is, like that of **I**, not known, the intermediate formation of the allylic aminosulfoxonium ylides **27a**, **27b**, and *ent*-**27c** may play an important role. Deprotonation of **8a**, **8b**, and *ent*-**8c** at the γ-position is expected to be a facile process because of the stabilization of the negative charge of **27a**, **27b**, and *ent*-**27c** by the aminosulfoxonium group and the double bond. For example *N*,*N*-dimethyl-*S*-methylphenylsulfoxonium tetrafluoroborate already has a pK_a value of 15.5, and the double bond is expected to raise the acidity of **8a**, **8b**, and *ent*-**8c** even further.[29] Cyclization of the allylic aminosulfoxonium salts **10a**, **10b**, and *ent*-**10c** should primarily lead to the silyl tetrahydrofuranium salts **26a**, **26b**, and *ent*-**26c**, respectively, which are desilylated either by DBU, the sulfonamide, or water upon aqueous workup[30] with formation of **9a**, **9b**, and *ent*-**9c**, respectively. In considering the low reactivity of for example silyl ethers of 3-bromomethyl-but-3-en-1-ol derivatives toward cyclization with formation of the corresponding 3-methylene tetrahydrofurans,[31] the facile cyclization of **10a**, **10b**, and *ent*-**10c** is noteworthy. This points to a high nucleofugacity of the allylic (dimethylamino)sulfoxonium group.

Recycling of the Chiral Auxiliary. Besides the 2,3-dihydrofurans **4a**−**h**, **6a**, and **6b** and the tetrahydrofurans **9a** and **9b** sulfinamide **16** with ≥98% ee was isolated in high yields. Thus a conversion of **16** to the sulfoximine **11**, the starting material for the synthesis of allylic sulfoximines, was desirable. To this end, sulfinamide **16** was treated with MeMgCl, which gave under inversion of configuration the sulfoxide **28** which

Scheme 7. Recycling of the Chiral Auxiliary



was isolated with ≥98% ee in 93% yield (Scheme 7). Since the conversion of **28** to sulfoximine **11** has already been described,[32] the synthesis of **28** from **16** represents a recycling of the chiral auxiliary.

Conclusion

We have described an asymmetric synthesis of highly substituted mono- and bicyclic 2-silyl-2,3-dihydrofurans from enantio- and diastereomerically pure silyloxy alkylidene carbene (dimethylamino)sulfoxonium ylides carrying two stereogenic centers. Key steps are the elimination of the ylides with formation of silyloxy alkylidene carbenes and the O,Si-bond insertion of the latter. The advantage of this synthesis is that it provides an access to enantio- and diasteriomerically pure 2,3-dihydrofurans carrying various aryl and alkyl substituents including sterically demanding ones. The results show that 1-alkenyl (dimethylamino)sulfoxonium salts can, with the intermediacy of alkylidene carbene (dimethylamino)sulfoxonium ylides, serve as versatile starting material for the generation of chiral alkylidene carbenes. Interestingly 1-alkenyl (dimethylamino)sulfoxonium salts show a synthetically highly useful dichotomy in their reactivity toward bases. While with strong bases an α-elimination of the aminosulfoxonium salts occurs, weak bases induce an isomerization to the allylic aminosulfoxonium salts whose (dimethylamino)sulfoxonium group shows a high nucleofugacity in intramolecular substitution by a silyloxy group leading to tetrahydrofurans. Thus, not only the α-(sulfonylamino)alkyl-substituted alkenyl aminosulfoxonium salts obtained through aminoalkylation of cyclic allylic sulfoximines with *N*-*tert*-butylsulfonyl iminoester are capable of undergoing a migratory cyclization but also the α-(silyloxy)alkyl-substituted alkenyl aminosulfoxonium salts secured through hydroxyalkylation of cyclic allylic sulfoximines with aldehydes.

Acknowledgment. Financial support of this work by the Deutsche Forschungsgemeinschaft (Collaborative Research Center "Asymmetric Synthesis with Chemical and Biological Methods" SFB 380) is gratefully acknowledged.

Supporting Information Available: General comments and materials, general experimental procedures, and analytical and spectroscopic data and MS spectrometric data for compounds **4a**−**h**, **5f**, **6a**, **6b**, *ent*-**6c**, ***ent*-8c**, **9a**, **9b**, *ent*-**9c**, *E*-**13a**, *Z*-**13a**, **15a**−**h**, **16**, *ent*-**17c**, **18a**, **18b**, *ent*-**18c**, and **28**, and X-ray crystallographic data of **9b** and *ent*-**9c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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