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Asymmetric Synthesis of *anti*-Homopropargylic Alcohols from Aldehydes and Chiral Sulfonimidoyl Substituted Bis(allyl)titanium Complexes through Generation and Elimination of Novel Chiral Alkylidenecarbene (Dimethylamino)sulfoxonium Ylides

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Abstract: A new method for the asymmetric synthesis of anti-configured homopropargylic alcohols **1** is described, which features the addition of chiral sulfonimidoyl substituted bis(allyl)titanium complexes **3** to aldehydes, the methylation of sulfonimidoyl substituted homoallylic alcohols **2** at the N-atom, and the elimination of alkenyl (dimethylamino)sulfoxonium salts **7** with LiN(H)*t*Bu. The reaction of isopropyl, cyclohexyl, and methyl substituted allylic titanium complexes **3a**−**c** with benzaldehyde, *p*-bromobenzaldehyde, *p*-chlorobenzaldehyde, *p*-methoxybenzaldehyde, (*E*)-3-phenylpropenal, and phenylpropynal afforded with high regio- and diastereoselectivities the anti-configured sulfonimidoyl substituted homoallylic alcohols **2a**−**j**, respectively. Only one allylic unit of the titanium complexes **3a**−**c** was transferred in the case of unsaturated aldehydes, and the starting allylic sulfoximines **2a**−**g** were recovered in approximately 50% yield. The methylation of the silyl protected alkenyl sulfoximines **6a**−**j** with Me_3OBF_4 gave in practically quantitative yields the (dimethylamino)sulfoxonium salts **7a**−**j**, respectively. Salts **7a**−**e**, **7g**, **7h**, and **7j** delivered upon treatment with 2 equiv of LiN(H)*t*Bu the enantio- and diastereomerically pure saturated and unsaturated alkynes **9a**−**e**, **9g**, **9h**, and **9j**, respectively, in high yields. Besides the alkynes the sulfinamide **8** (96% ee) was isolated. Aminosulfoxonium salts **9f** and **9i**, which carry a CC triple bond, also suffered an elimination under these conditions but did not yield the corresponding diynes. Elimination of salts **7a**−**e**, **7g**, **7h**, and **7j** proceeds most likely through deprotonation at the α-position with formation of the novel alkylidenecarbene aminosulfoxonium ylides **19a**−**e**, **19g**, **19h**, and **19j**, respectively. The ylides **19a**−**e**, **19g**, **19h**, and **19j** presumably eliminate sulfinamide **8** with generation of the chiral nonracemic (β-siloxyalkylidene)carbenes **20a**−**e**, **20g**, **20h**, and **20j**, which suffer a 1,2-H-shift with formation of alkynes **9**. Support for the formation of the putative alkylidenecarbenes **20** as intermediates comes from the elimination of the β-methyl substituted aminosulfoxonium salt **24**, which delivered the enantio- and diastereomerically pure 2,3-dihydrofuran derivative **28** upon treatment with LiN(H)*t*Bu in high yield. Here, the putative (β-siloxyalkylidene)carbene **26** suffers a 1,5-O,Si bond insertion rather than a 1,2-Me shift. Methylation of the alkenyl sulfoximine **6a** at the α-position with formation of **13** was achieved through deprotonation of the former with formation of the α-lithioalkenyl sulfoximine **11a** and its treatment MeI. Reaction of the α-methylated alkenyl aminosulfoxonium salt **14a** with LiN*i*Pr$_2$ at low temperatures gave the enantio- and diastereomerically pure anti-configured homoallenylic alcohol derivative **15**, while reaction of the salt with LiN*i*Pr$_2$ or LiN(H)*t*Bu at higher temperatures afforded the enantio- and diastereomerically pure nonterminal homopropargylic alcohol derivative **17**. Deprotonation of the alkenyl (dimethylamino)sulfoxonium salts **7a** and **7b** with *n*BuLi afforded the novel alkylidenecarbene aminosulfoxonium ylides **19a** and **19b**, respectively, which upon treatment with MeI yielded the methylated aminosulfoxonium salts **14a** and **14b**, respectively.

Introduction

Enantio- and diastereomerically pure homopropargylic alcohols of type **1** (Scheme 1) constitute an interesting class of compounds,[1] which have frequently served as important building blocks in natural product syntheses.[2] The high synthetic utility of alcohols **1** stems from the fact that terminal alkynes are among the most versatile functional groups for the further elaboration of a carbon skeleton.[1−3] Asymmetric synthesis of alcohols **1** from aldehydes with the concurrent formation of the two stereogenic C-atoms has been accomplished mainly by two

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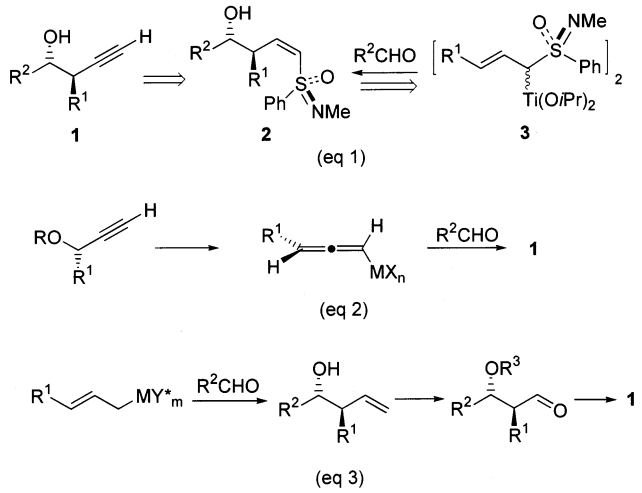
Scheme 1. Retrosynthesis and Synthesis of *anti*-Homopropargylic Alcohols



methods.[4] The first method entails the synthesis of chiral nonracemic allenylic metal compounds from the corresponding chiral nonracemic propargylic alcohols and the addition of the former to aldehydes (eq 2),[2q−x,5] and the second method encompasses the allylation of aldehydes with a chiral nonracemic allylic metal reagent with formation of the corresponding homoallylic alcohols,[6] which are then converted to **1** by a one-carbon homologation following conversion to the corresponding aldehydes (eq 3).[2i,l,o,7] While both methods are imaginative and efficient, their enantio- and diastereoselectivities tend to be variable and the allylic metal method requires the oxidative cleavage of a double bond, which imposes restriction upon R^1 and R^2. In addition, the large majority of applications of both methods have been confined so far to the synthesis of methyl substituted homopropragylic alcohols **1** (R^1 = Me).[8] Further routes leading to alcohols **1** include the addition of chiral nonracemic titanated allylic carbamates[6d,e] or chlorine substituted allylic boronates[6a,b,i] to aldehydes followed by the elimination of the corresponding aminocarbonyloxy[2n,9] or chlorine[10] substituted homoallylic alcohols, the ring opening of chiral oxiranes by alkynylmetal reagents,[2a−e,g,h,n,3a−c] the ring opening of chiral propargylic oxiranes with organometal reagents,[11] the base-catalyzed ring opening of chiral methylene oxetanes,[12] and the substitution of chiral bromoallenols with organometal reagents.[11] While the regioselective ring opening of oxiranes by alkynylmetal reagents is restricted to hydroxyalkyl substituted oxiranes, the other routes have been so far applied only to the synthesis of racemic homopropargylic alcohols[11] or even only to that of one particular derivative of *rac*-**1** where R^1 = Me.[9,10,12] Thus the scope of these routes for the synthesis of nonracemic alcohols **1**, which will crucially depend on the availability of the chiral nonracemic starting material[13] and the variability of the substituents, has yet to be determined. Therefore, we felt that it would be desirable to have a method which allows the asymmetric synthesis of alcohols **1**, carrying a wide range of groups R^1 and R^2 including unsaturated and highly branched ones, from aldehydes. We have recently shown that chiral sulfonimidoyl substituted bis(allyl)titanium complexes **3** (R^1 = Me, Et, *i*Pr, *c*C_6H_{11}, Ph) add with very high regio- and diastereoselectivity to aliphatic aldehydes and benzaldehyde to give enantio- and diastereomerically pure sulfonimidoyl functionalized homoallylic alcohols of type **2**,[14,15] which have served for example as starting material for the asymmetric synthesis of

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(8) For recent asymmetric syntheses of **1** (R^1 = H), see: (a) Yu, C.-M.; Le, J. Y.; So, B.; Hong, J. *Angew. Chem.* **1998**, *110*, 2504; *Angew. Chem., Int. Ed.* **1998**, *37*, 2392. (b) Denmark, S. E.; Wynn, T. *J. Am. Chem. Soc.* **2001**, *123*, 6199. (c) Evans, D. A.; Sweeny, Z. K.; Rovis, T.; Tedrow, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 12095.

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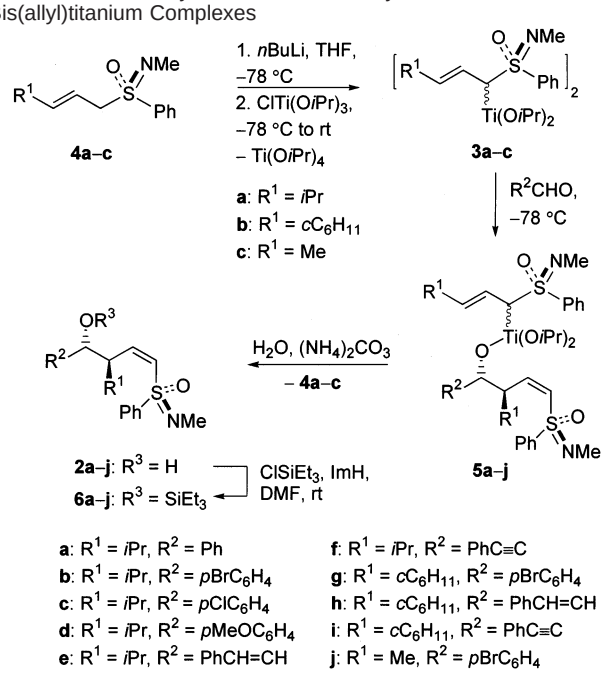
β-substituted and β,β-disubstiuted β-amino acids and of 1,3-amino alcohols having three contiguous stereogentic C-atoms.[16] The allylic sulfoximines required for the synthesis of titanium complexes **3** and *ent*-**3** are readily accessible from the corresponding aldehydes and (*S*)- or (*R*)-*N*,*S*-dimethyl-*S*-phenylsulfoximine, respectively.[14c] Thus, provided an efficient alkenyl sulfoximine to alkyne conversion could be devised (eq 1), the homoallylic alcohols **2** should serve as versatile starting material for the asymmetric synthesis of the 1,2-disubstituted homopropargylic alcohols **1**. A further prerequisite would be that not only alkyl and aryl substituted derivatives of **2** but also those containing unsaturated groups can be secured with high selectivities from the titanium complexes **3** and aldehydes. In this paper we describe a new method for the asymmetric synthesis of *anti*-homopropargylic alcohols of type **1** based on the addition of titanated allylic sulfoximines **3** to aliphatic, aromatic, and other unsaturated aldehydes and the generation and elimination of novel alkylidenecarbene aminosulfoxonium ylides derived from sulfoximines **2**.

Results and Discussion

Sulfonimidoyl Substituted Homoallylic Alcohols. Up to now only the reaction of bis(allyl)titanium complexes **3** with aliphatic aldehydes and benzaldehyde had been studied.[14] Although mono(allyl)titanium complexes derived from allyl and crotyl sulfoximine carrying an additional chiral substituent at the N-atom have been reported to react not only with saturated aldehydes but also with propenal with high selectivities,[15] diminished selectivities have been observed in the reaction of chiral allylic boron reagents with unsaturated aldehydes as compared to saturated aldehydes.[17] It was therefore of interest to see whether unsaturated aldehydes, such as for example (*E*)-3-phenylpropenal and phenylpropynal, would also react with the allylic titanium reagents with high selectivities. Included into the reactivity study of **3** with aldehydes were *p*-chlorobenzaldehyde and *p*-bromobenzaldehyde in order to see whether an elimination of the corresponding *p*-chlorophenyl and *p*-bromophenyl substituted homoallylic alcohol **2** ($R^2 = p\mathrm{ClC_6H_4}$, $p\mathrm{BrC_6H_4}$) with bases with formation of **1** ($R^2 = p\mathrm{ClC_6H_4}$, $p\mathrm{BrC_6H_4}$) without a concomitant aryne formation or halogen−metal exchange, depending on the base used, could be accomplished. The enantiomerically pure allylic sulfoximines **4a**−**c** (Scheme 2) were prepared from (*S*)-*N*,*S*-dimethyl-*S*-phenylsulfoximine[18] and the corresponding aldehydes in good yields by the addition−elimination−isomerization route according to the one-pot procedure described recently.[14c] Reaction of allylic sulfoximines **4a**−**c** with 1.1 equiv of *n*BuLi in tetrahydrofuran (THF) and titanation of the thus formed lithiated allylic sulfoximines with 1.1 equiv of $\mathrm{ClTi(O}i\mathrm{Pr)_3}$ gave the isopropyl, cyclohexyl, and methyl substituted bis(allyl)titanium complexes **3a**−**c**, respectively, together with equimolar amounts of $\mathrm{Ti(O}i\mathrm{Pr)_4}$ which was found previously to be essential for the reaction of the titanium complexes with aldehydes to occur.[14c] Treatment of titanium complexes **3a**−**c**, which were not isolated, with 1.5 equiv, based on sulfoximines **4a**−**c**, of benzaldehyde, *p*-bromobenzaldehyde, *p*-chlorobenzaldehyde, *p*-methoxybenzaldehyde, (*E*)-3-phenylpropenal, and phenylpropynal at −78 °C proceeded in each case with high regio- and diastereoselectivity and gave the mono(allyl)titanium complexes **5a**−**j** containing the homoallylic alcohols **2a**−**j**, respectively, as alkoxy ligands. Titanium complexes **5a**−**j** did not further react with the aldehydes at low temperatures and gave upon hydrolysis the diastereomerically pure *anti*-homoallylic alcohols **2a**−**j** together with the starting allylic sulfoximines **4a**−**c**. Homoallylic alcohols **2a**−**j** and allylic sulfoximines **4a**−**c**, which were readily separated by crystallization and chromatography, could be obtained in 45−48% and 40−50% isolated yield, respectively. We had found previously that reaction of mono(allyl)titanium complexes of type **5** with aldehydes occurs only at higher temperatures and proceeds with lower selectivities than that of the titanium complexes of type **3**.[14c] However, in the case of alkyl substituted complexes **5** (R^1, R^2 = alkyl) high selectivities were attained in the reaction with saturated aldehydes when $\mathrm{ClTi(O}i\mathrm{Pr)_3}$ was added to the reaction mixture.[14c] Surprisingly, this modification was not successful in the case of the reaction of titanium complexes **5a**−**j** with aromatic and unsaturated aldehydes. It seems that the selectivities of the reaction of mono(allyl)titanium complexes of type **5** with unsaturated aldehydes in the presence of $\mathrm{ClTi(O}i\mathrm{Pr)_3}$ are generally lower than that of the reaction of bis(allyl)titanium complexes **3** with saturated aldehydes.[19] In summary, in reactions of bis(allyl)titanium complexes of type **3** with aliphatic aldehydes in the presence of $\mathrm{ClTi(O}i\mathrm{Pr)_3}$ both allylic units can be utilized, whereas in the reaction with unsaturated aldehydes it is only one unit which can be transferred and half of the starting allylic sulfoximine is recovered. Assignment of the anti-configuration of alcohols **2a**−**j** was made on the basis of the NMR data in comparison

Scheme 2. Synthesis of Sulfonimidoyl Substituted Homoallylic Alcohols from Aldehydes and Sulfonimidoyl Substituted Bis(allyl)titanium Complexes



a: R^1 = *i*Pr, R^2 = Ph
b: R^1 = *i*Pr, R^2 = $p\mathrm{BrC_6H_4}$
c: R^1 = *i*Pr, R^2 = $p\mathrm{ClC_6H_4}$
d: R^1 = *i*Pr, R^2 = $p\mathrm{MeOC_6H_4}$
e: R^1 = *i*Pr, R^2 = PhCH=CH
f: R^1 = *i*Pr, R^2 = PhC≡C
g: R^1 = $c\mathrm{C_6H_{11}}$, R^2 = $p\mathrm{BrC_6H_4}$
h: R^1 = $c\mathrm{C_6H_{11}}$, R^2 = PhCH=CH
i: R^1 = $c\mathrm{C_6H_{11}}$, R^2 = PhC≡C
j: R^1 = Me, R^2 = $p\mathrm{BrC_6H_4}$

(15) For the highly selective synthesis of **2** (R^1 = H, Me) bearing a chiral substituent at the N-atom, see: (a) Reggelin, M.; Weinberger, H. *Angew. Chem.* **1994**, *106*, 489; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 444. (b) Reggelin, M.; Weinberger, H.; Gerlach, M.; Welcker, R. *J. Am. Chem. Soc.* **1996**, *118*, 4765. (c) Reggelin, M.; Zur, C. *Synthesis* **2000**, 1.
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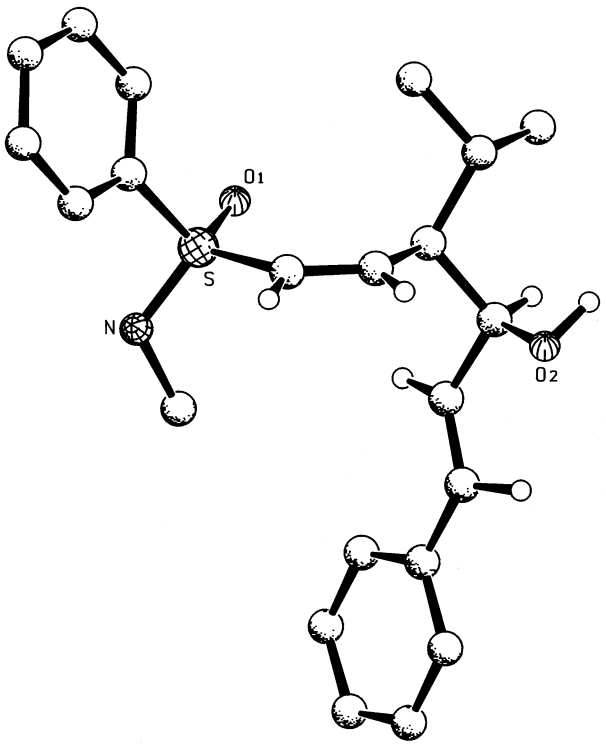

Figure 1. Structure of **2e** in the crystal.

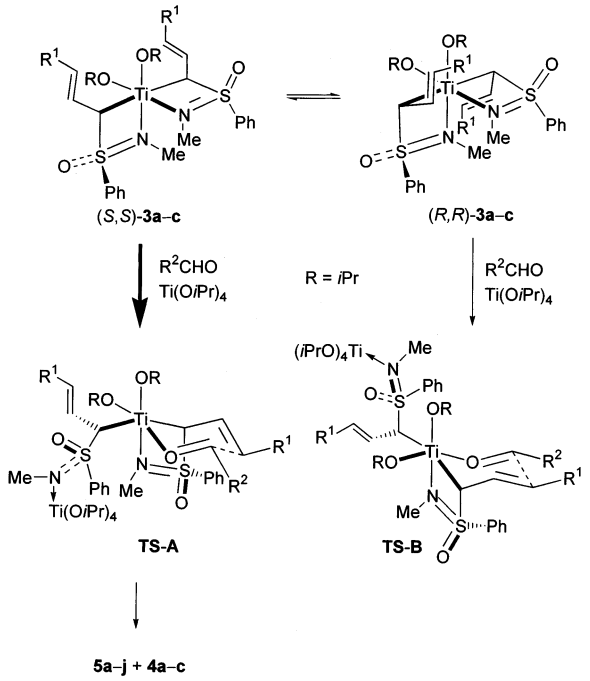

Figure 2. Reaction of sulfonimidoyl substituted bis(allyl)titanium complexes with aldehydes.

with previous structure determinations of further derivatives of **2**.[14c] A final proof of the absolute configuration of the allylic−homoallylic alcohol **2e** was provided by X-ray crystal structure analysis (Figure 1). The hydroxy sulfoximine **2e** features in the crystal an intermolecular hydrogen bond between the hydroxy group and the N-atom of the sulfonimidoyl group.[14c] Finally, silylation of the homoallylic alcohols **2a**−**j** afforded the triethylsilyl ethers **6a**−**j**, respectively, in high yields.

Stereochemical Consideration. According to NMR spectroscopy the bis(allyl)titanium complexes **3a**−**c** are configurationally labile with regard to the Cα-atoms and exist in solution mainly as equilibrium mixtures of the C_2-symmetric cis,cis,-trans-configured octahedral complexes (*R*,*R*)-**3a**−**c** and (*S*,*S*)-**3a**−**c** (Figure 2).[14,20a,b] According to NMR spectroscopy and crystal structure analysis of a derivative of **3**, bearing two phenyl groups at the γ-position,[14c] the allylic sulfoximine ligands of the titanium complexes are coordinated most likely in a bidentate fashion via the Cα-atom and the N-atom to the Ti-atom. Equilibration of the diastereomeric complexes (*R*,*R*)-**3a**−**c** and (*S*,*S*)-**3a**−**c** is fast at low temperatures[20a,b] and proceeds perhaps through a reversible 1,3-C/N-shift of the Ti-atom containing group of the type that has unequivocally been demonstrated for the mono(allyl)titanium tris(diethylamino) complexes derived from **4a**−**c**.[14c,20a,c] Formation of (*S*,*R*,*Z*)-configured homoallylic alcohols **2a**−**j** entails *Re*,*Re*,*Z* processes of the aldehydes with the titanium complexes **3a**−**c**. This can be rationalized on the basis of the Curtin−Hammett principle[21] by assuming that (1) the equilibration of the bis(allyl)titanium complexes (*R*,*R*)-**3a**−**c** and (*S*,*S*)-**3a**−**c** is faster than their reaction with the aldehydes, (2) the aldehydes react preferentially with the (*S*,*S*)-configured complexes (*S*,*S*)-**3a**−**c**, and (3) the reaction occurs through the chairlike six-membered transition states **TS-A**.[14c,15c] These TS's feature, besides a coordination of the aldehyde to the Ti-atom, pseudoequatorial R^1 and R^2 groups and a pseudoaxial sulfonimidoyl group which is coordinated through the N-atom to the Ti-atom and whose phenyl group adopts the *exo*-position. It seems surprising that the sulfonimidoyl group should adopt a pseudoaxial position in the **TS-A**. However, for the reactions of aldehydes with a number of allylic metal reagents, which bear a heteroatom based substituent at the α-position, transition-state models featuring a pseudoaxial position of that substituent have been proposed to account for the selective formation of the (*Z*)-configured homoallylic alcohol.[6] The origin of this effect is, however, a matter of debate. The alternative *Si*,*Si*,*Z* mode of bond formation between the aldehydes and the (*R*,*R*)-configured complexes (*R*,*R*)-**3a**−**c** via the analogous transition state **TS-B** is considered to be less favorable because here the phenyl group of the sulfonimidoyl group, which is coordinated to the Ti-atom, resides in the sterically more encumbered *endo*-position. Interestingly, in the reaction of bis(allyl)titanium complexes **3** with *N*-sulfonyl α-imino esters, which leads to (*S*,*R*,*E*)-configured homoallylic amines and requires *Si*,*Re*,*E* processes, the (*R*,*R*)-configured complexes (*R*,*R*)-**3** seem to be the faster reacting ones.[22] The essential role exerted by Ti(O*i*Pr)$_4$ in the addition of **3a**−**c** to the aldehydes may be that of providing for a free coordination site at the Ti-atom of the six-coordinate complexes, which is required for the coordination of the aldehyde through complexation of the sulfonimidoyl group of one allylic moiety.

Terminal Homopropargylic Alcohols. Treatment of alkenyl sulfoximines **6** with *n*BuLi or MeLi did not lead to an elimination of *N*-methyl phenylsulfinamide with formation of alkynes **9**. Instead, a quantitative lithiation of **6** at the α-position

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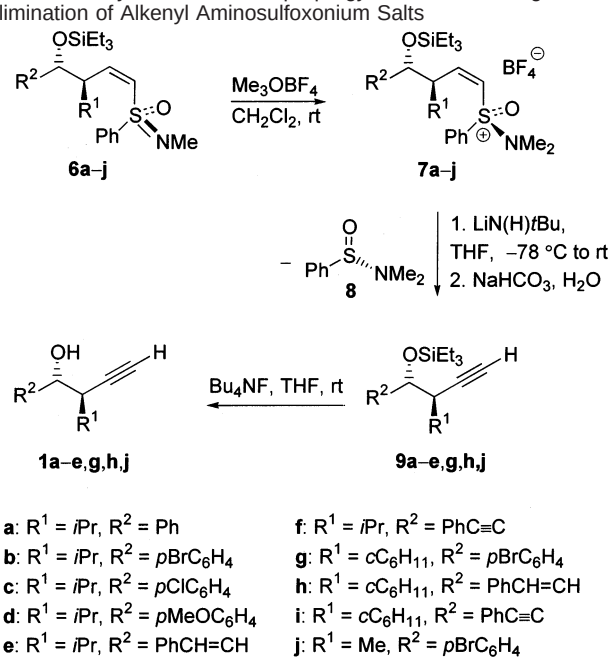
Table 1. Asymmetric Synthesis of *anti*-Homopropargylic Alcohols from Aldehydes[a,b]

compd	R^1	R^2	**2** yield (%)	**2** dr	**6** yield (%)	**7** yield (%)	**9** yield (%)	**1** yield (%)
a	*i*Pr	Ph	48 (84)	≥98:2	98	92	95	85
b	*i*Pr	*p*BrC_6H_4	48 (87)	≥98:2	98	96	89	97
c	*i*Pr	*p*ClC_6H_4	48 (87)	≥98:2	97	98	90	98
d	*i*Pr	*p*$MeOC_6H_4$	48 (87)	≥98:2	98	96	92	92
e	*i*Pr	PhCH=CH	48 (80)	≥98:2	97	98	90	97
f	*i*Pr	PhC≡C	47 (96)	≥98:2	97	95	*c*	*c*
g	*c*C_6H_{11}	*p*BrC_6H_4	48 (80)	≥98:2	96	96	90	97
h	*c*C_6H_{11}	PhCH=CH	45 (90)	≥98:2	98	96	90	97
i	*c*C_6H_{11}	PhC≡C	45 (87)	≥98:2	96	97	*c*	*c*
j	Me	*p*BrC_6H_4	48 (92)	≥98:2	97	99	91	98

[a] Isolated yields. [b] Numbers in parentheses refer to yields based on recovered sulfoximine **4**. [c] See text.

Scheme 3. Synthesis of Homopropargylic Alcohols through Elimination of Alkenyl Aminosulfoxonium Salts



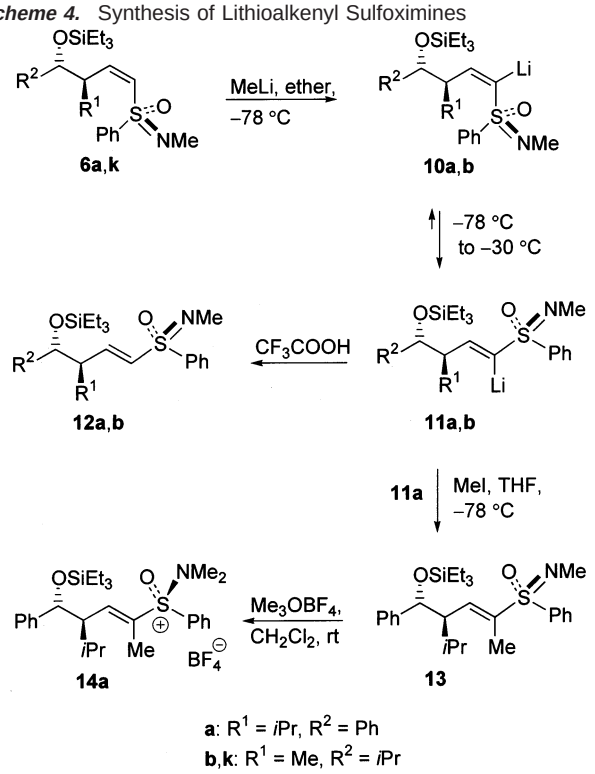
a: R^1 = *i*Pr, R^2 = Ph
b: R^1 = *i*Pr, R^2 = *p*BrC_6H_4
c: R^1 = *i*Pr, R^2 = *p*ClC_6H_4
d: R^1 = *i*Pr, R^2 = *p*$MeOC_6H_4$
e: R^1 = *i*Pr, R^2 = PhCH=CH
f: R^1 = *i*Pr, R^2 = PhC≡C
g: R^1 = *c*C_6H_{11}, R^2 = *p*BrC_6H_4
h: R^1 = *c*C_6H_{11}, R^2 = PhCH=CH
i: R^1 = *c*C_6H_{11}, R^2 = PhC≡C
j: R^1 = Me, R^2 = *p*BrC_6H_4

to the sulfonimidoyl group with formation of the corresponding stable α-lithioalkenyl sulfoximines occurred (vide infra).[14a] Therefore the sulfonimidoyl group of **6a**−**j** was converted through methylation to the (dimethylamino)sulfoxonium group,[18b] which ought to be a better leaving group than the sulfonimidoyl group.[23] Treatment of the *N*-methyl alkenyl sulfoximines **6a**−**j** with Me_3OBF_4 afforded in practically quantitative yields the aminosulfoxonium salts **7a**−**j**, respectively (Scheme 3). We were pleased to find that salts **7a**−**e**, **7g**, **7h**, and **7j** readily afforded alkynes **9a**−**e**, **9g**, **9h**, and **9j**, respectively, in high yields upon treatment with 2 equiv of LiN(H)*t*Bu in THF at −78 °C to room temperature and a subsequent aqueous quench of the reaction mixtures. The complete conversion of salts **7a**−**e**, **7g**, **7h**, and **7j** to alkynes **9a**−**e**, **9g**, **9h**, and **9j**, respectively, required the use of 2 equiv of the base. For example treatment of salt **7d** with only 1 equiv of LiN(H)*t*Bu in THF at −78 °C and a subsequent aqueous workup led only to a 40% conversion of the salt with formation of alkyne **9d**. A competing substitution of the *p*-bromophenyl and *p*-chlorophenyl substituted salts **7b** and **7c** or alkynes **9b** and **9c**, respectively, with formation of the corresponding arynes was not observed when only 2 equiv of LiN(H)*t*Bu were used in THF at −78 °C to room temperature. However, when the elimination of the *p*-bromophenyl substituted salt **7b** was carried out by using a large excess of LiN(H)*t*Bu (10 equiv), a mixture of the *p*- and *m*-*tert*-butylamino derivatives of alkyne **9a** in a ratio of 3:1 was isolated in 80% yield, indicating not only an elimination but also an aromatic substitution through the aryne mechanism. Reaction of the salts **7f** and **7i**, which carry a triple bond, with 2 equiv of LiN(H)*t*Bu did not give the corresponding homopropargyl alcohol derivatives. Instead a reaction product of yet unassigned structure was isolated in each case, which according to NMR and IR spectroscopy did not contain any triple bond and no dimethylamino group (vide infra). In the elimination of salts **7a**−**e**, **7g**, **7h**, and **7j** besides alkynes **9a**−**e**, **9g**, **9h**, and **9j**, respectively, (*S*)-*N*,*N*-dimethyl phenylsulfinamide (**8**) of 96% ee was isolated in 80−90% yield as the second reaction product. Since (*R*)-*N*,*N*-dimethyl tolylsulfinamide has already been successfully converted in two steps into (*R*)-*S*-methyl-*S*-tolylsulfoximine with high stereoselectivity,[18b] we are confident that sulfinamide **8** can be converted to (*S*)-*S*-methyl-*S*-phenylsulfoximine and thus the chiral auxiliary be recycled. Deprotection of the silyl ethers **9a**−**e**, **9g**, **9h**, and **9j** gave finally the homopropargylic alcohols **1a**−**e**, **1g**, **1h**, and **1j**, respectively, in high yields (Table 1).

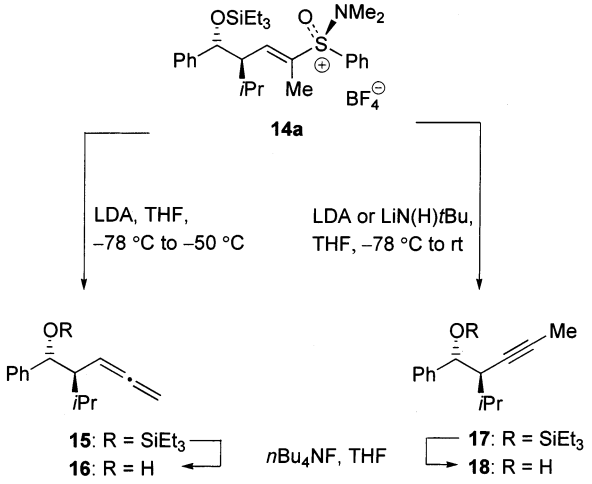
Nonterminal Homopropargylic Alcohols and Homoallenylic Alcohols. The observation of a facile lithiation of alkenyl sulfoximines **6** at the α-position led to the notion of a synthesis of nonterminal homopropargylic alcohols via introduction of a substituent at the α-position of **6** and a subsequent elimination by the sequence of reactions described above. Treatment of the alkenyl sulfoximines **6a** and **6k**[14c] with 1.2 equiv of MeLi at −78 °C in ether gave the (*Z*)-configured α-lithioalkenyl sulfoximines **10a** and **10b**, respectively, which upon warming of the reaction mixture to −30 °C suffered a complete isomerization to the (*E*)-isomers **11a** and **11b**, respectively (Scheme 4). Protonation of **11a** and **11b** afforded quantitatively the (*E*)-configured alkenyl sulfoximines **12a** and **12b**, respectively. Treatment of lithioalkenyl sulfoximine **11a** with MeI furnished the α-methylated alkenyl sulfoximine **13** in 98% yield. Methylation of sulfoximine **13** with Me_3OBF_4 at the N-atom proceeded uneventfully and gave the aminosulfoxonium salt **14a** in 98% yield. Reaction of salt **14a** with bases at different temperatures took a differing but synthetically interesting course (Scheme 5). Treatment of salt **14a** with 3 equiv of LiN*i*Pr_2 at −78 to −50 °C in THF afforded the homoallenylic alcohol derivative **15** in 89% yield. Deprotection of the silyl ether **15** yielded the parent alcohol **16**. Chiral nonracemic 1,2-disubstituted homoallenylic alcohols of type **15**, whose asymmetric synthesis has to the best of our knowledge not been described yet,[24] should be of considerable synthetic interest. When the

(23) (a) Johnson, C. R.; Haake, M.; Schroeck, C. W. *J. Am. Chem. Soc*. **1970**, *92*, 6594. (b) Johnson, C. R.; Lockard, J. P.; Kennedy, E. R. *J. Org. Chem.* **1980**, *45*, 264.

Scheme 4. Synthesis of Lithioalkenyl Sulfoximines



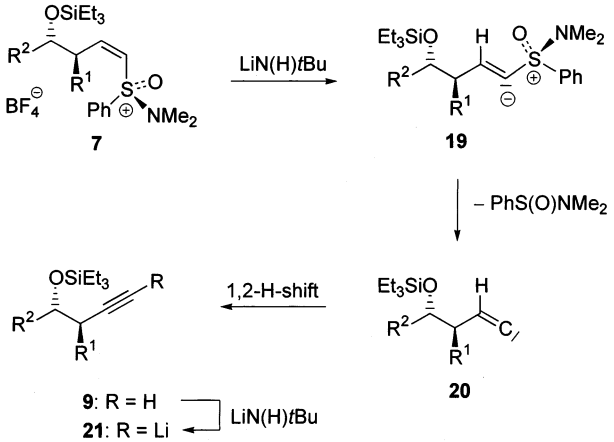
Scheme 5. Synthesis of an Internal Homopropargylic Alcohol and a Homoallenylic Alcohol from an Alkenyl Aminosulfoxonium Salt by Choice of the Reaction Conditions



elimination of salt **14a** was carried out by using either 3 equiv of LiN*i*Pr$_2$ or 10 equiv of LiN(H)*t*Bu at −78 °C and warming the reaction mixture to room temperature, the nonterminal alkyne **17** was isolated in 36 and 72% yield, respectively, instead. Deprotection of silyl ether **17** finally gave the homopropargylic alcohol **18**.

Alkylidenecarbene Aminosulfoxonium Ylides and Formation of a Chiral 2,3-Dihydrofuran Derivative. The facile conversion of the alkenyl aminosulfoxonium salts **7a**−**e**, **7g**, **7h**, and **7j** to the alkynes **9a**−**e**, **9g**, **9h**, and **9j**, respectively, which requires the use of 2 equiv of the lithium amide, brings

Scheme 6. Mechanistic Scheme for the Formation of Homopropargylic Alcohols from Alkenyl Aminosulfoxonium Salts via Alkylidenecarbenes



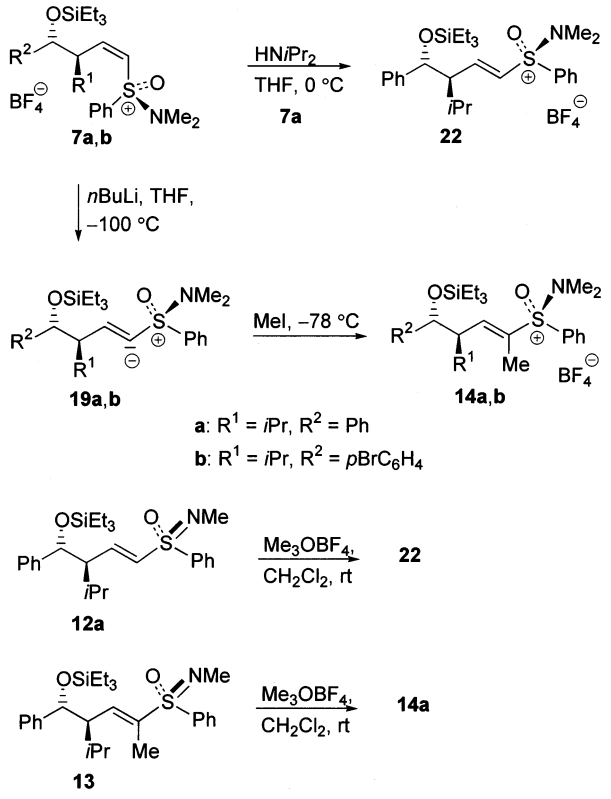
about the question as to the mechanism of this elimination. Because of the strong acidifying effect of the phenyl(dimethylamino)sulfoxonium group (pK_a [MeS(O)(NMe$_2$)PhBF$_4$] = 14.4),[25] salts **7** could perhaps react in the first step with the lithium amide with formation of the alkylidenecarbene aminosulfoxonium ylides **19** (Scheme 6). In the second step, ylides **19** could suffer a heterolysis with elimination of sulfinamide **8** and formation of alkylidenecarbenes **20**, which, in the last step, could undergo a 1,2-H-shift with formation of alkynes **9**. Finally, alkynes **9** would be expected to consume the second equivalent of the base to deliver acetylides **21**, which would give alkynes **6** upon aqueous workup. To verify the putative deprotonation of salts **7** with formation of the novel ylides **19** a number of experiments were conducted with salts **7a** and **7b**. Treatment of salt **7a** with HN*i*Pr$_2$ at 0 °C in THF led to its quantitative isomerization to the (*E*)-configured salt **22**, which was independently prepared by methylation of the alkenyl sulfoximine **12a** with Me$_3$OBF$_4$ in quantitative yield (Scheme 7). This observation may be rationalized by the formation of ylide **19a** as an intermediate on the way from the (*Z*)-isomer to the more stable (*E*)-isomer. However, an isomerization pathway, which involves the addition of the amine to the activated double bond[23b] of **7a** with formation of the corresponding ylide and a subsequent elimination of the amine delivering salt **22**, cannot be excluded. Therefore a more definite confirmation for the notion of a formation of ylides **19** upon reaction of salts **7** with strong bases was sought. Treatment of salts **7a** and **7b** with 1 equiv of *n*BuLi at −100 °C in THF followed by the addition of MeI resulted in the formation of the methyl substituted salts **14a** and **14b**, respectively, which were isolated in 94 and 46% yield, respectively. Salt **14a** was independently synthesized by methylation of sulfoximine **13**. These results unequivocally show that salts **7a** and **7b** are able to yield with strong bases the alkylidenecarbene aminosulfoxonium ylides **19a** and **19b**, respectively.

To obtain further insight into the mechanism of the elimination of salts **7**, we studied the reaction of the β-methyl substituted alkenyl aminosulfoxonium salt **24** with LiN(H)*t*Bu (Scheme 8). In this case the heterolysis of the alkylidenecarbene ylide **25** derived from salt **24** should deliver the methyl substituted (β-siloxyalkylidene)carbene **26**. Previous studies of

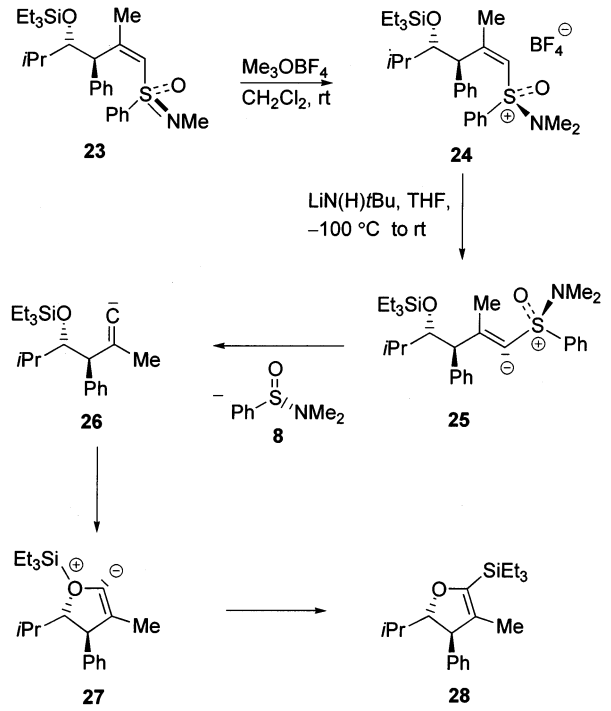
(24) (a) Henderson, M. A.; Heathcock, C. H. *J. Org. Chem.* **1988**, *53*, 4736. (b) Kimura, M.; Tanaka, S.; Tamaru, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1689. (c) Okamoto, S.; Sato, H.; Sato, F. *Tetrahedron Lett.* **1996**, *37*, 8865. (d) Hamada, T.; Mizojiri, R.; Urabe, H.; Sato, F. *J. Am. Chem. Soc.* **2000**, *122*, 7138.

(25) Bordwell, F. G.; Branca, J. C.; Johnson, C. R.; Vanier, N. R. *J. Org. Chem.* **1980**, *45*, 3884.

Scheme 7. Synthesis of Alkylidenecarbene Aminosulfoxonium Ylides



Scheme 8. Elimination of an Alkenyl Aminosulfoxonium Salt with Formation of a 2,3-Dihydrofuran Derivative



chiral racemic (β-siloxyalkylidene)carbenes, which were generated either from β-siloxy ketones and $Me_3SiC(Li)N_2$,[26a] through thermolysis of β-siloxy-α,β-expox-*N*-aziridinylimines,[26b] or through sulfinate addition to (β-siloxybutynyl)iodonium salts,[26c,d] had revealed an interesting and differing behavior of this type of alkylidenecarbenes depending on the substituents of the double bond. While (β-siloxyalkylidene)carbenes bearing a H-atom at the β-position of the double bond underwent a 1,2-H-shift with formation of alkynes, those carrying an alkyl group at the β-position of the double bond suffered an intramolecular 1,5-O,Si bond insertion with formation of a 2,3-dihydrofuran derivatives. Methylation of sulfoximine **23**, which was prepared with high regio- and diastereoselectivity from isobutyraldehyde and the corresponding chiral nonracemic bis(allyl)titanium complex,[14c,27] with Me_3OBF_4 proceeded quantitatively and gave salt **24**. Treatment of salt **24** with 2 equiv of LiN(H)*t*Bu at −100 °C in THF led to its rapid consumption with formation of the sulfinamide **8**. Remarkably, the enantio- and diastereomerically pure 2,3-dihydrofuran derivative **28** was isolated in 90% yield as the second elimination product and not the alkyne **17**. On the basis of these results, formation of alkynes **6** from salts **7** and of 2,3-dihydrofuran derivative **28** from salt **24** upon treatment with LiN(H)*t*Bu seems to proceed as follows. The deprotonation of salts **7** and **24** gives ylides **19** and **25**, respectively, which both suffer a heterolysis to deliver the (β-siloxyalkylidene)carbenes **20** and **26**, respectively. While alkylidenecarbenes **20** preferentially undergo a 1,2-H-shift with formation of alkynes **6**, alkylidenecarbene **26** preferentially undergoes a 1,5-O,Si bond insertion either concerted or via the oxonium ylide **27**, which suffers a [1,2]-silyl migration, to deliver 2,3-dihydrofuran derivative **28**. Thus, alkylidenecarbene aminosulfoxonium ylides **19** seem to behave in this respect in a manner similar to that of diazoalkenes,[29] alkylidenecarbene iodonium ylides,[30] and alkylidenecarbene oxonium ylides,[31] which readily yield alkynes through a 1,2-shift following heterolysis to alkylidenecarbenes.[3c,32] Formation of 2,3-dihydrofuran derivative **28** is also synthetically interesting since asymmetric synthesis of 2,3-dihydrofurans has found much attention recently,[28] and enantio- and diastereomerically pure 2,3-dihydrofurans of type **28** are not readily accessible yet.[28a]

Conclusion

In this paper, we described a new method for the asymmetric synthesis of anti-configured 1,2-disubstituted homopropargylic alcohols **1**, bearing the various groups R^1 and R^2, based on the highly regio- and diastereoselective addition of chiral nonracemic sulfonimidoyl substituted bis(allyl)titanium complexes **3** to aldehydes and a novel elimination of alkylidenecarbene (dimethylamino)sulfoxonium ylides derived from homoallylic

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(31) Sueda, T.; Nagaoka, T.; Satoru, G.; Ochiai, M. *J. Am. Chem. Soc*. **1996**, *118*, 10141.

(32) Stang, P. J. *Chem. Rev*. **1978**, *78*, 383.

alcohols carrying a (dimethylamino)sulfoxonium group. This method should be particularly well-suited for the synthesis of enantio- and diastereomerically pure homopropargylic alcohols **1** carrying sterically demanding and unsaturated substituents since enantio- and diastereomerically pure functionalized *anti*-homoallylic alcohols of type **2** can be obtained in a large variety with high selectivities through addition of titanium complexes **3** to aliphatic, aromatic, and unsaturated aldehydes. Although synthesis of homopropargylic alcohols **1** bearing two alkyl groups has not yet been demonstrated, we have no doubt that they can be made accessible by this method since the synthesis of the corresponding homoallylic alcohols **2** (R^1, R^2 = alkyl) has already been described.[14]

Although the mechanism of the elimination of the alkylidenecarbene aminosulfoxonium ylides awaits further studies, the available evidence points to a heterolysis of the novel alkylidenecarbene aminosulfoxonium ylides **19** with formation of chiral nonracemic (β-siloxyalkylidene)carbenes **20** which suffer a 1,2-H-shift. Evidence for the operation of such a mechanism was provided by the elimination of the methyl substituted alkylidenecarbene ylide **20**, which gave under 1,5-O,Si bond insertion the 2,3-dihydrofuran **28** and not through a 1,2-Me-shift the alkyne **17**. In this context it is tempting to speculate that the failure to isolate in the elimination of salts **7f** and **7i** the corresponding diynes might be due to an intramolecular reaction of the corresponding carbenes involving the triple bond at the γ,δ-position. The key alkylidenecarbene ylides **19** can be synthesized from the salts **7** upon treatment with *n*BuLi at low temperatures and methylated at the α-position. The elimination of the thus obtained α-methylated alkenyl aminosulfoxonium salts, which can also be prepared through methylation of the corresponding α-lithioalkenyl sulfoximines, could perhaps also provide for an asymmetric synthesis of homopropargylic alcohols with an internal triple bond and of hitherto little explored homoallenylic alcohols. Formation of 2,3-dihydrofuran derivative **28** suggests perhaps a new asymmetric synthesis of synthetically interesting highly substituted 2,3-dihydrofuran derivatives.

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Supporting Information Available: Complete experimental procedures and spectra and analytical data for all compounds generated in the course of the investigations reported here, including X-ray crystallographic data of **2e** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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