gen chloride.[11] The yield of **1** based on α,α-dichlorotoluene consumption also increases as hydrogen chloride increases. This result suggests that a higher mixing ratio of hydrogen chloride content suppress the decomposition of α,α-dichlorotoluene better. In the case of mole ratio of reactants higher than 1 : 6, however, about same amounts of products (**1-5**) were obtained.

In summary, we have shown that the direct synthesis of α,α-bis(silyl)toluenes successfully by reacting elemental silicon with a mixture of α,α-dichlorotoluene and hydrogen chloride in the presence of copper catalyst.

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6. Characterization data for 1,1,3,3-tetrachloro-2-phenyl-1,3-disilapropane (**1**); ^{1}H NMR ($CDCl_3$) δ 2.80 (t, J=1.9 Hz, 1H, C*H*), 5.71 (d, J=1.9 Hz, 2H, Si-*H*), 7.21-7.42 (m, 5H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 35.39 (*C*H), 127.22, 129.40, 129.63, 131.07 (*Ar*). HRMS (*m/e*): calcd for $C_7H_6Cl_4Si_2$ (M^+), 287.8919; found, 287.8914.
7. Characterization data for 1,1,1,3,3-pentachloro-2-phenyl-1,3-disilapropane (**2**); ^{1}H NMR ($CDCl_3$) δ 2.98 (d, J=1.9 Hz, 1H, C*H*), 5.74 (d, J=1.9 Hz, 1H, Si-*H*), 7.20-7.43 (m, 5H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 38.98 (*C*H), 127.50, 129.53, 129.77, 130.58 (*Ar*). HRMS (*m/e*): calcd for $C_7H_7Cl_5Si_2$ (M^+), 321.8529; found, 321.8539.
8. Characterization data for 1,1,1,3,3,3-hexachloro-2-phenyl-1,3-disilapropane (**3**); ^{1}H NMR ($CDCl_3$) δ 3.17 (s, 1H, CH), 7.26-7.42 (m, 5H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 42.25 (*C*H), 127.76, 129.36, 130.15, 130.32 (*Ar*). HRMS (*m/e*): calcd for $C_7H_6Cl_6Si_2$ (M^+), 355.8139; found, 355.8177.
9. Benzyldichlorosilane (**4**); ^{1}H NMR ($CDCl_3$) δ 2.76 (d, J= 2.0 Hz, 2H, CH_2), 5.54 (t, J=2.0 Hz, 1H, Si-*H*), 7.18-7.37 (m, 5H, Ar*H*).
10. Benzyltrichlorosilane (**5**); ^{1}H NMR ($CDCl_3$) δ 2.92 (s, 2H, CH_2), 7.29-7.36 (m, 5H, Ar*H*).
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Diels-Alder Reactions of α-Phenylthio-*o*-Quinodimethanes

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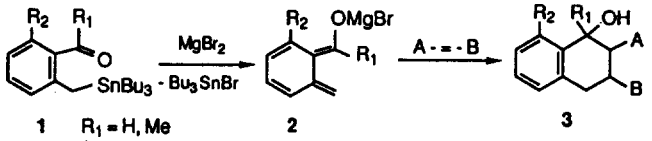
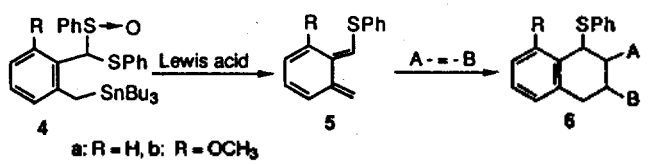
The generation and synthetic utility of *o*-quinodimethanes as the diene partner in Diels-Alder cycloaddition reactions is well documented.[1] In the previous report,[2] we found that the reactions of stannyl aldehydes and ketones **1** with anhydrous $MgBr_2$ at 0 ℃ in CH_2Cl_2 led to α-oxy-*o*-quinodimethanes **2**, which could be trapped as Diels-Alder adducts in good yields (Scheme 1).

As an extension of this study, we now wish to report a new and mild method for the generation of α-phenylthio-*o*-quinodimethanes **5** by the Lewis-acid promoted internal carbon-tin bond cleavage reaction of dithioacetal S-oxides **4** (Scheme 2). The method utilizes the potential of the C-Sn σ bond as a latent carbanionic nucleophile[3] and the sensitivity of sulfoxides as a leaving group in the presence of Lewis acids.[4] It is noteworthy that despite the well-known activating and regiodirecting effects of the sulfur substituents on diene in Diels-Alder reaction,[5] no report has yet been described concerning the generation and cycloadditions of *o*-quinodimethanes bearing the sulfur substituents at the α position.

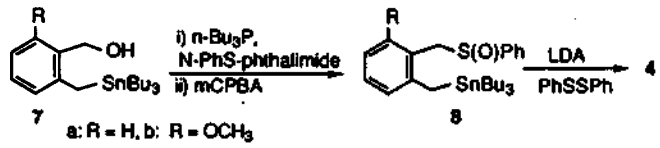
The requisite precursors **4** employed in the present study were easily prepared from the known stannyl alchols **7**[2,3] in three steps (Scheme 3). Reaction of **7** with *n*-Bu_3P and *N*-(phenylthio)phthalimide in benzene at room temperature[6] afforded their corresponding sulfides, which were subjected to *m*CPBA oxidation (1 equiv, −78°−−50 ℃/CH_2Cl_2/2 h) to give sulfoxides **8** in 70-75% overall yields. Sequential treat-



Scheme 1.

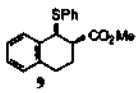
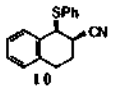
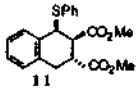
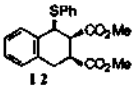
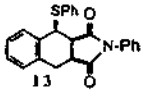
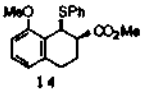
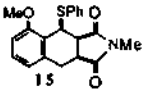
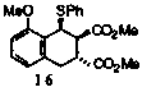


Scheme 2.



Scheme 3.

Table 1. Cycloadditions of α-Phenylthio-*o*-quinodimethanes with Dienophiles[a]

Entry	Stannane	Dienophile (Molar equiv)	Endo product	Ratio[b] (endo : exo)	Yield[c] %
1	**4a**	$CH_2=CHCO_2Me$ (3)	 **9**	3.4 : 1 3.6 : 1 3.0 : 1	48 36[d] 42[e]
2	**4a**	$CH_2=CHCN$ (3)	 **10**	9.5 : 1	67
3	**4a**	trans $MeO_2CCH=CHCO_2Me$ (2)	 **11**	1.1 : 1 1.2 : 1	58 45[d]
4	**4a**	cis $MeO_2CCH=CHCO_2Me$ (2)	 **12**	2.0 : 1	45
5[f]	**4a**	 (1.2)	 **13**	2.3 : 1 2.4 : 1	69 57[d]
6	**4b**	$CH_2=CHCO_2Me$ (3)	 **14**	3.0 : 1	42
7	**4b**	 (1.2)	 **15**	3.5 : 1	72
8[g]	**4b**	trans $MeO_2CCH=CHCO_2Me$ (2)	 **16**	7.2 : 1	61

[a] Unless otherwise noted, reactions were carried out at 0 ℃-rt in CH_2Cl_2 with 1.2 equiv of $ZnBr_2$. [b] Isomeric ratios (endo vs exo) were determined on the crude reaction mixture by 300 MHz ^1H NMR and/or isolation of pure isomers. [c] Isolated combined yields after flash column chromatography. [d] Reactions were carried out in CH_2Cl_2 at −20-0 ℃ with 2 equiv of CF_3CO_2H. [e] Reactions were carried out in CH_2Cl_2 at 0 ℃-rt with 1.2 equiv of $MgBr_2$. [f] Ref. 7.

ment of sulfoxides **8** with LDA (1.2 equiv, −78°-−50 ℃/1 h for **8a**, −78°-0 ℃/1.5 h for **8b**) and phenyl disulfide (1.1 equiv, −78°-0 ℃/1.5 h) in THF to produce **4** (**4a**; 82%, **4b**; 61%).

The *in situ* generation of α-phenylthio-*o*-quinodimethane intermediates **5** and their subsequent Diels-Alder trappings using electron-deficient olefins could be achieved by treatment of **4** with 1.2 equivalent of anhydrous zinc bromide in CH_2Cl_2 at the temperature ranging from 0 ℃ to room temperature. Table 1 lists up the results of a study of cycloadditions of **5** with various dienophiles. Use of $MgBr_2$ or trifluoroacetic acid instead of $ZnBr_2$ also afforded the cycloaddition adducts with similar regio- and stereoselectivities but in slightly lower yields.

The present method is operationally convenient and has been successfully employed on a scale ranging from 0.2-20 mmol. The mild reaction conditions required to effect both the generation of **5** and cycloadditions represent a useful feature of this method. As expected, cycloaddition with acrylonitrile (entry 2) took place both regio- and stereoselectively to give exclusively 1,2- *cis*, the *endo* adduct. On the other hand, analoguous reactions with methyl acrylate (entries 1 and 6) proceeded with less pronounced *endo* to *exo* selectivities. In the cycloaddition between **5b** and dimethyl fumarate a high *endo* to *exo* selectivity (7.2 : 1) was observed (entry 8). The latter case is interesting since it contrasts sharply with the related reaction of **5a**, which added to dimethyl fumarate (entry 3) with virtually no *endo* selectivity. Except for entry 8, cycloaddition reactions with symmetrical dienophiles generally proceeded with a modest degree of *endo* to *exo* selectivities.

In summary, we have shown that anhydrous zinc bromide can effectively promote the conversion of **4** to α-phenylthio-*o*-quinodimethanes **5**, which can then undergo Diels-Alder reactions. Although the observed stereoselectivities is far from optimal, the present method represents the first successful examples of cycloadditions involving α-phenylthio-*o*-quinodimethanes. Further investigations on the scope and some applications of this methodology are in progress.

A representative experimental procedure is as follows (Table 1, entry 5). To a cold (0 ℃) stirred solution of **4a** (251 mg, 0.40 mmol) and *N*-phenylmaleimide (83 mg, 0.48 mmol) in dry methylene chloride (2 mL) under argon was added anhydrous zinc bromide (108 mg, 0.48 mmol). After 1 h, the reaction mixture was allowed to warm up to room temperature over 1 h with stirring. The mixture was poured into ice-cold water, extracted with methylene chloride, dried, and concentrated. The residue obtained was redissolved in acetonitrile (25 mL) and then washed with hexane (10 mL, ×5) to remove organotin products. The acetonitrile layer was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel. Elution with hexane/ethyl acetate (4/1) gave *endo* adduct **13** (74 mg) and its *exo* isomer(32 mg) in 69% combined yield.

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2. Woo, S. H. *Tetrahedron Lett.* **1994**, *35*, 3975.
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Jr. J. W. *Tetrahedron Lett.* **1985**, *26*, 1395.
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7. **13**: mp 168.5-169.5 ℃. IR (KBr); 1710 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$); δ 3.24-3.49 (m, 3H), 3.60 (dd, 1H, J=9.6 Hz, J=5.4 Hz), 4.68 (d, 1H, J=5.4 Hz), 6.81-7.54 (m, 14H). ^{13}C NMR (75 MHz, $CDCl_3$); δ 28.33, 38.59, 45.73, 50.88, 126.59, 126.93, 126.99, 128.01, 128.22, 128.47, 128.73, 128.99, 129.16, 131.87, 133.26, 134.24, 134.89, 136.90, 175.59, 178.04. **16**: IR (thin film); 1738 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$); 2.85 (dd, 1H, J=17.1 Hz, J=11.9 Hz), 3.09 (s, 3H), 3.22 (dd, 1H, J=17.1 Hz, J=6.3 Hz), 3.26 (dd, 1H, J=11.6 Hz, J=3.7 Hz), 3.61 (ddd, 1H, J=11.9 Hz, J=11.6 Hz, J=6.3 Hz), 3.75 (s, 3H), 3.88 (s, 3H), 5.19 (d, 1H, J=3.7 Hz), 6.68-7.57 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$); δ 31.86, 37.70, 45.16, 46.65, 51.04, 52.04, 55.52, 108.27, 120.65, 124.28, 127.08, 128.50, 132.37, 133.65, 134.65, 136.11, 156.42, 171.40, 175.88.

Regio- and Stereoselective Oxyselenylation of Allylic Alcohol and It's Derivatives

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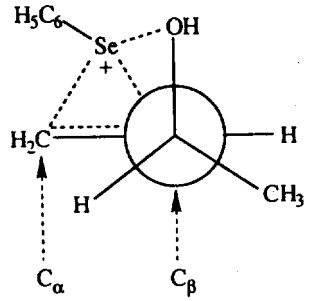
The electrophilic addition reaction of olefins with selenium species is of considerable interest with respect to the regio- and stereochemical outcome of this reaction[1-5] and versatile synthetic transformations of the phenylseleno group in the resultant product.[6] A couple of reports[2,5] showed that the phenylselenenyl chloride addition to allylic alcohols was performed in a highly regio- and stereoselective manner. Especially, the regio- and stereoselectivity are remarkably controlled in terminal acyclic allylic and cyclic allylic alcohol systems. However, the addition of phenylselenenyl chloride to internal acyclic allylic alcohol system afforded a relatively poor regioselectivity. In contrast to the systematic study of chloroselenylation to allylic alcohol systems, the oxyselenylation to olefins is limited to the addition reaction of cyclic and acyclic olefins substituted by the alkyl or phenyl group.[7-12] The solvent plays an important role in the formation of regioisomers in the oxyselenylation of cyclic system,[12] but the regiochemical outcome in the oxyselenylation of acyclic system is affected by the steric hindrance or temperature.[2,9] In spite of the synthetic importance of oxyselenylation in olefin systems, much less attention has been paid to the oxyselenylation of allylic alcohol systems which can be a potentially useful synthetic tool for the formation of regio- and stereocontrolled 1,2- or 1,3-diol compounds.[13,14] Although the hydroxyselenylation of 3-acetoxycyclohexene with N-phenylselenophthalimide in the presence of water and that of allylic alcohols with phenylselenenyl chloride in the presence of water were studied in recent years, the oxyselenylation of acyclic allylic alcohol derivatives has not been reported yet, specially from the regio- and stereochemical point of view.[15,16] In this communication, we wish to describe a regio- and stereochemical aspect in the oxyselenylation of acyclic allylic acohol derivatives with phenylselenenyl bromide in methanol.

The first examination of the oxyselenylation was performed on terminal allylic alcohols. When the reaction of 3-buten-2-ol (**1a**) with phenylselenenyl bromide was performed in CH_2Cl_2 solvent containing 10 equiv. of methanol at 25 ℃, the oxyselenylation adducts **2a**, **3a** and bromoselenylation adducts were obtained in a 40 : 3 : 57 ratio. Despite the high regioselectivity between oxyselenylation adducts **2a** and **3a** (93 : 7) was shown, the formation of bromoselenylation adduct was a serious drawback. However, the treatment of allylic alcohol **1a** with phenylselenenyl bromide in methanol solvent at 25 ℃ produced an anti-Markovnikov adduct **2a** and a Markovnikov adduct **3a** in 49% yield (**2a** : **3a**=93 : 7).[17,18] The bromoselenylation product was not observed in this reaction and the isomerization of **2a** to **3a** did not occur at all under the employed reaction condition. The regioselectivity of this reaction sharply contrasts to that obtained from the chloroselenylation of terminal allylic alcohols at 25 ℃, which afforded only Markovnikov adduct.[5] The high regioselectivity can be understood in terms of the steric hindrance between the attacking methanol and seleniranium ion intermediate [I] which was also suggested in the hydroxyselenylation of allylic alcohols.[16] Therefore, it is expected that the nucleophilic methanol attacks at the less hindered carbon site (C_α) rather than C_β.



[I]

The same reaction at a raised temperature (60 ℃) provided the relatively poor regioselectivity (**2a** : **3a**=81 : 19). Therefore, the similar treatment of other allyic alcohols with phenylselenenyl bromide was carried in methanol solvent at 25 ℃. When 3-acetoxy-1-butene (**1b**) was reacted with phenylselenenyl bromide under the suggested reaction condition, an anti-Markovnikov adduct **2b** and a small amount of the bromoselenylation adduct were isolated in 18% and 0.5% yield, respectively, although the improved regioselectivity was shown. The other regioisomer **3b** was not detected. The isolation of bromoselenylation adduct indicates that the seleniranium ion intermediate formed during methoxyselenylation was in equilibrium somewhat with bromoselenylation adduct. The formation of **2b** in a relatively low yield may be due