Reactions of *gem*-Dibromo Compounds with Trialkylmagnesate Reagents to Yield Alkylated Organomagnesium Compounds**

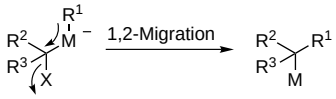
Atsushi Inoue, Junichi Kondo, Hiroshi Shinokubo, and Koichiro Oshima*[a]

Abstract: The reaction of *gem*-dibromocyclopropanes **5** with nBu$_3$MgLi affords butylated cyclopropylmagnesium species that can be trapped with various electrophiles. The reaction of dibromomethylsilanes **12** requires the addition of a catalytic amount of CuCN·2LiCl for smooth migration of the alkyl groups. The resultant α-silylpentylmagnesium compounds **16** react with electrophiles, such as acyl chlorides or α,β-unsaturated ketones to afford α- or γ-silyl ketones, respectively. Treatment of dibromodisilylmethanes with Me$_3$MgLi yields 1-bromo-1,1-disilylethanes **25** that can be converted into 1,1-disilylethenes **29** by dehydrobromination.

Keywords: ate complexes · carbenoids · Grignard reagents · magnesium · migrations

Introduction

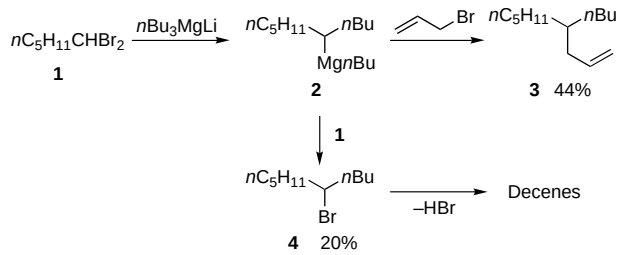
The utility of organometallic ate complexes in organic synthesis is well recognized, and numerous reports have been published on the reaction which makes use of various ate complexes that contain boron, copper, aluminum, zinc, manganese, zirconium, and other metals as the key atoms. Among reactions with ate complexes, the 1,2-migration of a ligand on a metal is a representative reaction pattern of ate-type carbenoids (Scheme 1).[1, 2] Organometallic ate complexes also induce halogen–metal exchange reactions.[3] The combination of these two reactions enables a variety of transformations starting from *gem*-dihalo compounds.[4, 5]



Scheme 1. 1,2-Migration of ate-type carbenoids.

We have already reported the halogen–magnesium exchange reaction with magnesium ate complexes.[6–8] The reaction proceeds at low temperatures of around $-78\,^{\circ}$C, and hence the exchange reaction of *gem*-dibromoalkanes is expected to provide ate-type carbenoid species that would undergo 1,2-migration of the alkyl group on magnesium to the adjacent carbon to form new organomagnesium reagents.

We started this research with the reaction of 1,1-dibromoalkane. Treatment of 1,1-dibromohexane (**1**) with nBu$_3$-MgLi followed by the addition of allyl bromide as an electrophile yielded 4-butyl-1-nonene (**3**, 44%) as well as 5-bromodecane (**4**, 20%) and decenes (Scheme 2). This result indicates that bromine–magnesium exchange and subsequent 1,2-migration of the butyl group affords the secondary alkylmagnesium species **2**. The coupling reaction of **2** with allyl bromide provides **3**. The magnesium compound **2** also abstracts bromine from dibromoalkane to afford **4**.



Scheme 2. Reaction of 1,1-dibromohexane with nBu$_3$MgLi.

To eliminate the possibility of these side reactions, we chose *gem*-dibromocyclopropanes and dibromomethylsilanes as substrates and investigated their reactions with magnesate reagents.

Results and Discussion

Reaction of *gem*-dibromocyclopropanes: Cyclopropane derivatives are versatile synthetic intermediates in organic synthesis. Double alkylation of *gem*-dihalocyclopropanes,

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[**] Preliminary accounts have already been published: Ref. [22].

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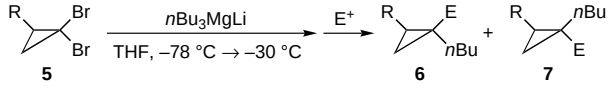
which can be readily prepared by the addition of dihalocarbenes to olefins, provided an expeditious route to a variety of functionalized cyclopropane derivatives. The reaction of *gem*-dibromocyclopropanes with dialkylcuprates,[5a,b] alkyllithiums,[5c,d] trialkylzincates,[5e,f] or trialkylmanganates[5g,h] have been reported to afford alkylated cyclopropylmetals, which could undergo further reactions with various electrophiles, such as alkyl halides and carbonyl compounds, to furnish double-alkylated cyclopropane derivatives. We have found that a magnesium ate complex (trialkylmagnesate) also effects this type of alkylative metalation.

Treatment of various *gem*-dibromocyclopropanes **5** with nBu$_3$MgLi at low temperatures followed by the addition of electrophiles afforded the expected products as diastereomeric mixtures (**6** and **7**). The results are summarized in Tables 1 and 2.

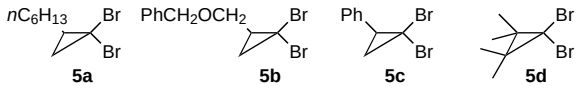
Several characteristics of this reaction are noteworthy:

1) The reaction should be performed at $-78\,^{\circ}$C to $-30\,^{\circ}$C. Treatment of **5a** with nBu$_3$MgLi at $0\,^{\circ}$C gave the desired product in modest yield together with a significant amount of 1,2-nonadiene. On the other hand, 1,2-migration of a butyl group did not go to completion at $-78\,^{\circ}$C. Quenching of the reaction mixture at $-78\,^{\circ}$C provided 1-bromo-2-hexylcyclopropane as a major product in addition to the butylated product.
2) A variety of electrophiles, such as iodine, allyl bromide, methyl iodide, benzaldehyde, and benzoyl chloride, can be employed. The use of allyl bromide as the electrophile required the coexistence of CuCN·2LiCl. Without the assistance of a copper salt, the intermediary tertiary cyclopropylmagnesium failed to react with allyl bromide because of steric hindrance.[9]
3) Stereoselectivities are somewhat lower than those observed in the reactions mediated by cuprates, zincates, or manganates. Interestingly, the reaction of **5e** or **5f** with nBu$_3$MgLi followed by the addition of benzaldehyde exhibited relatively high *exo* selectivity, although the yield was not satisfactory (vide infra).

Table 1. Reaction of *gem*-dibromocyclopropanes with nBu$_3$MgLi.



5 **6** **7**

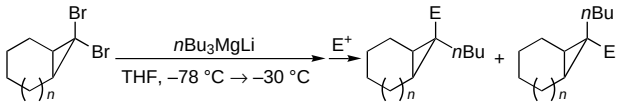


5a **5b** **5c** **5d**

Entry	Substrate	Electrophile	Product	Yield [%]	Ratio **6**/**7**
1	**5a**	H_3O^+	**6a/7a**	97	57/43
2		D_2O	**6b/7b**	97	56/44
3		I_2	**6c/7c**	80	62/38
4		CH_2=$CHCH_2Br$	**6d/7d**	65	51/49
5		MeI	**6e/7e**	74	45/55
6		PhCHO	**6f/7f**	78	44/56
7	**5b**	H_3O^+	**6g/7g**	91	48/52
8	**5c**	H_3O^+	**6h/7h**	86	81/19
9		CH_2=$CHCH_2Br$[a]	**6i/7i**	82	80/20
10	**5d**	I_2	**6j**	91	
11		CH_2=$CHCH_2Br$[a]	**6k**	73	

[a] In the presence of CuCN·2LiCl (30 mol%).

Table 2. Reaction of bicyclic *gem*-dibromocyclopropanes with nBu$_3$MgLi.

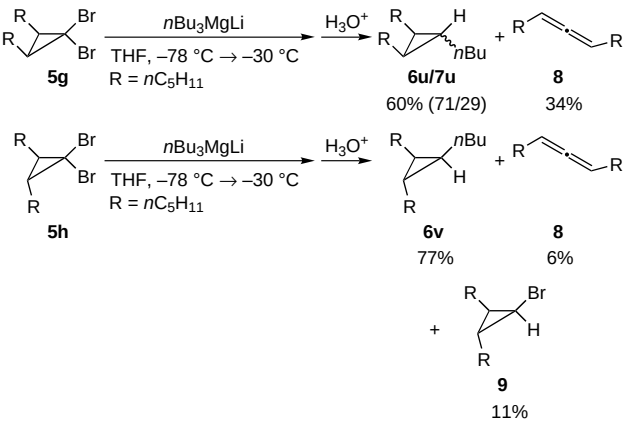


5e (n = 1) **5f** (n = 3) **6** **7**

Entry	Substrate	Electrophile	Product	Yield [%]	Ratio **6**:**7**
1	**5e**	H_3O^+	**6l/7l**	81	63/37
2		D_2O	**6m/7m**	82	63/37
3		I_2	**6n/7n**	91	61/39
4		CH_2=$CHCH_2Br$[a]	**6o/7o**	89	73/27
5		PhCOCl[b]	**6p/7p**	88	88/12
6		PhCHO	**6q/7q**	42[d]	27/73
7	**5f**	H_3O^+	**6r/7r**	97	58/42
8		I_2	**6s/7s**	86	64/36
9		PhCHO	**6t/7t**	35[e]	6/94
10		PhCHO[c]	**6t/7t**	43[f]	94/6

[a] In the presence of CuCN·2LiCl (30 mol%). [b] In the presence of CuCN·2LiCl (3.0 equiv). [c] In the presence of CuCN·2LiCl (3.0 equiv) and $BF_3\cdot OEt_2$ (3.0 equiv). [d] The product **6l** was also obtained in 47% yield. [e] The product **6r** was also obtained in 65%. [f] The products **6r** and **7r** were also obtained in 47% yield (45/55).

The use of 2,3-dialkyl-1,1-dibromocyclopropanes afforded disappointing results (Scheme 3). Steric hindrance of alkyl



Scheme 3. Reaction of 2,3-dialkyl-1,1-dibromocyclopropanes.

Abstract in Japanese: *gem*–ジブロモシクロプロパン**5**にnBu$_3$MgLiを作用させると、ブチル基が導入されたシクロプロピルマグネシウム種**11**が生成した。この**11**は種々の求電子剤によって収率良く捕捉することができた。ジブロモメチルシラン**12**との反応では、触媒量の銅塩によってブチル基の転位が促進されることが明らかとなった。生成したα–シリルペンチルマグネシウム種**16**は酸塩化物やα,β–不飽和ケトンで捕捉することにより、α–及びγ–シリルケトンへと導くことができた。また、ジブロモジシリルメタンとMe$_3$MgLiの反応では臭素の一つがメチル基に置換された生成物**25**を与えた。**25**は塩基によって脱臭化水素化することにより1,1–ジシリルエテン**29**へと変換することができた。

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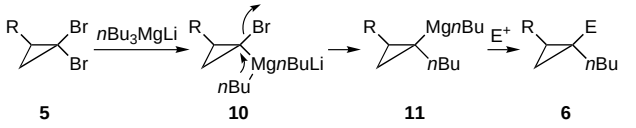
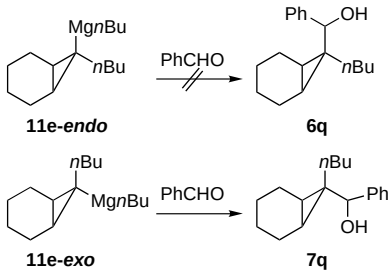
substituents on the cyclopropane ring retards 1,2-migration of the butyl group. In the reaction of **5g** or **5h**, migration of the butyl moiety competed with the formation of allene **8**.

We propose a similar reaction mechanism to the reactions with cuprates, zincates, and manganates (Scheme 4). Firstly, bromine–magnesium exchange occurs predominantly at the less hindered bromine atom to afford **10**. Next, the butyl



Scheme 4. Proposed mechanism of the reaction of *gem*-dibromocyclopropanes with nBu$_3$MgLi.

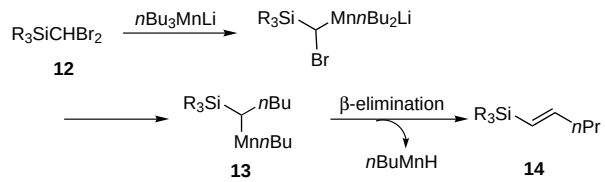
group on magnesium migrates to the adjacent carbon atom with concomitant elimination of the bromide ion and inversion of the configuration on the cyclopropane carbon. The resultant butylated cyclopropylmagnesium species **11** is eventually trapped by an electrophile with retention of configuration. The inverse stereoselectivity and the low yield in trapping with benzaldehyde are attributed to the low reactivity of the major diastereomer **11**-*endo* (Scheme 5). The



Scheme 5. Difference in the reaction between PhCHO and the *endo* or *exo* isomers of **11e**.

magnesium species **11**-*endo* fails to react with benzaldehyde and gives **6l** or **6r** after protonation. On the other hand, the other isomer, **11**-*exo*, is trapped with benzaldehyde to provide the cyclopropylbenzyl alcohol derivative.

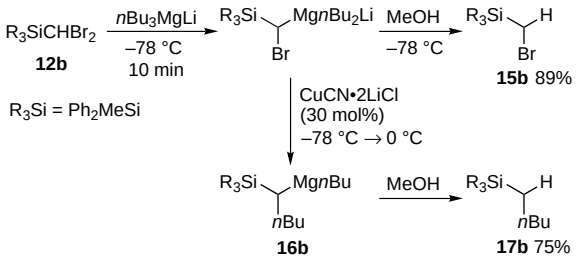
Copper(I)-catalyzed reaction of dibromomethylsilanes: We have previously reported synthesis of 1-alkenylsilanes **14** from dibromomethylsilanes **12**[10] via manganese carbenoids (Scheme 6).[5i,j] In this reaction, α-silylalkylmanganese **13** cannot be coupled with electrophiles because of its rapid conversion to alkenylsilane **14** by β-hydride elimination.



Scheme 6. Reaction of dibromomethylsilanes **12** with tributylmanganate.

We then investigated the reaction of dibromomethylsilanes with trialkylmagnesate. The reaction promised to be a facile method for the preparation of α-silylalkylmagnesium species, which are highly useful reagents in organic synthesis.[11]

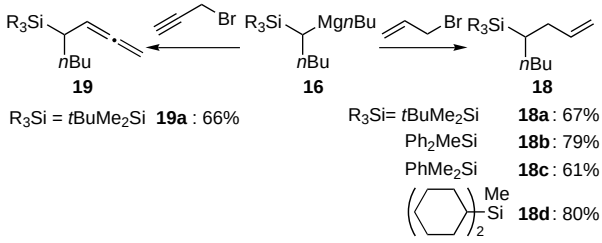
Treatment of dibromomethylsilane **12** with nBu$_3$MgLi induced clean bromine–magnesium exchange[6] to provide bromomethylsilane **15** upon quenching with methanol at $-78\,^{\circ}$C (Scheme 7). Warming the reaction mixture to room



Scheme 7. Bromine–magnesium exchange and the subsequent migration of an alkyl group.

temperature before quenching resulted in the migration of the butyl group to yield α-silylpentylmagnesium **16**.[12] A copper salt proved to facilitate this migration.[1a] The addition of CuCN·2LiCl (30 mol%) to the reaction mixture induced smooth migration of the butyl group at lower temperatures ($-30\,^{\circ}$C for **12a** and $0\,^{\circ}$C for **12b**) to afford **16** in good yield. Butyllithium or nBuMgBr instead of tributylmagnesate also induced metalation and the subsequent butylation. Under these conditions, however, the yields of the desired products were quite low.

The α-silylpentylmagnesium **16** could be trapped with allyl bromide to give **18** in good yield (Scheme 8). The reaction with propargyl bromide furnished exclusively the allenylated product **19**.



Scheme 8. Reaction of α-silylalkylmagnesium compounds **16** with allyl or propargyl bromide.

α-Silyl ketones are quite useful intermediates in organic synthesis.[13] Therefore, we undertook the preparation of α-silyl ketones with this new methodology.[14] The reaction of α-silylalkylmagnesium comopunds **16** with various acyl chlorides was examined.[15] The results are summarized in Table 3. The addition of acyl chlorides to the resulting solution of **16** furnished the corresponding α-silyl ketones **20** in good yields. 1,3-Dimethyl-2-imidazolidinone (DMI) proved to be an effective additive for the formation of α-silyl ketones. Without the use of DMI, the yield of product decreased (entry 7).

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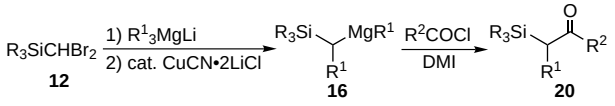
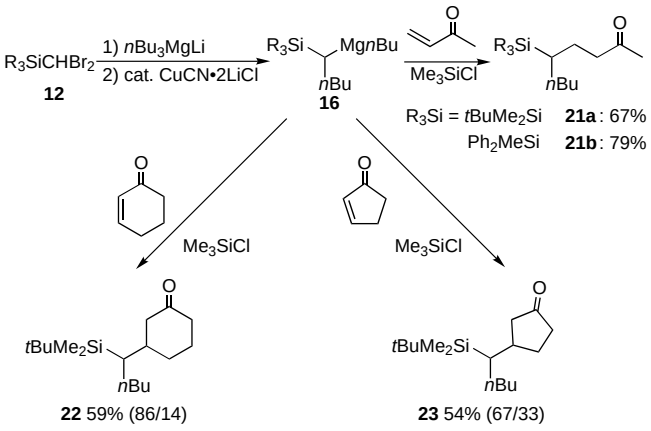
Table 3. Synthesis of α-silyl ketones from dibromomethylsilanes.[a]



Entry	Substrate	R_3Si	R^1	R^2	Product	Yield [%]
1	**12a**	tBuMe$_2$Si	nBu	CH_3	**20a**	60
2				cPr	**20b**	56
3				Ph	**20c**	66
4				(E)-CH_3CH=CH-	**20d**	53
5				(E)-PhCH=CH-	**20e**	51
6	**12b**	Ph$_2$MeSi	nBu	CH_3	**20f**	63
7				nPr	**20g**	49
8[b]				nPr	**20g**	74
9[b]				iPr	**20h**	63
10[b]				cPr	**20i**	69
11[b]				Ph	**20j**	77
12[b, c]		nC_6H_{13}	nPr		**20k**	85
13[c]				Ph	**20l**	70

[a] Reaction conditions: Magnesate was prepared from butyllithium (2.0 mmol) and butylmagnesium bromide (1.0 mmol) in THF (5 mL) at 0 °C. Dibromomethylsilanes (1.0 mmol) in THF (2 mL) were introduced at −78 °C. CuCN·2LiCl (0.3 mL, 1.0 M solution in THF, 0.3 mmol) was added. [b] DMI (2.0 mmol) was added before introduction of acyl chlorides. [c] Magnesate was prepared from hexyllithium (3.0 mmol) and $MgBr_2$ (1.0 mmol) in THF (5 mL) at 0 °C.

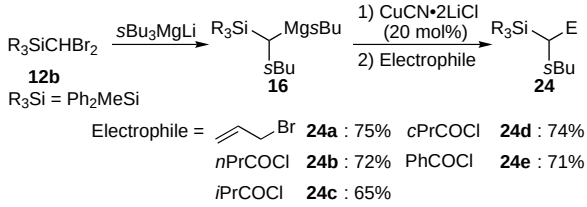
We also explored the conjugate addition of **16** to α,β-unsaturated ketones (Scheme 9). Addition of methyl vinyl ketone to the solution of **16** provided 5-silyl-2-nonanones **21a** and **21b** in good yields in the presence of Me_3SiCl.[16] The



Scheme 9. 1,4-Addition of α-silylalkylmagnesium compounds **16** toward enones.

addition of **16** to cyclohexenone or cyclopentenone also furnished the desired silylketones.

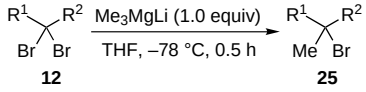
In the case of tri(*sec*-butyl)magnesate, which was prepared from *s*BuLi (3.0 equiv) and $MgBr_2$ (1.0 equiv), the migration of the secondary butyl group afforded the corresponding α-silylalkylmagnesium **16** smoothly without the assistance of a copper catalyst (Scheme 10). However, the addition of CuCN·2LiCl was beneficial for the acylation or allylation step to provide the coupling products **24** in good yields.



Scheme 10. Reaction of dibromomethylsilanes **12** with sBu$_3$MgLi.

Reaction of dibromomethylsilanes with Me$_3$MgLi: The reaction of dibromomethylsilane **12b** with Me_3MgLi gave a different result from the reaction of nBu$_3$MgLi. One of the two bromine atoms was substituted by the methyl group. This monomethylation reaction was successfully applied to dibromodisilylmethanes.[17] The results are summarized in Table 4.

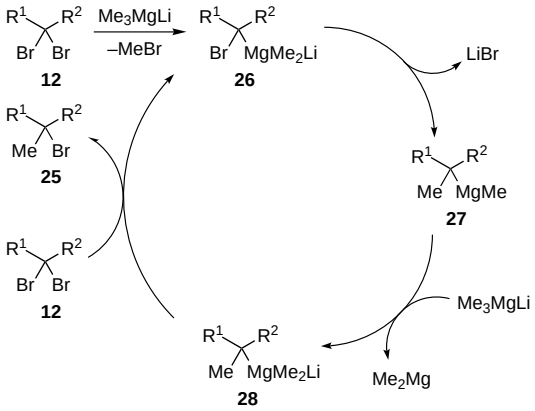
Table 4. Monomethylation of dibromodisilylmethanes with Me_3MgLi.[a]



Entry	Substrate	R^1	R^2	Product	Yield [%]
1	**12a**	Ph$_2$MeSi	H	**25a**	98
2	**12e**	Ph$_2$MeSi	Me	**25e**	89
3	**12f**	Ph$_2$MeSi	Me$_3$Si	**25f**	93
4	**12g**	Et$_3$Si	Et$_3$Si	**25g**	90
5	**12h**	tBuMe$_2$Si	Me$_3$Si	**25h**	82
6	**12i**	Me$_3$Si	Me$_3$Si	**25i**	89
7	**12j**	PhMe$_2$Si	PhMe$_2$Si	**25j**	80
8	**12k**	Ph$_2$MeSi	Ph$_2$MeSi	**25k**	90
9	**12l**	Ph$_2$MeSi	Et$_3$Ge	**25l**	93

[a] The substrate **12** (10 mmol) was treated with Me_3MgLi, prepared by mixing MeMgBr (THF solution, 10 mmol) and MeLi (Et_2O solution, 20 mmol), for 0.5 h in THF at −78 °C.

Substrates such as dibromomethylsilane (entry 1), 1,1-dibromoethylsilane (entry 2), and dibromodisilylmethanes (entries 3–8) could be converted into the corresponding monomethylated compounds **25** in good yields, regardless of the bulkiness of silyl substituents. Methylation of germylsilyldibromomethane also proceeded in good yield (entry 9). We propose the following mechanism[18] that involves the formation of the ate-type carbenoid species **26** through a bromine–magnesium exchange reaction (Scheme 11).[5, 6]

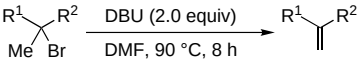


Scheme 11. Plausible mechanism of monomethylation.

The 1,2-migration of one of the methyl groups on magnesium provides **27** with concomitant elimination of the bromide anion. One of methyl groups in Me_3MgLi is transferred to **27** to form the ate complex **28**, which is more reactive than Me_3MgLi for the bromine–magnesium exchange reaction. The complex **28** abstracts the bromine atom from **12** to yield the monobromo compound **25** and the carbenoid **26**.

The resultant monomethylated products were converted into the corresponding 1,1-disilylethenes by dehydrobromination.[19, 20] Treatment of **25** with two equivalents of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in DMF at 90 °C for eight hours provided 1,1-disilylethenes **29** (Table 5). In each case, the desired product was obtained in good yield.

Table 5. Dehydrobromination of **25** with DBU.[a]



25 **29**

Entry	Substrate	R^1	R^2	Product	Yield [%]
1	**25f**	Ph_2MeSi	Me_3Si	**29f**	98
2	**25g**	Et_3Si	Et_3Si	**29g**	98
3	**25h**	tBuMe$_2$Si	Me_3Si	**29h**	85
4	**25i**	Me_3Si	Me_3Si	**29i**	83
5	**25j**	$PhMe_2Si$	$PhMe_2Si$	**29j**	97
6	**25k**	Ph_2MeSi	Ph_2MeSi	**29k**	89
7	**25l**	Ph_2MeSi	Et_3Ge	**29l**	85

[a] A solution of **25** (9.0 mmol) and DBU (18.0 mmol) in DMF (30 mL) was stirred for 8 h at 90 °C.

Conclusion

We have investigated the reactions of *gem*-dibromo compounds with trialkylmagnesate reagents (R_3MgLi). The halogen–magnesium exchange reaction and subsequent 1,2-migration of the alkyl group on magnesium affords the alkylated organomagnesium species in the presence or absence of a copper catalyst. The resultant organomagnesium species can be trapped with a variety of electrophiles. Trimethylmagnesate (Me_3MgLi) shows a different reactivity. The reagent induces monomethylation of dibromomethylsilanes or dibromodisilylmethanes.

Experimental Section

General: ^{1}H NMR (300 MHz) and ^{13}C NMR (75.3 MHz) spectra were recorded on a Varian GEMINI 300 spectrometer in $CDCl_3$ as a solvent, and chemical shifts were given in δ with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25 mm layer of Merck silica gel $60F_{254}$. Column chromatography was performed on silica gel (Wakogel 200 mesh). The analyses were carried out at the Elemental Analysis Center of Kyoto University. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone before use. Grignard reagents were prepared from the corresponding alkyl halide and Mg turnings (Nacalai tesque, INC). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Aldehydes were distilled and stored under argon.

Synthesis of *gem*-dibromocyclopropanes 5: Aqueous sodium hydroxide (10 mL, 50 w/w%) was added dropwise to a mixture of an alkene (20 mmol), bromoform (2.6 mL, 30 mmol), benzyltriethylammonium chloride (0.1 g), dichloromethane (2 mL), and ethanol (0.08 mL) at 0 °C. After stirring for 24 h, water was added (50 mL). The mixture was extracted with hexane and the organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by chromatography on a silica gel column gave provided *gem*-dibromocyclopropanes **5**.

*1,1-Dibromo-2-hexylcyclopropane (**5a**)*: $R_f = 0.71$ (hexane); IR (neat): $\tilde{\nu}$ = 2922, 2852, 1111, 1042, 677 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 0.89$ (t, $J = 6.9$ Hz, 3H), 1.18 (dd, $J = 6.9$, 7.2 Hz, 1H), 1.23–1.67 (m, 11H), 1.73 (dd, $J = 6.9$, 9.9 Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 14.1$, 22.6, 28.3, 28.5, 29.0, 29.7, 31.5, 31.7, 32.6; elemental analysis calcd (%) for $C_9H_{16}Br_2$: C 38.06, H 5.68; found: C 37.77, H 5.44.

*2-(Benzyloxymethyl)-1,1-dibromocyclopropane (**5b**)*: $R_f = 0.42$ (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu}$ = 3026, 2856, 1496, 1454, 1372, 1155, 1094, 1029, 735, 696, 680 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.37$ (dd, $J = 7.2$, 7.5 Hz, 1H), 1.80 (dd, $J = 7.2$, 10.5 Hz, 1H), 1.89–2.01 (m, 1H), 3.58 (dd, $J = 7.2$, 10.8 Hz, 1H), 3.63 (dd, $J = 5.7$, 10.8 Hz, 1H), 4.57 (d, $J = 12.0$ Hz, 1H), 4.61 (d, $J = 12.0$ Hz, 1H), 7.26–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$): δ = 26.0, 26.6, 30.2, 71.5, 73.0, 127.9, 127.9, 128.5, 138.1; elemental analysis calcd (%) for $C_{11}H_{12}Br_2O$: C 41.28, H 3.78; found: C 41.11, H 3.71.

*1,1-Dibromo-2-phenylcyclopropane (**5c**)*: $R_f = 0.41$ (hexane); IR (neat): $\tilde{\nu}$ = 1605, 1498, 1452, 1425, 1108, 1040, 766, 734, 696, 679 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.02$ (dd, $J = 7.8$, 8.4 Hz, 1H), 2.14 (dd, $J = 7.8$, 10.5 Hz, 1H), 2.97 (dd, $J = 8.4$, 10.5 Hz, 1H), 7.22–7.30 (m, 2H), 7.30–7.40 (m, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 27.2$, 28.3, 35.9, 127.7, 128.4, 129.0, 136.1; elemental analysis calcd (%) for $C_9H_8Br_2$: C 39.17, H 2.92; found: C 39.02, H 3.03.

*1,1-Dibromo-2,2,3,3-tetramethylcyclopropane (**5d**)*: IR (Nujol): $\tilde{\nu}$ = 1105, 1031, 994, 952, 863, 792, 774 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.25$ (s, 12H); ^{13}C NMR ($CDCl_3$) $\delta = 21.7$, 29.7, 58.9. We were not able to perform an analysis on this compound because of its sublimation.

*7,7-Dibromobicyclo[4.1.0]heptane (**5e**)*: $R_f = 0.72$ (hexane); IR (neat): $\tilde{\nu}$ = 2936, 2852, 1462, 1444, 1334, 1165, 1020, 729 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.00–1.25 (m, 2H), 1.30–1.43 (m, 2H), 1.50–1.62 (m, 2H), 1.76–1.90 (m, 2H), 1.92–2.07 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 20.1$, 20.6, 27.0, 40.7; elemental analysis calcd (%) for $C_7H_{10}Br_2$: C 33.11, H 3.97; found: C 33.20, H 3.95.

*9,9-Dibromobicyclo[6.1.0]nonane (**5f**)*: $R_f = 0.69$ (hexane); IR (neat): $\tilde{\nu}$ = 2920, 2848, 1467, 1164, 1060, 858, 815, 760, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.07–1.25 (m, 2H), 1.30–1.70 (m, 10H), 2.00–2.10 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 25.3$, 26.3, 27.8, 33.2, 37.0; elemental analysis calcd (%) for $C_9H_{14}Br_2$: C 38.33, H 5.00; found: C 38.28, H 4.83.

*cis-1,1-Dibromo-2,3-dipentylcyclopropane (**5g**)*: $R_f = 0.80$ (hexane); IR (neat): $\tilde{\nu}$ = 2952, 2922, 2854, 1466, 1379, 716 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.90 (t, $J = 6.9$ Hz, 6H), 1.24–1.59 (m, 18H); ^{13}C NMR ($CDCl_3$): $\delta = 13.9$, 22.5, 26.9, 28.1, 31.6, 33.8, 38.3; elemental analysis calcd (%) for $C_{13}H_{24}Br_2$: C 45.91, H 7.11; found: C 46.02, H 6.99.

*trans-1,1-Dibromo-2,3-dipentylcyclopropane (**5h**)*: $R_f = 0.83$ (hexane); IR (neat): $\tilde{\nu}$ = 2952, 2924, 2854, 1466, 1379, 1137, 1046, 722 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 0.90$ (t, $J = 6.9$ Hz, 6H), 1.01–1.11 (m, 2H), 1.24–1.52 (m, 14H), 1.52–1.68 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 13.9$, 22.5, 27.9, 31.4, 32.6, 37.0, 39.4; elemental analysis calcd (%) for $C_{13}H_{24}Br_2$: C 45.91, H 7.11; found: C 46.01, H 6.84.

General procedure for the reaction of *gem*-dibromocyclopropanes 5 with *n*Bu$_3$MgLi: Butyllithium (1.5 mL, 1.6 M solution in hexane, 2.4 mmol) was added to a solution of butylmagnesium bromide (1.2 mL, 1.0 M solution in THF, 1.2 mmol) in THF (5 mL) at 0 °C, and the mixture was stirred for 10 min. The resulting solution was cooled to −78 °C, and a solution of the corresponding **5** (1.0 mmol) in THF (2 mL) was added dropwise. After the reaction mixture was gradually warmed to −30 °C over a period of 2 h, the corresponding electrophile (3.0 mmol) was added. After stirring for 1 h at 0 °C, the reaction was quenched with saturated aqueous NH_4Cl. The mixture was extracted with ethyl acetate, and the organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by chromatography on a silica gel column provided **6** and **7** as diastereomeric mixtures.

Spectral data for **6a**, **7a**, **6e**, **7e**, **6h**, **7h**,[4b] **6f**, **7f**, **6g**, **7g**, **6l**, **7l**,[4e] **6c**, **7c**, **6d**, **7d**, **6i**, **7i**, **6o**, **7o**, **6t**, **7t**,[4g] **6r**, and **7r**[21] were identical with those reported

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in the literature. Alcohols (**6f**, **7f**, **6q**, **7q**, **6t**, and **7t**) were converted into the corresponding ketones by Jones oxidation for data collection.

*1-Butyl-1-iodo-2,2,3,3-tetramethylcyclopropane (**6j**)*: $R_f = 0.83$ (hexane); IR (neat): $\tilde{\nu} = 2942, 2864, 1460, 1378, 1105, 1005, 935, 828\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.92$ (t, $J = 7.2$ Hz, 3H), 1.05 (s, 6H), 1.23 (s, 6H), 1.32 (tq, $J = 7.5, 7.2$ Hz, 2H), 1.47–1.60 (m, 2H), 1.74–1.81 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 14.1, 16.7, 22.4, 25.8, 28.6, 33.4, 39.0, 49.9$. This compound is very sensitive to light or a trace of acid, and we were not able to perform an analysis or mass spectrometry.

*1-Allyl-1-butyl-2,2,3,3-tetramethylcyclopropane (**6k**)*: $R_f = 0.89$ (hexane); IR (neat): $\tilde{\nu} = 2996, 2924, 2870, 1640, 1468, 1379, 1110, 994, 909\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.87$ (t, $J = 6.9$ Hz, 3H), 0.98 (s, 6H), 0.99 (s, 6H), 1.15–1.36 (m, 6H), 2.13 (d, $J = 6.6$ Hz, 2H), 4.98 (d, $J = 10.2$ Hz, 1H), 5.00 (d, $J = 17.1$ Hz, 1H), 5.71 (ddt, $J = 10.2, 17.1, 6.6$ Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 14.1, 18.6, 18.7, 22.9, 23.3, 27.5, 28.7, 29.1, 32.4, 115.2, 138.4$; elemental analysis calcd (%) for $C_{14}H_{26}$: C 86.52, H 13.48; found: C 86.50, H 13.78.

*endo-7-Butyl-7-iodobicyclo[4.1.0]heptane (**6n**)*: $R_f = 0.80$ (hexane); IR (neat): $\tilde{\nu} = 2924, 2852, 1461, 1444, 1378, 1170, 1124, 819\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.66–0.77$ (m, 2H), 0.90 (t, $J = 7.2$ Hz, 3H), 1.12–1.40 (m, 6H), 1.40–1.59 (m, 4H), 1.59–1.67 (m, 2H), 2.02–2.16 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 14.1, 20.7, 21.2, 21.9, 23.9, 31.7, 39.3, 47.8$; elemental analysis calcd (%) for $C_{11}H_{19}I$: C 47.49, H 6.88; found: C 47.27, H 6.90.

*exo-7-Butyl-7-iodobicyclo[4.1.0]heptane (**7n**)*: $R_f = 0.74$ (hexane); IR (neat): $\tilde{\nu} = 2918, 2854, 1467, 1450, 1378, 1209, 1168, 1112, 1049, 926, 748\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.94$ (t, $J = 7.2$ Hz, 3H), 1.08–1.42 (m, 6H), 1.42–1.60 (m, 8H), 1.76–1.92 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 14.1, 18.6, 21.7, 22.3, 24.5, 28.8, 32.4, 35.2$; elemental analysis calcd (%) for $C_{11}H_{19}I$: C 47.49, H 6.88; found: C 47.20, H 6.86.

*endo-7-Benzoyl-7-butylbicyclo[4.1.0]heptane (**6p**)*: $R_f = 0.61$ (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu} = 2928, 2854, 1674, 1598, 1449, 1354, 1215, 1174, 935, 713, 690\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.78$ (t, $J = 6.9$ Hz, 3H), 0.84–1.00 (m, 2H), 1.06–1.32 (m, 8H), 1.53–1.62 (m, 2H), 1.74–1.94 (m, 4H), 7.41–7.51 (m, 2H), 7.51–7.58 (m, 1H), 8.02–8.08 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 13.8, 20.7, 21.3, 21.3, 22.4, 29.4, 35.0, 40.5, 128.5, 129.6, 132.7, 137.1, 201.1$; elemental analysis calcd (%) for $C_{18}H_{24}O$: C 84.32, H 9.44; found: C 84.56, H 9.64.

*exo-7-Benzoyl-7-butylbicyclo[4.1.0]heptane (**7p**)*: $R_f = 0.54$ (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu} = 2926, 2856, 1673, 1448, 1270, 1212, 1020, 710\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.73$ (t, $J = 6.9$ Hz, 3H), 1.08–1.22 (m, 4H), 1.24–1.46 (m, 4H), 1.50–1.64 (m, 4H), 1.71–1.80 (m, 2H), 1.96–2.12 (m, 2H), 7.42 (dd, $J = 6.6, 7.2$ Hz, 2H), 7.50 (t, $J = 7.2$ Hz, 1H), 7.78 (d, $J = 6.6$ Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 13.7, 18.4, 18.6, 22.0, 22.8, 26.5, 29.4, 37.2, 128.3, 128.4, 131.8, 137.6, 204.5$; elemental analysis calcd (%) for $C_{18}H_{24}O$: C 84.32, H 9.44; found: C 84.59, H 9.66.

*endo-9-Butyl-9-iodobicyclo[6.1.0]nonane (**6s**)*: $R_f = 0.86$ (hexane); IR (neat): $\tilde{\nu} = 2906, 2852, 1466, 1173, 1111, 943, 741\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.18–0.29$ (m, 2H), 0.90 (t, $J = 7.5$ Hz, 3H), 1.10–1.71 (m, 16H), 1.79 (dd, $J = 2.1, 13.8$ Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 14.1, 21.8, 26.7, 27.3, 29.1, 30.0, 31.5, 34.0, 46.9$; elemental analysis calcd (%) for $C_{13}H_{23}I$: C 50.99, H 7.57; found: C 51.28, H 7.63.

*exo-9-Butyl-9-iodobicyclo[6.1.0]nonane (**7s**)*: $R_f = 0.82$ (hexane); IR (neat): $\tilde{\nu} = 2920, 2852, 1466, 1178, 1113, 741\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.92$ (t, $J = 6.9$ Hz, 3H), 1.00–1.17 (m, 2H), 1.24–1.64 (m, 16H), 2.06 (dd, $J = 1.8, 13.8$ Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 14.0, 19.1, 21.7, 22.3, 26.0, 28.6, 31.8, 32.7, 34.8$; elemental analysis calcd (%) for $C_{13}H_{23}I$: C 50.99, H 7.57; found: C 51.02, H 7.39.

*1-Butyl-2,3-dipentylcyclopropane (2,3-cis, **6u**/**7u** = 71/29)*: $R_f = 0.85$ (hexane); IR (neat): $\tilde{\nu} = 2954, 2920, 2852, 1467, 1378, 725\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.02$ (tt, $J = 5.1, 6.3$ Hz, 1H), 0.31–0.43 (m, 2H), 0.79–0.98 (m, 9H), 1.00–1.44 (m, 22H); ^{13}C NMR ($CDCl_3$): $\delta = 14.0, 14.1, 17.7, 17.8, 22.5, 22.6, 22.8, 23.1, 23.4, 25.3, 28.1, 28.4, 29.9, 30.0, 31.8, 31.9, 32.1, 32.5, 32.6, 34.2$; elemental analysis calcd (%) for $C_{17}H_{34}$: C 85.63, H 14.37; found: C 85.64, H 14.61.

*r-1-Butyl-2-c,3-t-dipentylcyclopropane (**6v**)*: $R_f = 0.94$ (hexane); IR (neat): $\tilde{\nu} = 2954, 2918, 2850, 1467, 1378, 723\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.03$ (tt, $J = 4.8, 6.6$ Hz, 1H), 0.30–0.43 (m, 2H), 0.84–0.94 (m, 9H), 1.02–1.42 (m, 22H); ^{13}C NMR ($CDCl_3$): $\delta = 14.0, 14.1, 22.6, 22.6, 23.3, 23.4, 25.4, 28.1, 28.4, 29.3, 29.9, 31.7, 31.8, 32.5, 34.5$; elemental analysis calcd (%) for $C_{17}H_{34}$: C 85.63, H 14.37; found: C 85.68, H 14.62.

Synthesis of dibromomethylsilanes 12: The solution of LDA (lithium diisopropylamide) was prepared by the slow addition of butyllithium (39 mL, 1.6 M solution in hexane, 62 mmol) to a solution of diisopropylamine (8.8 mL, 63 mmol) in THF (40 mL) at 0 °C. The resulting solution was added to a solution of dibromomethane (4.2 mL, 60 mmol) and trialkylchlorosilane (60 mmol) in THF (50 mL) dropwise at −78 °C. After stirring for 0.5 h at −78 °C, the resulting mixture was poured into 1 M HCl and extracted with hexane. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica-gel column chromatography provided **12a–d**. Spectral data for **12a**,[9b] **12b**, and **12d**[4i] were identical with those reported in the literature.

*(Dibromomethyl)dimethylphenylsilane (**12c**)*: $R_f = 0.40$ (hexane/ethyl acetate 80:1); IR (neat): $\tilde{\nu} = 2968, 1427, 1252, 1117, 820, 787, 735, 698, 644, 617\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.57$ (s, 6H), 5.25 (s, 1H), 7.35–7.50 (m, 3H), 7.60–7.65 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = -5.0, 35.2, 128.0, 130.3, 133.9, 134.6$; elemental analysis calcd (%) for $C_9H_{12}Br_2Si$: C 35.09, H 3.93; found: C 35.32, H 3.74.

General procedure for the preparation of 1-silylpentylmagnesium species and its reaction with electrophiles: Butyllithium (1.2 mL, 1.6 M solution in hexane, 2.0 mmol) was added to a solution of butylmagnesium bromide (1.0 mL, 1.0 M solution in THF, 1.0 mmol) in THF (5 mL) at 0 °C, and the mixture was stirred for 10 min. The resulting solution was cooled to −78 °C, and a solution of **12** (1.0 mmol) in THF (2 mL) was added dropwise. After the mixture was stirred for 10 min, $CuCN \cdot 2LiCl$ (0.3 mL, 1.0 M solution in THF, 0.3 mmol) was added, and the mixture was allowed to gradually warm to −30 °C over a period of 2 h. Allyl bromide (0.26 mL, 3.0 mmol) was added at −30 °C. After stirring for 1 h at 0 °C, the reaction was quenched with saturated aqueous NH_4Cl. The mixture was extracted with hexane, and the organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica-gel column chromatography provided **18**.

*(Bromomethyl)methyldiphenylsilane (**15b**)*: $R_f = 0.37$ (hexane/ethyl acetate 40:1); IR (neat): $\tilde{\nu} = 2928, 1428, 1385, 1254, 1115, 999, 804, 765, 733, 696\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.75$ (s, 3H), 2.93 (s, 2H), 7.36–7.48 (m, 6H), 7.55–7.60 (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta = -5.2, 14.7, 128.1, 130.0, 134.5, 134.7$; elemental analysis calcd (%) for $C_{14}H_{15}BrSi$: C 57.73, H 5.19; found: C 57.72, H 5.18.

*Methylpentyldiphenylsilane (**17b**)*: $R_f = 0.49$ (hexane/ethyl acetate 80:1); IR (neat): $\tilde{\nu} = 2918, 1428, 1251, 784, 729, 697\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.55$ (s, 3H), 0.85 (t, $J = 6.9$ Hz, 3H), 1.07 (t, $J = 8.0$ Hz, 2H), 1.20–1.38 (m, 6H), 7.31–7.40 (m, 6H), 7.49–7.56 (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta = -4.6, 13.9, 14.0, 22.1, 23.4, 35.8, 127.8, 129.1, 134.6, 137.7$; elemental analysis calcd (%) for $C_{18}H_{24}Si$: C 80.53, H 9.01; found: C 80.44, H 8.85.

*4-(tert-Butyldimethylsilyl)-1-octene (**18a**)*: $R_f = 0.87$ (hexane); IR (neat): $\tilde{\nu} = 2924, 2854, 1465, 1254, 908, 825, 806, 761\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = -0.06$ (s, 3H), −0.05 (s, 3H), 0.75–0.90 (m, 1H), 0.87 (t, $J = 6.9$ Hz, 3H), 0.89 (s, 9H), 1.14–1.38 (m, 5H), 1.38–1.52 (m, 1H), 1.97–2.10 (m, 1H), 2.22–2.34 (m, 1H), 4.94 (d, $J = 9.9$ Hz, 1H), 4.98 (d, $J = 16.8$ Hz, 1H), 5.78 (ddt, $J = 9.9, 16.8, 6.9$ Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = -6.4, -6.3, 14.0, 17.4, 22.3, 22.9, 27.2, 29.1, 31.1, 34.4, 114.8, 139.5$; elemental analysis calcd (%) for $C_{14}H_{30}Si$: C 74.25, H 13.35; found: C 74.00, H 13.11.

*4-(Methyldiphenylsilyl)-1-octene (**18b**)*: $R_f = 0.55$ (hexane); IR (neat): $\tilde{\nu} = 3064, 2920, 2854, 1638, 1428, 1252, 1110, 998, 908, 785, 732, 698\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.59$ (s, 3H), 0.80 (t, $J = 7.2$ Hz, 3H), 1.10–1.62 (m, 7H), 2.01–2.15 (m, 1H), 2.28–2.40 (m, 1H), 4.90 (d, $J = 10.2$ Hz, 1H), 4.92 (d, $J = 17.4$ Hz, 1H), 5.75 (ddt, $J = 10.2, 17.4, 7.2$ Hz, 1H), 7.30–7.40 (m, 6H), 7.48–7.59 (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta = -5.3, 13.8, 22.7, 23.5, 28.9, 31.4, 34.2, 115.0, 127.8, 129.1, 134.6, 137.1, 139.2$; elemental analysis calcd (%) for $C_{21}H_{28}Si$: C 81.75, H 9.15; found: C 81.74, H 9.20.

*4-(Dimethylphenylsilyl)-1-octene (**18c**)*: $R_f = 0.64$ (hexane); IR (neat): $\tilde{\nu} = 2920, 2854, 1639, 1428, 1112, 995, 908, 814, 766, 731, 698\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.28$ (s, 6H), 0.82 (t, $J = 6.9$ Hz, 3H), 0.90–0.95 (m, 1H), 1.08–1.48 (m, 6H), 1.96–2.09 (m, 1H), 2.17–2.28 (m, 1H), 4.88–4.98 (m, 2H), 5.73 (ddt, $J = 10.2, 17.4, 7.2$ Hz, 1H), 7.31–7.38 (m, 3H), 7.47–7.54 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = -3.8, -3.8, 13.9, 22.8, 25.0, 28.7, 31.1, 34.0, 114.9, 127.7, 128.8, 137.0, 139.2, 139.3$; elemental analysis calcd (%) for $C_{16}H_{26}Si$: C 77.97, H 10.63; found: C 77.68, H 10.37.

*4-(Dicyclohexylmethylsilyl)-1-octene (**18d**)*: $R_f = 0.82$ (hexane); IR (neat): $\tilde{\nu} = 2925, 2848, 1638, 1446, 1249, 1098, 997, 907, 889, 846, 770, 738\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = -0.13$ (s, 3H), 0.72–0.90 (m, 3H), 0.88 (t, $J =$ 6.9 Hz, 3H), 1.06–1.52 (m, 16H), 1.58–1.84 (m, 10H), 1.95–2.07 (m, 1H), 2.21–2.32 (m, 1H), 4.89–8.02 (m, 2H), 5.79 (ddt, $J = 9.9, 16.8, 6.9$ Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = -8.7, 14.0, 22.3, 22.6, 22.9, 23.9, 24.0, 27.1, 28.4, 28.4, 28.4, 28.5, 29.8, 31.5, 32.1, 35.0, 114.3, 140.3$; elemental analysis calcd (%) for $C_{21}H_{40}Si$: C 78.67, H 12.57; found: C 78.52, H 12.73.

*4-(tert-Butyldimethylsilyl)-1,2-octadiene (**19a**)*: $R_f = 0.80$ (hexane); IR (neat): $\tilde{\nu} = 2952, 2924, 2854, 1951, 1466, 1362, 1250, 834\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = -0.06$ (s, 3H), −0.06 (s, 3H), 0.88 (t, $J = 7.2$ Hz, 3H), 0.90 (s, 9H), 1.12–1.58 (m, 7H), 4.63 (d, $J = 6.9$ Hz, 1H), 4.64 (d, $J = 6.6$ Hz, 1H), 4.98 (ddd, $J = 6.6, 6.9, 9.3$ Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = -7.3, -7.2, 14.0, 17.4, 22.3, 25.9, 27.2, 29.3, 31.6, 74.6, 92.4, 208.7$; HRMS (*m*/*z*) calcd for $C_{14}H_{28}Si$: 224.1960; found: 224.1955.

Procedure for the synthesis of α-silylketones 20a–l with acyl halide as the electrophile: Butyllithium (1.2 mL, 1.6 M solution in hexane, 2.0 mmol) was added to a solution of butylmagnesium bromide (1.0 mL, 1.0 M solution in THF, 1.0 mmol) in THF (5 mL) at 0 °C, and the mixture was stirred for 10 min. The resulting solution was cooled to −78 °C, and a solution of **12** (1.0 mmol) in THF (2 mL) was added dropwise. The mixture was stirred for 10 min, $CuCN \cdot 2LiCl$ (0.3 mL, 1.0 M solution in THF, 0.3 mmol) was added, and the mixture was allowed to warm gradually to 0 °C over a period of 3 h. DMI (0.22 mL, 2.0 mmol) and the corresponding acyl chloride (2.5 mmol) were successively added. After stirring for 1 h at 0 °C, the reaction was quenched with saturated aqueous NH_4Cl. The mixture was extracted with ethyl acetate and the organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica-gel column chromatography gave **20**.

*3-(tert-Butyldimethylsilyl)-2-heptanone (**20a**)*: $R_f = 0.54$ (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu} = 2926, 2856, 1692, 1467, 1353, 1252, 1167, 836, 772\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = -0.02$ (s, 3H), 0.03 (s, 3H), 0.85 (t, $J =$ 7.1 Hz, 3H), 0.92 (s, 9H), 1.04–1.34 (m, 4H), 1.34–1.48 (m, 1H), 1.96–2.03 (m, 1H), 2.07 (s, 3H), 2.47 (dd, $J = 1.8, 11.9$ Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = -7.2, -5.2, 13.8, 17.7, 22.4, 26.7, 28.0, 32.0, 33.1, 46.1, 211.2$; elemental analysis calcd (%) for $C_{13}H_{28}SiO$: C 68.35, H 12.35; found: C 68.17, H 12.55.

*2-(tert-Butyldimethylsilyl)-1-cyclopropyl-1-hexanone (**20b**)*: $R_f = 0.54$ (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu} = 2928, 2856, 1676, 1466, 1378, 1252, 1140, 1071, 836\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.02$ (s, 3H), 0.04 (s, 3H), 0.77–0.84 (m, 2H), 0.86 (t, $J = 7.2$ Hz, 3H), 0.94 (s, 9H), 0.94–1.00 (m, 1H), 1.00–1.08 (m, 1H), 1.08–1.20 (m, 1H), 1.20–1.36 (m, 3H), 1.36–1.49 (m, 1H), 1.82 (tt, $J = 4.5, 7.8$ Hz, 1H), 1.94–2.09 (m, 1H), 2.62 (dd, $J = 2.1, 11.7$ Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = -7.1, -6.0, 10.4, 11.1, 13.8, 17.7, 22.0, 22.4, 26.8, 27.7, 33.1, 46.6, 212.5$; elemental analysis calcd (%) for $C_{15}H_{30}SiO$: C 70.80, H 11.88; found: C 70.66, H 12.14.

*2-(tert-Butyldimethylsilyl)-1-phenyl-1-hexanone (**20c**)*: $R_f = 0.54$ (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu} = 2928, 2854, 1654, 1597, 1580, 1466, 1447, 1252, 1227, 1003, 833, 731, 688\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = -0.26$ (s, 3H), 0.03 (s, 3H), 0.84 (t, $J = 6.9$ Hz, 3H), 0.91 (s, 9H), 1.12–1.40 (m, 4H), 1.50–1.65 (m, 1H), 2.16–2.32 (m, 1H), 3.42 (dd, $J = 2.1, 11.7$ Hz, 1H), 7.44 (dd, $J = 6.6, 7.2$ Hz, 2H), 7.52 (t, $J = 7.2$ Hz, 1H), 7.90 (d, $J = 6.6$ Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta = -7.4, -5.8, 13.8, 18.1, 25.6, 26.9, 28.7, 33.3, 39.2, 128.1, 128.5, 132.4, 140.0, 203.9$; elemental analysis calcd (%) for $C_{18}H_{30}SiO$: C 74.42, H 10.41; found: C 74.68, H 10.52.

*(E)-5-(tert-Butyldimethylsilyl)-2-nonen-4-one (**20d**)*: $R_f = 0.48$ (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu} = 2928, 2854, 1679, 1657, 1628, 1466, 1256, 1143, 1065, 969, 822, 770\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = -0.08$ (s, 3H), 0.03 (s, 3H), 0.84 (t, $J = 7.2$ Hz, 3H), 0.92 (s, 9H), 1.03–1.35 (m, 4H), 1.38–1.51 (m, 1H), 1.87 (dd, $J = 1.8, 6.9$ Hz, 3H), 1.96–2.11 (m, 1H), 2.61 (dd, $J = 2.1, 11.7$ Hz, 1H), 6.12 (dq, $J = 15.6, 1.8$ Hz, 1H), 6.77 (dq, $J = 15.6, 6.9$ Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = -7.2, -6.0, 13.8, 17.9, 17.9, 22.5, 26.8, 27.8, 33.0, 43.1, 133.5, 140.4, 202.5$; elemental analysis calcd (%) for $C_{15}H_{30}SiO$: C 70.80, H 11.88; found: C 71.00, H 11.61.

*(E)-4-(tert-Butyldimethylsilyl)-1-phenyl-1-octen-3-one (**20e**)*: $R_f = 0.44$ (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu} = 2926, 2854, 1673, 1642, 1609, 1466, 1450, 1252, 1138, 1070, 835, 688\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = -0.22$ (s, 3H), 0.08 (s, 3H), 0.85 (t, $J = 6.9$ Hz, 3H), 0.95 (s, 9H), 1.10–1.39 (m, 4H), 1.49–1.58 (m, 1H), 2.05–2.20 (m, 1H), 2.75 (dd, $J = 2.4, 12.0$ Hz, 1H), 6.73 (d, $J = 15.9$ Hz, 1H), 7.36–7.42 (m, 3H), 7.52 (d, $J = 15.9$ Hz, 1H), 7.52–7.58 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = -7.0, -5.9, 13.8, 18.0, 22.5, 26.9, 27.9, 33.1, 44.6, 127.8, 128.3, 129.0, 130.2, 135.0, 140.7, 202.2$; elemental analysis calcd (%) for $C_{20}H_{32}SiO$: C 75.88, H 10.19; found: C 76.17, H 9.90.

*3-(Methyldiphenylsilyl)-2-heptanone (**20f**)*: $R_f = 0.43$ (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu} = 2924, 1687, 1428, 1353, 1255, 1167, 1111, 790, 735, 699\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.64$ (s, 3H), 0.81 (t, $J = 6.9$ Hz, 3H), 1.05–1.34 (m, 4H), 1.34–1.48 (m, 1H), 1.71 (s, 3H), 1.96–2.11 (m, 1H), 2.98 (dd, $J = 2.1, 11.4$ Hz, 1H), 7.31–7.45 (m, 6H), 7.47–7.53 (m, 2H), 7.55–7.60 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = -6.4, 13.7, 22.3, 27.3, 32.5, 32.9, 47.7, 128.1, 128.2, 129.8, 129.9, 134.4, 134.8$ (2C), 134.9, 210.6; elemental analysis calcd (%) for $C_{20}H_{26}SiO$: C 77.36, H 8.44; found: C 77.59, H 8.51.

*5-(Methyldiphenylsilyl)-4-nonanone (**20g**)*: $R_f = 0.53$ (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu} = 2954, 1691, 1429, 1254, 1112, 789\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.64$ (s, 3H), 0.64 (t, $J = 7.4$ Hz, 3H), 0.81 (t, $J = 6.9$ Hz, 3H), 1.05–1.32 (m, 5H), 1.32–1.52 (m, 2H), 1.80 (ddd, $J = 6.0, 8.7, 16.8$ Hz, 1H), 1.98 (ddd, $J = 6.0, 8.7, 16.8$ Hz, 1H), 2.00–2.14 (m, 1H), 2.94 (dd, $J = 2.1, 11.7$ Hz, 1H), 7.30–7.45 (m, 6H), 7.46–7.53 (m, 2H), 7.55–7.61 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = -6.5, 13.5, 13.7, 16.8, 22.4, 27.4, 32.9, 46.5, 47.4, 128.0, 128.1, 129.8, 129.8, 134.7, 134.7, 134.8, 135.1, 212.6$; elemental analysis calcd (%) for $C_{22}H_{30}SiO$: C 78.05, H 8.93; found: C 78.07, H 9.12.

*2-Methyl-4-(methyldiphenylsilyl)-3-octanone (**20h**)*: $R_f = 0.49$ (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu} = 2956, 2924, 1689, 1466, 1428, 1112, 1057, 788, 736, 697\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.58$ (d, $J = 6.9$ Hz, 3H), 0.64 (s, 3H), 0.80 (t, $J = 7.2$ Hz, 3H), 0.96 (d, $J = 6.9$ Hz, 3H), 1.00–1.42 (m, 5H), 1.97 (sept, $J = 6.9$ Hz, 1H), 2.00–2.15 (m, 1H), 3.14 (dd, $J = 2.4, 11.7$ Hz, 1H), 7.29–7.44 (m, 6H), 7.46–7.52 (m, 2H), 7.54–7.61 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = -6.5, 13.8, 16.1, 19.0, 22.5, 27.6, 33.1, 42.1, 45.3, 128.0, 128.1, 129.8$ (2C), 134.7, 134.8, 134.8, 135.2, 215.9; elemental analysis calcd (%) for $C_{22}H_{30}SiO$: C 78.05, H 8.93; found: C 77.86, H 9.19.

*1-Cyclopropyl-2-(methyldiphenylsilyl)-1-hexanone (**20i**)*: $R_f = 0.50$ (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu} = 2926, 2854, 1675, 1429, 1378, 1254, 1112, 792, 736, 721, 697\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.30$ (dddd, $J = 2.7, 6.6, 7.5, 9.0$ Hz, 1H), 0.57–0.68 (m, 1H), 0.64 (s, 3H), 0.71–0.93 (m, 2H), 0.81 (t, $J = 7.2$ Hz, 3H), 1.08–1.35 (m, 4H), 1.36–1.49 (m, 2H), 1.99–2.14 (m, 1H), 3.13 (dd, $J = 2.4, 11.4$ Hz, 1H), 7.30–7.45 (m, 6H), 7.50–7.56 (m, 2H), 7.56–7.61 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 5.9, 10.5, 11.1, 13.8, 22.3, 22.5, 27.0, 32.9, 48.3, 127.9, 128.0, 129.6, 129.7, 134.8, 134.9, 134.9, 135.2, 211.6$; elemental analysis calcd (%) for $C_{22}H_{28}SiO$: C 78.52, H 8.39; found: C 78.23, H 8.49.

*2-(Methyldiphenylsilyl)-1-phenyl-1-hexanone (**20j**)*: $R_f = 0.53$ (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu} = 2922, 2854, 1659, 1447, 1429, 1344, 1255, 1228, 1112, 1002, 790, 732, 697\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.57$ (s, 3H), 0.80 (t, $J = 7.2$ Hz, 3H), 1.16–1.42 (m, 4H), 1.55–1.68 (m, 1H), 2.20–2.36 (m, 1H), 3.86 (dd, $J = 2.4, 11.4$ Hz, 1H), 7.13–7.20 (m, 2H), 7.20–7.28 (m, 3H), 7.33–7.42 (m, 6H), 7.54–7.60 (m, 2H), 7.64–7.70 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = -5.7, 13.8, 22.4, 28.2, 33.0, 41.0, 127.7, 128.0, 128.0, 128.1, 129.5, 129.7, 132.0, 134.4, 134.7, 134.8, 134.9, 139.7, 203.3$; elemental analysis calcd (%) for $C_{25}H_{28}SiO$: C 80.59, H 7.57; found: C 80.40, H 7.47.

*5-(Methyldiphenylsilyl)-4-undecanone (**20k**)*: $R_f = 0.52$ (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu} = 2928, 2856, 1690, 1464, 1429, 1254, 1111, 791, 737, 700\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.64$ (s, 3H), 0.64 (t, $J = 7.5$ Hz, 3H), 0.83 (t, $J = 6.9$ Hz, 3H), 1.08–1.32 (m, 9H), 1.32–1.49 (m, 2H), 1.80 (ddd, $J =$ 6.0, 8.7, 16.8 Hz, 1H), 1.97 (ddd, $J = 6.0, 8.7, 16.8$ Hz, 1H), 2.03–2.15 (m, 1H), 2.94 (dd, $J = 2.4, 11.4$ Hz, 1H), 7.30–7.44 (m, 6H), 7.46–7.51 (m, 2H), 7.55–7.59 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = -6.4, 13.5, 13.9, 16.8, 22.5, 27.7, 29.0, 30.7, 31.5, 46.5, 47.4, 128.0, 128.1, 129.8, 129.8, 129.8, 134.7, 134.7, 134.8, 135.1$; HRMS (*m*/*z*) calcd for $C_{24}H_{34}OSi$ 366.2379; found: 366.2362.

*2-(Methyldiphenylsilyl)-1-phenyl-1-octanone (**20l**)*: $R_f = 0.49$ (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu} = 2926, 2855, 1661, 1429, 1342, 1256, 1217, 1113, 791, 733, 698\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.55$ (s, 3H), 0.80 (t, $J = 6.9$ Hz, 3H), 1.08–1.40 (m, 8H), 1.52–1.64 (m, 1H), 2.18–2.32 (m, 1H), 3.84 (dd, $J = 2.4, 11.4$ Hz, 1H), 7.12–7.25 (m, 5H), 7.32–7.42 (m, 6H), 7.53–7.60 (m, 2H), 7.62–7.69 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = -5.7, 13.9, 22.4, 28.5, 29.0, 30.8, 31.5, 41.1, 127.7, 128.0, 128.0, 128.1, 129.5, 129.7, 132.0, 134.5, 134.8, 134.9, 139.8, 203.3$; elemental analysis calcd (%) for $C_{27}H_{32}OSi$: C 80.95, H 8.05; found: C 80.70, H 8.16.

Procedure for the conjugate addition of α-silylpentylmagnesium to enones: Butyllithium (1.2 mL, 1.6 M solution in hexane, 2.0 mmol) was added to a solution of butylmagnesium bromide (1.0 mL, 1.0 M solution in THF, 1.0 mmol) in THF (5 mL) at 0 °C, and the mixture was stirred for 10 min. The resulting solution was cooled to −78 °C, and a solution of **12**

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(1.0 mmol) in THF (2 mL) was added dropwise. The mixture was stirred for 10 min, CuCN · 2 LiCl (0.3 mL, 1.0 M solution in THF, 0.3 mmol) was added, and the mixture was allowed to warm gradually to 0 °C over a period of 3 h. Then the mixture was cooled to −78 °C and a mixture of the corresponding enone (4.0 mmol) and chlorotrimethylsilane (0.51 mL, 4.0 mmol) in THF (2 mL) was added. The reaction mixture was gradually warmed to 0 °C and then poured into saturated aqueous NH_4Cl and extracted with ethyl acetate. The organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica-gel column chromatography provided **21**, **22**, or **23**.

*5-(tert-Butyldimethylsilyl)-2-nonanone (**21a**)*: $R_f = 0.51$ (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu} = 2926, 2854, 1720, 1467, 1362, 1252, 1155, 828, 805, 763\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = -0.06$ (s, 6H), 0.65–0.75 (m, 1H), 0.88 (t, $J = 7.1$ Hz, 3H), 0.89 (s, 9H), 1.15–1.38 (m, 5H), 1.40–1.60 (m, 2H), 1.72–1.86 (m, 1H), 2.13 (s, 3H), 2.40 (ddd, $J = 6.0, 10.5, 16.5$ Hz, 1H), 2.44 (ddd, $J = 6.0, 10.5, 16.5$ Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = -6.5, -6.4, 13.9, 17.3, 22.0, 23.0, 24.1, 27.2, 29.3, 29.8, 31.2, 43.3, 209.6$; elemental analysis calcd (%) for $C_{15}H_{32}SiO$: C 70.24, H 12.57; found: C 70.30, H 12.42.

*5-(Methyldiphenylsilyl)-2-nonanone (**21b**)*: $R_f = 0.60$ (hexane/ethyl acetate 5:1); IR (neat): $\tilde{\nu} = 2920, 2854, 1714, 1428, 1358, 1253, 1109, 785, 735, 719, 699\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.58$ (s, 3H), 0.79 (t, $J = 7.2$ Hz, 3H), 1.08–1.40 (m, 6H), 1.46–1.90 (m, 3H), 1.95 (s, 3H), 2.24 (ddd, $J = 6.0, 9.6, 16.5$ Hz, 1H), 2.35 (ddd, $J = 6.0, 9.6, 16.5$ Hz, 1H), 7.30–7.39 (m, 6H), 7.50–7.56 (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta = -5.7, 13.8, 22.7, 23.1, 23.9, 29.4, 29.6, 31.4, 43.3, 127.9, 127.9, 129.2, 129.2, 134.8, 136.9, 136.9, 209.4$; elemental analysis calcd (%) for $C_{22}H_{30}SiO$: C 78.05, H 8.93; found: C 77.90, H 8.80.

*3-[1-(tert-Butyldimethylsilyl)pentyl]-1-cyclohexanone (**22**, 86:14 mixture of diastereomers)*: $R_f = 0.49$ (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu} = 2928, 2850, 1711, 1462, 1254, 823, 805, 764\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = -0.03$ (s, 2.58H), −0.03 (s, 0.42H), 0.01 (s, 0.42H), 0.02 (s, 2.58H), 0.65–0.72 (m, 0.14H), 0.77–0.84 (m, 0.86H), 0.84–0.93 (m, 1.68H), 0.88 (s, 7.74H), 0.89 (t, $J = 6.9$ Hz, 2.58H), 1.18–1.45 (m, 6H), 1.48–1.78 (m, 3H), 1.94–2.10 (m, 2H), 2.14–2.42 (m, 4H); ^{13}C NMR ($CDCl_3$) (major isomer): $\delta = -5.8, -5.1, 14.0, 17.3, 23.1, 25.8, 26.7, 27.1, 28.6, 31.7, 34.1, 40.9, 41.2, 46.6, 212.7$; elemental analysis calcd (%) for $C_{17}H_{34}SiO$: C 72.27, H 12.13; found: C 72.16, H 12.16.

*3-[1-(tert-Butyldimethylsilyl)pentyl]-1-cyclopentanone (**23**, 67:33 mixture of diastereomers)*: $R_f = 0.53$ (hexane/ethyl acetate 5:1); IR (neat): $\tilde{\nu} = 2924, 2854, 1744, 1466, 1252, 1155, 825, 763\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = -0.03$ (s, 4.02H), −0.01 (s, 0.99H), 0.00 (s, 0.99H), 0.78–0.96 (m, 4H), 0.91 (s, 9H), 1.16–1.52 (m, 6H), 1.60–2.48 (m, 7H); ^{13}C NMR ($CDCl_3$): $\delta = -5.8, -5.5, -5.4, -5.0, 13.9, 17.4, 17.5, 23.1, 23.2, 26.4, 26.7, 27.0, 27.2, 27.2, 28.0, 29.6, 33.9, 34.1, 38.9, 38.9, 39.1, 39.1, 43.0, 45.3, 220.1$; elemental analysis calcd (%) for $C_{16}H_{32}SiO$: C 71.57, H 12.01; found: C 71.31, H 12.28.

Procedure for the introduction of a *sec*-butyl group: *sec*-Butyllithium (2.0 mL, 1.0 M solution in hexane-cyclohexane, 2.0 mmol) was added to a solution of *sec*-butylmagnesium bromide (1.0 mL, 1.0 M solution in THF, 1.0 mmol) in THF (5 mL) at 0 °C, and the mixture was stirred for 10 min. The resulting solution was cooled to −78 °C and a solution of (dibromomethyl)methyldiphenylsilane (**12b**, 370 mg, 1.0 mmol) in THF (2 mL) was added dropwise. The mixture was allowed to warm to ambient temperature gradually. CuCN · 2 LiCl (0.2 mL, 1.0 M solution in THF, 0.2 mmol) and the corresponding electrophile (3.0 mmol) were successively added at 0 °C. After stirring for 1 h at 0 °C, the reaction was quenched with saturated aqueous NH_4Cl. The mixture was extracted with hexane and the organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica-gel column chromatography provided **24**.

*5-Methyl-4-(methyldiphenylsilyl)-1-heptene (**24a**)*: $R_f = 0.46$ (hexane/ethyl acetate 80:1); IR (neat): $\tilde{\nu} = 3071, 2959, 1638, 1460, 1427, 1252, 1109, 997, 908, 787, 737, 700\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.64$ (s, 1.5H), 0.65 (s, 1.5H), 0.76 (t, $J = 7.5$ Hz, 1.5H), 0.79 (d, $J = 6.6$ Hz, 1.5H), 0.82 (t, $J = 7.2$ Hz, 1.5H), 0.90 (d, $J = 7.2$ Hz, 1.5H), 1.15–1.33 (m, 2H), 1.51–1.62 (m, 1H), 1.62–1.76 (m, 1H), 2.19–2.36 (m, 2H), 4.83–4.94 (m, 2H), 5.71–5.79 (m, 1H), 7.34–7.38 (m, 6H), 7.50–7.59 (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta = -4.3, -3.7, 12.3, 12.5, 17.7, 19.2, 28.3, 29.1, 29.8, 30.5, 30.7, 32.3, 35.1, 35.4, 114.4, 114.7, 127.8, 127.8, 127.9, 129.0, 129.3, 134.3, 134.8, 134.9, 134.9, 137.6, 137.8, 138.2, 140.2, 140.7$; HRMS ($m/z$) calcd for $C_{21}H_{28}Si$: 308.1960; found: 308.1945.

*6-Methyl-5-(methyldiphenylsilyl)-4-octanone (**24b**, ≈1:1 mixture of two diastereomers)*: $R_f = 0.49$ (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu} = 2961, 2874, 1690, 1464, 1429, 1254, 1111, 1038, 793, 737, 700\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.57$ (t, $J = 7.5$ Hz, 1.5H), 0.60 (t, $J = 7.5$ Hz, 1.5H), 0.70 (t, $J = 7.5$ Hz, 1.5H), 0.72 (s, 1.5H), 0.73 (d, $J = 6.3$ Hz, 1.5H), 0.75 (s, 1.5H), 0.79 (t, $J = 7.5$ Hz, 1.5H), 0.88 (d, $J = 6.3$ Hz, 1.5H), 0.85–1.15 (m, 2H), 1.22–1.44 (m, 2H), 1.69 (ddd, $J = 5.7, 9.0, 17.4$ Hz, 0.5H), 1.75 (ddd, $J = 5.7, 9.0, 17.4$ Hz, 0.5H), 1.90–2.03 (m, 1H), 2.04–2.16 (m, 0.5H), 2.18–2.31 (m, 0.5H), 2.85 (d, $J = 10.8$ Hz, 0.5H), 2.87 (d, $J = 9.9$ Hz, 0.5H), 7.26–7.35 (m, 3H), 7.35–7.41 (m, 3H), 7.47–7.53 (m, 2H), 7.55–7.61 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = -5.4, -5.2, 10.8, 11.4, 13.4, 13.4, 16.1, 16.2, 18.8, 19.1, 29.2, 29.8, 30.0, 35.4, 48.7, 48.9, 52.4, 52.6, 127.9, 128.0, 129.5, 129.5, 129.5, 134.6, 134.7, 135.1, 135.1, 135.5, 135.6, 135.8, 136.0, 213.4, 213.6$; elemental analysis calcd (%) for $C_{22}H_{30}OSi$: C 78.05, H 8.93; found: C 78.30, H 8.94.

*2,5-Dimethyl-4-(methyldiphenylsilyl)-3-heptanone (**24c**, ≈1:1 mixture of two diastereomers)*: $R_f = 0.56$ (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu} = 2966, 1688, 1454, 1429, 1381, 1254, 1109, 1042, 791, 700\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.36$ (d, $J = 6.6$ Hz, 1.5H), 0.38 (d, $J = 6.6$ Hz, 1.5H), 0.46–0.75 (m, 0.5H), 0.70 (t, $J = 7.5$ Hz, 1.5H), 0.73 (s, 1.5H), 0.76 (s, 1.5H), 0.76 (d, $J = 6.6$ Hz, 1.5H), 0.81 (t, $J = 7.5$ Hz, 1.5H), 0.87 (d, $J = 6.6$ Hz, 1.5H), 0.96 (d, $J = 7.5$ Hz, 1.5H), 0.98 (d, $J = 7.5$ Hz, 1.5H), 1.00–1.26 (m, 0.5H), 1.33–1.53 (m, 1H), 1.84–2.06 (m, 1H), 2.06–2.29 (m, 1H), 3.05 (d, $J = 10.5$ Hz, 0.5H), 3.08 (d, $J = 10.2$ Hz, 0.5H), 7.26–7.42 (m, 6H), 7.47–7.53 (m, 2H), 7.57–7.62 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = -5.2, -5.0, 11.4, 11.5, 15.9, 18.6, 18.7, 18.7, 19.4, 29.1, 30.1, 35.1, 35.2, 43.0, 43.1, 51.1, 51.9, 127.9, 128.0, 129.5, 129.5, 129.5, 134.7, 134.7, 135.3, 135.3, 135.5, 136.0, 136.2, 216.2, 216.5$; elemental analysis calcd (%) for $C_{22}H_{30}OSi$: C 78.05, H 8.93; found: C 78.16, H 9.16.

*1-Cyclopropyl-3-methyl-2-(methyldiphenylsilyl)-1-pentanone (**24d**, ≈1:1 mixture of two diastereomers)*: $R_f = 0.44$ (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu} = 2963, 2930, 1674, 1429, 1377, 1254, 1111, 1063, 797, 737, 700\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.16–0.26$(m, 0.5H), 0.24–0.35 (m, 0.5H), 0.50–0.67 (m, 2H), 0.67–0.83 (m, 1H), 0.71 (s, 1.5H), 0.72 (t, $J = 7.5$ Hz, 1.5H), 0.73 (s, 1.5H), 0.78 (d, $J = 6.9$ Hz, 1.5H), 0.81 (t, $J = 7.5$ Hz, 1.5H), 0.92 (d, $J = 6.6$ Hz, 1.5H), 0.91–1.07 (m, 0.5H), 1.07–1.24 (m, 0.5H), 1.35–1.58 (m, 2H), 1.95–2.15 (m, 0.5H), 2.15–2.32 (m, 0.5H), 3.09 (d, $J = 10.8$ Hz, 0.5H), 3.11 (d, $J = 9.6$ Hz, 0.5H), 7.26–7.40 (m, 6H), 7.52–7.58 (m, 2H), 7.58–7.64 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = -4.7, -4.4, 10.1, 10.3, 10.6, 11.2, 11.3, 11.4, 18.9, 19.3, 23.4, 23.4, 29.3, 29.9, 34.8, 35.2, 54.3, 54.7, 127.8, 128.0, 129.4, 129.4, 129.5, 134.8, 134.8, 135.1, 135.2, 135.6, 135.8, 136.0, 212.8, 213.0$; elemental analysis calcd (%) for $C_{22}H_{28}OSi$: C 78.52, H 8.39; found: C 78.34, H 8.51.

*3-Methyl-2-(methyldiphenylsilyl)-1-phenyl-1-pentanone (**24e**, ≈1:1 mixture of two diastereomers)*: $R_f = 0.42$ (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu} = 2963, 2930, 1659, 1429, 1263, 1204, 1111, 789, 735, 718, 698\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.67$ (s, 1.5H), 0.71 (s, 1.5H), 0.71 (t, $J = 7.4$ Hz, 1.5H), 0.78 (t, $J = 7.7$ Hz, 1.5H), 0.86 (d, $J = 6.9$ Hz, 1.5H), 0.94 (d, $J = 6.6$ Hz, 1.5H), 0.98–1.12 (m, 0.5H), 1.12–1.28 (m, 0.5H), 1.41–1.58 (m, 1H), 2.22–2.36 (m, 0.5H), 2.36–2.51 (m, 0.5H), 3.81 (d, $J = 10.5$ Hz, 0.5H), 3.83 (d, $J = 9.9$ Hz, 0.5H), 7.12–7.23 (m, 5H), 7.24–7.40 (m, 6H), 7.40–7.48 (m, 2H) , 7.52–7.60 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = -4.6, -4.4, 11.0, 11.5, 19.0, 19.5, 29.4, 30.2, 35.8, 36.1, 46.9, 47.1, 127.6, 127.6, 127.9, 128.0, 128.1, 128.1, 129.2, 129.4, 129.4, 131.9, 131.9, 134.7, 134.8, 135.1, 135.1, 135.2, 135.6, 135.8, 140.0, 140.3$; HRMS ($m/z$) calcd for $C_{25}H_{28}OSi$ 372.1909; found: 372.1912.

Preparation of dibromodisilylmethanes

Method A: Butyllithium (2.6 mL, 1.6 M solution in hexane, 4.2 mmol) was added dropwise to a solution of diisopropylamine (0.63 mL, 4.5 mmol) in THF (4 mL) at 0 °C, and the mixture was stirred for 0.5 h. The resulting solution of LDA was cooled to −78 °C, and a solution of a dibromomethylsilane (4.0 mmol) in THF (8 mL) was added dropwise at −78 °C. The mixture was stirred for 0.5 h, and the corresponding trialkylchlorosilane or iodomethane (5.0 mmol) was added. After stirring for 0.5 h at −78 °C, the mixture was poured into 1 M HCl and extracted with hexane. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica-gel column chromatography provided the corresponding dibromodisilylmethane.

Method B: The solution of LDA (lithium diisopropylamide) was prepared by the slow addition of butyllithium (39 mL, 1.6 M solution in hexane, 62 mmol) to a solution of diisopropylamine (8.8 mL, 63 mmol) in THF (40 mL) at 0 °C. The resulting solution was added to a solution of dibromomethane (4.2 mL, 30 mmol) and trialkylchlorosilane (65 mmol) in

THF dropwise at −78 °C. After stirring for 2 h at room temperature, the resulting mixture was poured into 1M HCl and extracted with hexane. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica-gel column chromatography or recrystallization provided the corresponding dibromodisilylmethane.

Method C: Butyllithium (25 mL, 1.6M solution in hexane, 40 mmol) was slowly added to a solution of (chloro)methyldiphenylsilane (8.4 mL, 40 mmol) and carbon tetrabromide (6.63 g, 20 mmol) in THF (50 mL) at −78 °C under an argon atmosphere. The cooling bath was removed and the mixture was stirred for 2 h at room temperature. Then, 1M HCl was added to the reaction mixture and the whole mixture was extracted with chloroform. The organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Recrystallization from hexane/ethyl acetate afforded **12k**.

Spectral data for **12f**[18c] (prepared by method A from **12b** and chlorotrimethylsilane), and **12i**[18a] (prepared by method B), were identical with those reported in the literature.

*1,1-Dibromo-1-(methyldiphenylsilyl)ethane (**12e**, prepared by method A from **12b** and iodomethane)*: $R_f = 0.31$ (hexane/ethyl acetate 40:1); IR (neat): $\tilde{\nu} = 1427$, 1256, 1113, 1049, 999, 793, 733, 698 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 0.90$ (s, 3H), 2.59 (s, 3H), 7.36–7.51 (m, 6H), 7.78–7.84 (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta = -4.6$, 37.0, 58.4, 127.9, 130.3, 132.6, 136.0; elemental analysis calcd (%) for $C_{15}H_{16}Br_2Si$: C 46.90, H 4.20; found: C 47.09, H 4.21.

*Dibromobis(triethylsilyl)methane (**12g**, prepared by method A from (dibromomethyl)triethylsilane and chlorotriethylsilane)*: $R_f = 0.74$ (hexane); IR (neat): $\tilde{\nu} = 2955$, 2878, 1462, 1414, 1379, 1242, 1009, 818, 743, 679 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 0.90$ (q, $J = 7.8$ Hz, 12H), 1.10 (t, $J = 7.8$ Hz, 18H); ^{13}C NMR ($CDCl_3$): $\delta = 4.8$, 8.3, 58.2; elemental analysis calcd (%) for $C_{13}H_{30}Br_2Si_2$: C 38.81, H 7.52; found: C 38.63, H 7.62.

*Dibromo(tert-butyldimethylsilyl)(trimethylsilyl)methane (12h, prepared by method A from **12a** and chlorotrimethylsilane)*: $R_f = 0.77$ (hexane); IR (neat): $\tilde{\nu} = 2932$, 2860, 1464, 1252, 847, 772, 691 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 0.26$ (s, 6H), 0.33 (s, 9H), 1.11 (s, 9H); ^{13}C NMR ($CDCl_3$): $\delta = -3.55$, −0.58, 20.64, 57.30; elemental analysis calcd (%) for $C_{10}H_{24}Br_2Si_2$: C 33.34, H 6.71; found: C 33.30, H 6.83.

*Dibromobis(dimethylphenylsilyl)methane (**12j**, prepared by method B)*: $R_f = 0.61$ (hexane/ethyl acetate 30:1); m.p. 63 °C; IR (Nujol): $\tilde{\nu} = 1427$, 1252, 1117, 839, 785, 735, 700, 640 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 0.33$ (s, 12H), 7.32–7.46 (m, 6H), 7.67 (dd, $J = 1.5$, 7.8 Hz, 4H); ^{13}C NMR ($CDCl_3$): $\delta = -3.1$, 56.0, 127.6, 130.1, 135.2, 135.6; elemental analysis calcd (%) for $C_{17}H_{22}Br_2Si_2$: C 46.16, H 5.01; found: C 46.08, H 4.94.

*Dibromobis(methyldiphenylsilyl)methane (**12k**, prepared by method C)*: m.p. 174 °C; IR (Nujol): $\tilde{\nu} = 1429$, 1252, 1103, 814, 789, 719, 700 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 0.27$ (s, 6H), 7.35 (dd, $J = 7.2$, 8.1 Hz, 8H), 7.44 (t, $J = 7.2$ Hz, 4H), 7.79 (d, $J = 8.1$ Hz, 8H); ^{13}C NMR ($CDCl_3$): $\delta = -2.7$, 50.2, 127.6, 130.1, 134.1, 136.5; elemental analysis calcd (%) for $C_{27}H_{26}Br_2Si_2$: C 57.25, H 4.63; found: C 56.98, H 4.53.

*Dibromo(methyldiphenylsilyl)(triethylgermyl)methane (**12l**, prepared by method A from **12a** and chlorotriethylgermane)*: $R_f = 0.47$ (hexane/ethyl acetate 40:1); IR (neat): $\tilde{\nu} = 2950$, 2870, 1460, 1427, 1252, 1111, 1014, 813, 696 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 0.82–0.92$ (m, 6H), 0.87 (s, 3H), 0.96–1.04 (m, 9H), 7.37–7.47 (m, 6H), 7.86–7.92 (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta = -2.1$, 6.4, 9.2, 53.3, 127.7, 130.0, 134.3, 136.3; elemental analysis calcd (%) for $C_{20}H_{28}Br_2GeSi$: C 45.42, H 5.34; found: C 45.14, H 5.22.

Procedure for the monomethylation of dibromodisilylmethanes 12 with Me_3MgLi: A solution of lithium trimethylmagnesate, [prepared by mixing methylmagnesium bromide (10.8 mL, 0.93M solution in THF, 10 mmol) and methyllithium (17.5 mL, 1.14M solution in Et_2O, 20 mmol) in THF (15 mL)] was added to a solution of **12** (10 mmol) in THF (50 mL) at −78 °C under an argon atmosphere. After stirring for 0.5 h at −78 °C, the mixture was carefully poured into 1M HCl and extracted with AcOEt. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica-gel column chromatography or recrystallization provided **25**.

*(1-Bromoethyl)methyldiphenylsilane (**25a**)*: $R_f = 0.36$ (hexane/ethyl acetate 40:1); IR (neat): $\tilde{\nu} = 2956$, 1428, 1254, 1114, 1006, 790, 731, 697 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 0.73$ (d, $J = 0.6$ Hz, 3H), 1.74 (dd, $J = 0.6$, 7.5 Hz, 3H), 3.86 (q, $J = 7.5$ Hz, 1H), 7.34–7.47 (m, 6H), 7.55–7.60 (m, 2H), 7.60–7.66 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = -6.3$, 20.9, 33.9, 128.0, 128.0, 129.9 (2C), 134.2, 134.3, 135.1, 135.1; elemental analysis calcd (%) for $C_{15}H_{17}BrSi$: C 59.01, H 5.61; found: C 59.07, H 5.60.

*2-Bromo-2-(methyldiphenylsilyl)propane (**25e**)*: $R_f = 0.36$ (hexane/ethyl acetate 40:1); IR (neat): $\tilde{\nu} = 3071$, 2951, 1427, 1254, 1111, 1088, 893, 791, 727, 700 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 0.78$ (s, 3H), 1.86 (s, 6H), 7.35–7.48 (m, 6H), 7.71–7.77 (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta = -5.1$, 31.3, 53.7, 127.9, 129.8, 134.1, 135.7; elemental analysis calcd (%) for $C_{16}H_{19}BrSi$: C 60.18, H 6.00; found: C 60.23, H 5.96.

*1-Bromo-1-(methyldiphenylsilyl)-1-(trimethylsilyl)ethane (**25f**)*: $R_f = 0.44$ (hexane/ethyl acetate 40:1); IR (neat): $\tilde{\nu} = 2955$, 1427, 1252, 1109, 964, 841, 802, 736, 721, 700 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = -0.10$ (s, 9H), 0.79 (s, 3H), 1.92 (s, 3H), 7.30–7.48 (m, 6H), 7.72 (dd, $J = 1.8$, 7.8 Hz, 2H), 7.86 (dd, $J = 1.8$, 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta = -2.2$, −1.8, 23.7, 43.9, 127.5, 127.8, 129.5, 129.6, 135.0, 135.3, 135.8, 136.0; elemental analysis calcd (%) for $C_{18}H_{25}BrSi_2$: C 57.28, H 6.68; found: C 57.53, H 6.67.

*1-Bromo-1,1-bis(triethylsilyl)ethane (**25g**)*: $R_f = 0.84$ (hexane); IR (neat): $\tilde{\nu} = 2955$, 2878, 1462, 1416, 1379, 1242, 1007, 970, 777, 735 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 0.76$ (q, $J = 8.4$ Hz, 6H), 0.78 (q, $J = 7.8$ Hz, 6H), 1.04 (t, $J = 7.8$ Hz, 9H), 1.04 (t, $J = 8.4$ Hz, 9H), 1.82 (s, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 4.0$, 8.3, 25.0, 47.2; elemental analysis calcd (%) for $C_{14}H_{33}BrSi_2$: C 49.82, H 9.86; found: C 49.80, H 9.56.

*1-Bromo-1-(tert-butyldimethylsilyl)-1-(trimethylsilyl)ethane (**25h**)*: $R_f = 0.77$ (hexane); IR (neat): $\tilde{\nu} = 2956$, 2854, 1467, 1252, 966, 840, 822, 766 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 0.11$ (s, 3H), 0.17 (s, 3H), 0.15 (s, 9H), 1.02 (s, 9H), 1.85 (s, 3H); ^{13}C NMR ($CDCl_3$): $\delta = -4.3$, −4.1, −1.2, 20.1, 24.3, 28.3, 45.9; elemental analysis calcd (%) for $C_{11}H_{27}BrSi_2$: C 44.72, H 9.21; found: C 44.42, H 9.42.

*1-Bromo-1,1-bis(trimethylsilyl)ethane (**25i**)*: $R_f = 0.72$ (hexane); IR (neat): $\tilde{\nu} = 2955$, 1252, 966, 841, 760, 691 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 0.14$ (s, 18H), 1.71 (s, 3H); ^{13}C NMR ($CDCl_3$): $\delta = -1.6$, 23.0, 45.0; elemental analysis calcd (%) for $C_8H_{21}BrSi_2$: C 37.93, H 8.36; found: C 37.78, H 8.49.

*1-Bromo-1,1-bis(dimethylphenylsilyl)ethane (**25j**)*: $R_f = 0.46$ (hexane/ethyl acetate 40:1); m.p. 73 °C; IR (Nujol): $\tilde{\nu} = 1587$, 1427, 1258, 1111, 966, 827, 783, 739, 702, 671 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 0.25$ (s, 6H), 0.26 (s, 6H), 1.82 (s, 3H), 7.32–7.44 (m, 6H), 7.59 (dd, $J = 1.8$, 7.8 Hz, 4H); ^{13}C NMR ($CDCl_3$): $\delta = -3.9$, −3.4, 23.5, 44.1, 127.6, 129.5, 135.1, 136.7; elemental analysis calcd (%) for $C_{18}H_{25}BrSi_2$: C 57.28, H 6.68; found: C 57.39, H 6.71.

*1-Bromo-1,1-bis(methyldiphenylsilyl)ethane (**25k**)*: m.p. 126 °C; IR (Nujol): $\tilde{\nu} = 1429$, 1254, 1103, 999, 964, 797, 735, 698 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 0.23$ (s, 6H), 2.12 (s, 3H), 7.26–7.43 (m, 12H), 7.58 (dd, $J = 1.2$, 7.8 Hz, 4H), 7.76 (dd, $J = 1.2$, 7.8 Hz, 4H); ^{13}C NMR ($CDCl_3$): $\delta = -3.4$, 24.5, 42.3, 127.6, 127.7, 129.6, 134.8, 135.3, 136.0, 136.3; elemental analysis calcd (%) for $C_{28}H_{29}BrSi_2$: C 67.05, H 5.63; found: C 66.86, H 5.87.

*1-Bromo-1-(methyldiphenylsilyl)-1-(triethylgermyl)ethane (**25l**)*: $R_f = 0.51$ (hexane/ethyl acetate 40:1); IR (neat): $\tilde{\nu} = 2948$, 2868, 1458, 1428, 1253, 1109, 1014, 791, 734, 698 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 0.75$ (t, $J = 7.5$ Hz, 6H), 0.79 (s, 3H), 0.96 (t, $J = 7.5$ Hz, 9H), 2.03 (s, 3H), 7.30–7.45 (m, 6H), 7.72 (dd, $J = 1.5$, 7.8 Hz, 2H), 7.85 (dd, $J = 1.5$, 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta = -2.6$, 5.0, 6.5, 9.4, 25.9, 127.5, 127.7, 129.4, 129.6, 135.1, 135.3, 135.7, 136.0; elemental analysis calcd (%) for $C_{21}H_{31}BrGeSi$: C 54.35, H 6.73; found: C 54.58, H 6.67.

Procedure for the synthesis of 1,1-disilylethenes 29 by dehydrobromination of 1-bromo-1,1-disilylethanes 25: A solution of **25** (9.0 mmol) and DBU (2.7 mL, 18.0 mmol) in DMF (40 mL) was stirred for 8 h at 90 °C. The mixture was carefully poured into 1M HCl and extracted with AcOEt. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica-gel column chromatography or recrystallization provided **29**. Spectral data for **29i** were identical with those reported in the literature.[19a]

*1-(Methyldiphenylsilyl)-1-(trimethylsilyl)ethene (**29f**)*: $R_f = 0.52$ (hexane/ethyl acetate 40:1); IR (neat): $\tilde{\nu} = 2957$, 1427, 1250, 1113, 972, 839, 789, 737, 723, 700 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = -0.04$ (s, 9H), 0.68 (s, 3H), 6.24 (d, $J = 5.1$ Hz, 1H), 6.55 (d, $J = 5.1$ Hz, 1H), 7.30–7.40 (m, 6H), 7.48 (dd, $J = 2.1$, 7.5 Hz, 4H); ^{13}C NMR ($CDCl_3$): $\delta = -2.7$, −0.4, 127.7, 129.2, 135.3, 136.8, 144.9, 150.8; elemental analysis calcd (%) for $C_{18}H_{24}Si_2$: C 72.90, H 8.16; found: C 72.86, H 8.06.

*1,1-Bis(triethylsilyl)ethene (**29g**)*: $R_f = 0.85$ (hexane); IR (neat): $\tilde{\nu} = 2955$, 1462, 1416, 1236, 1005, 966, 814, 733 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 0.61$ (q,

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$J = 7.8$ Hz, 12H), 0.90 (t, $J = 7.8$ Hz, 18H), 6.37 (s, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 3.5$, 7.2, 143.3, 147.4; HRMS (m/z) calcd for $C_{14}H_{32}Si_2$ 256.2043; found: 256.2034.

1-(tert-Butyldimethylsilyl)-1-(trimethylsilyl)ethene (**29h**): $R_f = 0.81$ (hexane); IR (neat): $\tilde{\nu} = 2957$, 1472, 1408, 1362, 1248, 1148, 966, 837, 770, 675 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 0.08$ (s, 6H), 0.09 (s, 9H), 0.85 (s, 9H), 6.34 (d, $J = 4.8$ Hz, 1H), 6.43 (d, $J = 4.8$ Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = -4.4$, 0.1, 17.1, 26.9, 142.9, 152.0; elemental analysis calcd (%) for $C_{11}H_{26}Si_2$: C 61.60, H 12.22; found: C 61.39, H 12.48.

1,1-Bis(dimethylphenylsilyl)ethene (**29j**): $R_f = 0.53$ (hexane/ethyl acetate 80:1); IR (neat): $\tilde{\nu} = 1564$, 1427, 1248, 1111, 968, 841, 781, 729, 700, 640 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 0.25$ (s, 12H), 6.41 (s, 2H), 7.25–7.36 (m, 6H), 7.38–7.44 (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta = -2.0$, 127.7, 128.9, 134.2, 139.0, 144.0, 151.0; elemental analysis calcd (%) for $C_{18}H_{24}Si_2$: C 72.90, H 8.16; found: C 73.02, H 8.31.

1,1-Bis(methyldiphenylsilyl)ethene (**29k**): m.p. 123 °C; IR (Nujol): $\tilde{\nu} = 1427$, 1261, 1113, 980, 829, 789, 739, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 0.34$ (s, 6H), 6.41 (s, 2H), 7.18–7.32 (m, 12H), 7.35 (d, $J = 7.5$ Hz, 8H); ^{13}C NMR ($CDCl_3$): $\delta = -2.8$, 127.6, 129.1, 135.1, 136.4, 146.7, 149.6; elemental analysis calcd (%) for $C_{28}H_{28}Si_2$: C 79.94, H 6.71; found: C 79.83, H 6.80.

1-(Methyldiphenylsilyl)-1-(triethylgermyl)ethene (**29l**): $R_f = 0.49$ (hexane); IR (neat): $\tilde{\nu} = 2948$, 1428, 1251, 1111, 1015, 965, 808, 788, 735, 718, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 0.66$ (s, 3H), 0.69 (q, $J = 7.8$ Hz, 6H), 0.91 (t, $J = 7.8$ Hz, 9H), 6.29 (d, $J = 4.5$ Hz, 1H), 6.41 (d, $J = 4.5$ Hz, 1H), 7.30–7.42 (m, 6H), 7.45–7.54 (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta = -3.0$, 4.6, 8.7, 127.7, 129.2, 135.2, 136.8, 143.8, 149.1; elemental analysis calcd (%) for $C_{21}H_{30}GeSi$: C 65.83, H 7.89; found: C 65.67, H 7.81.

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[1] a) P. Kocienski, C. Barber, *Pure Appl. Chem.* **1990**, *62*, 1933; b) A. Sidduri, M. J. Rozema, P. Knochel, *J. Org. Chem.* **1993**, *58*, 2694; c) A. Sidduri, P. Knochel, *J. Am. Chem. Soc.* **1992**, *114*, 7579; d) A. N. Kasatkin, R. J. Whitby, *Tetrahedron Lett.* **2000**, *41*, 6211, and references therein.

[2] a) R. W. Hoffmann, O. Knopff, A. Kusche, *Angew. Chem.* **2000**, *112*, 1521; *Angew. Chem. Int. Ed.* **2000**, *39*, 1462; b) R. W. Hoffmann, B. Hölzer, O. Knopff, K. Harms, *Angew. Chem.* **2000**, *112*, 3206; *Angew. Chem. Int. Ed.* **2000**, *39*, 3072; c) A. Shibli, J. P. Varghese, P. Knochel, I. Marek, *Synlett* **2001**, 818; d) G. Köbrich, *Bull. Soc. Chim. Fr.* **1969**, 2712.

[3] a) Y. Kondo, N. Takazawa, C. Yamazaki, T. Sakamoto, *J. Org. Chem.* **1994**, *59*, 4717; b) M. Uchiyama, M. Koike, M. Kameda, Y. Kondo, T. Sakamoto, *J. Am. Chem. Soc.* **1996**, *118*, 8733; c) M. Uchiyama, M. Kameda, O. Mishima, N. Yokoyama, M. Koike, Y. Kondo, T. Sakamoto, *J. Am. Chem. Soc.* **1998**, *120*, 4934; d) Y. Kondo, T. Matsudaira, J. Sato, N. Murata, T. Sakamoto, *Angew. Chem.* **1996**, *108*, 818; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 736.

[4] a) T. Harada, D. Hara, K. Hattori, A. Oku, *Tetrahedron Lett.* **1988**, *29*, 3821; b) T. Harada, T. Katsuhira, A. Oku, *J. Org. Chem.* **1992**, *57*, 5805; c) T. Harada, T. Katsuhira, D. Hara, Y. Kotani, K. Maejima, R. Kaji, A. Oku, *J. Org. Chem.* **1993**, *58*, 4897; d) T. Harada, Y. Kotani, T. Katsuhira, A. Oku, *Tetrahedron Lett.* **1991**, *32*, 157; e) T. Harada, T. Katsuhira, A. Osada, K. Iwazaki, K. Maejima, A. Oku, *J. Am. Chem. Soc.* **1996**, *118*, 11377; f) T. Harada, T. Kaneko, T. Fujiwara, A. Oku, *J. Org. Chem.* **1997**, *62*, 8966; g) T. Harada, T. Kaneko, T. Fujiwara, A. Oku, *Tetrahedron* **1998**, *54*, 9317; h) R. Inoue, H. Shinokubo, K. Oshima, *J. Org. Chem.* **1998**, *63*, 910; i) K. Oshima, *J. Organomet. Chem.* **1999**, *575*, 1.

[5] For the reaction of *gem*-dibromocyclopropanes, see: a) K. Kitatani, T. Hiyama, H. Nozaki, *J. Am. Chem. Soc.* **1976**, *98*, 2362; b) K. Kitatani, T. Hiyama, H. Nozaki, *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1600; c) K. Kitatani, H. Yamamoto, T. Hiyama, H. Nozaki, *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2158; d) R. Hässig, H. Siegel, D. Seebach, *Chem. Ber.* **1982**, *115*, 1990; e) T. Harada, K. Hattori, T. Katsuhira, A. Oku, *Tetrahedron Lett.* **1989**, *30*, 6035; f) T. Harada, T. Katsuhira, K. Hattori, A. Oku, *J. Org. Chem.* **1993**, *58*, 2958; g) R. Inoue, H. Shinokubo, K. Oshima, *Tetrahedron Lett.* **1996**, *37*, 5377; h) H. Kakiya, R. Inoue, H. Shinokubo, K. Oshima, *Tetrahedron* **2000**, *56*, 2131; for the reaction of dibromomethylsilanes, see: i) H. Kakiya, R. Inoue, H. Shinokubo, K. Oshima, *Tetrahedron Lett.* **1997**, *38*, 3275; j) H. Kakiya, H. Shinokubo, K. Oshima, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2139.

[6] a) K. Kitagawa, A. Inoue, H. Shinokubo, K. Oshima, *Angew. Chem.* **2000**, *112*, 2594; *Angew. Chem. Int. Ed.* **2000**, *39*, 2481; b) A. Inoue, K. Kitagawa, H. Shinokubo, K. Oshima, *J. Org. Chem.* **2001**, *66*, 4333; c) A. Boudier, L. O. Bromm, M. Lotz, P. Knochel, *Angew. Chem.* **2000**, *112*, 4584; *Angew. Chem. Int. Ed.* **2000**, *39*, 4414.

[7] a) G. Wittig, F. J. Meyer, G. Lange, *Justus Liebigs Ann. Chem.* **1951**, *571*, 167; b) T. Greiser, J. Kopf, D. Thoennes, E. Weiss, *Chem. Ber.* **1981**, *114*, 209; c) D. Thoennes, E. Weiss, *Chem. Ber.* **1978**, *111*, 3726; d) L. M. Seitz, T. L. Brown, *J. Am. Chem. Soc.* **1966**, *88*, 4140; e) R. E. Mulvey, *Chem. Commun.* **2001**, 1049.

[8] For the use of a magnesate reagent, see: a) M. Yasuda, M. Ide, Y. Matsumoto, M. Nakata, *Synlett* **1998**, 899; b) M. Yasuda, M. Ide, Y. Matsumoto, M. Nakata, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1417; c) M. Ide, M. Yasuda, M. Nakata, *Synlett* **1998**, 936; d) M. Ide, M. Yasuda, M. Nakata, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2491; e) E. C. Ashby, L.-C. Chao, J. Laemmle, *J. Org. Chem.* **1974**, *39*, 3258; f) H. G. Richey, Jr., J. Farkas, Jr., *Tetrahedron Lett.* **1985**, *26*, 275; g) H. G. Richey, Jr., J. Farkas, Jr., *Organometallics* **1990**, *9*, 1778.

[9] a) P. Knochel, M. C. P. Yeh, S. C. Berk, J. Talbert, *J. Org. Chem.* **1988**, *53*, 2390; b) P. Knochel, R. D. Singer, *Chem. Rev.* **1993**, *93*, 2117; c) P. Knochel, *Synlett* **1995**, 393.

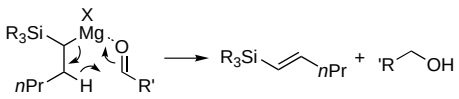
[10] a) C. Bacquet, D. Masure, J. F. Normant, *Bull. Soc. Chim. Fr.* **1975**, 1797; b) H. Shinokubo, K. Miura, K. Oshima, K. Utimoto, *Tetrahedron* **1996**, *52*, 503.

[11] a) J. S. Panek in *Comprehensive Organic Synthesis*, *Vol. 1* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, p. 579; b) D. J. Peterson, *J. Org. Chem.* **1968**, *33*, 780; c) K. Itami, K. Mitsudo, J. Yoshida, *Tetrahedron Lett.* **1999**, *40*, 5533; d) A. G. Brook, J. M. Duff, D. G. Anderson, *Can. J. Chem.* **1970**, *48*, 561; e) G. R. Buell, R. J. P. Corriu, C. Guerin, L. Spialter, *J. Am. Chem. Soc.* **1970**, *92*, 7424.

[12] E. Negishi, K. Akiyoshi, *J. Am. Chem. Soc.* **1988**, *110*, 646.

[13] a) E. W. Colvin, *Silicon Reagents in Organic Synthesis*, Academic Press, London, **1988**, p. 77; b) K. Utimoto, M. Obayashi, H. Nozaki, *J. Org. Chem.* **1976**, *41*, 2940; c) M. Obayashi, K. Utimoto, H. Nozaki, *Tetrahedron Lett.* **1978**, 1383; d) M. Obayashi, K. Utimoto, H. Nozaki, *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2646; e) D. Enders, D. Ward, J. Adam, G. Raade, *Angew. Chem.* **1996**, *108*, 1059; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 981; f) D. Enders, J. Adam, D. Klein, T. Otten, *Synlett* **2000**, 1371.

[14] The reaction of **16** with aldehydes resulted in formation of the reduced alcohols and 1-alkeneylsilanes.



[15] Reaction of α-silylalkylmetals with acyl chloride, see: a) F. C. Whitmore, L. H. Sommer, J. Gold, R. E. V. Strien, *J. Am. Chem. Soc.* **1947**, *69*, 1551; b) T. H. Chan, E. Chang, E. Vinokur, *Tetrahedron Lett.* **1970**, 1137; c) D. E. Seitz, A. Zapata, *Synthesis* **1981**, 557.

[16] a) S. Matsuzawa, Y. Horiguchi, E. Nakamura, I. Kuwajima, *Tetrahedron* **1989**, *45*, 349; b) H. Andringa, I. Oosterveld, L. Brandsma, *Synth. Commun.* **1991**, *21*, 1393.

[17] a) K. Yoon, D. Y. Son, *J. Organomet. Chem.* **1997**, *545–546*, 185; b) C. Eaborn, W. Clegg, P. B. Hitchcock, M. Hopman, K. Izod, P. N. O'Shaughnessy, J. D. Smith, *Organometallics* **1997**, *16*, 4728; c) N. Wiberg, K.-S. Joo, K. Polborn, *J. Organomet. Chem.* **1996**, *524*, 147.

[18] Bromine–magnesium exchange of one of the two bromines and the subsequent addition of methyl iodide did not give the methylation product in comparable yield. Therefore, the mechanism including the reaction of carbenoid species **26** with MeBr is not plausible.

[19] For preparations of 1,1-disilylalkenes, see: a) B.-T. Gröbel, D. Seebach, *Chem. Ber.* **1977**, *110*, 852; b) G. Fritz, J. Grobe, *Z. Anorg. Allg. Chem.* **1961**, *309*, 77; c) I. Fleming, C. D. Floyd, *J. Chem. Soc. Perkin Trans. 1* **1981**, 969; d) I. Fleming, U. Ghosh, *J. Chem. Soc. Perkin Trans. 1* **1994**, 257; e) K. Narasaka, N. Saito, Y. Hayashi, H. Ichida, *Chem. Lett.* **1990**, 1411; f) D. M. Hodgson, P. J. Comina, M. G. B. Drew, *J. Chem. Soc. Perkin Trans. 1* **1997**, 2279; g) E. Negishi, L. D. Boardman, H. Sawada, V. Bagheri, A. T. Stoll, J. M. Tour, C. L. Rand, *J. Am. Chem. Soc.* **1988**, *110*, 5383; h) C. Flann, T. C. Malone, L. E. Overman, *J. Am. Chem. Soc.* **1987**, *109*, 6097.

[20] For reaction of 1,1-disilylalkenes, see: a) B.-T. Gröbel, D. Seebach, *Angew. Chem.* **1974**, *86*, 102; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 83; b) D. Seebach, R. Bürstinghaus, B.-T. Gröbel, M. Kolb, *Justus Liebigs Ann. Chem.* **1977**, 830; c) B.-T. Gröbel, D. Seebach, *Chem. Ber.* **1977**, *110*, 867; d) M. Kira, T. Hino, Y. Kubota, N. Matsuyama, H. Sakurai, *Tetrahedron Lett.* **1988**, *29*, 6939. See also Refs. [19f–h].

[21] Y. Gai, M. Julia, J.-N. Verpeaux, *Bull. Soc. Chim. Fr.* **1996**, *133*, 817.

[22] a) J. Kondo, A. Inoue, H. Shinokubo, K. Oshima, *Angew. Chem.* **2001**, *113*, 2146; *Angew. Chem. Int. Ed.* **2001**, *40*, 2085; b) A. Inoue, J. Kondo, H. Shinokubo, K. Oshima, *Chem. Lett.* **2001**, 956.

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  0947-6539/02/0807-1740 $ 20.00+.50/0