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Thermal [3,3]-rearrangement of 1,1-disubstituted allyl carboxylates: lone pair participation and the geminal bond participation

Yuji Naruse *, Aya Deki, Katsura Yamada

Department of Chemistry, Gifu University 1-1 Yanagido, Gifu 501-1193, Japan

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ABSTRACT

The diastereoselectivity of the [3,3]-rearrangement of 1,1-disubsstituted allyl carboxylates was studied. In this heteroatom-containing system, the transition state has a boat-like transition structure (TS) because of the participation of the lone pairs and the secondary orbital interaction. Although the TS for the [1,3]-rearrangement has a far higher barrier, it does not proceed in the usual antarafacial manner due to the cyclic orbital interaction among two lone pairs of the carboxylate and the allylic lumo. In conjunction with the geminal bond participation, delocalization to the σ-bond at the Z-position shows a bonding character in the transition state of the [3,3]-rearrangement. Therefore, we predicted that a more electron-withdrawing σ-bond prefers the Z-position in the product. We designed the 1,1-disubstituted substrates with trimethylsilyl and pentyl groups, and found that the trimethylsilyl group prefers the Z-position despite its steric bulkiness. We confirmed our prediction by experimentation. This Z-selectivity was improved when a trimethylgermyl group was used.

1. Introduction

Recently, we have shown that the bonds geminal to the reaction center take part in the reaction and alter the reactivity/selectivity in the pericyclic reaction, as well as the aldol reaction.[1] Such geminal bond participation is under the control of phase continuity requirements (Fig. 1).[2] Phase discontinuity of the cyclic orbital interaction among the two σ-bonds geminal to the reaction center and the accepting bond results in the predominance of the bonding character of one geminal σ-bond and suppresses the other delocalization.[1]

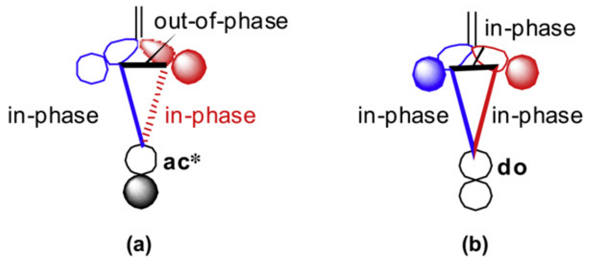

Figure 1. Phase continuity condition in (a) cyclic orbital interaction from the geminal bonds to the accepting orbital (**ac***) and (b) that from the donating orbital (**do**) to the geminal bonds.

Introduction of a heteroatom to the system alters the reactivity/selectivity for two main reasons. First, the more polar nature of the bonds changes the bond energies and the overlaps. Second, this can result in the presence of lone pairs. Lone pairs are more electron-donating than σ-bonds, and are not suitable as an accepting orbital.

We have demonstrated that a more electron-donating σ-bond prefers the Z-position of the product in Cope rearrangements.[3] We sought to modify this reaction by introducing two oxygens in the [3,3]-rearrangement of 1,1-disubstituted allyl carboxylates. We report here a successful realization of this venture.

2. Results and discussion

We chose allyl formate **1a** as a model substrate to clarify the effect of the geminal bond participation on selectivity. We located the transition state (TS) structure at the B3LYP/6-31G(d) level (Scheme 1, Figs. 2 and 3).[4] Interestingly, the transition structure prefers a boat conformation and no chair-like TS structure was found, in contrast to the chair-form in the carbocongener Cope reaction.[3] To probe the electronic structure in the TS, we subjected them to the bond model analysis.[5,6] In the transition state, the Lewis index (coefficient of the ground state) C_G of the reactant and ionic models are 1.105 and 0.888, respectively (Fig. 4). Thus, the TS has a considerable ion-pair character composed of an allyl cation and a formate ion. This ion-pair picture of the TS helps us to

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* Corresponding author. Tel.: +81 58 293 2615; fax: +81 58 293 2794; e-mail address: naruse@gifu-u.ac.jp (Y. Naruse).

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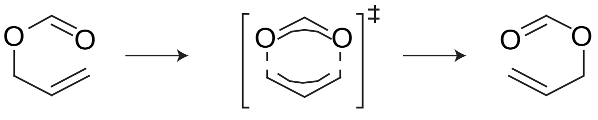
understand the boat-form TS structure (Fig. 5). The HOMO of the formate (−0.1583 a.u.) is the antisymmetric π-orbital (π_2). However, the antisymmetric combination of the lone pairs on the oxygens (n_{Oa}) and the symmetrical combination together with the out-of-phase σ_{CH} orbital ($n_{Os}-\sigma_{CH}$) have almost the same energy (−0.1814 a.u. and −0.1600 a.u., respectively). On the other hand, in the allyl part, the lumo is low (−0.2169 a.u.) and the nlumo is also fairly low (−0.0143 a.u.). These orbitals prefer to interact with the lone pairs (NHOMO $n_{Os}-\sigma_{CH}$ and HOMO−2n_{Oa}) than with the π-system (π_1 and HOMO π_2), where the π_1 orbital is quite low in energy (−0.3169 a.u.). With the lone pairs, the π-planes of the formate and the allyl cation should be perpendicular to each other. However, the orbital at the center carbon in the nlumo, which is out-of-phase to those at the terminal carbons, can interact with the back lobes of the lone pairs in the NHOMO. The overlap between the NHOMO and the nlumo can be increased by tilting into a boat form (Fig. 6). This secondary orbital interaction should stabilize the TS.



1a

Scheme 1. [3,3]-Rearrangement of **1a**.

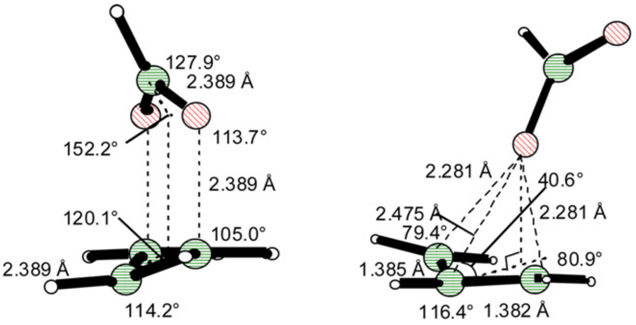


Figure 2. [3,3]- and [1,3]-TS structures calculated at the B3LYP/6-31G(d).

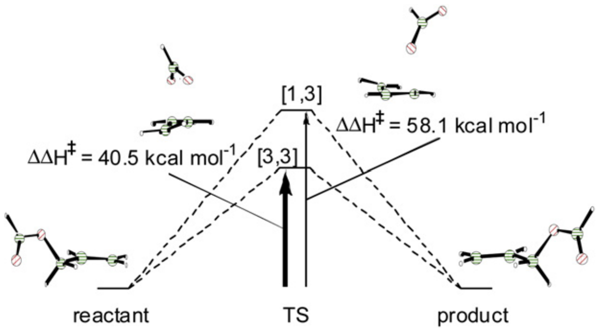


Figure 3. Reaction coordinates of the [3,3]- and [1,3]-rearrangement.

C_G = 1.105
(a) Reactant bond model
(or product bond model)

C_G = 0.888
(b) Ion-pair bond model

Figure 4. Bond models and Lewis index (C_G) for the transition structure of the [3,3] rearrangement of allyl formate **1a** (RHF/6-31G(d)).

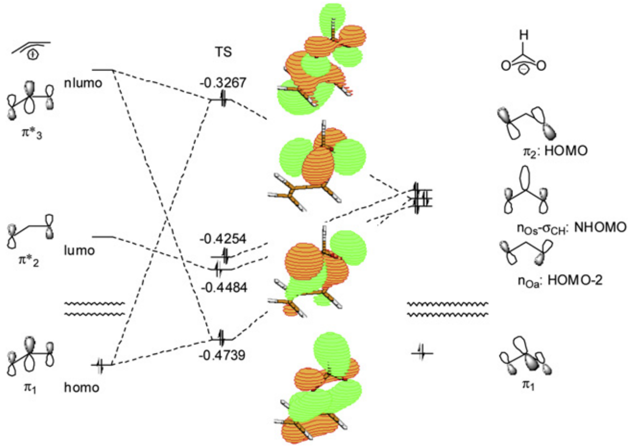


Figure 5. Orbital interaction diagram of the TS (orbital energies in a.u.; MP2/6-31G(d)//B3LYP/6-31G(d)).

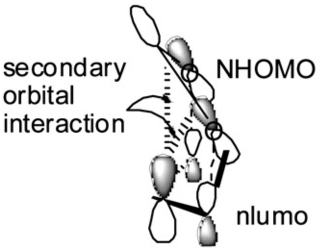
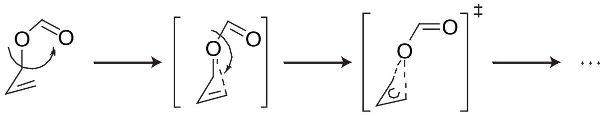


Figure 6. Secondary orbital interaction in the TS of **1a**.

Another route to the product is [1,3]-rearrangement of the carboxylate.[8] This reaction path is not important since the enthalpy of activation is considerably higher ($\Delta\Delta H^{\ddagger}$=58.1 kcal mol^{-1}) than that of [3,3]-rearrangement ($\Delta\Delta H^{\ddagger}$=40.5 kcal mol^{-1}) (Fig. 3). However, it is noteworthy that [1,3]-rearrangement does not occur in the usual antarafacial manner (Fig. 2). In the initial stage of the reaction, the IRC calculation[7] shows that the carboxylate group rotates around the C–O bond, and then the dissociation and formation of C–O bonds occur (Scheme 2). Out-of-phase combination of the lone pairs on the oxygen terminal and the allylic lumo satisfy the phase continuity (Fig. 7a).[2] Cyclic delocalization among them should



Scheme 2. Reaction route for the [1,3]-rearrangement of **1a**.

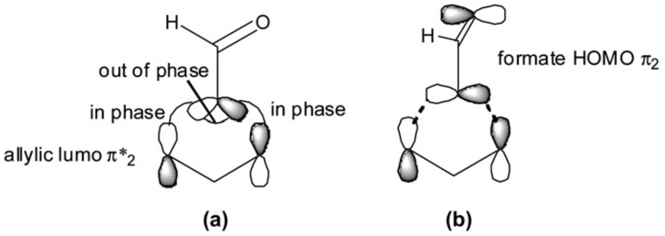


Figure 7. Phase conditions of (a) the lone pair participation in the TS and (b) the ordinary antarafacial TS of **1a**.

provide greater stability than the interaction between the formate HOMO and the allylic lumo (Fig. 7b).

In the TS of the [3,3]-rearrangement, the difference in delocalization from the donor to the geminal σ-bonds of the substituents is greater than that from the geminal σ-bonds (Fig. 8 and Table 1). This is in sharp contrast to the situation in Cope rearrangement. The greatest difference in interaction is between the lone pair on the oxygen and the σ* orbital of the geminal bonds (Fig. 9). With these results in hand, we can predict that a more electron-withdrawing σ-bond should occupy the Z-position in the product.

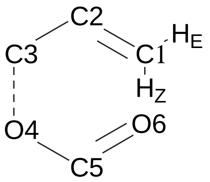


Figure 8. Atom numbering in the TS.

Table 1
IBE values[9] (a.u.) of the bond interactions in the transition state for the [3,3]-rearrangement of **1a** (RHF/6-31G(d))

Interaction	IBE (a.u.)
$\pi_{C5-O6}-\sigma^*_{C1-HZ}$	0.0018
$\pi_{C5-O6}-\sigma^*_{C1-HE}$	−0.0044
$n_{O6a}-\sigma^*_{C1-HZ}$	−0.0019
$n_{O6a}-\sigma^*_{C1-HE}$	−0.0008
$n_{O6b}-\sigma^*_{C1-HZ}$	−0.0137
$n_{O6b}-\sigma^*_{C1-HE}$	0.0050
$\sigma_{C1-HZ}-\pi^*_{C5-O6}$	−0.0010
$\sigma_{C1-HE}-\pi^*_{C5-O6}$	−0.0042

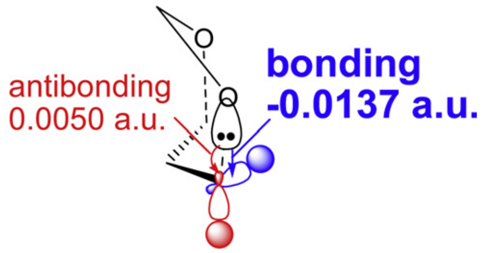
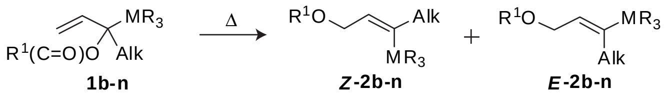


Figure 9. IBE values (a.u.) in the transition state of **1a**.

We designed silyl- and alkyl-substituted substrates as good candidates to test our prediction (Scheme 3). The σ* orbital energy level of a Si–C bond is lower than that of a C–C bond. Thus, the Si–C bond is more electron-withdrawing than a C–C bond, and the silyl group should occupy the Z-position in the product.



1b: $MR_3 = SiH_3$; Alk = Me; $R^1 = H$
1c: $MR_3 = SiMe_3$; Alk = Me; $R^1 = Me$
1d: $MR_3 = SiMe_3$; Alk = nC_5H_{11}; $R^1 = Me$
1e: $MR_3 = SiMe_3$; Alk = nC_5H_{11}; $R^1 = CH_2Cl$
1f: $MR_3 = SiMe_3$; Alk = Me; $R^1 = CHCl_2$
1g: $MR_3 = SiMe_3$; Alk = nC_5H_{11}; $R^1 = CHCl_2$
1h: $MR_3 = SiH_3$; Alk = nC_5H_{11}; $R^1 = CF_3$
1i: $MR_3 = GeH_3$; Alk = Me; $R^1 = Me$
1j: $MR_3 = GeMe_3$; Alk = Me; $R^1 = Me$
1k: $MR_3 = GeMe_3$; Alk = nC_5H_{11}; $R^1 = Me$
1l: $MR_3 = SiH_3$; Alk = nC_5H_{11}; $R^1 = CHCl_2$
1m: MR_3 = 1-methyl-1-silacyclopropyl; Alk = Me; R^1 = Me
1n: MR_3 = 1-methyl-1-silacyclobutyl; Alk = Me; R^1 = Me

Scheme 3.

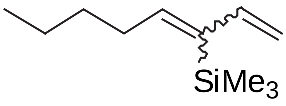
We performed a calculation for **1b** ($MR_3{=}SiH_3$, $Alk{=}CH_3$, $R^1{=}H$) at the B3LYP/6–31G(d) level. As expected, the Z-product is preferred by 2.0 kcal mol^{-1}. The difference in the enthalpies of activation corresponds to a selectivity of 94:6 under the kinetic control conditions (Table 2).

Table 2
Calculated enthalpies of activation, differences in calculated enthalpies of activation, calculated selectivities and heats of reaction for *Z*- and *E*-products (B3LYP/6-31G(d), in kcal mol^{-1})

Molecule	$\Delta H^{\ddagger}_{Z}$	$\Delta H^{\ddagger}_{E}$	$\Delta\Delta H^{\ddagger a}$	Calcd select.	$-\Delta H_Z{}^{b}$	$-\Delta H_E{}^{b}$
1b	31.4	33.4	2.0	94:6	5.9	6.1
1c	26.1	26.3	0.2	58:42	2.8	5.2
1f	27.7	28.1	0.3	63:37	3.4	4.7
1i	24.8	27.1	2.3	98:2	4.6	3.5
1j	25.7	27.3	1.6	94:6	9.0	7.6
1m	31.8	32.7	0.9	82:18	4.8	5.4
1n	24.7	26.1	1.4	91:9	4.5	5.4

[a] $\Delta\Delta H^{\ddagger}{=}\Delta H^{\ddagger}_{E}-\Delta H^{\ddagger}_{Z}$.
[b] $-\Delta H_{Z/E}{=}H_{\text{substrate}}-H_{Z/E\text{-product}}$.

We prepared substrate **1c** from 2-trimethylsilyl-3-buten-2-ol[10], and subjected it to the rearrangement reaction. However, the reaction proceeded at the higher temperature (>240 °C, 24 h), only to give the desired rearranged product in a small amount with much of the by-products. To avoid the loss during purification of the volatile product and to determine major by-products, we prepared **1d**[11,13] ($MR_3{=}SiMe_3$; $Alkyl{=}nC_5H_{11}$; $R^1{=}CH_3$) as illustrated in Figure 10. If difference in the steric repulsion of the trimethylsilyl group would be reduced using a longer chain alkyl group, the selectivity should be enhanced. The yield was determined by ^1H NMR analysis in comparison with the internal standard naphthalene, and the stereochemistry was confirmed by NOE experiments with the purified products. The major product was the *Z*-isomer *Z*-**2d** ($MR_3{=}SiMe_3$; $Alkyl{=}nC_5H_{11}$; $R^1{=}CH_3$), which agrees with our prediction (Table 3). However, the selectivity, *Z*/*E*=6:4, remained almost the same to **1c**. The reactivity and yield were improved by the introduction of halogen to the carboxylates (**1e**, **1g**, **1h**). However, this was accompanied by the



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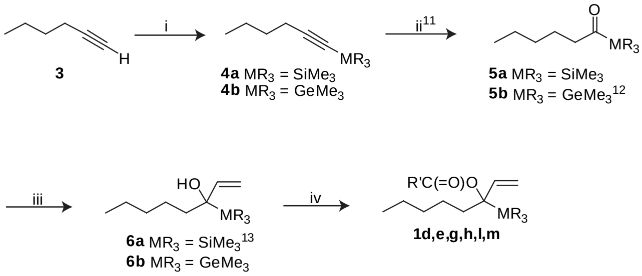

(i) BuLi-TMEDA, R_3MCl; (ii) BH_3SMe_2, Me_3NO; (iii) $CH_2{=}CHMgBr$
(iv) R'COCl, $CH_2{=}CHMgBr$

Figure 10. Reaction scheme for preparation of the substrates.

Table 3
Reaction conditions, observed yield and selectivity in the thermal [3,3]-rearrangement

Substrate	Reacn condx	Yield/%[a]	*Z*/*E* ratio	Other by-product (%)
1c	[b]	[b]	—	—
1d	200 °C, 48 h	48	58:42	n.d.[c]
1e	200 °C, 1.5 h	73	57:43	**7** (19)
1g	200 °C, 20 min	81	60:40	**7** (19)
1h	150 °C, 20 min	81	55:45	**7** (19)
1k	200 °C, 72 h	44	63:37	
1l	200 °C, 30 min	80	67:33	

[a] Determined by ^{1}H NMR compared with the internal standard of naphthalene.
[b] See text.
[c] Not determined.

production of some **7**[14], while the selectivities also remained almost the same.

We wondered what the decrease in selectivity comes from. To probe the question, we performed the bond model analysis for a C–Y bond (Y=CH_3, SiH_3, $SiMe_3$) in CH_3Y. The σ* orbital energy level of the C–Si bond is considerably increased by methyl substituents on silicon (Table 4). The steric bulkiness by trimethyl substitution on the silicon atom should also result in lower selectivity.

Table 4
The bond orbital energy level of σ^*_{CM} in CH_3MR_3 (RHF/6-31G(d))

MR_3	σ^*_{CM}
CH_3	0.679
SiH_3	0.508
$SiMe_3$	0.613
GeH_3	0.348
$GeMe_3$	0.374
1-methyl-1-silacyclopropyl	0.559
1-methyl-1-silacyclobutyl	0.571

We further considered the substrates to improve the Z-selectivity. To enhance the *Z*-selectivity, the substituent σ-bond should be more electron-withdrawing. We planned to (i) use a heavier atom to lower the σ^*_{CM} level and (ii) introduce a strained structure to lower the σ^*_{CSi} orbital energy level. First, we used a trimethylgermyl group. A C–Ge bond is more electron-accepting than a C–Si bond. Let us suppose that two alkyl groups on the silicon atom form a small ring. The ring bond should be rich in p-character so that the s-character of the C–Si bond must be increased. Thus, the σ* orbital energy level should be lowered. In fact, we subjected the model compounds 1,1-dimethylsilirane and 1,1-dimethyl-1-siletane to the bond model analysis. The hybrid of the silicon of the ring bond is $sp^{6.17}$ and $sp^{5.74}$, respectively. The C–Si bond with a methyl group is $sp^{3.80}$ and $sp^{3.88}$, respectively, and we found that the σ^*_{CSi} orbital energy levels are lower than that of tetramethylsilane (Table 4).

We designed **1i**, **1j**, **1m**, and **1n** and calculated the transition structures. All of the substrates showed a Z-preference with higher selectivities. Note that the TS of the germyl-substituted **1i** to *Z*-**2i** showed a O···Ge distance of 2.728 Å, which is much shorter than the sum of the van der Waals radii of oxygen and germanium (3.62 Å) (Fig. 11). The carboxylate could be hypercoordinated to the germyl group, in contrast to the situation in **1c**. On the other hand, the O···Ge distance for the TS to *E*-**2i** is 2.811 Å, and weaker hypercoordination should be expected. *Z*-selectivity should be further enhanced due to hypercoordination.

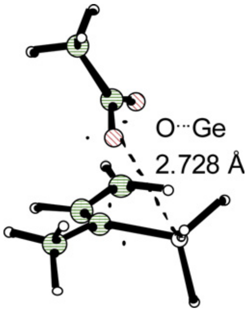

Figure 11. TS structure for the reaction from **1i** to *Z*-**2i**.

We prepared the corresponding substrate **1k**–**l**[11,12] from readily available reagents, which were subjected to the reaction. *Z*-selectivities of 63:37 and 67:33 were observed for **1k** and **1l**, which are higher than those for **1d** and **1g** (Table 3) to confirm our predicition.[15]

3. Conclusion

The TS of the [3,3]-rearrangement of the 1,1-disubstituted allyl carboxylates has a boat form configuration due to secondary orbital interaction of the lone pairs. The [1,3]-rearrangement, although its reaction barrier is far higher than the [3,3]-rearrangement, proceeds not in the usual antarafacial manner due to the lone pair participation. The geminal bond participation controls the stereoselectivity in the [3,3]-rearrangement. The bond model analysis showed that electron-withdrawing σ-bond substituents prefer to occupy the Z-position. We successfully designed *Z*-selective reactions using silyl and germyl substituents.

4. Experimental section

4.1. 3-(3-Hydroxy-1-octenyl)trimethylsilane 6a[13]

To a stirred solution of hexanoyltrimethylsilane **5a**[11] (4.1 g, 25 mmol) in THF (24 mL) was added vinylmagnesium bromide (1.0 M in THF, 47 mL, 47 mmol) dropwise at −75 °C. After 3 h, the reaction was quenched by adding 1 N HCl, and the resulting mixture was extracted by ether several times. The combined extracts were dried over $NaSO_4$, concentrated in vacuo, and purified by column chromatography on SiO_2 (SGC) gave a colorless oil (3.4 g, 70%). ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9H), 0.86 (t, ^3J (H,H)=6.8 Hz, 3H), 1.24 (m, 4H), 1.26 (s, 1H), 1.47–1.66 (m, 2H), 4.97 (dd, ^3J (H,H)=1.0, 17.2 Hz, 1H), 5.01 (dd, ^3J (H,H)=1.0, 11.6 Hz, 1H), 5.86 (dd, ^3J (H,H)= 11.6, 17.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −4.4, 14.1, 21.9, 22.7, 32.3, 36.5, 72.1, 109.7, 143.1.MS (EI) 73(100). IR: 3480 (br), 2880–3020, 1625, 1466, 1247, 997, 905, 840, 751 cm^{-1}.

4.2. 1-Hexynyltrimethylgermane 4b

Compound **4b** was prepared in analogous fashion[11] as 1-hexynyltrimethylsilane **4a** from 1-hexyne **3** (91%). ^{1}H NMR ($CDCl_3$) δ 0.30 (s, 9H), 0.89 (t, ^3J (H,H)=7.6 Hz, 3H), 1.34–1.51 (m, 4H), 2.20 (t, ^3J (H,H)=6.8 Hz, 2H).

4.3. 1-Hexanoyltrimetylgermane 5b[12]

Compound **5b** was prepared in analogous fashion[11] as 1-hexanoyltrimethylsilane **5a**[11] (21%). ^{1}H NMR ($CDCl_3$) δ 0.42 (s, 9H). 0.86 (t, ^3J (*H,H*)=7.2 Hz, 3H), 1.20–1.31 (m, 4H), 1.47–1.50 (m, 2H) 2.59 (t, ^3J (H,H)=7.6 Hz, 2H).

4.4. 3-(3-Hydroxy-1-octenyl)trimethylgermane 6b

Compound **6b** was prepared in analogous fashion as 3-(3-hydroxy-1-octenyl)trimethylsilane **6a** (64%). ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 9H), 0.86 (t, ^3J (H,H)=6.8 Hz, 3H), 1.21–1.31 (m, 4H), 1.54 (br s, 1H), 1.54–1.60 (m, 1H), 1.65–1.70 (m, 1H), 4.95 (dd, ^3J (H,H)=0.8, 16.8 Hz, 1H), 4.96 (dd, ^3J (H,H)=0.8, 11.2 Hz, 1H), 5.90 (dd, *J*=11.2, 16.8 Hz, 1H); ^{13}C NMR ($CDCl_3$)δ−4.5, 14.1, 22.5, 22.6, 32.3, 27.9, 74.9, 108.6, 143.4. MS (EI) 121 (29), 119 (100), 118 (22), 117 (73), 115 (51). IR:

3402 (br), 2800–2950, 1685, 1466, 1409, 1377, 1329, 827, 604 cm^{-1}. Anal. Calcd (%) for $C_{11}H_{24}GeO$ (244.95): C 53.94, H 9.88; found: C 54.11, H 9.82.

4.5. 3-(3-Acetoxyoct-1-enyl)trimethylsilane 1d, general procedure

To a stirred solution of **5a** (1.3 g, 6.8 mmol) in ether (52 mL) was added vinylmagnesium bromide (1.0 M in THF, 9.4 mL, 9.4 mmol) dropwise at −75 °C, followed by acetyl chloride (1.0 mL, 15 mmol). The reaction mixture was stirred overnight, gradually being warmed to rt. It was poured into satd NH_4Cl aq, and extracted with ether several times. The combined extracts were dried over $NaSO_4$, concentrated in vacuo and purified by SGC gave a colorless oil (0.62 g, 38%). ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9H), 0.81 (t, ^{3}J (H,H)=6.8 Hz, 3H), 1.20–1.30 (m, 6H), 1.53–1.60 (m, 1H), 1.99 (s, 3H), 2.06–2.12 (m, 1H), 4.92 (dd, ^{3}J (H,H)=1.6, 18.8 Hz, 1H), 4.93 (dd, ^{3}J (H,H)=1.6, 10.8 Hz, 1H), 5.68 (dd, ^{3}J (H,H)=10.8, 18.8 Hz, 1H); (C_6D_6) δ 0.23 (s, 9H), 1.08 (t, ^{3}J (H,H)=7.6 Hz, 3H), 1.37–1.63 (m, 6H), 1.82 (td-like m, 1H), 1.91 (s, 3H), 2.51 (td-like m, 1H), 5.25 (dd, ^{3}J (H,H)=1.5, 14.6 Hz, 1H), 5.32 (dd, ^{3}J (H,H)=1.5, 17.1 Hz, 1H), 5.89 (dd, ^{3}J (H,H)=14.6, 17.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −1.9, 14.2, 20.6, 23.0, 23.4, 32.5, 34.2, 81.6, 110.3, 140.5, 169.9. MS (EI) 73 (100). IR: 2880–2950, 1733, 1628, 1368, 1265, 840, 755, 628 cm^{-1}. Anal. Calcd (%) for $C_{13}H_{22}O_2Si$ (286.98): C 64.41, H 10.81; found: C 64.22, H 10.83.

4.6. 3-(3-(Chloroacetoxy)oct-1-enyl)trimethylsilane 1e

Ethylmagnesium chloride was used instead of vinylmagnesium bromide. Yield: 24%. ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 9H), 0.86 (t, ^{3}J (H,H)= 6.8 Hz, 3H), 1.25 (m, 6H), 1.60 (m, 1H), 2.16 (m, 1H), 4.05 (s, 2H), 5.01 (dd, ^{3}J (H,H)=1.6, 12.4 Hz, 1H), 5.05 (dd, ^{3}J (H,H)=1.6, 16.8 Hz, 1H), 5.74 (dd, ^{3}J (H,H)=16.8, 12.4 Hz, 1H); (C_6D_6) δ 0.34 (s, 9H), 1.08 (t, ^{3}J (H,H)=6.8 Hz, 3H), 1.33–1.63 (m, 6H), 1.77 (m, 1H), 2.47 (m, 1H), 3.66 (s, 2H), 5.19 (dd, ^{3}J (H,H)=1.6, 11.2 Hz, 1H), 5.32 (dd, ^{3}J (H,H)= 1.6, 17.2 Hz, 1H), 5.81 (dd, ^{3}J (H,H)=11.2, 17.2 Hz, 1H); ^{13}C NMR (C_6D_6) δ −2.1, 14.2, 22.9, 23.2, 32.4, 33.9, 40.9, 84.2, 111.0, 139.6, 166.2. MS (EI) 73 (100), 199 (19). IR: 2880–2950, 1733, 1466, 1411, 1316, 1250, 841 cm^{-1}. Anal. Calcd (%) for $C_{13}H_{25}ClO_2Si$ (276.87): C 56.39, H 9.10, Cl 12.80; found C 56.64, H 9.09, Cl 12.69.

4.7. 3-(3-(Dichloroacetoxy)oct-1-enyl)trimethylsilane 1g

Ethylmagnesium chloride was used instead of vinylmagnesium bromide. Yield: 31%. ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9H), 0.85 (t, ^{3}J (H,H)= 6.8 Hz, 3H), 1.20–1.36 (m, 6H), 1.65–1.71 (m, 2H), 2.16–2.23 (m, 1H), 5.07 (dd, ^{3}J (H,H)=11.2, 0.9 Hz, 1H), 5.05 (dd, ^{3}J (H,H)=17.2, 0.9 Hz, 1H), 5.74 (dd, ^{3}J (H,H)=17.2, 11.2 Hz, 1H), 5.92 (s, 1H); (C_6D_6) δ 0.32 (s, 9H), 1.07 (t, ^{3}J (H,H)=6.8 Hz, 3H), 1.38 (m, 2H), 1.45 (m, 2H), 1.53–1.62 (m, 2H), 1.77 (m, 1H), 2.48 (m, 2H), 5.18 (dd, ^{3}J (H,H)=1.6, 11.2 Hz, 1H), 5.37 (dd, ^{3}J (H,H)=1.6, 17.6 Hz, 1H), 5.61 (s, 1H), 5.76 (dd, ^{3}J (H,H)=11.2, 17.6 Hz, 1H); ^{13}C NMR (C_6D_6) δ −2.4, 14.2, 22.9, 23.1, 32.2, 33.7, 65.4, 85.2, 111.4, 138.8, 183.4. MS (EI) 73 (100), 185 (14), 189 (2), 199 (29), 311 (1). IR: 2880–2950, 1741, 1251, 839 cm^{-1}. Anal. Calcd (%) for $C_{13}H_{24}Cl_2O_2Si$ (311.32): C 50.15, H 7.77, Cl 22.78; found C 50.28, H 7.59, Cl 22.75.

4.8. 3-(3-(Trifluoroacetoxy)oct-1-enyl)trimethylsilane 1h

Ethylmagnesium chloride was used instead of vinylmagnesium bromide, and trifluoroacetic anhydride was used as an acylating agent. Yield: 86%. ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 9H), 0.85 (t, ^{3}J (H,H)= 7.6 Hz, 3H), 1.20–1.36 (m, 6H), 1.71 (m, 1H), 2.25 (m, 1H), 5.06 (dd, ^{3}J (H,H)=1.2, 16.8 Hz, 1H), 5.09 (dd, ^{3}J (H,H)=1.2, 11.2 Hz, 1H), 5.74 (dd, ^{3}J (H,H)=11.2, 16.8 Hz, 1H), (C_6D_6) δ 0.23 (s, 9H), 1.03 (t, ^{3}J (H,H)= 7.6 Hz, 3H), 1.26–1.59 (m, 6H), 1.75 (m, 1H), 2.47 (m, 1H), 5.12 (d, ^{3}J (H,H)=11.2 Hz, 1H), 5.28 (d, ^{3}J (H,H)=17.6 Hz, 1H), 5.66 (dd, ^{3}J (H, H)=11.2, 17.6 Hz, 1H); ^{13}C NMR (C_6D_6) δ −2.9, 14.1, 22.7, 22.9, 32.1, 33.4, 88.7, 111.8, 115.5 (q, ^{3}J (H,H)=286.3 Hz), 137.6, 156.6 (q, ^{3}J (H, H)=41.0 Hz). MS (EI) 73 (100), 199 (13). IR: 2880–3020, 1778, 1632, 1378, 1253, 1219, 1170, 841 cm^{-1}. Anal. Calcd (%) for $C_{13}H_{23}F_3O_2Si$ (298.14): C 52.68, H 7.74; found: C 52.90, H 7.74.

4.9. 3-(3-Acetoxyoct-1-enyl)trimethylgermane 1k

Yield: 38%. ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 9H), 0.85 (t, ^{3}J (H,H)=7.6 Hz, 3H), 1.20–1.30 (m, 6H), 1.57–1.61 (m, 1H), 2.05 (s, 3H), 2.06–2.12 (m, 1H), 4.95 (d, ^{3}J (H,H)=10.8 Hz, 1H), 4.95 (d, ^{3}J (H,H)=17.6 Hz, 1H), 5.68 (dd, ^{3}J (H,H)=10.8, 17.6 Hz, 1H); (C_6D_6) δ 0.54 (s, 9H), 1.08 (t, ^{3}J (H,H)=7.2 Hz, 3H), 1.37–1.67 (m, 6H), 1.84 (m, 1H), 1.91 (s, 3H), 2.50 (m, 1H), 5.18 (dd, ^{3}J (H,H)=1.6, 11.2 Hz, 1H), 5.32 (dd, ^{3}J (H,H)= 1.6, 17.2 Hz, 1H), 5.89 (dd, ^{3}J (H,H)=11.2, 17.6 Hz, 1H); ^{13}C NMR (C_6D_6) δ −1.6, 14.2, 20.6, 23.0, 23.6, 32.4, 35.1, 82.8, 109.5, 140.6, 169.8. MS (EI) 115 (59), 117 (85), 118 (25), 119 (100), 121 (32). IR: 2880–2950, 1734, 1628, 1368, 1261, 820, 592 cm^{-1}. Anal. Calcd (%) for $C_{13}H_{22}O_2Si$ (286.98): C 54.41, H 9.13; found: C 54.63, H 9.25.

4.10. 3-(3-(Dichloroacetoxy)oct-1-enyl)trimethylgermane 1l

Ethylmagnesium chloride was used instead of vinylmagnesium bromide. Yield: 48%. ^{1}H NMR ($CDCl_3$) δ 0.22 (s, 9H), 0.85 (t, ^{3}J (H,H)= 7.2 Hz, 3H), 1.22–1.30 (m, 6H), 1.65–1.72 (m, 1H), 2.14–2.21 (m, 1H), 5.01 (dd, ^{3}J (H,H)=0.8, 10.8 Hz, 1H), 4.95 (dd, ^{3}J (H,H)=0.8, 17.6 Hz, 1H), 5.68 (dd, ^{3}J (H,H)=10.8, 17.6 Hz, 1H); (C_6D_6) δ 0.47 (s, 9H), 1.07 (t, ^{3}J (H,H)=7.2 Hz, 3H), 1.34–1.48 (m, 4H), 1.54–1.63 (m, 2H), 1.79 (m, 1H), 2.45 (m, 1H), 5.15 (dd, ^{3}J (H,H)=1.6, 11.2 Hz, 1H), 5.35 (dd, ^{3}J (H,H)=1.6, 17.2 Hz, 1H), 5.80 (dd, ^{3}J (H,H)=11.2, 17.6 Hz, 1H); ^{13}C NMR (C_6D_6) δ −2.1, 14.2, 22.9, 23.3, 32.2, 34.6, 65.3, 87.1, 110.4, 139.0, 163.4. MS (EI) 115 (56), 117 (76), 118 (24), 119 (100), 121 (22). IR: 2880–2950, 1734, 1629, 1466, 1411, 1307, 1196, 906, 826, 596 cm^{-1}.

4.11. Thermal rearrangement of the allyl esters, general procedure: 3-(1-acetoxyoct-2-enyl)trimethylsilane 2d

A benzene-*d*$_6$ solution of **1d** (19 mg, 0.080 mmol) and naphthalene as the internal standard (4.2 mg) was sealed in an NMR tube, and heated with a Kugel Rohr apparatus monitoring the temperature with a thermometer. Completion of the reaction was determined by measuring by ^{1}H NMR (48 h). The yield (48%) and the diastereoselectivity (*Z*/*E*=58:42) were determined by ^{1}H NMR. ^{1}H NMR (C_6D_6) δ 0.29 (s, 9H for *E*-isomer), 0.36 (s, 9H for *Z*-isomer), 1.08 and 1.09 (overlapping two t's, ^{3}J (H,H)=7.0 Hz, 3H), 1.36–1.60 (m, 6H), 1.89 (s, 3H for *E*-isomer), 1.90 (s, 3H for *Z*-isomer), 2.28 (t, ^{3}J (H,H)=7.6 Hz, 2H for *Z*-isomer), 2.34 (t, ^{3}J (H,H)=7.6 Hz, 2H for *E*-isomer), 4.95 (d, ^{3}J (H,H)=6.4 Hz, 2H for *Z*-isomer), 4.98 (d, ^{3}J (H, H)=6.0 Hz, 2H for *E*-isomer), 6.21 (t, ^{3}J (H,H)=6.0 Hz, 1H for *E*-isomer), 6.38 (t, ^{3}J (H,H)=6.4 Hz, 1H for *Z*-isomer). MS (EI) 73 (100), 75 (43), 117 (51), 149 (13), 199 (7), 214 (5), 239 (6), 242 (4). IR: 2880–2960, 1744, 1248, 1376, 1229, 1026, 838 cm^{-1}. Anal. Calcd (%) for $C_{13}H_{22}O_2Si$ (242.43): C 64.41, H 10.81%; found: C 64.17, H 10.57.

4.12. 3-(1-Chloroacetoxyoct-2-enyl)trimethylsilane 2e

A mixture of *E*- and *Z*-isomers. ^{1}H NMR (C_6D_6) δ 0.27 (s, 9H for *E*-isomer), 0.32 (s, 9H for *Z*-isomer), 1.08 and 1.09 (overlapping two t's, ^{3}J (H,H)=7.0 Hz, 3H), 1.36–1.60 (m, 6H), 2.24 (t, ^{3}J (H,H)=7.7 Hz, 2H for *Z*-isomer), 2.29 (t, ^{3}J (H,H)=7.7 Hz, 2H for *E*-isomer), 3.63 (s, 2H for *E*-isomer), 3.63 (s, 2H for *Z*-isomer), 4.87 (d, ^{3}J (H,H)=6.2 Hz, 2H for *Z*-isomer), 4.88 (d, ^{3}J (H,H)=7.0 Hz, 2H for *E*-isomer), 6.09 (t, ^{3}J (H,H)=7.0 Hz, 1H for *E*-isomer), 6.26 (t, ^{3}J (H,H)=6.2 Hz, 1H for *Z*-isomer). IR: 2883–2953, 1741, 1249, 1169, 838 cm^{-1}. Anal. Calcd (%)

for $C_{13}H_{26}O_2Si$ (276.87): C 56.39, H 9.10 Cl 12.80%; found: C 56.57, H 9.07, Cl 13.05%.

4.13. 3-(1-(Dichloroacetoxy)oct-2-enyl)trimethylsilane 2g

A mixture of *E*- and *Z*-isomers. ^{1}H NMR (C_6D_6) δ 0.24 (s, 9H for *E*-isomer), 0.29 (s, 9H for *Z*-isomer), 1.08 and 1.09 (overlapping two t's, ^3J (H,H)=7.0 Hz, 3H), 1.36–1.60 (m, 6H), 2.24 (t, ^3J (H,H)=7.7 Hz, 2H for *Z*-isomer), 2.29 (t, ^3J (H,H)=7.7 Hz, 2H for *E*-isomer), 4.82 (d, ^3J (H,H)=6.2 Hz, 2H for *Z*-isomer), 4.83 (d, ^3J (H,H)=7.0 Hz, 2H for *E*-isomer), 5.60 (s, 1H for *Z*-isomer), 5.61 (s, 1H for *E*-isomer), 6.03 (t, ^3J (H,H)=6.2 Hz, 1H for *E*-isomer), 6.20 (t with hyperfine coupling, ^3J (H,H)=7.0 Hz, 1H for *Z*-isomer). MS (EI) 73 (100), 93 (45), 95 (17), 157 (12), 159 (8), 161 (2), 185 (13), 187 (9), 189 (2). IR: 2859–2957, 1767, 1456, 1250, 1162, 838 cm^{-1}.

4.14. 3-(1-(Trifluoroacetoxy)oct-2-enyl)trimethylsilane 2h

A mixture of *E*- and *Z*-isomers. ^{1}H NMR (C_6D_6) δ 0.20 (s, 9H for *E*-isomer), 0.25 (s, 9H for *Z*-isomer), 1.08 and 1.09 (overlapping two t's, ^3J (H,H)=7.0 Hz, 3H), 1.31–1.46 (m, 6H), 2.16 (t, ^3J (H,H)=7.7 Hz, 2H for *Z*-isomer), 2.20 (t, ^3J (H,H)=7.7 Hz, 2H for *E*-isomer), 4.72 (d, ^3J (H,H)=7.2 Hz, 2H for *Z*-isomer), 4.87 (d, ^3J (H,H)=7.2 Hz, 2H for *E*-isomer), 6.09 (t, ^3J (H,H)=7.2 Hz, 1H for *E*-isomer), 6.26 (t with hyperfine coupling, ^3J (H,H)=7.2 Hz, 1H for *Z*-isomer). MS (EI) 73 (100), 77 (81), 82(30), 121(32), 149(3), 171(7). IR: 2861–2960, 1786, 1251, 1223, 1151, 839 cm^{-1}.

4.15. 3-(1-Acetoxyoct-2-enyl)trimethylgermane 2k

A mixture of *E*- and *Z*-isomers. ^{1}H NMR (C_6D_6) δ 0.41 (s, 9H for *E*-isomer), 0.49 (s, 9H for *Z*-isomer), 1.07 and 1.08 (overlapping two t's, ^3J (H,H)=7.0 Hz, 3H), 1.36–1.56 (m, 6H), 1.90 (s, 3H for *E*-isomer), 1.90 (s, 3H for *Z*-isomer), 2.32 (t, ^3J (H,H)=7.7 Hz, 2H for *Z*-isomer), 2.42 (t, ^3J (H,H)=7.7 Hz, 2H for *E*-isomer), 4.90 (d, ^3J (H,H)=7.2 Hz, 2H for *Z*-isomer), 4.96 (d, ^3J (H,H)=7.0 Hz, 2H for *E*-isomer), 6.10 (t, ^3J (H,H)=7.0 Hz, 1H for *E*-isomer), 6.26 (t with hyperfine coupling, ^3J (H,H)=7.2 Hz, 1H for *Z*-isomer). MS(EI) 41 (28), 43 (41), 55 (22), 57 (27), 115 (49), 117 (79), 118 (12), 119 (100), 121 (39). IR: 2883–2959, 1744, 1229, 1023, 825 cm^{-1}.

4.16. 3-(1-(Dichloroacetoxy)oct-2-enyl)trimethylgermane 2l

A mixture of *E*- and *Z*-isomers. ^{1}H NMR (C_6D_6) δ 0.37 (s, 9H for *E*-isomer), 0.43 (s, 9H for *Z*-isomer), 1.08 and 1.09 (overlapping two t's, ^3J (H,H)=7.0 Hz, 3H), 1.30–1.51 (m, 6H), 2.25 (t, ^3J (H,H)=7.7 Hz, 2H for *Z*-isomer), 2.32 (t, ^3J (H,H)=7.7 Hz, 2H for *E*-isomer), 4.79 (d, ^3J (H,H)=7.6 Hz, 2H for *Z*-isomer), 4.80 (d, ^3J (H,H)=6.8 Hz, 2H for *E*-isomer), 5.61 (s, 2H for *E*-isomer), 5.62 (s, 2H for *Z*-isomer), 5.92 (t, ^3J (H,H)=6.8 Hz, 1H for *E*-isomer), 6.16 (t, ^3J (H,H)=7.6 Hz, 1H for *Z*-isomer). MS (EI) 115 (55), 117 (74), 118 (24), 119 (100), 121 (21), 135 (41), 137 (68), 138 (17), 139 (92), 141 (39), 171 (5), 173 (9), 174 (2), 175 (12), 177 (8), 227 (11), 229 (22), 230 (5), 231 (31), 232 (4), 233 (18). IR: 2883–2959, 1740, 1280, 1166, 826, 598 cm^{-1}.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.06.016. These data include MOL files and InChIKeys of the most important compounds described in this article.

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6. The Slater determinant Ψ of the electronic structure is expanded into the electron configurations Φ of a given bond model in the bond orbital basis. In the ground configuration Φ_G, all of the electrons occupy the bonding orbital(s) of the bond(s) or the nonbonding lone pair(s).

$$\Psi = C_G\Phi_G + \Sigma C_T\Phi_T + \cdots$$

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8. We did not consider the stepwise ionic route since the enthalpies of activation should be far higher.
9. IBE is derived as follows:

$$\mathrm{IB}E\mathrm{ij} = P\mathrm{ij}(H\mathrm{ij} + F\mathrm{ij})$$

where Pij, Hij, and Fij are the elements of the density, Fock and core Hamiltonian matrices of the bond orbitals of i and j, respectively. See Ref. 5b.

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