

Headline Articles

"*Syn-Effect*" in the Conversion of (*E*)-α,β-Unsaturated Esters into the Corresponding β,γ-Unsaturated Esters and Aldehydes into Silyl Enol Ethers

Samar Kumar Guha, Atsushi Shibayama, Daisuke Abe, Maki Sakaguchi, Yutaka Ukaji,* and Katsuhiko Inomata*

Division of Material Sciences, Graduate School of Natural Science and Technology, Kanazawa University, Kakuma, Kanazawa, Ishikawa 920-1192

Received June 28, 2004; E-mail: inomata@cacheibm.s.kanazawa-u.ac.jp

The stereochemistry in the conversion of (*E*)-α,β-unsaturated esters into the corresponding β,γ-unsaturated esters, and that in the conversion of aldehydes into the silyl enol ethers, were investigated. The *Z*/*E* ratios of the resulting β,γ-unsaturated esters and the silyl enol ethers varied according to the γ-substituents of the (*E*)-α,β-unsaturated esters and the α-substituents of the aldehydes, respectively. This phenomenon was rationalized by a "*syn-effect*", which may be attributed primarily to a $\sigma \rightarrow \pi^*$ interaction and/or 6π-electron homoaromaticity.

Previously, we investigated the stereochemistry in the isomerization of α-unsubstituted (*E*)-vinylic sulfones to the corresponding allylic sulfones, and that in the desulfonylation reaction of α,α-dialkylated allylic sulfones with a base.[1a,b] In both cases, the sterically unfavorable (*Z*)-allylic sulfones and (*Z*)-alkadienes were predominantly formed, respectively. These results were rationalized by "*conformational acidity*", which essentially implies a "*syn-effect*".[2] We proposed that the "*syn-effect*" is primarily caused by 6π-electron homoaromaticity and/or a $\sigma \rightarrow \pi^*$ interaction.[1b] Very recently, we investigated the "*syn-effect*" in the conversion of α-fluorinated (*E*)-vinylic sulfones to the corresponding allylic sulfones, and also in the desilylation reaction of γ-silylated allylic and vinylic sulfones to the corresponding allylic sulfones; it was ultimately found that the $\sigma \rightarrow \pi^*$ interaction is the most important factor for the "*syn-effect*".[1c,d]

It is well known that treatment of dienolates derived from α,β-unsaturated carbonyl compounds with electrophiles, such as proton or alkyl halides, affords deconjugated β,γ-unsaturated carbonyl compounds.[3,4] The reaction of ethyl (*E*)-2-alkenoates with lithium amides in the presence of HMPA was reported to give sterically unfavored (*Z*)-3-alkenoates as the main products. The stereoselectivity was explained by the stability of the produced anion or cyclic transition model during deprotonation.[3a,b,d] Furthermore, the deconjugative α-alkylation of (*E*)-4-methylthio-2-butenoate produced a mixture of (*E*)- and (*Z*)-4-methylthio-3-butenoates,[4a] while the deconjugative α-alkylation and aldol reaction of (*E*)-4-methoxy-2-butenoate gave (*Z*)-4-methoxy-3-butenoates selectively.[4b,c] However, there was no explanation about the stereochemical outcomes. A rational elucidation for the origin of these puzzling phenomena has been strongly desired. In order to determine the exact origin of these deconjugation reactions starting from (*E*)-α,β-unsaturated esters, (*E*)-α,β-unsaturated esters **1** bearing various substituents at the γ-position were converted to the corresponding β,γ-unsaturated esters **2**, and the stereochemical outcome of the *Z*/*E* ratios of products **2** was well rationalized herein by the "*syn-effect*".[5]

Furthermore, in the preparation of silyl enol ethers from aldehydes, a mixture of (*Z*)- and (*E*)-isomers could be produced. Although the *Z*/*E* ratios were reported to be altered depending on the α-substituents of the aldehydes and the reaction conditions, a reasonable interpretation for the stereochemistry was not hitherto offered.[6] In the present work, the reaction of aldehydes **5** with silylating agents in the presence of a base was also systematically investigated, and the stereochemistry of the resulting silyl enol ethers **6**–**8** was also elucidated by the "*syn-effect*".

Results and Discussion

Preparation of (*E*)-α,β-Unsaturated Esters. (*E*)-α,β-Unsaturated esters **1a**–**e**,**h** containing an alkyl or a benzyloxy group at the γ-position were prepared by the Horner–Emmons–Wadsworth reaction in good yields. In the cases where trace amounts of (*Z*)-isomers were formed, they were separated from the (*E*)-isomers by column chromatography or preparative TLC. The γ-phenyl substituted (*E*)-α,β-unsaturated ester **1f** was prepared according to Scheme 1. Ethyl (phenylthio)acetate (**3**) was treated with sodium hydride, followed by the addition of (2-bromoethyl)benzene in the presence of

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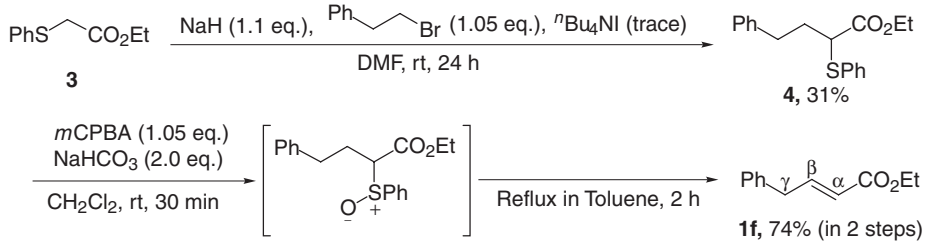
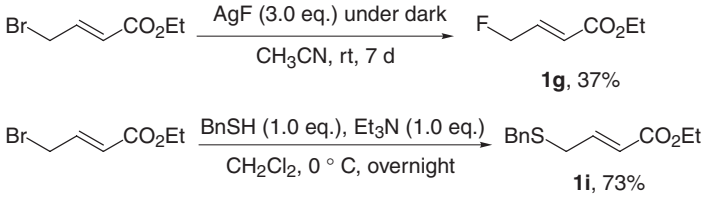
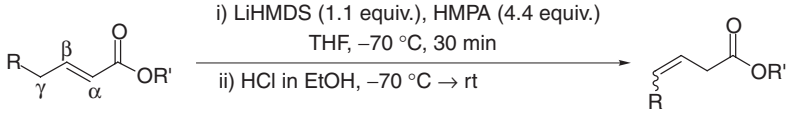


Scheme 1.



Scheme 2.

Table 1. Conversion of (*E*)-α,β-Unsaturated Esters to the Corresponding β,γ-Unsaturated Esters



1 **2**

Entry	**1**	R	R′	**1**/**2**[a]	*Z*/*E* of **2**[a]	Yield of **2**/%[b]
1	**a**	CH_3	CH_3CH_2	0/100	91/9	42
2	**b**	CH_3	$CH_3(CH_2)_7$	0/100	94/6	83[c]
3	**c**	CH_3CH_2	CH_3CH_2	0/100	85/15	70
4	**d**	$(CH_3)_2CH$	CH_3CH_2	0/100	70/30	68
5	**e**	$(CH_3)_3C$	CH_3CH_2	28/72	0/100	47
6	**f**	Ph	CH_3CH_2	0/100	16/84	99
7	**g**	F	CH_3CH_2	0/100	100/0	55
8[d]	**h**	BnO	CH_3CH_2	0/100	100/0	78
9	**i**	BnS	CH_3CH_2	7/93	44/56	84

a) The ratios were determined by 400 MHz ^{1}H NMR spectra. b) Isolated yields. c) The yield was improved by careful workup after preliminary report.[5] d) Quenched with $Et_3N\cdot HCl$ in EtOH instead of aq. HCl in EtOH to avoid the hydrolysis of a vinyl ether moiety.

a catalytic amount of a quaternary ammonium iodide to give the alkylated (phenylthio)acetate intermediate **4**. This phenylthio intermediate **4** was converted to the γ-phenyl substituted (*E*)-α,β-unsaturated ester **1f** by oxidizing with *m*CPBA, followed by refluxing in toluene.

γ-Fluoro and γ-benzylthio substituted (*E*)-α,β-unsaturated esters **1g**,**i** were prepared according to Scheme 2 by treating ethyl (*E*)-4-bromo-2-butenoate with AgF or BnSH in the presence of Et_3N, respectively.

Conversion of (*E*)-α,β-Unsaturated Esters to the Corresponding β,γ-Unsaturated Esters. (*E*)-α,β-Unsaturated esters **1** bearing various substituents at the γ-position were converted to the corresponding β,γ-unsaturated esters **2** by treating with lithium hexamethyldisilazide (LiHMDS) in the presence of HMPA, followed by quenching with aq. HCl diluted in EtOH. The results of the isomerization reactions are summarized in Table 1.

The *Z*-selectivity with respect to the γ-alkyl substituents decreased along with their bulkiness: $CH_3- > CH_3CH_2- > (CH_3)_2CH- > (CH_3)_3C-$ (Entries 1,3–5). Namely, the methyl group realized high *Z*-selectivity, whereas the (*E*)-product was exclusively obtained in the case of the ^{t}Bu substituent. In the case of the γ-phenyl substituent, high *E*-selectivity was observed (Entry 6). γ-Fluoro and γ-benzyloxy groups were found to show complete *Z*-selectivity (Entries 7,8), while γ-benzylthio substituted 2-alkenoate **1i** afforded almost a 1/1 mixture of (*Z*)- and (*E*)-3-alkenoates **2i** (Entry 9). In the cases of γ-methyl and γ-fluoro substituted esters **1a**,**g**, the isolated yields of products **2a**,**g** were slightly lower compared with other γ-substituents (Entries 1,7). This is due to the high volatility of those products. In fact, the use of ester **1b** derived from a higher alcohol realized a better chemical yield (Entry 2). The relative degree of the "*syn-effect*", depending on the γ-substituents R of (*E*)-α,β-unsaturated esters **1**, was found for their conversion to the corresponding β,γ-unsaturated esters **2** as follows:

$$F- \approx BnO- > CH_3- > CH_3CH_2- > (CH_3)_2CH-$$
$$> BnS- > Ph- > (CH_3)_3C-$$

It seems to be possible to rationalize the relative degree of the Z/E ratios by the "*syn-effect*" in the transition state of deprotonation. It was reported that a C–CH_3 eclipsed conformation of ethyl (*E*)-2-pentenoate (**1a**) was preferred due to hyperconjugation of the C–H bond at the γ-position to the $\pi^*_{C=C}$ orbital of an electron-deficient olefin moiety.[7] In the transition state of deprotonation, the hyperconjugation of a developing anion generated by the interaction of H_γ with a base becomes more effective in the eclipsed conformations, **A** and **B**, in both of which the developing anion is aligned with the $\pi^*_{C=C}$ orbital (Fig. 1), and the other conformations can be neglected. Our recent proposal that the $\sigma \rightarrow \pi^*$ interaction is the most probable explanation for the "*syn-effect*" is very consistent with this consideration. During the deprotonation of γ-alkyl-2-butenoates **1a**–**d**, the CC eclipsed *syn*-conformation **A** might be preferred rather than CH eclipsed form **B**, because a hyperconjugative electron donation by the C–$H_{\gamma 2}$ bond is more effective than that by the C–C bond,[7,8] since $H_{\gamma 2}$ can also interact with a base to afford the developing anion. In the cases of γ-fluoro and γ-benzyloxy substituted α,β-unsaturated esters **1g**,**h**, the CH eclipsed form **B** is unfavorable due to the low donor ability of the C–F and C–O bonds,[8c,9] resulting in an exclusive formation of (*Z*)-**2g**,**h** via conformation **A**.

In the cases of **1a**–**c**,**g**,**h**, it is also possible to stabilize the *syn*-conformation at the transition state by 6π-electron homoaromaticity (an "aromatic" 6π-electron system as another origin of "*syn-effect*") involving the developing charge at the γ-position and a pseudo p-orbital of the δ-CH_2 (Fig. 2a, R = CH_2R'), or a lone pair of electrons in a p-orbital of the hetero atom (Fig. 2b, R = XR′), respectively.[2,10]

In the case of ^{i}Pr-substituted ester **1d**, 6π-electron homoaromaticity is difficult to be considered; however, the sterically unfavorable (*Z*)-isomer was still obtained as the major product (70%, Entry 4). Therefore, it is obvious that the "*syn-effect*" arises from the $\sigma \rightarrow \pi^*$ interaction. In the case of ^{t}Bu- and Ph-substituted esters **1e**,**f**, (*E*)-β,γ-unsaturated esters **2e**,**f** were obtained as the major products. This result is probably due to the bulkiness of those groups, which excludes a *syn*-conformation at the transition state. Especially in the case of the Ph group, the steric repulsion between the α-proton of the ester and the *o*-proton of the benzene ring avoids CC eclipsed form **A** in Fig. 1 (Fig. 3a). In the case of γ-benzylthio substituted ester **1i**, the contribution of the empty d-orbital of the S-atom, such as $\sigma_{C-H} \rightarrow$ d, is still unclear, but $\sigma_{C-S} \rightarrow \pi^*$ interaction (Fig. 3b) might be responsible for the predominance of the CH eclipsed form **B** (R = SBn) in Fig. 1 to increase the *E*-selectivity.[11] The order in the relative degree of the "*syn-effect*" of the benzylthio substituent was different from the previous result observed in the conversion of vinylic sulfones to the corresponding allylic sulfones, probably due to the difference between the present electron-deficient conjugated olefinic system and the non-conjugated olefinic system in vinylic sulfones.

Previously, Krebs, Kende, and Galatsis obtained comparable results in the deconjugation of γ-Me, Et, and ^{i}Pr substituted (*E*)-α,β-unsaturated esters.[3a,b,d] Although Galatsis proposed a cyclic transition state, the difference by the substituents could not be explained by it. Kende proposed that the predominant formation of the (*Z*)-β,γ-unsaturated ester was probably due to the stability of the generated 2-butenyl anion system, that is, due to the greater $A^{1,2}$ strain than that of the $A^{1,3}$ strain

Fig. 1.

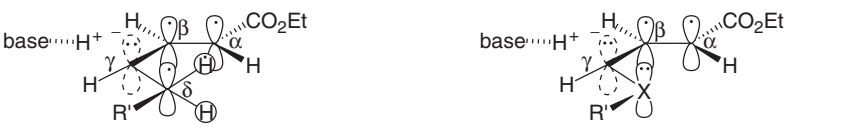


Fig. 2.

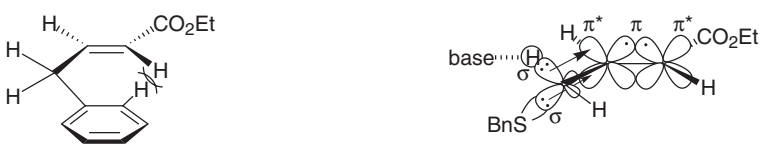


Fig. 3.

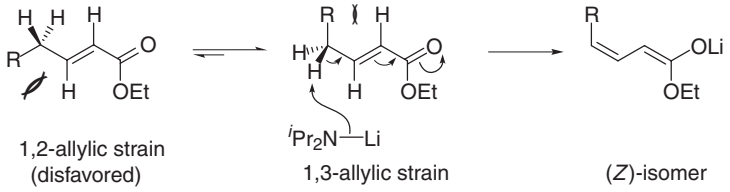


Fig. 4.

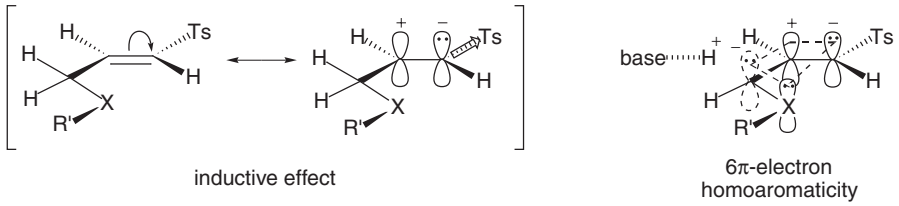


Fig. 5.

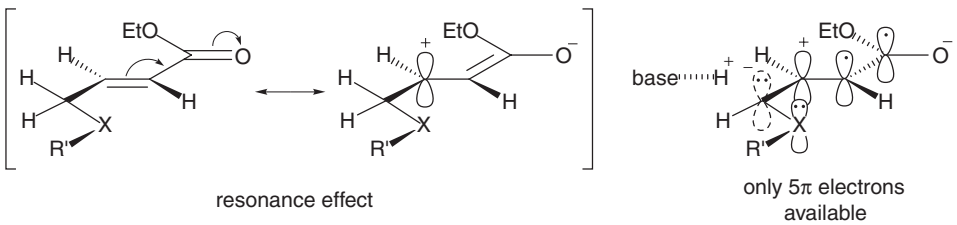


Fig. 6.

(Fig. 4), or homoaromaticity.[10] If the former proposal is correct, in the conversion of the γ-^{t}Bu substituted (*E*)-α,β-unsaturated ester to the corresponding β,γ-unsaturated ester, the (*Z*)-isomer should be the major product. This was not actually observed, but only the (*E*)-β,γ-unsaturated ester was obtained. Thus, it is clear that the "*syn-effect*" does not arise from the difference between the $A^{1,2}$ and $A^{1,3}$ strains. The latter, homoaromaticity, is consistent with our proposal for the origin of the "*syn-effect*".

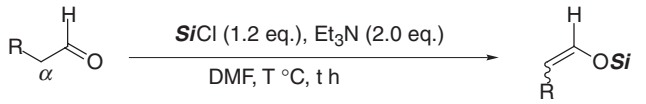
It should be noted that the *Z*/*E* ratios in the present isomerization were higher compared with the previous case observed in the conversion of (*E*)-vinylic sulfones to the corresponding allylic sulfones. In the isomerization of (*E*)-vinylic sulfones to the corresponding allylic sulfones, 6π-electron homoaromaticity (Fig. 5) seems to be possible, together with the $\sigma \rightarrow \pi^*$ interaction to stabilize the *syn*-conformation at the transition state.[1a] On the other hand, in the isomerization of (*E*)-α,β-unsaturated esters to the corresponding β,γ-isomers, due to the mesomeric character of the carbonyl group, the contribution of 6π-electron homoaromaticity must be decreased. Namely, only 5π electrons are available in the conjugated system with *syn*-conformation (Fig. 6). However, in the case of benzyloxy and fluoro substituents, complete *Z*-selectivity was observed. This fact indicates that the effect of the $\sigma \rightarrow \pi^*$ interaction is more enhanced in the isomerization of (*E*)-α,β-unsaturated esters to the corresponding β,γ-unsaturated esters than in the isomerization of (*E*)-vinylic sulfones to the corresponding allylic sulfones.

Conversion of Aldehydes into Silyl Enol Ethers. Silyl enol ether, one of the most important and isolable active intermediates used in organic synthesis, can be prepared from a carbonyl compound by a treatment with a silylating agent in the presence of a base.[12] In the preparation of silyl enol ethers from aldehydes, the *Z*/*E* ratios of the products were reported to vary according to the α-substituents of the aldehydes.[6] In order to determine the exact origin of the phenomena, we systematically investigated the reaction of various α-substituted aldehydes with silylating agents in the presence of a base. The *Z*/*E* ratio of the resulting silyl enol ethers was also well rationalized by the "*syn-effect*".

First, the reaction of various aldehydes with chlorosilanes and Et_3N in DMF was examined.[6d] The results are given in Table 2. The *Z*/*E* ratios of the silyl enol ethers obtained from decanal were around 60/40 regardless of the kind of chlorosilanes and the reaction temperature (Entries 2–4). Then, reactions of various kinds of aldehydes **5** were carried out using $Ph_2MeSiCl$ as a silylating agent at 60 °C (Entries 1,5–7) or 25 °C (Entries 8,9). The corresponding silyl enol ethers **6** were obtained in good chemical yields, except for a bulky aldehyde **5d** (Entry 6). In the case of aliphatic aldehydes **5a–d** (Entries 1,2,5,6), the ratio of the (*Z*)-isomer of **6** decreased in the order of $R = CH_3 > CH_3(CH_2)_7 > (CH_3)_2CH > (CH_3)_3C$. A striking *Z*-selectivity was observed in the reaction of (benzyloxy)-acetaldehyde (**5f**) (Entry 8).

It is also possible to explain the relative degree of the *Z*/*E* ratios of the resulting silyl enol ethers by a $\sigma \rightarrow \pi^*$ interaction in the transition state of the deprotonation of aldehydes, as in the case of (*E*)-α,β-unsaturated esters described above. Namely, due to the low donor ability of the C–C bond compared with the C–H bond, the CC eclipsed conformation **C** (Fig. 7) would be preferred to the conformation **D** at the deprotonation of aldehydes, affording the (*Z*)-silyl enol ethers as the

Table 2. Conversion of Aldehydes to the Corresponding Silyl Enol Ethers by Using Silyl Chlorides



5 **6** (***Si*** = Ph_2MeSi) or **7** (***Si*** = Me_3Si)

Entry	**5**	R	***Si***	T/°C	t/h	Z/E of **6**,**7**[a)]	Yield of **6**,**7**/%[a)]	
1	**a**	CH_3	Ph_2MeSi	60	96	74/26	**6a**	76
2	**b**	$CH_3(CH_2)_7$	Ph_2MeSi	60	48	58/42	**6b**	93
3	**b**	$CH_3(CH_2)_7$	Ph_2MeSi	25	143	58/42	**6b**	85
4	**b**	$CH_3(CH_2)_7$	Me_3Si	60	25	60/40	**7b**	88
5	**c**	$(CH_3)_2CH$	Ph_2MeSi	60	96	54/46	**6c**	>99
6	**d**	$(CH_3)_3C$	Ph_2MeSi	60	96	30/70	**6d**	50
7	**e**	Ph	Ph_2MeSi	60	48	67/33	**6e**	72
8	**f**	BnO	Ph_2MeSi	25	23	100/0	**6f**	85
9	**g**	BnS	Ph_2MeSi	25	29	37/63	**6g**	84

a) Yields and Z/E ratios were determined by 400 MHz ^{1}H NMR spectra of the crude products.

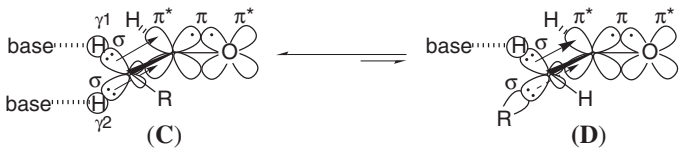


Fig. 7.

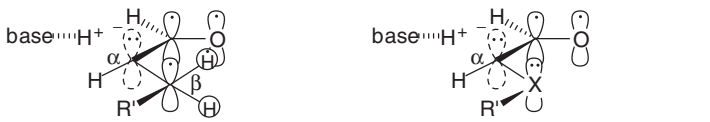


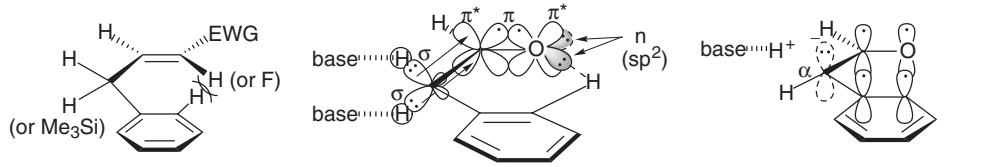
Fig. 8.

major products. In the case of benzyloxy-substituted aldehyde **5f**, conformation **D** is much less favored due to the low donor ability of the C–O bond compared with the C–C bond. As a result, a higher Z-selectivity was observed.

In the cases of **5a**,**b**,**f**, it is also possible to stabilize the *syn*-conformation at the transition state by 6π-electron homoaromaticity involving the developing anion at the α-position and a pseudo p-orbital of the β-CH_2 (Fig. 8a, R = CH_2R'), or a lone pair of electrons in a p-orbital of the hetero atom (Fig. 8b, R = XR′).

In the cases of ^{i}Pr- and ^{t}Bu-substituted aldehydes **5c**,**d**, 6π-electron homoaromaticity is difficult to be considered; still, remarkable amounts (54% and 30%, respectively) of the sterically unfavorable (Z)-isomers were obtained (Entries 5,6). It is thus clear that the "*syn-effect*" arises from the $\sigma \rightarrow \pi^*$ interaction, even in the present case. In the case of (benzylthio)acetaldehyde (**5g**), the $\sigma_{C-S} \rightarrow \pi^*$ interaction might be responsible for the predominance of the CH eclipsed form **D** in Fig. 7 (R = SBn) to increase the E-selectivity (Entry 9), as discussed concerning the isomerization of γ-benzylthio substituted α,β-unsaturated ester **1i**. All of the reactions so far investigated concerning the "*syn-effect*" for phenyl substituted substrates, namely the isomerization of γ-phenyl α-unsubstituted and α-fluorinated (E)-vinylic sulfones, the desulfonylation of δ-phenyl-α,α-dialkylated (E)-allylic sulfones, the desilylation reaction of γ-silylated (E)-allylic sulfones,[1] and the isomerization of γ-phenyl substituted (E)-α,β-unsaturated esters **1f**, exclusively or predominantly gave the corresponding (E)-olefins because of an unfavorable steric repulsion between an aromatic proton at the *ortho*-position and an olefinic α-proton (Fig. 9a). However, in the present case for α-phenyl substituted aldehyde **5e**, there is not such olefinic proton for unfavorable congestion with an aromatic proton at the *ortho*-position, but rather a favorable hydrogen bond with a carbonyl oxygen (Fig. 9b),[13] which allows a $\sigma \rightarrow \pi^*$ interaction, which enhances the degree of the "*syn-effect*" for the phenyl group (Entry 7) than that in the previous cases. Furthermore, 6π-electron homoaromaticity can also work to stabilize the *syn*-conformation at the transition state by the participation of π-bonding electrons of the phenyl group (Fig. 9c), due to the absence of a steric repulsion between the olefinic protons, as in Fig. 9a.

The fact that (Z)-silyl enol ether was still produced in the case of ^{t}Bu substituted aldehyde **5d** (Entry 6), in which 6π-electron homoaromaticity is very unlikely, might strongly sug-



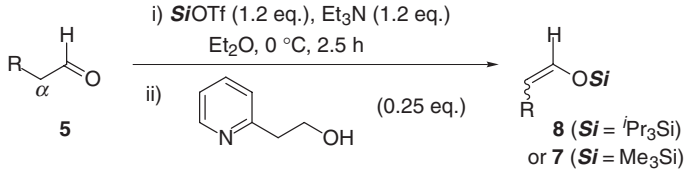
a) steric repulsion between *o*-H of Ph group and an olefinic atom

b) $\sigma \rightarrow \pi^*$ interaction and hydrogen bonding between *o*-H of Ph group and O atom

c) 6π-electron homoaromaticity in α-phenyl substituted system

Fig. 9.

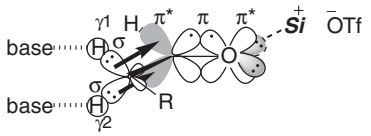
Table 3. Conversion of Aldehydes to the Corresponding Silyl Enol Ethers by Using Silyl Triflates



5 **8** (***Si*** = ^{i}Pr$_3$Si) or **7** (***Si*** = Me$_3$Si)

Entry	**5**	R	***Si***	*Z*/*E* of **8**,**7**[a]	Yield of **8**,**7**/%[b]	
1	**a**	CH_3	^{i}Pr$_3$Si	96/4	**8a**	71
2	**b**	$CH_3(CH_2)_7$	Me$_3$Si	87/13[c]	**7b**	35[c]
3	**b**	$CH_3(CH_2)_7$	^{i}Pr$_3$Si	93/7	**8b**	71
4	**c**	$(CH_3)_2CH$	^{i}Pr$_3$Si	88/12	**8c**	72
5	**d**	$(CH_3)_3C$	^{i}Pr$_3$Si	84/16	**8d**	63
6	**e**	Ph	^{i}Pr$_3$Si	60/40	**8e**	54
7	**f**	BnO	^{i}Pr$_3$Si	96/4	**8f**	77
8	**g**	BnS	^{i}Pr$_3$Si	37/63	**8g**	92

a) The ratios were determined by 400 MHz ^{1}H NMR spectra. The ratios were confirmed not to be changed during the purification by column chromatography on silica gel. b) Isolated yields. c) Yield and *Z*/*E* ratio were determined by 400 MHz ^{1}H NMR spectrum of the crude products.



enhanced $\sigma \rightarrow \pi^*$ interaction

Fig. 10.

gest that the $\sigma \rightarrow \pi^*$ interaction works at the stage of deprotonation, even in this case. Therefore, if the reaction is carried out under the conditions that the $\sigma \rightarrow \pi^*$ interaction is enhanced by polarizing and lowering in energy of the π^* orbital, the *Z*-selectivity is anticipated to be increased. Based on this hypothesis, a more Lewis-acidic silyl triflate than silyl chloride was next used as a silylating agent (Table 3), which can activate the carbonyl group strongly (Fig. 10).[14–16]

When decanal (**5b**) was treated with trimethylsilyl triflate and Et_3N in Et_2O at 0 °C, a remarkable enhancement of the *Z*/*E* ratio was observed (Entry 2). When triisopropylsilyl triflate (TIPSOTf) was used, both the *Z*-selectivity and the chemical yield were further increased (Entry 3).[17] Then, the conversion of various kinds of aldehydes **5** to the corresponding silyl enol ethers **8** was carried out using TIPSOTf. An enhancement of the *Z*/*E* ratios was observed in the case of aliphatic aldehydes **5a**–**d**, while keeping the same order of the *Z*-preference (Entries 1,3–5) as that using silyl chloride. To our surprise, the silylation of 3,3-dimethylbutanal (R = ^{t}Bu) (**5d**) with TIPSOTf realized a dramatic increase of the *Z*-selectivity (Entry 5), which strongly suggested that the $\sigma \rightarrow \pi^*$ interaction worked effectively, as anticipated. The highest *Z*-selectivity was also observed in the case of benzyloxy substituted aldehyde **5f** (Entry 7). In the reaction of (benzylthio)acetaldehyde (**5g**), not only the $\sigma_{C-H} \rightarrow \pi^*$ interaction, but also the $\sigma_{C-S} \rightarrow \pi^*$ interaction[11] seemed to be enhanced together to scarcely alter the *Z*/*E* ratio (Entry 8). Furthermore, a slight decrease of the *Z*-selectivity for phenylacetaldehyde (**5e**) was observed when TIPSOTf was used as a silylating agent (Entry 6). This result might have been due to the weakened hydrogen bond in *syn*-conformation caused by a decrease of the electron density of the carbonyl oxygen by coordinating to a strongly Lewis-acidic silyl group.

As described above, the stereochemistry in the conversion of aldehydes into the corresponding silyl enol ethers by a treatment with silyl chlorides or silyl triflates and a base was well rationalized by the "*syn-effect*", which was accounted for by the $\sigma \rightarrow \pi^*$ interaction and/or 6π-electron homoaromaticity. In the reaction using silyl triflates, with which a strong $\sigma \rightarrow \pi^*$ interaction was anticipated, a higher *Z*-selectivity was observed, especially in the case of aliphatic aldehydes.[18]

In conclusion, both in the conversion of (*E*)-α,β-unsaturated esters to the corresponding β,γ-unsaturated esters and in the conversion of various α-substituted aldehydes to the corresponding silyl enol ethers, their stereochemical outcomes were

well rationalized by the "*syn-effect*" in the transition state of deprotonation, which arose from the $\sigma \rightarrow \pi^*$ interaction and/or 6π-electron homoaromaticity. It is noteworthy that the highest *Z*-selectivity was observed for fluoro and/or benzyloxy substituent of the examined substrates.

Experimental

The ^{1}H NMR spectra were recorded on JEOL JNM-GX 400, Lambda 400, and Lambda 300 NMR spectrometers. The chemical shifts were determined in the δ-scale relative to $Si(CH_3)_4$ ($\delta = 0$) as an internal standard. The IR spectra were measured by a JASCO FT/IR-230 spectrometer and the MS spectra were recorded with Hitachi M-80 and JEOL SX-102A mass spectrometers, respectively. All glass equipment was flame-dried under a vacuum before use. THF and Et_2O were freshly distilled from sodium diphenylketyl. All other solvents were distilled and stored over drying agents. Thin-layer chromatography (TLC), and flash column chromatography were performed using Merck's silica gel 60 PF_{254} (Art. 7749) and Cica-Merck's silica gel 60 (No. 9385-5B), respectively. Commercially available reagents were used without further purification, unless otherwise noted.

(*E*)-α,β-Unsaturated esters **1a**,**c**–**e**,**h** containing an alkyl or a benzyloxy group at the γ-position were prepared by the Horner–Emmons–Wadsworth reaction using $(EtO)_2P(O)CH_2COOEt$ in good yields.[19] In the cases where trace amounts of (*Z*)-isomers were formed, they were separated from the (*E*)-isomers by column chromatography or preparative TLC.

Octyl (*E*)-2-Pentenoate (1b). To a suspension of NaH (60% dispersion in mineral oil) (360 mg, 9.0 mmol) in THF (10 mL) was added a solution of $(EtO)_2P(O)CH_2COO(CH_2)_7CH_3$ (2.77 g, 9.0 mmol) in THF (5 mL) dropwise at 0 °C under a N_2 atmosphere. After stirring for 30 min, CH_3CH_2CHO (0.65 mL, 9.0 mmol) was added to the mixture at the same temperature. After stirring overnight at room temperature, a saturated aqueous NH_4Cl solution was added to the reaction mixture. After evaporation of the organic solvent, the residue was extracted with Et_2O, followed by washing with brine, and dried over Na_2SO_4. The solvent was removed and the crude product was purified by column chromatography (SiO_2, hexane/AcOEt = 5/1, v/v) to give **1b** in 77% yield (1.47 g). An oil; IR (neat) 2956, 2927, 2856, 1724, 1656, 1462, 1380, 1335, 1308, 1288, 1265, 1178, 1123, 1088, 1038, 979, 859 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, J = 7.31 Hz), 1.07 (3H, t, J = 7.31 Hz), 1.20–1.40 (10H, m), 1.65 (2H, p, J = 6.83 Hz), 2.23 (2H, dp, J = 1.72, 7.31 Hz), 4.12 (2H, t, J = 6.83 Hz), 5.82 (1H, dt, J = 15.63, 1.72 Hz), 7.01 (1H, dt, J = 15.63, 7.31 Hz). HRMS (EI) Found: m/z 212.1773. Calcd for $C_{13}H_{24}O_2$: 212.1777.

Ethyl 4-Phenyl-2-(phenylthio)butanoate (4). To a suspension of NaH (60% dispersion in mineral oil) (264 mg, 6.6 mmol) in DMF (20 mL) was added ^{n}Bu$_4$NI (155 mg, 0.42 mmol), followed by the addition of a solution of ethyl (phenylthio)acetate (**3**) (1.176 g, 6.0 mmol) in DMF (5 mL) under a N_2 atmosphere. After stirring for a few minutes at room temperature, (2-bromoethyl)benzene (0.86 mL, 6.3 mmol) was added dropwise to the reaction mixture. After stirring for 24 h, the reaction mixture was diluted with Et_2O, quenched with phosphate-buffer solution (pH 7), and the organic substances were extracted with Et_2O. The organic phase was then washed with H_2O and brine, dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane/AcOEt = 20/1, v/v) to give **4** in 31% yield (550 mg). An oil; IR (neat) 3060, 3026, 2980, 2932, 1731, 1603, 1583, 1496, 1480, 1454, 1440, 1389, 1260, 1151, 1093, 1025, 748, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (3H, t, J = 7.07 Hz), 2.01–2.11 (1H, m), 2.16–2.26 (1H, m), 2.76 (2H, t, J = 7.56 Hz), 3.62 (1H, t, J = 7.08 Hz), 4.06–4.16 (2H, m), 7.15–7.33 (8H, m), 7.41–7.44 (2H, m). MS (EI) m/z 301 ($M^+ + 1$, 11.39%), 300 (M^+, 56.44), 196 (25.79), 191 (21.91), 145 (11.63), 123 (32.01), 117 (68.37), 110 (17.98), 91 (100.00), 65 (18.35), 58 (10.41).

Ethyl (*E*)-4-Phenyl-2-butenoate (1f). To a solution of ethyl 4-phenyl-2-(phenylthio)butanoate (**4**) (225 mg, 0.75 mmol) in CH_2Cl_2 (3 mL), finely powdered $NaHCO_3$ (126 mg, 1.50 mmol) was added. After cooling to 0 °C, a solution of *m*CPBA (ca. 70% pure, 194 mg, 0.788 mmol) in CH_2Cl_2 (3 mL) was added dropwise to the mixture. After stirring for 30 min, H_2O was added. The organic solvent was removed and the organic substances were extracted by AcOEt. The combined extracts were washed by brine and dried over Na_2SO_4. After evaporating the solvent, the crude product was purified by a preparative TLC (SiO_2, hexane/AcOEt = 5/1, v/v) to give the corresponding sulfoxide. The sulfoxide was then refluxed in toluene for 2 h to afford **1f** in 74% yield (106 mg). An oil; IR (neat) 3085, 3062, 3029, 2981, 2936, 2904, 1719, 1654, 1603, 1495, 1454, 1367, 1323, 1271, 1202, 1161, 1042, 984, 751, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.27 (3H, t, J = 7.15 Hz), 3.51 (2H, dd, J = 1.47, 6.79 Hz), 4.17 (2H, q, J = 7.15 Hz), 5.81 (1H, dt, J = 15.59, 1.47 Hz), 7.09 (1H, dt, J = 15.59, 6.79 Hz), 7.16–7.34 (5H, m). MS (EI) m/z 190 (M^+, 28.21%), 145 (17.90), 117 (44.24), 115 (26.98), 91 (15.00), 77 (6.06), 58 (100.00).

Ethyl (*E*)-4-Fluoro-2-butenoate (1g).[20] To a suspension of AgF (5.709 g, 45.0 mmol) in CH_3CN (50 mL) was added a solution of ethyl (*E*)-4-bromo-2-butenoate (2.896 g, 15.0 mmol) in CH_3CN (10 mL) under a N_2 atmosphere in the dark. After stirring for 7 days at room temperature, the reaction mixture was filtered through celite. After evaporating the solvent, the product was purified by column chromatography (SiO_2, hexane/Et_2O = 8/1, v/v) to give **1g** in 37% yield (735 mg). An oil; IR (neat) 2984, 2939, 1723, 1668, 1449, 1380, 1368, 1308, 1277, 1237, 1180, 1085, 1037, 998, 968, 912 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (3H, t, J = 7.07 Hz), 4.22 (2H, q, J = 7.07 Hz), 5.06 (2H, ddd, J = 2.20, 3.90, 46.11 Hz), 6.12 (1H, dq, J = 15.86, 2.20 Hz), 6.96 (1H, ddt, J = 15.86, 22.69, 3.90 Hz). MS (CI) m/z 133 ($M^+ + 1$, 100.00%), 117 (1.59), 105 (1.10), 99 (1.13).

Ethyl (*E*)-4-Benzylthio-2-butenoate (1i). To a solution of BnSH (68 mg, 0.548 mmol) in CH_2Cl_2 (2.5 mL) was added Et_3N (0.08 mL, 0.548 mmol) at 0 °C and stirred for 30 min. Then, a solution of ethyl (*E*)-4-bromo-2-butenoate (106 mg, 0.548 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise at 0 °C. After stirring overnight at 0 °C, the reaction mixture was quenched with a phosphate buffer solution (pH 7). The organic substances were extracted with CH_2Cl_2, followed by washing with H_2O and brine, and dried over Na_2SO_4. After evaporating the solvent, the residue was purified by preparative TLC (SiO_2, hexane/Et_2O = 8/1, v/v) to give **1i** in 73% yield (94 mg). An oil; IR (neat) 3060, 3027, 2980, 2920, 1717, 1652, 1600, 1494, 1454, 1418, 1395, 1367, 1315, 1267, 1199, 1149, 1042, 979, 748, 703 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (3H, t, J = 7.07 Hz), 3.10 (2H, dd, J = 0.98, 7.32 Hz), 3.66 (2H, s), 4.21 (2H, q, J = 7.07 Hz), 5.83 (1H, dt, J = 15.37, 0.98 Hz), 6.87 (1H, dt, J = 15.37, 7.32 Hz), 7.24–7.34 (5H, m). MS (EI) m/z 236 (M^+, 23.53%), 145 (36.34), 123 (72.84), 114 (96.10), 99 (34.42), 91 (100.00), 65 (61.93), 45 (62.78), 39 (64.58), 29 (81.79).

The Representative Procedure for Conversion of (*E*)-α,β-Unsaturated Esters to the Corresponding β,γ-Unsaturated Esters. To a solution of hexamethyldisilazane (0.12 mL, 0.55 mmol) in THF (1 mL) was added a solution of ^{n}BuLi (0.36 mL, 0.55 mmol, 1.52 M in hexane) at 0 °C under a N_2 atmosphere. After stirring for 15 min, HMPA (0.38 mL, 2.2 mmol) was added and stirred for another 30 min at 0 °C. After that, the reaction mixture was cooled to −70 °C, and a solution of octyl (*E*)-2-pentenoate (**1b**) (106 mg, 0.50 mmol) in THF (0.5 mL) was added to the mixture, and the resulting solution was stirred for 30 min. The reaction mixture was then quenched with a solution of aqueous HCl diluted in EtOH cooled to −70 °C, and allowed to warm up to room temperature. The solvent was evaporated and the residue was extracted with Et_2O, followed by washing with H_2O and brine, dried over Na_2SO_4. After evaporating the solvent, the crude product was purified by column chromatography (SiO_2, hexane/Et_2O = 20/1, v/v) to give the β,γ-unsaturated ester **2b** in 83% yield (88 mg, Z/E = 94/6).

The physical and spectral data of the resulting β,γ-unsaturated esters **2** are given in the following:

Ethyl 3-Pentenoate (2a): (Z/E = 91/9). An oil, IR (neat) 3032, 2982, 2960, 1739, 1655, 1447, 1402, 1371, 1322, 1247, 1178, 1098, 1037, 941, 851, 746, 680 cm^{-1}; ^{1}H NMR of (*Z*)-form (400 MHz, $CDCl_3$) δ 1.259 (3H, t, J = 7.02 Hz), 1.64 (3H, dd, J = 0.91, 6.41 Hz), 3.08 (2H, d, J = 7.02 Hz), 4.15 (2H, q, J = 7.02 Hz), 5.54–5.70 (2H, m); ^{1}H NMR of (*Z*)-form (400 MHz, C_6D_6) δ 0.96 (3H, t, J = 7.02 Hz), 1.38 (3H, ddt, J = 1.83, 6.72, 0.92 Hz), 2.92 (2H, ddq, J = 1.83, 7.02, 0.92 Hz), 3.93 (2H, q, J = 7.02 Hz), 5.48 (1H, dtq, J = 10.68, 1.83, 6.72, Hz), 5.71 (1H, dtq, J = 10.68, 7.02, 1.83 Hz); ^{1}H NMR of (*E*)-form (400 MHz, $CDCl_3$) δ 1.264 (3H, t, J = 7.02 Hz), 1.70 (3H, d, J = 4.89 Hz), 3.01 (2H, d, J = 5.19 Hz), 4.14 (2H, q, J = 7.02 Hz), 5.54–5.70 (2H, m); ^{1}H NMR of (*E*)-form (400 MHz, C_6D_6) δ 0.96 (3H, t, J = 7.02 Hz), 1.48 (3H, ddt, J = 1.53, 6.72, 1.22 Hz), 2.85 (2H, ddq, J = 1.53, 7.02, 1.22 Hz), 3.93 (2H, q, J = 7.02 Hz), 5.33 (1H, dtq, J = 15.26, 1.53, 6.72 Hz), 5.58 (1H, dtq, J = 15.26, 7.02, 1.53 Hz). MS (CI) m/z 129 ($M^+ + 1$, 100.00%), 113 (25.62), 112 (9.27), 85 (12.82), 81 (11.25), 79 (9.66), 73 (16.04), 71 (14.18), 69 (14.53).

Octyl 3-Pentenoate (2b): (Z/E = 94/6). An oil; IR (neat) 3032, 2956, 2927, 2857, 1740, 1660, 1467, 1403, 1378, 1321, 1288, 1248, 1166, 1099, 1016, 966, 723, 679 cm^{-1}; ^{1}H NMR of (*Z*)-form (400 MHz, $CDCl_3$) δ 0.88 (3H, t, J = 7.07 Hz), 1.20–1.40 (10H, m), 1.59–1.67 (2H, m), 1.64 (3H, dd, J = 1.46, 6.59 Hz), 3.09 (2H, dd, J = 1.29, 6.83 Hz), 4.08 (2H, t, J = 6.83 Hz), 5.53–5.71 (2H, m); ^{1}H NMR of (*Z*)-form (400 MHz, C_6D_6) δ 0.89 (3H, t, J = 7.07 Hz), 1.10–1.30 (10H, m), 1.40–1.50 (2H, m), 1.41 (3H, ddt, J = 1.96, 6.83, 0.98 Hz), 2.96 (2H, ddq, J = 7.07, 1.96, 0.98 Hz), 4.01 (2H, t, J = 6.83 Hz), 5.50 (1H, dtq, J = 10.71, 1.96, 6.83 Hz), 5.72 (1H, dtq, J = 10.71, 7.07, 1.96 Hz); ^{1}H NMR of (*E*)-form (400 MHz, $CDCl_3$) δ 0.88 (3H, t, J = 7.07 Hz), 1.20–1.40 (10H, m), 1.59–1.67 (2H, m), 1.70 (3H, dd, J = 1.22, 4.88 Hz), 3.01 (2H, dd, J = 1.24, 5.60 Hz), 4.08 (2H, t, J = 6.83 Hz), 5.53–5.71 (2H, m); ^{1}H NMR of (*E*)-form (400 MHz, C_6D_6) δ 0.89 (3H, t, J = 7.07 Hz), 1.10–1.30 (10H, m), 1.40–1.50 (2H, m), 1.50 (3H, ddt, J = 1.72, 6.59, 1.22 Hz), 2.89 (2H, ddq, J = 1.48, 7.07, 1.22 Hz), 4.01 (2H, t, J = 6.83 Hz), 5.35 (1H, dtq, J = 15.12, 1.48, 6.59 Hz), 5.60 (1H, dtq, J = 15.12, 7.07, 1.72 Hz). MS (EI) m/z 213 ($M^+ + 1$, 20.16%), 212 (100.00), 157 (14.96), 113 (7.73), 112 (31.72), 101 (67.93), 100 (89.74), 99 (3.72), 83 (46.06), 67 (6.42).

Ethyl 3-Hexenoate (2c): (Z/E = 85/15). An oil; IR (neat) 3040, 2967, 2936, 2876, 1739, 1653, 1459, 1402, 1367, 1327, 1254, 1177, 1113, 1038, 970, 940, 870, 850 cm^{-1}; ^{1}H NMR of (*Z*)-form (400 MHz, $CDCl_3$) δ 0.98 (3H, t, J = 7.56 Hz), 1.26 (3H, t, J = 7.07 Hz), 2.06 (2H, p, J = 7.56 Hz), 3.07 (2H, d, J = 6.34 Hz), 4.143 (2H, q, J = 7.07 Hz), 5.49–5.64 (2H, m); ^{1}H NMR of (*Z*)-form (400 MHz, C_6D_6) δ 0.82 (3H, t, J = 7.33 Hz), 0.94 (3H, t, J = 7.02 Hz), 1.82–1.89 (2H, m), 2.92 (2H, ddt, J = 1.83, 7.32, 0.92 Hz), 3.93 (2H, q, J = 7.02 Hz), 5.44 (1H, dtt, J = 10.68, 1.83, 7.32 Hz), 5.67 (1H, dtt, J = 10.68, 1.53, 7.32 Hz); ^{1}H NMR of (*E*)-form (400 MHz, $CDCl_3$) δ 0.99 (3H, t, J = 7.56 Hz), 1.26 (3H, t, J = 7.07 Hz), 2.06 (2H, p, J = 7.56 Hz), 3.01 (2H, d, J = 6.59 Hz), 4.138 (2H, q, J = 7.07 Hz), 5.49–5.64 (2H, m); ^{1}H NMR of (*E*)-form (400 MHz, C_6D_6) δ 0.85 (3H, t, J = 7.33 Hz), 0.94 (3H, t, J = 7.02 Hz), 1.82–1.89 (2H, m), 2.88 (2H, dq, J = 7.02, 1.22 Hz), 3.93 (2H, q, J = 7.02 Hz), 5.36–5.46 (1H, m), 5.60 (1H, dtt, J = 15.57, 1.53, 7.02 Hz). MS (CI) m/z 143 ($M^+ + 1$, 100.00%), 142 (M^+, 4.51), 115 (1.85), 97 (0.98), 79 (15.20), 60 (6.08).

Ethyl 5-Methyl-3-hexenoate (2d): (Z/E = 70/30). An oil; IR (neat) 2960, 2871, 1740, 1465, 1367, 1325, 1300, 1250, 1179, 1123, 1038, 971, 942, 721 cm^{-1}; ^{1}H NMR of (*Z*)-form (400 MHz, $CDCl_3$) δ 0.97 (6H, d, J = 6.59 Hz), 1.26 (3H, t, J = 7.07 Hz), 2.50–2.63 (1H, m), 3.08 (2H, dd, J = 1.46, 4.15 Hz), 4.142 (2H, q, J = 7.07 Hz), 5.36–5.56 (2H, m); ^{1}H NMR of (*Z*)-form (400 MHz, C_6D_6) δ 0.87 (6H, d, J = 6.59 Hz), 1.00 (3H, t, J = 7.07 Hz), 2.36–2.48 (1H, m), 2.93 (2H, dd, J = 1.46, 7.07 Hz), 3.95 (2H, q, J = 7.07 Hz), 5.30 (1H, ddt, J = 9.51, 10.98, 1.46 Hz), 5.47–5.57 (1H, m); ^{1}H NMR of (*E*)-form (400 MHz, $CDCl_3$) δ 0.99 (6H, d, J = 6.83 Hz), 1.26 (3H, t, J = 7.07 Hz), 2.25–2.35 (1H, m), 3.00 (2H, dd, J = 0.73, 5.61 Hz), 4.136 (2H, q, J = 7.07 Hz), 5.36–5.56 (2H, m); ^{1}H NMR of (*E*)-form (400 MHz, C_6D_6) δ 0.91 (6H, d, J = 6.83 Hz), 0.99 (3H, t, J = 7.07 Hz), 2.10–2.22 (1H, m), 2.87 (2H, d, J = 6.83 Hz), 3.94 (2H, q, J = 7.07 Hz), 5.39 (1H, ddt, J = 6.59, 15.37, 1.22 Hz), 5.47–5.57 (1H, m). MS (CI) m/z 157 ($M^+ + 1$, 100.00%), 156 (M^+, 4.63), 111 (2.24), 109 (1.04), 79 (1.87), 69 (1.04), 60 (2.68).

Ethyl 5,5-Dimethyl-3-hexenoate (2e): (Z/E = 0/100). An oil; IR (neat) 2959, 2900, 2869, 1740, 1658, 1480, 1464, 1366, 1269, 1245, 1180, 1150, 1035, 973 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 (9H, s), 1.26 (3H, t, J = 7.07 Hz), 3.00 (2H, dd, J = 1.22, 6.83 Hz), 4.14 (2H, q, J = 7.07 Hz), 5.44 (1H, dt, J = 15.61, 6.83 Hz), 5.58 (1H, dt, J = 15.61, 1.22 Hz). MS (EI) m/z 170 (M^+, 4.25%), 130 (100.00), 128 (37.12), 113 (11.26), 102 (12.31), 83 (9.85), 57 (16.83).

Ethyl 4-Phenyl-3-butenoate (2f): (Z/E = 16/84). An oil; IR (neat) 3027, 2981, 2937, 2905, 1737, 1600, 1496, 1448, 1369, 1322, 1295, 1251, 1159, 1028, 966, 746, 693 cm^{-1}; ^{1}H NMR of (*Z*)-form (400 MHz, $CDCl_3$) δ 1.27 (3H, t, J = 7.07 Hz), 3.33 (2H, dd, J = 1.71, 7.32 Hz), 4.17 (2H, q, J = 7.07 Hz), 5.90 (1H, dt, J = 11.46, 7.32 Hz), 6.63 (1H, d, J = 11.46 Hz), 7.20–7.38 (5H, m); ^{1}H NMR of (*E*)-form (400 MHz, $CDCl_3$) δ 1.28 (3H, t, J = 7.07 Hz), 3.24 (2H, dd, J = 1.46, 7.07 Hz), 4.17 (2H, q, J = 7.07 Hz), 6.30 (1H, dt, J = 15.86, 7.07 Hz), 6.49 (1H, d, J = 15.86 Hz), 7.20–7.38 (5H, m).[21] MS (EI) m/z 190 (M^+, 16.65%), 117 (49.15), 115 (14.22), 91 (10.23), 77 (6.38), 58 (100.00).

Ethyl 4-Fluoro-3-butenoate (2g): (Z/E = 100/0). An oil; IR (neat) 2955, 2924, 2851, 1735, 1670, 1654, 1459, 1376, 1261, 1031 cm^{-1}; ^{1}H NMR of (*Z*)-form (300 MHz, $CDCl_3$) δ 1.21 (3H, t, J = 7.14 Hz), 3.18 (2H, dt, J = 7.14, 1.65 Hz), 4.16 (2H, q, J = 7.14 Hz), 5.03 (1H, ddt, J = 4.77, 41.4, 7.14 Hz),

6.55 (1H, ddt, $J = 4.77$, 84.03, 1.65 Hz). MS (EI) m/z 133 ($M^+ + 1$, 7.96%), 132 (M^+, 2.94), 117 (13.41), 113 (9.33), 103 (9.07), 99 (43.19), 87 (100.00), 59 (52.85).

Ethyl 4-Benzyloxy-3-butenoate (2h):[22] ($Z/E = 100/0$). An oil; IR (neat) 3060, 3032, 2981, 2930, 2910, 2880, 1736, 1669, 1497, 1455, 1401, 1367, 1325, 1294, 1179, 1112, 1062, 1030, 736, 698 cm^{-1}; ^1H NMR of (Z)-form (400 MHz, $CDCl_3$) δ 1.25 (3H, t, $J = 7.07$ Hz), 3.17 (2H, dd, $J = 1.71$, 7.07 Hz), 4.13 (2H, q, $J = 7.07$ Hz), 4.62 (1H, dt, $J = 6.10$, 7.07 Hz), 4.81 (2H, s), 6.17 (1H, dt, $J = 6.10$, 1.71 Hz), 7.30–7.36 (5H, m). HRMS (EI) Found: m/z 220.1095. Calcd for $C_{13}H_{16}O_3$: 220.1099.

Ethyl 4-Benzylthio-3-butenoate (2i):[22] ($Z/E = 44/56$). An oil; IR (neat) 3061, 3029, 2932, 2870, 1735, 1653, 1603, 1495, 1454, 1369, 1314, 1255, 1160, 1096, 1071, 1028, 939, 860, 758, 701 cm^{-1}; ^1H NMR of (Z)-form (400 MHz, $CDCl_3$) δ 1.25 (3H, t, $J = 7.02$ Hz), 3.14 (2H, dd, $J = 1.83$, 7.02 Hz), 3.87 (2H, s), 4.13 (2H, q, $J = 7.02$ Hz), 5.74 (1H, dt, $J = 9.46$, 7.02 Hz), 6.12 (1H, dt, $J = 9.46$, 1.83 Hz), 7.22–7.32 (5H, m); ^1H NMR of (E)-form (400 MHz, $CDCl_3$) δ 1.24 (3H, t, $J = 7.02$ Hz), 3.06 (2H, dd, $J = 1.22$, 7.02 Hz), 3.89 (2H, s), 4.12 (2H, q, $J = 7.02$ Hz), 5.70 (1H, dt, $J = 14.96$, 7.02 Hz), 6.08 (1H, dt, $J = 14.96$, 1.22 Hz), 7.22–7.32 (5H, m). MS (EI) m/z 237 ($M^+ + 1$, 10.84%), 236 (M^+, 74.97), 190 (12.73), 163 (13.58), 148 (6.58), 129 (9.82), 123 (7.21), 91 (100.00), 65 (39.37), 39 (18.75), 29 (26.75).

The Representative Procedure for Conversion of Aldehydes to the Corresponding Silyl Enol Ethers Using Silyl Chloride. To a mixed solution of chloro(methyl)diphenylsilane (400 mg, 1.72 mmol) and octanal (**5b**) (224 mg, 1.43 mmol) in DMF (1.0 mL) was added Et_3N (0.41 mL, 2.86 mmol) at 0 °C. The mixture was immediately heated at 60 °C. After stirring for 48 h at 60 °C, the reaction mixture was cooled to room temperature. Cold pentane (20 mL) and 5% aqueous HCl (8 mL) were added to the mixture and the organic substances were extracted. The organic layer was washed by 5% aqueous $NaHCO_3$ three times and dried over Na_2SO_4. After evaporating the solvent, the crude products **6b** (538 mg) were analyzed by measuring the ^1H NMR spectrum to determine their yields and Z/E ratio. A sample for physical and spectral data was obtained by purification by column chromatography (SiO_2, hexane/$Et_2O = 60/1$, v/v).

In a similar way, other aldehydes **5a**,**c**–**g**, were converted to the corresponding silyl enol ethers **6a**,**c**–**g** and **7b**. The physical and spectral data of **6a**–**g**, **7b** are given in the following:

1-(Methyldiphenylsiloxy)-1-propene (6a): ($Z/E = 74/26$). An oil; IR (neat) 3070, 3047, 2952, 2917, 2861, 1662, 1590, 1488, 1428, 1402, 1362, 1257, 1122, 1065, 998, 837, 793, 773, 729, 698, 672 cm^{-1}; ^1H NMR of (Z)-form (400 MHz, $CDCl_3$) δ 0.694 (3H, s), 1.64 (3H, dd, $J = 1.83$, 6.71 Hz), 4.56 (1H, dq, $J = 5.80$, 6.71 Hz), 6.21 (1H, dq, $J = 5.80$, 1.83 Hz), 7.36–7.42 (6H, m), 7.59–7.61 (4H, m); ^1H NMR of (E)-form (400 MHz, $CDCl_3$) δ 0.689 (3H, s), 1.48 (3H, dd, $J = 1.83$, 6.71 Hz), 5.09 (1H, dq, $J = 11.90$, 6.71 Hz), 6.25 (1H, dq, $J = 11.90$, 1.83 Hz), 7.28–7.61 (10H, m). MS (EI) m/z 254 (M^+, 9.98%), 239 (12.67), 197 (100.00), 195 (27.21), 183 (21.48), 181 (11.75), 165 (10.64), 137 (90.18), 121 (10.54), 105 (20.48), 91 (8.76), 77 (9.63), 58 (9.80), 43 (37.42), 28 (16.96).

1-(Methyldiphenylsiloxy)-1-decene (6b): ($Z/E = 58/42$). An oil; IR (neat) 3070, 3050, 3028, 2955, 2924, 2854, 1656, 1590, 1466, 1428, 1399, 1377, 1256, 1180, 1121, 1092, 998, 834, 793, 728, 698 cm^{-1}; ^1H NMR of (Z)-form (400 MHz, $CDCl_3$) δ 0.686 (3H, s), 0.87 (3H, t, $J = 6.10$ Hz), 1.22–1.30 (12H, m), 2.13–2.18 (2H, m), 4.50 (1H, dt, $J = 5.80$, 7.33 Hz), 6.19 (1H, dt, $J = 5.80$, 1.52 Hz), 7.36–7.44 (6H, m), 7.58–7.60 (4H, m); ^1H NMR of (E)-form (400 MHz, $CDCl_3$) δ 0.690 (3H, s), 0.87 (3H, t, $J = 6.10$ Hz), 1.22–1.30 (12H, m), 1.80–1.85 (2H, m), 5.08 (1H, dt, $J = 11.91$, 7.33 Hz), 6.24 (1H, dt, $J = 11.91$, 1.22 Hz), 7.28–7.62 (10H, m). MS (EI) m/z 352 (M^+, 1.88%), 351 (6.24), 337 (30.95), 274 (6.82), 253 (24.06), 197 (100.00), 137 (13.00), 105 (5.23), 83 (9.52).

1-(Trimethylsiloxy)-1-decene (7b): ($Z/E = 60/40$). An oil; IR (neat) 3030, 2957, 2925, 2854, 1656, 1466, 1400, 1253, 1162, 1092, 922, 845, 751 cm^{-1}; ^1H NMR of (Z)-form (400 MHz, $CDCl_3$) δ 0.16 (9H, s), 0.87 (3H, t, $J = 6.83$ Hz), 1.18–1.38 (12H, m), 2.03–2.08 (2H, m), 4.47 (1H, dt, $J = 5.83$, 7.31 Hz), 6.12 (1H, dt, $J = 5.83$, 1.48 Hz); ^1H NMR of (E)-form (400 MHz, $CDCl_3$) δ 0.17 (9H, s), 0.87 (3H, t, $J = 6.83$ Hz), 1.18–1.38 (12H, m), 1.84–1.96 (2H, m), 4.98 (1H, dt, $J = 11.95$, 7.35 Hz), 6.17 (1H, dt, $J = 11.95$, 1.48 Hz). MS (EI) m/z 229 ($M^+ + 1$, 1.06%), 228 (M^+, 5.54), 213 (11.33), 185 (8.80), 155 (0.20), 143 (8.15), 129 (73.17), 115 (4.30), 75 (35.91), 73 (100.00).

3-Methyl-1-(methyldiphenylsiloxy)-1-butene (6c): ($Z/E = 54/46$). An oil; IR (neat) 3070, 3050, 3024, 2957, 2926, 2868, 1655, 1590, 1490, 1465, 1457, 1429, 1400, 1308, 1248, 1153, 1120, 1073, 998, 880, 795, 760, 735, 698 cm^{-1}; ^1H NMR of (Z)-form (400 MHz, $CDCl_3$) δ 0.69 (3H, s), 0.97 (6H, d, $J = 6.72$ Hz), 2.85–3.00 (1H, m), 4.37 (1H, dd, $J = 5.80$, 8.85 Hz), 6.09 (1H, d, $J = 5.80$ Hz), 7.36–7.44 (6H, m), 7.58–7.61 (4H, m); ^1H NMR of (E)-form (400 MHz, $CDCl_3$) δ 0.81 (3H, s), 0.92 (6H, d, $J = 7.02$ Hz), 2.10–2.25 (1H, m), 5.06 (1H, dd, $J = 7.93$, 11.90 Hz), 6.25 (1H, d, $J = 11.90$ Hz), 7.29–7.62 (10H, m). MS (EI) m/z 282 (M^+, 62.96%), 267 (80.67), 197 (100.00), 189 (12.87), 137 (19.57).

3,3-Dimethyl-1-(methyldiphenylsiloxy)-1-butene (6d): ($Z/E = 30/70$). An oil; IR (neat) 3070, 3051, 3023, 2953, 2862, 1652, 1590, 1477, 1461, 1428, 1406, 1360, 1283, 1254, 1205, 1119, 1088, 997, 934, 918, 852, 797, 731, 698, 677 cm^{-1}; ^1H NMR of (Z)-form (400 MHz, $CDCl_3$) δ 0.69 (3H, s), 1.16 (9H, s), 4.33 (1H, d, $J = 6.41$ Hz), 6.01 (1H, d, $J = 6.41$ Hz), 7.37–7.44 (6H, m), 7.58–7.61 (4H, m); ^1H NMR of (E)-form (400 MHz, $CDCl_3$) δ 0.69 (3H, s), 0.95 (9H, s), 5.18 (1H, d, $J = 12.21$ Hz), 6.21 (1H, d, $J = 12.21$ Hz), 7.29–7.62 (10H, m). MS (EI) m/z 296 (M^+, 48.89%), 281 (100.00), 239 (10.65), 197 (99.97), 137 (71.98), 105 (33.64).

1-(Methyldiphenylsiloxy)-2-phenylethene (6e): ($Z/E = 67/33$). An oil; IR (neat) 3069, 3050, 3025, 2959, 1643, 1593, 1492, 1447, 1428, 1302, 1261, 1212, 1200, 1144, 1119, 1083, 1075, 1029, 998, 925, 892, 792, 765, 731, 696 cm^{-1}; ^1H NMR of (Z)-form (400 MHz, $CDCl_3$) δ 0.78 (3H, s), 5.35 (1H, d, $J = 6.41$ Hz), 6.41 (1H, d, $J = 6.41$ Hz), 7.10–7.70 (15H, m); ^1H NMR of (E)-form (400 MHz, $CDCl_3$) δ 0.77 (3H, s), 6.14 (1H, d, $J = 12.21$ Hz), 7.01 (1H, d, $J = 12.21$ Hz), 7.10–7.70 (15H, m). MS (EI) m/z 316 (M^+, 77.69%), 223 (20.93), 197 (100.00), 180 (72.19), 165 (10.48), 105 (15.65), 91 (18.12), 77 (9.35).

2-Benzyloxy-1-(methyldiphenylsiloxy)ethene (6f): ($Z/E = 100/0$). An oil; IR (neat) 3068, 3048, 2959, 2871, 1667, 1589, 1496, 1454, 1428, 1396, 1362, 1298, 1254, 1119, 1024, 973, 910, 835, 793, 730, 698 cm^{-1}; ^1H NMR of (Z)-form (400 MHz, $CDCl_3$) δ 0.71 (3H, s), 4.76 (2H, s), 5.43 (1H, d, $J = 3.36$ Hz), 5.53 (1H, d, $J = 3.36$ Hz), 7.24–7.62 (15H, m). MS (EI) m/z 346 (M^+, 19.75%), 269 (11.01), 255 (6.77), 239 (1.80), 197 (100.00), 178 (23.52), 163 (15.80), 137 (14.02), 105 (16.93), 91 (84.40), 65 (10.22).

2-Benzylthio-1-(methyldiphenylsiloxy)ethene (6g): (Z/E = 37/63). An oil; IR (neat) 3068, 3040, 3025, 2959, 2920, 1615, 1593, 1494, 1453, 1428, 1255, 1229, 1120, 1088, 1026, 998, 894, 856, 794, 734, 698 cm^{-1}; ^1H NMR of (*Z*)-form (400 MHz, $CDCl_3$) δ 0.70 (3H, s), 3.85 (2H, s), 5.01 (1H, d, J = 5.19 Hz), 6.37 (1H, d, J = 5.19 Hz), 7.15–7.62 (15H, m); ^1H NMR of (*E*)-form (400 MHz, $CDCl_3$) δ 0.65 (3H, s), 3.61 (2H, s), 5.53 (1H, d, J = 11.59 Hz), 6.52 (1H, d, J = 11.59 Hz), 7.15–7.62 (15H, m). MS (EI) m/z 364 ($M^+ + 2$, 8.82%), 363 ($M^+ + 1$, 22.21), 362 (M^+, 75.03), 271 (24.05), 197 (100.00), 165 (6.66), 105 (9.11), 91 (58.94), 65 (6.52), 43 (10.92).

The Representative Procedure for Conversion of Aldehydes to the Corresponding Silyl Enol Ethers Using TIPSOTf. To a solution of triisopropylsilyl trifluoromethanesulfonate (TIPSOTf) (379 mg, 1.2 mmol) in Et_2O (1.5 mL) was added Et_3N (0.17 mL, 1.2 mmol) at 0 °C. After stirring for 30 min, a solution of CH_3CH_2CHO (**5a**) (58 mg, 1.0 mmol) in Et_2O (0.5 mL) was added to the mixture and stirred for 2 h at 0 °C. The reaction mixture was then quenched with 2-(2-hydroxyethyl)pyridine (0.03 mL, 0.25 mmol), and the solvent was evaporated. The crude product was purified by silica-gel column chromatography using hexane as the eluent to give **8a** (151 mg, 71%) as a mixture of Z/E isomers (Z/E = 96/4).

In a similar way, other aldehydes **5b–g** were converted to the corresponding silyl enol ethers **8b–g**,**7b**. The physical and spectral data of **8a–g** are given in the following:

1-(Triisopropylsiloxy)-1-propene (8a): (Z/E = 96/4). An oil; IR (neat) 3040, 2945, 2894, 2868, 1660, 1465, 1403, 1385, 1362, 1260, 1179, 1130, 1065, 1014, 996, 920, 883, 685 cm^{-1}; ^1H NMR of (*Z*)-form (400 MHz, $CDCl_3$) δ 1.08 (18H, d, J = 6.10 Hz), 1.11–1.21 (3H, m), 1.59 (3H, dd, J = 1.71, 6.59 Hz), 4.45 (1H, dq, J = 5.86, 6.59 Hz), 6.29 (1H, dq, J = 5.86, 1.71 Hz); ^1H NMR of (*E*)-form (400 MHz, $CDCl_3$) δ 1.08 (18H, d, J = 6.10 Hz), 1.11–1.21 (3H, m), 1.51 (3H, dd, J = 1.48, 6.83 Hz), 5.00 (1H, dq, J = 11.70, 6.83 Hz), 6.31 (1H, dq, J = 11.70, 1.48 Hz). MS (EI) m/z 214 (M^+, 19.75%), 171 (100.00), 143 (56.05), 129 (14.99), 115 (50.37), 101 (32.47), 85 (16.08), 73 (23.72), 61 (53.78), 59 (15.72).

1-(Triisopropylsiloxy)-1-decene (8b): (Z/E = 93/7). An oil; IR (neat) 2925, 2867, 1655, 1465, 1400, 1259, 1097, 996, 882 cm^{-1}; ^1H NMR of (*Z*)-form (400 MHz, $CDCl_3$) δ 0.88 (3H, t, J = 6.83 Hz), 1.07 (18H, d, J = 6.10 Hz), 1.12–1.17 (3H, m), 1.27–1.36 (12H, m), 2.04–2.20 (2H, m), 4.35 (1H, m), 6.25 (1H, d, J = 5.85 Hz). ^1H NMR of (*E*)-form (400 MHz, $CDCl_3$) δ 0.88 (3H, t, J = 6.83 Hz), 1.06 (18H, d, J = 5.85 Hz), 1.12–1.17 (3H, m), 1.27–1.36 (12H, m), 1.82–1.92 (2H, m), 4.98 (1H, dt, J = 11.95, 6.59 Hz), 6.27 (1H, d, J = 11.95 Hz). MS (EI) m/z 312 (M^+, 2.90%), 269 (100.00), 241 (3.14), 227 (3.45), 213 (2.02), 183 (1.28), 171 (3.27), 157 (3.50), 129 (3.01), 99 (4.70).

3-Methyl-1-(triisopropylsiloxy)-1-butene (8c): (Z/E = 88/12). An oil; IR (neat) 3026, 2947, 2897, 2868, 1654, 1465, 1403, 1250, 1154, 1083, 1014, 996, 920, 882, 684 cm^{-1}; ^1H NMR of (*Z*)-form (400 MHz, $CDCl_3$) δ 0.962 (6H, d, J = 6.83 Hz), 1.08 (18H, d, J = 6.10 Hz), 1.11–1.17 (3H, m), 2.83 (1H, m), 4.24 (1H, dd, J = 5.85, 8.78 Hz), 6.15 (1H, d, J = 5.85 Hz); ^1H NMR of (*E*)-form (400 MHz, $CDCl_3$) δ 0.966 (6H, d, J = 6.59 Hz), 1.06 (18H, d, J = 6.34 Hz), 1.11–1.17 (3H, m), 2.20 (1H, m), 4.97 (1H, dd, J = 7.81, 11.95 Hz), 6.28 (1H, d, J = 11.95 Hz). MS (EI) m/z 242 (M^+, 24.11%), 227 (3.35), 199 (100.00), 171 (2.09), 157 (3.73), 131 (35.95), 103 (36.59), 75 (26.67), 61 (22.82), 59 (15.56).

3,3-Dimethyl-1-(triisopropylsiloxy)-1-butene (8d): (Z/E = 84/16). An oil; IR (neat) 3024, 2946, 2868, 1655, 1464, 1409, 1385, 1360, 1285, 1249, 1206, 1097, 1050, 996, 920, 883, 847, 716, 675 cm^{-1}; ^1H NMR of (*Z*)-form (300 MHz, $CDCl_3$) δ 1.05–1.20 (3H, m), 1.08 (18H, d, J = 5.87 Hz), 1.13 (9H, s), 4.19 (1H, d, J = 6.60 Hz), 6.07 (1H, d, J = 6.60 Hz); ^1H NMR of (*E*)-form (300 MHz, $CDCl_3$) δ 1.00 (9H, s), 1.05–1.20 (3H, m), 1.08 (18H, d, J = 5.87 Hz), 5.09 (1H, d, J = 12.10 Hz), 6.41 (1H, d, J = 12.10 Hz). MS (EI) m/z 256 (M^+, 13.87%), 241 (21.27), 213 (100.00), 185 (39.81), 157 (28.45), 143 (5.21), 131 (20.27), 103 (17.06), 75 (29.77), 57 (42.76).

2-Phenyl-1-(triisopropylsiloxy)ethene (8e): (Z/E = 60/40). An oil; IR (neat) 3062, 3030, 2945, 2893, 2867, 1644, 1602, 1496, 1464, 1416, 1267, 1151, 1088, 1069, 1030, 922, 883, 693 cm^{-1}; ^1H NMR of (*Z*)-form (400 MHz, $CDCl_3$) δ 1.13 (18H, d, J = 5.12 Hz), 1.17–1.28 (3H, m), 5.26 (1H, d, J = 6.59 Hz), 6.50 (1H, d, J = 6.59 Hz), 7.09–7.27 (3H, m), 7.64 (2H, d, J = 8.05 Hz); ^1H NMR of (*E*)-form (400 MHz, $CDCl_3$) δ 1.12 (18H, d, J = 4.64 Hz), 1.17–1.28 (3H, m), 6.04 (1H, d, J = 12.20 Hz), 7.08 (1H, d, J = 12.20 Hz), 7.09–7.27 (5H, m). MS (EI) m/z 276 (M^+, 63.27%), 233 (100.00), 191 (18.83), 163 (47.06), 161 (45.40), 147 (13.23), 103 (20.70), 89 (18.93), 75 (15.09).

2-Benzyloxy-1-(triisopropylsiloxy)ethene (8f): (Z/E = 96/4). An oil; IR (neat) 2944, 2867, 1664, 1465, 1398, 1362, 1253, 1134, 1015, 883, 733, 695 cm^{-1}; ^1H NMR of (*Z*)-form (400 MHz, $CDCl_3$) δ 1.09 (18H, d, J = 6.34 Hz), 1.13–1.21 (3H, m), 4.82 (2H, s), 5.35 (1H, d, J = 3.42 Hz), 5.60 (1H, d, J = 3.42 Hz), 7.28–7.37 (5H, m). ^1H NMR of (*E*)-form (400 MHz, $CDCl_3$) δ 1.05 (18H, d, J = 5.86 Hz), 1.13–1.21 (3H, m), 4.63 (2H, s), 6.39 (1H, d, J = 10.25 Hz), 6.52 (1H, d, J = 10.25 Hz), 7.28–7.37 (5H, m). MS (EI) m/z 306 (M^+, 27.05%), 263 (75.62), 157 (52.35), 129 (16.89), 115 (35.70), 91 (100.00), 59 (29.24).

2-Benzylthio-1-(triisopropylsiloxy)ethene (8g): (Z/E = 37/63). An oil; IR (neat) 3062, 3028, 2945, 2867, 1604, 1495, 1233, 1179, 1097, 1070, 883, 696 cm^{-1}; ^1H NMR of (*Z*)-form (400 MHz, $CDCl_3$) δ 1.07 (18H, d, J = 6.34 Hz), 1.05–1.18 (3H, m), 3.84 (2H, s), 4.90 (1H, d, J = 4.88 Hz), 6.47 (1H, d, J = 4.88 Hz), 7.18–7.34 (5H, m). ^1H NMR of (*E*)-form (400 MHz, $CDCl_3$) δ 1.01 (18H, d, J = 6.10 Hz), 1.05–1.18 (3H, m), 3.65 (2H, s), 5.45 (1H, d, J = 11.47 Hz), 6.59 (1H, d, J = 11.47 Hz), 7.18–7.34 (5H, m). MS (EI) m/z 322 (M^+, 60.58%), 279 (11.43), 245 (8.57), 188 (2.20), 157 (12.15), 91 (100.00).

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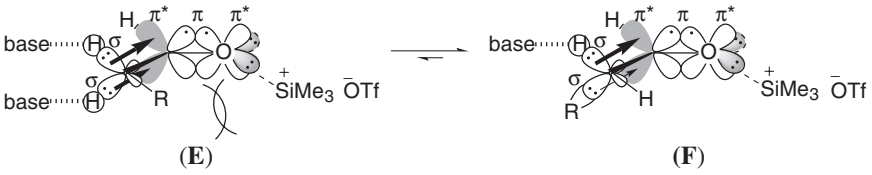

transition state in *syn*-coordination by trimethylsilyl triflate

Fig. 11.

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