Synthesis and Reactions of Neutral Hypercoordinate Allylsilicon Compounds Having a Tropolonato Ligand

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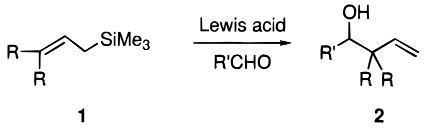
A novel intramolecular allylic migration from silicon to carbon was observed during the reaction of allylmethyldichlorosilane with tropolone in the presence of triethylamine to give an isomeric mixture of pentacoordinate silicon compounds having allylated tropolonato ligand. The molecular structure of the major isomer was determined by X-ray analysis. Reaction of diprenyldichlorosilane with tropolone at low temperature (−35 °C) gave the first hexacoordinate allylsilicon compound, diprenylbis(tropolonato)silicon, which underwent the allylic migration at room temperature to give the neutral pentacoordinate allylic silicon compound. The activation parameters for the rearrangement in $CDCl_3$ were determined by NMR to be $\Delta H^{\ddagger} = 77.6$ kJ/mol and $\Delta S^{\ddagger} = -60.3$ J/(mol·K). Facile allylation of aldehyde was performed with the neutral pentacoordinate allylic silicon compounds to give the corresponding homoallylic alcohols in good yields (70−90%) at room temperature without any catalyst.

Introduction

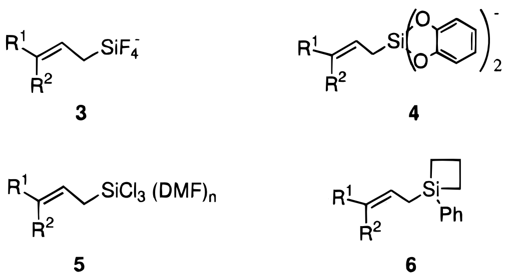
In recent years, the use of organosilicon compounds, such as α-silylcarbanions, silyl enol ethers, allylsilanes, vinylsilanes, alkynylsilanes, etc., as reagents in organic synthesis has become a field of considerable importance.[1] Among these silicon reagents, allyltrimethylsilane (**1**) is one of the most important,[2] since the reactions of allyltrimethylsilane with carbonyl compounds give the corresponding homoallylic alcohols (**2**) (eq 1) in a regiospecific manner, which can be converted to many important building blocks for natural product synthesis.



(1)

Whereas the reactions are usually promoted by Lewis acids such as $TiCl_4$, $AlCl_3$, $SnCl_4$, and $BF_3{\cdot}OEt_2$, novel regiospecific and highly stereoselective allylations of carbonyl compounds without any catalysts have been recently developed by applying high reactivity of pentacoordinate allylsilicates (**3**−**5**)[3,4] and 1-allylsilacyclobutane (**6**)[5] (Chart 1).

Chart 1



The high reactivity of the pentacoordinate allylsilicates is attributed to the significant Lewis acidity to give the corresponding hexacoordinate silicon compounds, in which the nucleophilicity of the γ-carbon of the allylsilicates is enhanced by the effective $\sigma-\pi$ conjugation.[3] The origin of the high regio- and stereoselectivity of the allylations is ascribed to the six-membered ring transition states. However, as far as we are aware, hexacoordinate allylsilicon compounds have never been isolated and their intrinsic reactivity has not been known to date.

Although a number of hexacoordinate silicon compounds have been isolated and characterized,[6] those having two Si−C bonds are very rare. We have recently reported the successful synthesis of neutral hexacoordinate dialkyl- and diarylsilicon compounds (**8**) having two tropolonato ligands by the reaction of tropolone with the corresponding dimethoxysilanes (eq 2).[7] The tropolonato ligand is suggested to be useful to stabilize hexacoordinate silicon compounds due to the contribu-

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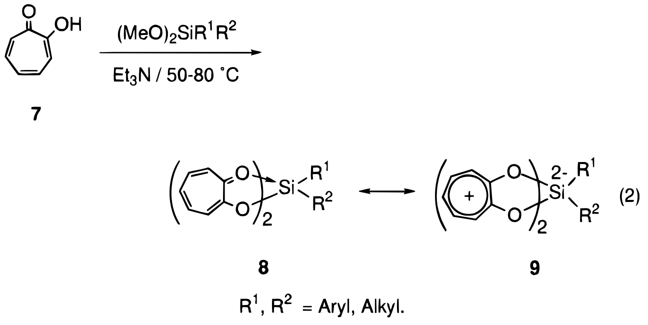
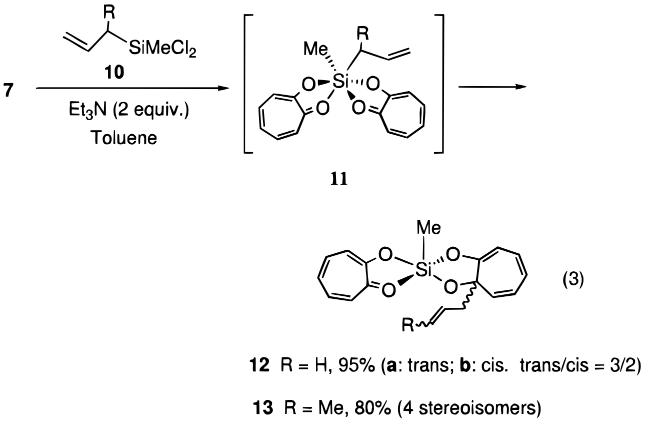
tion of a canonical structure of **9**, where tropolonato rings serve as the intramolecular countercations for the silicate dianion.



In this paper, we report the first isolation of neutral hexacoordinate and pentacoordinate allylsilicon compounds, facile intramolecular allylic migration of the hexacoordinate allylsilicon compounds, and high reactivity of the neutral pentacoordinate allylsilicon compounds toward aldehydes.

Results and Discussion

Allylic Migration during Reactions of Tropolone with Allyldichloro(methyl)silane and Related Silicon Compounds. During the course of our study of the preparation of hexacoordinate allylsilicon compounds having tropolonato ligand, rather unusual intramolecular allylic migration from silicon to carbon was discovered. Thus, treatment of tropolone with allyldichloro(methyl)silane (**10**) in toluene at room temperature for 3 h in the presence of 2 equiv of triethylamine afforded yellow prisms of an isomeric mixture of pentacoordinate silicon compounds **12a,b** in 95% yield with the **12a**/**12b** ratio of 3/2 (eq 3). Similarly, a reaction of



tropolone with 1-methylallyldichloro(methyl)silane gave a mixture of four stereoisomers of the migration product **13**. No evidence for the intermediacy of hexacoordinate allylic silicon compounds **11** was obtained by low-temperature NMR study of the reactions. The structures of **12** and **13** were confirmed by means of NMR spectroscopy and X-ray chromatography. The ^{29}Si NMR resonances of *trans* and *cis* isomers of **12** found at −69.5 and −68.5 ppm, respectively, are indicative of the pentacoordinate structure around silicon.

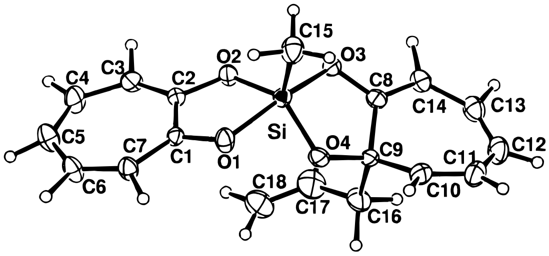


Figure 1. ORTEP drawings of **12a**, showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity. Selected bond distances (Å): Si−O1 = 1.834(4), Si−O2 = 1.731(4), Si−O3 = 1.739(4), Si−O4 = 1.656(4), C1−C2 = 1.420(6), C1−C7 = 1.387(7), C3−C2 = 1.382, C4−C3 = 1.374(8), C5−C4 = 1.356(8), C7−C6 = 1.381(8), C6−C5 = 1.366(8). O1−C1 = 1.299(6), O2−C2 = 1.322(5). Selected bond angles (deg): O1−Si−O2 = 84.1(1), O1−Si−O3 = 165.8(1), O2−Si−O4 = 128.7(2), O2−Si−C15 = 112.5(1), O4−Si−C15 = 118.7(2), O1−Si−C15 = 96.4(2).

The molecular structure of **12a** was confirmed by X-ray analysis.[8] An ORTEP drawing of **12a** is shown in Figure 1 with selected bond distances and angles. The X-ray analysis of **12a** confirmed the distorted trigonal bipyramidal geometry around silicon atom (O1−Si−O2 = 84.1°, O1−Si−O3 = 165.8°, O2−Si−O4 = 128.7°) with a methyl and an allyl groups at the *trans*-positions to each other regarding the five-membered ring as illustrated in Figure 1. The bond lengths of Si−O2 (1.731(4) Å), Si−O3 (1.739(4) Å), and Si−O4 (1.656(4) Å) are comparable with those in the penta- and hexacoordinate silicate anions having catecholato ligand.[9] The Si−O1 bond distance (1.83(4) Å) is longer than the other Si−O bonds of **12a** but even shorter than the shortest Si−O coordination bond distance among the reported (1.91 Å).[10] All the four oxygens of the seven-membered rings are regarded to be covalently bonded to the silicon atom. All the C−C bond distances in the tropolonato ring are significantly longer than 1.337(6) Å for a typical carbon−carbon double bond but shorter than C_{sp^2}−C_{sp^2} single bonds found in related tropolone derivatives.[11] The degree of the bond alternation observed in the seven-membered ring in **12a** is remarkably reduced from that of the seven membered ring in tropolonyl *p*-chlorobenzoate; the ring of **12a** more closely resemble a tropylium oxide structure rather than cycloheptatrienone.[11b] The less extent bond alternation in **12** may suggest the significant contribution of a canonical structure where the tropolone ring serves as

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[8] The data collection and structural analysis for **12a** were carried out as follows. The reflection intensities were collected on a Rigaku AFC-5R diffractometer with a rotating anode (45 kV, 200 mA) using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). Crystal data (150 K): orthorhombic, space group: *Pbca* (No. 61), a = 14.398 (4) Å, b = 14.107 (5) Å, c = 16.476 (1) Å, γ = 90.0 (0)°, V = 3346.7 (47) Å^3, Z = 8, D_{calcd} = 1.30 g cm^{-3}. A total of 4327 reflections was measured, and of these 2299 reflections [$F_o > 2\sigma(F_o)$] were used in refinement. R = 0.072, and R_w = 0.067. All calculations were performed by an ACOS-2200 computer at Tohoku University with the applied library program UNICS III (Sakurai, T.; Kobayashi, K. *Rikagaku Kenkyusho Hokoku* **1979**, *55*, 69).

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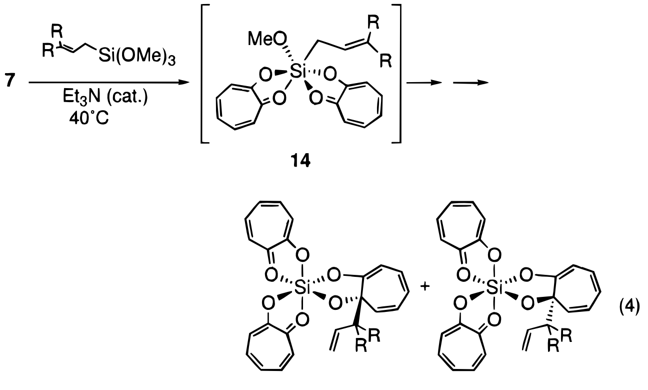
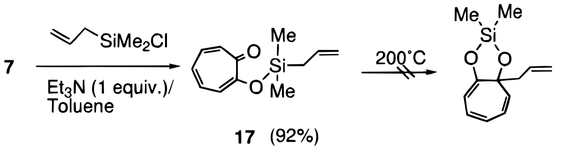
an intramolecular countercation for the silicate anion, as previously found in the diphenylbis(tropolonato)silicon compound.

The reactions of allyltrimethoxysilane and prenyltrimethoxysilane with tropolone gave the corresponding hexacoordinate tris(tropolonato)silicon compounds, **15** and **16**, respectively, in which a tropolone ring bears an allylic group as shown in eq 4. As evidenced by NMR, **15** (or **16**) was obtained as a diastereomeric mixture of **15a**,**b** (or **16a**,**b**), since the octahedral tris(tropolonato)silicon and the allyl-substituted carbon are both chiral (see Experimental Section). On the other hand, the reaction of allydimethylchlorosilane with tropolone gave only a tetracoordinate silane (**17**); no allylic migration occurred even when **17** was heated at 200 °C (eq 5). It is suggested that hypercoordination at silicon atom is required for the allylic migration from silicon to tropolonato carbon.



(4)

15a R = H **15b** R = H
(55% yield as a mixture of **15a** and **15b**)
16a R = Me **16b** R = Me
(76% yield as a mixture of **16a** and **16b**)



17 (92%)

(5)

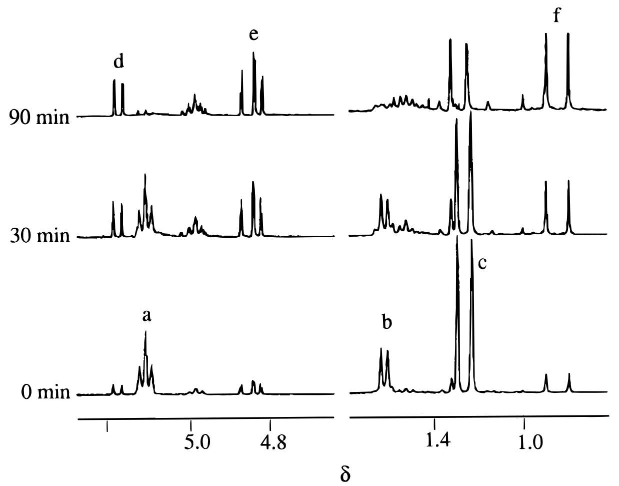
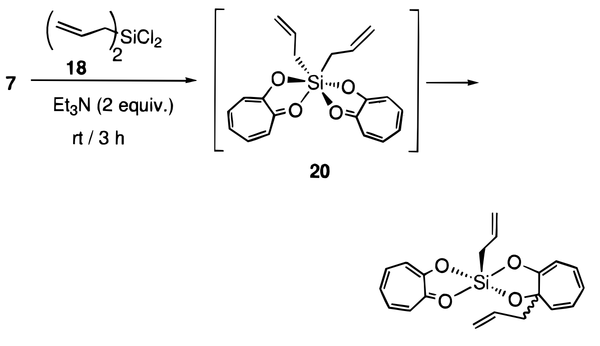


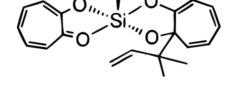
Figure 2. Isomerization of **22** to **23** monitored by ^{1}H NMR spectroscopy in $CDCl_3$ at 294 K. The time course shows the decrease of olefinic (a, 1H), allylic (b, 2H), and methyl protons (c, 6H)) of the prenyl group in **22** and the accompanying increase of olefinic (d, 1H and e, 2H) and methyl (f, 6H) protons of the 1,1-dimethylallyl group in **23**.

Isolation of Pentacoordinate and Hexacoordinate Allylsilicon Compounds. Interestingly, when diallyldichlorosilane (**18**) was treated with tropolone at room temperature, one of the allyl group migrated from the silicon atom to the seven-membered ring carbon to give a pentacoordinate allylsilicon compounds (**21**) (eq 6); no further migration of the other allyl group to silicon occurred even at 80 °C. The ^{29}Si NMR resonance of **21** appeared at −73 ppm. Again, no evidence for the hexacoordinate silicon intermediate (**20**) was obtained by a low-temperature NMR study of the reaction. However, when the reaction of diprenyldichlorosilane (**19**) with tropolone was carried out at −35 °C, hexacoordinate diprenylbis(tropolonato)silicon compound (**22**) was isolated as orange prisms from the reaction mixture (eq 7). The *cis* configuration of the two allylic groups in **22** is assigned on the basis of the X-ray structural analysis as well as the dynamic behavior of the ^{1}H and ^{13}C NMR spectra for dimethyl- and diphenylbis(tropolonato)silicon compounds reported in a previous paper.[7] The ^{29}Si NMR resonance of **22** (−111.5 ppm) is indicative of the hexacoordinate silicon structure. To the best of our knowledge, **22** is the first hexacoordinate allylic silicon compound isolated. The hexacoordinate diprenylsilicon compound **22** readily underwent prenyl migration from silicon to carbon to give the corresponding pentacoordinate prenylsilicon compound **23** upon standing for 3 h in solution at room temperature.



21 (90%)

(6)



23 (90%)

(7)

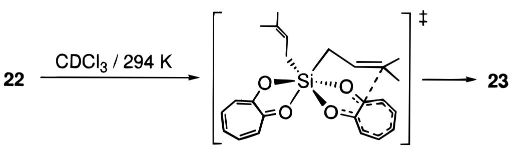
The isomerization of **22** to **23** was monitored at various temperatures by ^{1}H NMR spectroscopy; a typical run is shown in Figure 2. The time-course of the ^{1}H NMR spectra shown in Figure 2 indicates that the hexacoordinate silicon compound **22** is easily converted to the pentacoordinate silicon compound **23** (eq 8). The

$$\mathbf{22} \xrightarrow[\text{CDCl}_3\,/\,294\text{ K}]{k} \mathbf{23} \qquad (8)$$

$$k = 4.8 \times 10^{-5}\ \text{s}^{-1}\ (294\ \text{K})$$
$$\Delta H^{\ddagger} = 77.6\ \text{kJ}\bullet\text{mol}^{-1}$$
$$\Delta S^{\ddagger} = -60.3\ \text{J}\bullet\text{mol}^{-1}\bullet\text{K}^{-1}$$

rate constant at 298 K, the activation enthalpy ($\Delta H^{\ddagger}$), and the activation entropy ($\Delta S^{\ddagger}$) were determined as 4.8 $\times$ 10^{-5} s^{-1}, 77.6 kJ/mol, and -60.3 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, respectively, by monitoring the signal intensity as a function of time elapsed at the various temperatures. The activation enthalpy is compared to the barrier of 77.3 kJ/mol for the reaction of pentacoordinate allylsilicate with formaldehyde calculated by ab initio MO method, where the reaction is supposed to proceed via a six-membered cyclic transition state.[12] In addition, the negative activation entropy is consistent with the cyclic transition state (**24**) for the rearrangement.

The migration from **22** to **23** will proceed via a cyclic chair form **24** (eq 9) analogous to the transition states for the allylation of α-hydroxy ketones. These results are suggestive of the transient existence of the hexacoordinate allylsilicon intermediates like **11** and **20** during the formation of **12** and **21**, respectively. The much higher migratory aptitude of *hexacoordinate* allylsilicon compounds as compared to the corresponding *pentacoordinate* allylsilicon compounds gives a strong experimental support to the mechanism via a cyclic transition state having a hexacoordinate silicon atom like **25**, proposed for the reactions of pentacoordinate allylsilicon compounds with aldehydes (eq 10); the cyclic transition state will be favored since the hexacoordination at silicon will increase the electron-donating ability of the silyl group and, in turn, the nucleophilicity of the allylic γ-carbon due to the enhanced hyperconjugation.



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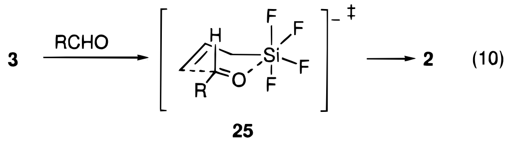
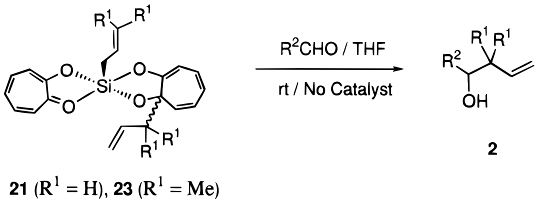


(10)

Allylation of Aldehydes with Pentacoordinate Allylsilicon Compounds 21 and 23. Allylation of carbonyl compounds with anionic pentacoordinate allylsilicates has been well established as a useful synthetic method for homoallylic alcohols in regiospecific and highly stereoselective manner.[3] Recently, Kobayashi et al. have found a facile allylation of aldehydes with allyltrichlorosilane in DMF, where it is assumed that neutral pentacoordinate allylsilicon compounds coordinated by a DMF molecule are the reactive species.[4] However, there is no systematic study of the comparison of reactivity between neutral and anionic pentacoordinate allylsilicon compounds until now. We have investigated the reactions of the isolated neutral pentacoordinate allylic silicon compounds **21** and **23** with benzaldehyde and nonanal.

Table 1. Reactions of Pentacoordinate Allylsilicon Compounds 21 and 23 with Aldehydes

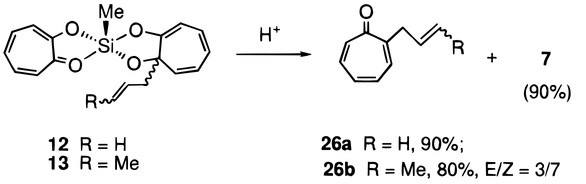


(11)

R^1	R^2	time/h	yield of **2**/%
H	n-C_8H_{17}	12	85
H	Ph	12	90
Me	n-C_8H_{17}	40	70
Me	Ph	40	72

As shown in Table 1, **21** and **23** reacted with not only benzaldehyde but also nonanal at room temperature without any catalyst to produce the corresponding homoallylic alcohols (**2a**–**d**) in high yields after hydrolysis. The reactions of **23** with nonanal and benzaldehyde gave 3,3-dimethyl-1-dodecenyl-3-ol (**2c**) and 2,2-dimethyl-1-phenylbut-3-en-1-ol (**2d**) as a sole regioisomer, respectively. The reason of the higher reactivity of **21** and **23**[13] compared to the corresponding anionic bis(catecholato)allylsilicates, which reacts with benzaldehyde but does not with aliphatic aldehydes, may be attributed to the stronger Lewis acidity of the former.[14]

Regiospecific Formation of 2-Allyltropones via Hydrolysis of 12 and 13. When **12** and **13** were treated with acidic aqueous solutions, 2-allyltropones (**26**) were obtained regiospecifically, in which the C-C bond formation occurred at the γ-carbon of the allylsilanes; the yields were quantitative, and the *E*/*Z* ratio in **26b** was 3/7 (eq 12).



(12)

Whereas a number of methods to prepare 2-alkyltropones by the reactions of tropolone and its derivatives with organometallic reagents such as Grignard reagents and alkyllithium reagents have been reported,[15,16] most of the known routes have drawback in the low regioselectivity.[17] The present procedure provides a novel method for the regiospecific synthesis of 2-allyltropones, while the overall yields of **26** do not exceed 50% based on the utilized tropolone.

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Experimental Section

General Methods. ^{1}H (300 MHz), ^{13}C (75.4 MHz), and ^{29}Si (59.6 MHz) NMR spectra were measured on a Bruker AC300P NMR spectrometer. ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR spectra were measured on a Bruker AM600P NMR spectrometer. ^{1}H and ^{13}C NMR chemical shifts were referenced to internal residual protons in chloroform-*d* (^{1}H δ 7.24) or CD_2Cl_2 (^{1}H δ 5.26). ^{29}Si NMR chemical shifts were relative to Me_4Si in ppm. Mass spectra and high-resolution mass spectra were obtained on a JEOL JMS D-300 Mass spectrometer. Electronic spectra were recorded on a Shimadzu UV2000 and a Milton Roy SP-3000 spectrometer. GLC analysis was conducted by using a Shimadzu 8A gas chromatograph.

All reactions were conducted in oven-dried or flame-dried glassware under atmospheres of dry argon or nitrogen. All solvents were purified before use.

Methyl[1-(3-propenyl)cyclohepta-2,4,6-trien-1,2-diolato)(tropolonato)silicon Compounds (12a,b). To a toluene solution of tropolone (**7**) (1 g, 8.2 mmol) and triethylamine (1 g, 9.9 mmol) was added allyldichloro(methyl)silane (682 mg, 4.1 mmol), under argon, and the resultant mixture was stirred for 3 h at room temperature. Filtration of the precipitated $Et_3N{\cdot}HCl$ under argon followed by removal of the solvent under vacuum afforded the solid of a mixture of **12a**,**b** with a trans/cis ratio of 3/2 as determined by ^{1}H NMR spectroscopy. During the recrystalization of the mixture from toluene under argon, **12b** isomerized to **12a** and finally gave the pure **12a**.

12a (trans-isomer): yellow crystals; mp 240 °C (dec); ^{1}H NMR (600 MHz, CD_2Cl_2) δ 0.16 (s, 3 H), 1.78 (ddt, $J = 13.8$, 7.8, 1.0 Hz, 1 H), 1.87 (ddt, $J = 13.8$, 6.5, 1.0 Hz, 1 H), 4.68 (ddt, $J = 17.1$, 1.4, 1.3 Hz, 1 H), 4.72 (ddt, $J = 10.2$, 1.4, 1.3 Hz, 1 H), 5.31 (d, $J = 11.1$ Hz, 1 H), 5.60 (dddd, $J = 17.1$, 10.2, 7.8, 6.5 Hz, 1 H), 5.64 (d, $J = 7.2$ Hz, 1 H), 5.98 (dd, $J = 10.8$, 7.1 Hz, 1 H), 5.99 (dd, $J = 11.1$, 7.1 Hz, 1 H), 6.29 (dd, $J = 10.8$, 7,2 Hz, 1 H), 7.61 (tt, $J = 9.82$, 1.07 Hz, 1 H), 7.78 (dd, $J = 10.1$, 1.1 Hz, 1 H), 7.79 (dd, $J = 11.0$, 1.1 Hz, 1 H), 7.87 (ddd, $J = 10.1$, 9.8, 1.1 Hz, 1 H), 7.99 (ddd, $J = 11.0$, 9.8, 1.1 Hz, 1 H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ −0.17, 37.0, 79.0, 95.8, 117.9, 120.9, 123.9, 126.3, 127.4, 128.9, 129.4, 134.0, 134.3, 142.8, 145.0, 154.0, 169.5, 175.4; ^{29}Si NMR (59 MHz, CD_2Cl_2) δ −69.36 ppm; MS *m/z* (%) 326 (M^+, 1.3), 285 ($M^+ - 41$, 100), 279 (39), 257 (7.6); high-resolution MS *m/z* found 326.0973, calcd for $C_{18}H_{18}O_4Si$ 326.0976. Anal. Calcd for $C_{18}H_{18}O_4Si$: C, 66.26; H, 5.52. Found: C, 66.00; H, 5.60.

12b (cis-isomer): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 0.33 (s, 3 H), 1.91 (ddt, $J = 13.8$, 7.3, 1.0 Hz, 1 H), 1.95 (ddt, $J = 13.8$, 7.5, 1.0 Hz, 1 H), 4.95 (ddt, $J = 17.1$, 1.4, 1.3 Hz, 1 H), 5.05 (ddt, $J = 10.2$, 1.4, 1.3 Hz, 1 H), 5.13 (d, $J = 10.4$ Hz, 1 H), 5.61 (d, $J = 7.5$ Hz, 1 H, H), 5.83 (dddd, $J = 17.1$, 10.2, 7.5, 7.3 Hz, 1 H), 6.01 (dd, $J = 10.8$, 6.3 Hz, 1 H), 6.07 (dd, $J = 10.4$, 6.3 Hz, 1 H), 6.31 (dd, $J = 10.8$, 7.5 Hz, 1 H), 7.59 (tt, $J = 9.8$, 1.1 Hz, 1 H), 7.59 (tt, $J = 9.8$, 1.1 Hz, 1 H), 7.79 (dd, $J = 10{,}9$, 1.1 Hz, 1 H), 7.85 (dd, $J = 10.3$, 1.1 Hz, 1 H), 7.91 (ddd, $J = 10.3$, 9.8, 1.1 Hz, 1 H), 8.00 (ddd, $J = 10.9$, 9.8, 1.1 Hz, 1 H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 1.5, 37.8, 79.7, 96.1, 118.4, 120.9, 124.0, 126.4, 126.6, 129.1, 129.3, 134.0, 134.4, 143.0, 145.0, 154.9, 169.5, 175.5; ^{29}Si NMR (59 MHz, CD_2Cl_2) δ −68.23; MS *m/z* (%) 326 (M^+, 0.2), 285 (40), 279 (78), 149 (100).

Methyl[1-(3-butenyl)cyclohepta-2,4,6-trien-1,2-diolato)]-(tropolonato)silicon Compounds (13a,b). The title compounds were obtained as a mixture of four isomers in 80% by a similar procedure as above using methyl(1-methylallyl)-dichlorosilane as an allylsilane. Among the four isomers, the NMR data of (*Z*)-3-butenyl isomers (**13a**,**b**) were analyzed as follows. **13a** (trans-isomer): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 0.23 (s, 3 H), 1.26 (d, $J = 4.6$ Hz, 3 H), 1.89−2.08 (m, 2 H), 5.28 (d, $J = 10.0$ Hz, 1 H), 5.27 (m, 1 H), 5.57 (m, 1 H), 5.77 (d, $J = 7.2$, 1 H), 6.03 (dd, $J = 10.4$, 6.3 Hz, 1 H), 6.08 (dd, $J = 10.0$, 6.3 Hz, 1 H), 6.32 (dd, $J = 10.4$, 7.2 Hz, 1 H), 7.60 (tt, $J = 9.8$, 1.07 Hz, 1 H), 7.77 (dd, $J = 10.9$, 1.1 Hz, 1 H), 7.78 (dd, $J = 10.9$, 1.0 Hz, 1 H), 7.87 (ddd, $J = 10.1$, 9.8, 1.0 Hz, 1 H), 7.79 (ddd, $J = 10.9$, 9.8, 1.1 Hz, 1 H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ −0.4, 12.8, 30.0, 78.9, 96.2, 120.9, 123.4, 125.0, 126.5, 127.0, 127.5, 128.7, 129.3, 134.0, 142.2, 144.2, 154.9, 169.3, 174.0; ^{29}Si NMR (59 MHz, CD_2Cl_2) δ −69.2. **13b** (cis-isomer): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 0.40 (s, 3 H), 1.54 (d, $J = 5.7$ Hz, 3 H), 1.89−2.08 (m, 2 H), 5.45 (d, $J = 10.0$ Hz, 1 H), 5.27 (m, 1 H), 5.57 (m, 1 H), 5.75 (d, $J = 7.2$, 1 H), 6.04 (dd, $J = 10.4$, 6.3 Hz, 1 H), 6.09 (dd, $J = 10.0$, 6.3 Hz, 1 H), 6.35 (dd, $J = 10.4$, 7.2 Hz, 1 H), 7.58 (tt, $J = 9.8$, 1.1 Hz, 1 H), 7.78 (dd, $J = 10.9$, 1.1 Hz, 1 H), 7.84 (dd, $J = 10.3$, 1.1 Hz, 1 H), 7.90 (ddd, $J = 10.3$, 9.8, 1.0 Hz, 1 H), 8.00 (ddd, $J = 10.8$, 9.8, 1.0 Hz, 1 H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 1.3, 12.8, 30.5, 79.7, 95.7, 120.7, 123.6, 125.8, 125.9, 127.0, 127.5, 128.9, 129.3, 133.9, 142.2, 144.1, 154.9, 169.3, 173.9; ^{29}Si NMR (59 MHz, CD_2Cl_2) δ −68.2.

The NMR spectra of a mixture of (*E*)-3-butenyl isomers (**13c**,**d**) were too complex to be analyzed.

[1-(3-Propenyl)cyclohepta-2,4,6-trien-1,2-diolato)]bis-(tropolonato)silicon Compounds (15a,b). A mixture of trimethoxyallylsilane (1 mL), tropolone (500 mg, 4.1 mmol) and triethylamine (4.5 mmol) was heated 80 °C for 4 h under argon atmosphere. A precipitate was collected and washed with dry ether giving a yellow powder, which decomposed at 280 °C. The GC-MS and NMR analyses have shown that the solid is a mixture of two racemic diastereomers (**15a**,**b**, **15a**/**15b** = 1:1) in the total yield of 55%. GC-MS of the two isomers: *m/z* (relative intensity) 432 (M^+, 0.26), 391 ($M^+ - 41$, 100) for **15a** (or **15b**) and *m/z* (relative intensity) 432 (M^+, 0.20), 391 ($M^+ - 41$, 100), 363 (12), 325 (51) for **15b** (or **15a**). The NMR spectral data for each isomer were analyzed on the basis of 2D ^{1}H−^{1}H and ^{13}C−^{1}H COSY experiments as follows. **15a** (or **15b**): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 1.75 (1 H, ddt, $J = 13.3$, 7.2, 1.3 Hz), 1.79 (1 H, ddt, $J = 13.3$, 7.2, 1.3 Hz), 4.45 (1 H, ddt, $J = 17.1$, 2.5, 1.3 Hz), 4.74 (1 H, ddt, $J = 10.2$, 2.5, 1.3 Hz), 4.89 (1 H, d, $J = 10.9$), 5.43 (1 H, d, $J = 7.0$ Hz), 5.62 (1 H, ddt, $J = 17.1$, 10.2, 7.1, 6.7 Hz), 5.90 (1 H, dd, $J = 10.9$, 6.3 Hz), 6.19 (1 H, dd, $J = 10.8$, 6.3 Hz), 6.19 (1 H, dd, $J = 10.8$, 7.0 Hz), 7.37 (1 H, t, $J = 9.8$ Hz), 7.39 (1 H, t, $J = 10.0$ Hz), 7.47 (1 H, d, $J = 10.6$ Hz), 7.48 (1 H, d, $J = 10.3$ Hz), 7.64 (1 H, d, $J = 10.8$ Hz), 7.69 (1 H, d, $J = 10.8$ Hz), 7.73 (1 H, dd, $J = 10.6$, 9.78 Hz), 7.74 (1 H, dd, $J = 10.3$, 10.0 Hz), 7.78 (1 H, dd, $J = 10.8$, 9.8 Hz), 7.82 (1 H, dd, $J = 10.8$, 10.0 Hz); ^{13}C NMR (150.9 MHz, CD_2Cl_2) δ 36.0, 76.0, 94.2, 114.7, 119.3, 121.5, 124.9, 125.0, 125.2, 125.4, 127.5, 127.6, 130.4, 130.5, 134.5, 141.6, 141.8, 141.9, 141.9, 154.0, 171.3, 171.4, 171.8, 172.2. **15b** (or **15a**): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 1.849 (1 H, ddt, $J = 13.6$, 6.7, 1.3 Hz), 1.94 (1 H, ddt, $J = 13.6$, 6.7, 1.3 Hz), 4.78 (1 H, ddt, $J = 17.1$, 2.5, 1.3 Hz), 4.89 (1 H, ddt, $J = 10.3$, 2.5, 1.3 Hz), 5.25 (1 H, d, $J = 10.9$ Hz), 5.44 (1 H, d, $J = 6.9$ Hz), 5.93 (1 H, dd, $J = 10.8$, 6.3 Hz), 5.96 (1 H, dd, $J = 10.9$, 6.3 Hz), 5.97 (1 H, ddt, $J = 17.1$, 10.2, 7.2 Hz), 6.19 (1 H, dd, $J = 10.8$, 6.9 Hz), 7.38 (1 H, t, $J = 9.8$ Hz), 7.41 (1 H, t, $J = 10.0$ Hz), 7.48 (1 H, d, $J = 10.6$ Hz), 7.49 (1 H, d, 10.3 Hz), 7.64 (1 H, d, $J = 10.8$ Hz), 7.72 (1 H, d, $J = 10.8$ Hz), 7.73 (1 H, dd, $J = 10.6$, 9.8 Hz), 7.76 (1 H, dd, $J = 10.3$, 1.0 Hz), 7.79 (1 H, dd, $J = 10.8$, 9.8 Hz), 7.93 (1 H, dd, $J = 10.8$, 10.0 Hz); ^{13}C NMR (150.9 MHz, CD_2Cl_2) δ 63.3, 76.4, 94.3, 115.1, 119.5, 121.5, 124.9, 125.2, 125.3, 125.5, 127.5, 127.8, 130.5, 130.6, 134.9, 141.7, 141.9, 141.9, 142.0, 154.2, 171.4, 171.5, 172.1, 172.8). ^{29}Si CP-MAS NMR (59.6 MHz) of the mixture showed a singlet at δ −137.5. High-resolution MS of the mixture: found, 391.0642 ($M^+ - 41$); calcd for $C_{21}H_{15}O_6Si$, 391.0646.

[1-(1′,1′-Dimethyl-2′-propenyl)cyclohepta-2,4,6-trien-1,2-diolato)]bis(tropolonato)silicon Compounds (16a,b). A similar reaction of tropolone with prenyltrimethoxysilane gave an isomeric mixture of **16a**,**b** (**16a**/**16b** = 1:1). GC-MS: *m/z* (relative intensity) 391 ($M^+ - 69$, 100), 363 (9.7), 146 (37.7), 122 (79.9), 91 (35.9) for **16a** (or **16b**) and *m/z* (relative intensity) 391 ($M^+ - 69$, 100), 363 (12), 325 (51) for **16b** (or **16a**). The NMR spectral data for each isomer were analyzed on the basis of 2D ^{1}H−^{1}H and ^{13}C−^{1}H COSY experiments as follows. **16a** (or **16b**): ^{1}H NMR (300 MHz, CD_2Cl_2) δ 0.76 (s, 3 H), 0.88 (s, 3 H), 4.61 (dd, J = 9.9, 2.1 Hz, 1 H), 4.74 (dd, J = 17.4, 2.1 Hz, 1 H), 4.75 (d, J = 11.5 Hz, 1 H), 5.61 (d, J = 7.5 Hz, 1 H), 5.93 (dd, J = 10.9, 6.3 Hz, 1 H), 5.94 (dd, J = 11.5, 6.3 Hz, 1 H), 5.97 (dd, J = 10.8, 7.5 Hz, 1 H), 5.79 (ddt, J = 17.4, 9.9, 2.1 Hz, 1 H), 7.37−7.85 (m, 10 H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 20.2, 20.8, 49.5, 82.1, 98.9, 109.1, 120.8, 123.0, 124.8, 125.0, 126.3, 127.4, 127.7, 128.0, 131.4, 131.5, 134.5, 142.6, 142.8, 142.9, 146.6, 150.4, 171.3, 171.4, 171.8, 172.2. **16b** (or **16a**): ^{1}H NMR (300 MHz, CD_2Cl_2) δ 0.78 (s, 3 H), 0.95 (s, 3 H), 4.66 (dd, J = 9.9, 2.1 Hz, 1 H), 4.70 (dd, J = 17.4, 2.1 Hz, 1 H), 5.20 (d, J = 11.5 Hz, 1 H), 5.69 (d, J = 7.5 Hz, 1 H), 5.94 (dd, J = 10.9, 6.3 Hz, 1 H), 5.96 (dd, J = 11.5, 6.3 Hz, 1 H), 6.05 (dd, J = 10.8, 7.5 Hz, 1 H), 6.16 (ddt, J = 17.4, 9.9, 2.1 Hz, 1 H), 7.37−7.85 (m, 10 H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 20.2, 21.0, 49.7, 83.3, 98.6, 110.1, 121.0, 123.2, 125.0, 125.2, 126.6, 127.7, 128.2, 131.6, 131.7, 134.7, 142.8, 42.9, 143.0, 143.1, 146.7, 151.1, 172.4, 172.5, 173.3, 174.0. Anal. Calcd for a mixture of **16a**,**b** ($C_{26}H_{24}O_6Si$): C, 67.82; H, 5.25. Found: C, 67.65; H, 5.00.

2-(Allyldimethylsiloxy)cyclohepta-2,4,6-trien-1-one (17). To a stirred solution of tropolone (1 g, 8.2 mmol) and triethylamine (1 g) in toluene (20 mL) was added dropwise allyldimethylchlorosilane (1.5 g, 8.5 mmol) at room temperature. After additional stirring for 4 h at 60 °C, filtration of a precipitate, and removal of the solvent, the residual oil was distilled by using a Kugelrohr to give the title compound in the yield of 1.6 g (89%). **17**: Pale yellow oil; bp 110−115 °C/0.05 mmHg; yield 57%; ^{1}H NMR (300 MHz, D_6H_6 ppm) δ 0.32 (6 H, s,), 1.77 (2 H, d, J = 8.1 Hz), 4.84 (1 H, dd, J = 10.5 and 1.5 Hz), 4.90 (1 H, dd, J = 17.1 and 1.5 Hz), 5.85 (1 H, ddd, J = 11.1, 17.1 and 8.1 Hz), 7.36−6.867 (5 H, m); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 0.7, 27.5, 113.4, 123.9, 128.2, 128.8, 128.9, 134.9, 135.9, 137.7, 172.5; ^{29}Si NMR (59 MHz, D_6H_6, ppm) δ 12.8; MS m/z (relative intensity) 205 ($M^+ - 15$, 3), 179 ($M^+ - 41$), 149 (27). Anal. Calcd for $C_{12}H_{16}O_2Si$: C, 65.41; H, 7.32. Found: C, 65.15; H, 7.30.

Allyl[1-(3-propenyl)cyclohepta-2,4,6-trien-1,2-diolato]-(tropolonato)silicon Compounds (21a,b). A similar procedure as described above using diallyldichlorosilane instead of allylmethyldichlororosilane, the title compounds (**21a**,**b**) were obtained as a trans/cis mixture (**21a**/**21b** = 1:1) in 90% yield. **21a** (trans-isomer): ^{1}H NMR (300 MHz, CD_2Cl_2) δ 1.66 (m, 1 H), 1.64 (m, 1 H), 1.78 (ddt, J = 13.8, 7.8, 1.0 Hz, 1 H), 1.87 (ddt, J = 13.9, 6.5, 1.0 Hz, 1 H), 4.53 (dd, J = 17.0, 1.4, 1.4 Hz, 1 H), 4.64 (dd, J = 17.1 and 1.4 Hz, 1 H), 4.70 (dd, J = 10.2, 1.4 Hz, 1 H), 4.72 (dd, J = 10.2, 1.4 Hz, 1 H), 5.10 (d, J = 11.1 Hz, 1 H), 5.60 (dddd, J = 17.1, 10.2, 7.8, 6.5 Hz, 1 H), 5.7 (m, 1 H), 5.64 (d, J = 7.2 Hz, 1 H), 5.98 (dd, J = 10.8, 7.1 Hz, 1 H), 5.99 (dd, J = 11.1, 7,1 Hz, 1 H), 6.29 (dd, J = 10.8, 7.2 Hz, 1 H), 7.61 (tt, J = 9.8, 1.1 Hz, 1 H), 7.78 (dd, J = 10.1, 1.1 Hz, 1 H), 7.79 (dd, J = 11.0, 1.1 Hz, 1 H), 7.87 (ddd, J = 10.1, 9.8, 1.1 Hz, 1 H), 7.99 (ddd, J = 11.0, 9.8, 1.1 Hz, 1 H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 26.1, 37.2, 78.6, 95.4, 113.4, 117.9, 120.6, 123.5, 125.8, 126.4, 128.2, 128.8, 133.8, 133.9, 135,3, 142.8, 144.9, 155.3, 169.3, 175.0; ^{29}Si NMR (59 MHz, CD_2Cl_2) δ −73.1. **21b** (cis-isomer): ^{1}H NMR (300 MHz, CD_2Cl_2) δ 1.83 (m, 1 H), 1.85 (m, 1 H), 1.81 (ddt, J = 13.8, 7.8, 1.0 Hz, 1 H), 1.95 (ddt, J = 13.9, 6.5, 1.0 Hz, 1 H), 4.90 (dd, J = 17.0, 1.4 Hz, 1 H), 4.96 (dd, J = 10.2 and 1.4 Hz, 1 H), 4.95 (ddt, J = 17.1, 1.4, 1.3 Hz, 1 H), 5.05 (ddt, J = 10.6, 1.4, 1.3 Hz, 1 H), 5.26 (d, J = 11.0 Hz, 1 H), 5.60−5.80 (m, 1 H), 5.61 (d, J = 7.5 Hz, 1 H), 5.83 (dddd, J = 17.1, 10.2, 7.5, 7.3 Hz, 1 H), 6.01 (dd, J = 10.8, 6.3 Hz, 1 H), 6.07 (dd, J = 10.4, 6.3 Hz, 1 H), 6.31(dd, J = 10.8, 7.5 Hz, 1 H), 7.59 (tt, J = 9.8, 1.1 Hz, 1 H), 7.79 (dd, J = 10.9, 1.1 Hz, 1 H), 7.85 (dd, J = 10.3, 1.1 Hz, 1 H), 7.91 (ddd, J = 10.3, 9.8, 1.1 Hz, 1 H), 8.00 (ddd, J = 10.9, 9.8, 1.1 Hz, 1 H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 26.8, 37.4, 79.1, 95.7, 113.6, 118.0, 120.6, 123.5, 125.9, 126.9, 128.2, 129.3, 133.7, 133.9, 135.4, 142.7, 144.8, 156.4, 169.4, 175.3; ^{29}Si NMR (59 MHz, CD_2Cl_2) δ −73.1. Anal. Calcd for $C_{20}H_{20}O_4Si$: C, 68.15; H, 5.72. Found: C, 68.01; H, 5.80.

Diprenylbis(tropolonato)silicon Compound (22). To a cooled toluene solution (−35 °C) of tropolone (1 g, 8.2 mmol) and triethylamine (1 g, 9.9 mmol) was added diprenyldichlorosilane (980 mg, 4.1 mmol), under argon, and the resulted mixture was stirred for 3 h at −35 °C. Filtration of the precipitated $Et_3N{\cdot}HCl$ under argon followed by removal of solvent in vacuo afforded the title compound, **22**, quantitatively. Recrystallization from a cooled mixture of dichloromethane and ether under argon gave a pure sample of **22**: orange crystals; ^{1}H NMR (300 MHz, $CDCl_3$, 294 K) δ 1.23 (s, 6 H), 1.29 (s, 6 H), 1.64 (d, J = 8.7 Hz, 4 H), 5.18 (tq, J = 8.7 Hz and 1.0 Hz, 2 H), 7.03 (t, J = 9.38 Hz, 2 H), 7.26 (d, J = 10.8 Hz, 4 H), 7.51 (dd, J = 10.8 and 9.4 Hz, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$, 294 K) δ 16.8, 25.5, 29.7, 123.1, 124.1, 127.7, 128.5, 140.9, 173.6; ^{29}Si NMR (59 MHz, $CDCl_3$) δ −111.5; MS m/z (relative intensity) 338 (14), 159 (17), 149 (16), 131 (24) 122 (45), 105 (67), 94 (63), 91(100). Anal. Calcd for $C_{24}H_{28}O_4Si$: C, 70.55; H, 6.91. Found: C, 69.95; H, 7.00. The ^{1}H and ^{13}C NMR data apparently show that the two tropolonato ligands are magnetically equivalent and also each ring should have a mirror plane. The origin is ascribed to the facile degenerate rearrangement of **22** with the *cis* configuration of the two prenyl groups at 294 K.[7]

Prenyl[1-(1,1-dimethyl-3-propenyl)cyclohepta-2,4,6-trien-1,2-diolato)](tropolonato)silicon Compound (23). Thermal isomerization of **22** afforded a sole stereoisomer of the title compound, while the stereochemistry could not be determined on the unambiguous basis. **23**: Yellow prism, mp 139−140 °C, ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.78 (s, 3 H), 0.88 (s, 3 H), 1.25 (s, 3 H), 1.33 (s, 3 H) 1.61−1.46 (m, 2 H), 4.66 (dd, J = 10.9, 2.1 Hz, 1 H), 4.70 (dd, J = 17.5, 2.1 Hz, 1 H), 4.95 (ddq, J = 9.3, 10.3, 1.1 Hz), 5.31 (d, J = 11.5 Hz, 1 H), 5.89 (dd, J = 11.1, 6.7 Hz, 1 H), 5.95 (dd, J = 10.9, 17.5 Hz, 1 H) 5.98 (d, J = 7.5 Hz, 1 H), 6.13 (dd, J = 7.6, 7.12, 11.1 Hz, 1 H), 6.16 (dd, J = 6.7, 11.5 Hz, 1 H), 7.53 (ddt, J =10.5, 9.8, 1.0 Hz, 1 H), 7.77 (dd, J = 10.8, 1.0 Hz, 1 H), 7.78 (dd, J = 10.9, 1.1 Hz, 1 H), 7.87 (ddt, J = 10.8, 10.5, 1.07 Hz, 1 H), 7.96 (ddt, J = 9.8, 10.3, 1.0 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.2, 18.4, 19.2, 21.6, 25.2, 49.8, 83.2, 100.7, 111.8, 120.6, 121.6, 124.6, 124.8, 126.9, 128.2, 128.9, 132.4, 137.6, 142.2, 143.9, 144.3, 149.8, 169.5, 174.4; ^{29}Si NMR (59 MHz, $CDCl_3$) δ −77.97; MS m/z (relative intensity) 408 (9), 407 (29), 339 (100), 159 (41) 149 (33), 131 (45), 122 (82), 105 (21), 94 (37), 91 (26). Anal. Calcd for $C_{24}H_{28}O_4Si$: C, 70.55; H, 6.91. Found: C, 70.15; H, 7.01.

Allylation of Aldehydes with 21 and 23. To a THF (10 mL) solution of **21** (or **23**) (1.42 mmol) was added an aldehyde (1.35 mmol) at room temperature under argon, and then the resultant mixture was stirred for 12−40 h. Usual workup, and then purification by silica gel column chromatography, provided the corresponding homoallyl alcohol. Physical data for all homoallyl alcohols described in this paper are available in the literature.[4−7]

Hydrolysis of Pentacoordinate Silicon Compounds (12a,b). Typically, a mixture of a solution of a pentacoordinate silicon compound (**12a**,**b**) (2 mmol) and 1 N HCl solution in methanol (10 mL) was stirred for 4 h. The usual workup, and then purification by silica gel column chromatography, provided the corresponding 2-allyltropone. The following are the physical data for the products.

2-(2′-Propenyl)cyclohepta-2,4,6-trien-1-one (26a):[16] ^{1}H NMR ($CDCl_3$) δ 3.35 (2 H, d, J = 6.6 Hz), 5.10 (dd, J = 9.3 and 1.5 Hz, 1 H), 5.12 (dd, J = 17.0, 1.50 Hz, 1 H), 5.89 (1 H, ddt, J = 17.0, 10.4 and 6.6 Hz), 6.86−6.98 (m, 2 H), 7.02−7.08 (m, 2 H), 7.21 (dd, J = 8.3 and 1.3 Hz); ^{13}C NMR δ 38.8, 117.3, 132.7, 133.7, 134.9, 135.0, 135.4, 140.3, 153.5, 186.6; MS (m/z (%)) 146 (M^+, 45.7), 131 ($M^+ - 15$, 100), 117 (39).

(*E*)-2-(2′-Butenyl)cyclohepta-2,4,6-trien-1-one (26b-*E*): $_{1}$H NMR ($CDCl_3$) δ 1.62 (dd, J = 6.2 and 1.1 Hz, 3 H), 3.25 (d, J = 5.7 Hz, 2 H), 5.40−5.50 (m, 2 H), 6.83−7.14 (m, 4 H), 7.24

(d, $J = 9.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 17.9, 37.6, 127.4, 128.2, 134.7, 135.1, 140.3, 140.6, 141.3, 154.4, 186.7; MS (70 eV, m/z (%)) 160 (M^+, 25), 145 ($M^+ - 15$, 100), 131 ($M^+ - 29$.3), 127 (16.7), 115 (32), 91 (28). Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.57; H, 7.70.

(*Z*)-2-(2′-Butenyl)cyclohepta-2,4,6-trien-1-one (26b-*Z*): $_1$H NMR ($CDCl_3$) δ 1.60 (dd, $J = 6.2$, 1.1 Hz, 3 H), 3.33 (d, $J = 7.2$ Hz, 2 H), 5.47 (d, quart, $J = 11.3$, 7.2 Hz, 1 H), 5.64 (dt, quart, $J = 11.3$, 6.2, 1.1 Hz, 1 H), 6.83−7.14 (m, 4 H), 7.22 (d, $J = 9.5$ Hz, 1 H); ^{13}C NMR $CDCl_3$) δ 12.7, 31.9, 126.4, 127.1, 132.5, 133.8, 134.3, 135.4, 140.1, 154.1, 186.9; MS (70 eV, m/z (%)) 160 (M^+, 25.7), 145 ($M^+ - 15$, 100), 131 ($M^+ - 29$, 88), 127 (27), 115 (35), 91 (33). Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.30; H, 7.60.

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Supporting Information Available: Crystallographic data with complete tables of X-ray parameters, bond lengths, bond angles, and thermal and positional parameters for **12a** (9 pages). Ordering information is given on any current masthead page.

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