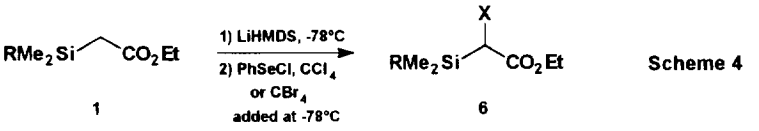


Scheme 4

Table 1. Preparation of α-halogeno and α-phenylseleno-α-silylacetic esters (Scheme 4).

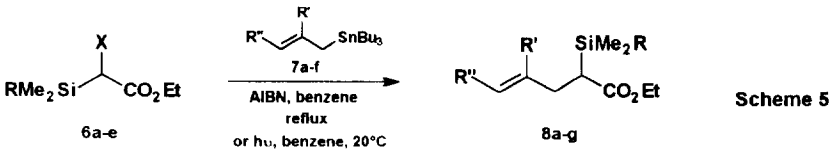
Entry	α-Silyl ester	R	Product	X	Yield (%)[a]
1	1a	t-BuO	6a	Cl	72
2	1a	t-BuO	6b	Br	70
3	1a	t-BuO	6c	PhSe	87[b]
4	1b	i-PrO	6d	PhSe	68
5	1c	Ph	6e	PhSe	89

[a] Crude yields. Esters **6** were used in the next step without further purification. [b] Isolated yield after purification.

The substrates **6a-e** were then reacted with allyltri-n-butyltin reagents **7a-f**[11] in benzene under reflux in the presence of AIBN or irradiated using a 300W sunlamp (Scheme 5). The allylated products **8** were obtained in good to excellent yields, after purification by kugelrohr distillation or flash chromatography (Table 2), except for entry 7 where the starting material was recovered unchanged. The nature of the radical precursor had little influence on the outcome of the reaction as shown by the excellent yields of **8a** obtained independently from **6a**, **6b** or **6c** (entry 1-3). As expected, the reaction conditions left unchanged the carbonyl group attached to the allylic moiety giving rise to the corresponding α-allyl-α-silylester **8c** in 67% yield (entry 5). Homoallylsilanes **8d-8g** and dienylester **8f** were also obtained under similar conditions (entry 6, 9 and 8 respectively).

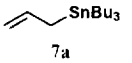
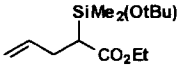
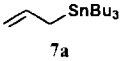
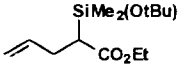
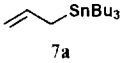
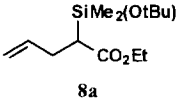
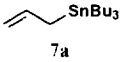
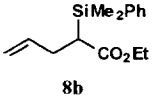
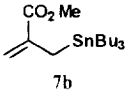
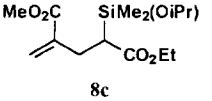
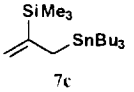
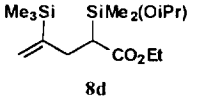
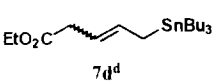
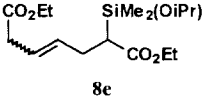
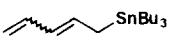
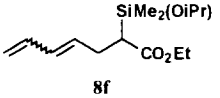
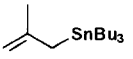
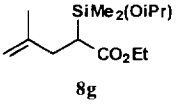
In order to obtain some information concerning the reactivity and the nature of the radical generated during our reaction, we carried out an investigation on the competitive allylation rate of the α-silylacetic ester **6d** with electronically differentiated allylstannanes (Scheme 6). The results summarized in Table 3 indicate that a relative rate enhancement is observed in the sense Me_3Si > Me > H. The small differences in allylation rate between **7a**, **7c** and **7f** do not allow for a clear-cut rationalization of our results. However, examination of the relative stability of the radical intermediates would offer a satisfactory explanation, assuming that a Me_3Si group is a better stabilizing group than a methyl group, which is in turn better than a hydrogen atom (Scheme 7).[12,13] Some reports indeed suggest that an α-silyl group stabilizes an alkyl radical by about 2.6 kcal/mol.[14] This could therefore offer a satisfactory explanation to our observations.

Concerning the nature of this α-silyl radical, we supposed that the silicon centre reduces the electrophilicity of the radical centre. This would explain the similar reactivity of our α-silyl radical and α-sulfinylated radical towards allylstannanes **7a,c,f**.[15] It is known that α-sulfinylated radicals behave like ambiphilic radicals, probably due to the electron donating ability of the sulfur centre on sulfoxide. A similar behaviour might be envisioned for α-silyl radicals such as **5** and may account for their reactivity.

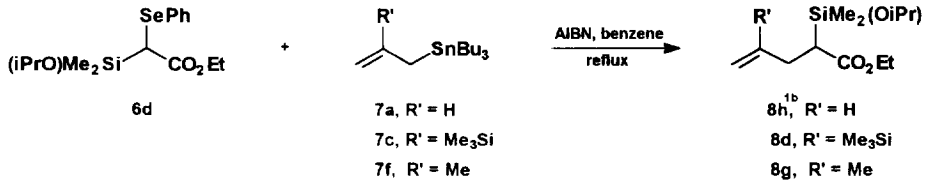


Scheme 5

Table 2. Radical allylation of α-halogeno and α-phenylseleno-α-silylacetic esters 6 (Scheme 5).

Entry	Substrate	R	X	Stannane	Product	Yield (%)[a,b]
1	6a	t-BuO	Br	 7a	 8a	97
2	6b	t-BuO	Cl	 7a	 8a	86
3	6c	t-BuO	PhSe	 7a	 8a	95
4	6e	Ph	PhSe	 7a	 8b	65 (68[c])
5	6d	i-PrO	PhSe	 7b	 8c	67
6	6d	i-PrO	PhSe	 7c	 8d	44
7	6d	i-PrO	PhSe	 7d[d]	 8e	N.R.[e]
8	6d	i-PrO	PhSe	 7e[f]	 8f	62
9	6d	i-PrO	PhSe	 7f	 8g	58

[a] Isolated yields after purification by distillation or flash chromatography. [b] AIBN, benzene, reflux. [c] hυ, benzene, 20°C. [d] 7:3 *E/Z* mixture. [e] No Reaction : **6d** was recovered unchanged. [f] 83:17 *E/Z* mixture.

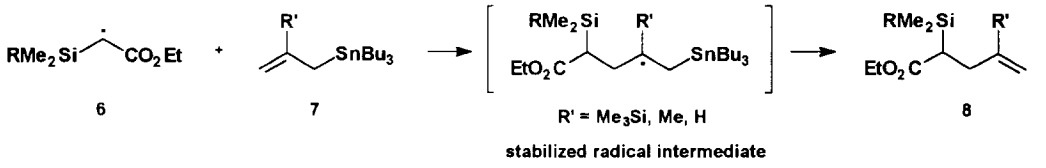


Scheme 6

Table 3. Competitive allylation of α-silylacetic ester 6d (Scheme 6).

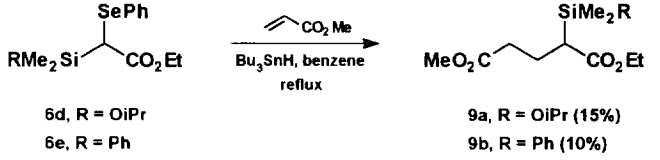
Entry	Allylstannanes[a]	α-Silylesters	Ratio[b]
1	7c/7f	8d/8g	1.7/1
2	7f/7a	8g/8h	1.6/1
3	7c/7a	8d/8h	1.9/1

[a] An equimolar amount of the allylstannanes were reacted with **6d**. [b] Estimated using 360 MHz ^{1}H NMR.



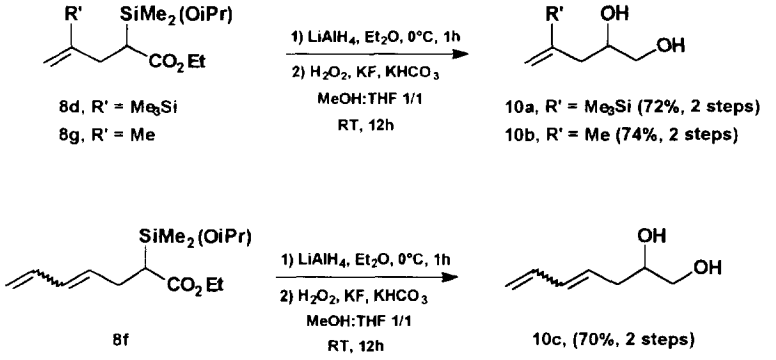
Scheme 7

It is, however, still premature to deduce the nature of the radical formed by this process only from these preliminary results. Experimental evidence has yet to be produced to support the ambiphilic nature of these radicals since our various attempts to add α-silylacetic ester radicals to electron-rich[16] and electron-poor olefins (Scheme 8) gave poor results which did not allow us to draw definitive conclusions.



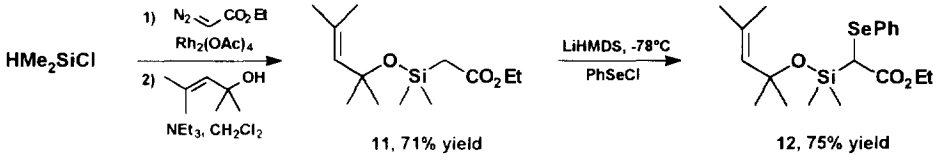
Scheme 8

The homoallylsilanes **8d** and **8f-g** were then reduced to the corresponding β-hydroxysilane using $LiAlH_4$ in ether and were directly subjected to the Tamao oxidation[17] to afford the homoallylic-1,2-diols **10a**, **10b** and **10c** in good overall yields (Scheme 9). This strategy thus affords an alternative route to those already known for the synthesis of homoallylic-1,2-diols.[1b]



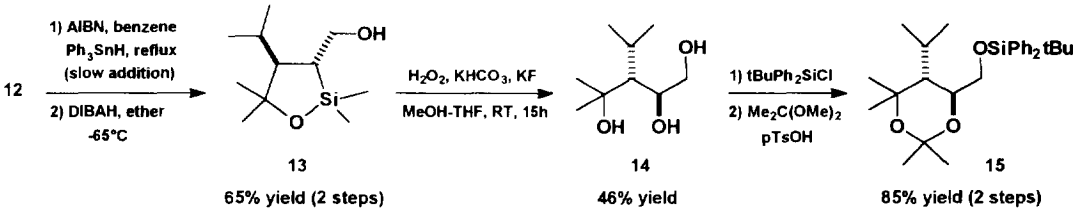
Scheme 9

Finally, we examined an example of an intramolecular version of our methodology starting from the α-(allyloxysilyl)acetic ester **11**. This allylic ether was designed as the best candidate for the preliminary studies on the *5-exo-trig* cyclization process, since the competing *6-endo-trig* process is disfavoured here for steric reasons.[18] **11** was prepared in a one pot process, by rhodium-carbene insertion into the Si-H bond of HMe_2SiCl, followed by displacement of the chlorine atom by the appropriate allylic alcohol (Scheme 10).[1b] Alkylation of **11** using LiHMDS then afforded the suitable α-phenylseleno-α-silylacetic ester **12** in a pure enough state to be used without further purification.



Scheme 10

12 was allowed to react in benzene under reflux in the presence of Ph_3SnH, added slowly to minimize the reduction of the α-silyl radical.[18] Two diastereoisomeric cyclic esters were formed in a 7:3 *trans/cis* ratio (^1H NMR). Surprisingly, reduction of the ester function using DIBAH furnished the siloxane **13** as the sole diastereoisomer (Scheme 11). The good overall yield obtained for the sequence **12** → **13** suggests that epimerization occurred during the reduction step, leading to the more stable *trans* diastereoisomer. Tamao oxidation[17] then gave the expected triol **14** in moderate yield. The relative stereochemistry was assigned from ^1H NMR of the cyclic acetonide **15** prepared after silylation of the primary alcohol function and acetalization.[19]



Scheme 11

In summary, we have realized a short access to new homoallylsilanes which are useful intermediates in the preparation of various synthons. The radical process described here is particularly mild and is an efficient alternative to the ionic process where Peterson elimination may sometimes occur. Competitive allylation reactions afford a better insight into the reactivity of these α-silylacetic ester radicals but do not provide a conclusive answer as to the nature of these new radicals. Finally, the intramolecular radical reaction of these substrates offers an entry into polyhydroxylated systems.

EXPERIMENTAL SECTION

^1H NMR and ^{13}C NMR spectra were recorded on a BRUKER 250FT (250 MHz) and BRUKER WH-360FT (360 MHz) using $CDCl_3$ as internal reference unless otherwise indicated. The chemical shifts (δ) and coupling constants (J) are expressed in ppm and Hz respectively. IR spectra were recorded on a Perkin-Elmer 1710 spectrophotometer. All commercial products were used without further purifications.

CH_2Cl_2, hexamethyldisilazane and triethylamine were distilled from CaH_2. THF was distilled from sodium and benzophenone. Chlorosilanes were distilled before use from magnesium. Ph_3SnH was obtained by reduction of Ph_3SnCl using $LiAlH_4$.

Elemental analyses were performed by the I. Beetz laboratory, W-8640 Kronach (D). Mass spectra were recorded on a Nermag R10-10C (NH_3).

Alkylation of α-silylacetic ester 1b. A 1.6M solution of n-BuLi in hexane (0.64 ml, 1.03 mmol) was added at -20°C to a solution of hexamethyldisilazane (0.26 ml, 1.22 mmol) in dry THF (4 ml). The solution was stirred at -5°C for 15 minutes then cooled to -60°C and a solution of the ester **1b** (0.2 g, 0.98 mmol) in dry THF (1 ml) was added dropwise. The mixture was stirred at -60°C for one hour, then a solution of ethyl bromoacetate (0.16 ml, 1.47 mmol) in dry THF (1 ml) was added dropwise. The mixture was slowly allowed to warm to 0°C over 2 hours then treated with a saturated solution of $NaHCO_3$ and the organic layer decanted. The aqueous layer was extracted with ether and the combined extracts were washed with brine, dried ($MgSO_4$) and evaporated in vacuo to give a yellow oil which was purified using flash chromatography (petroleum ether/EtOAc/NEt_3 98:1.5:0.5) to afford the ester **3a** (90 mg, 39%) : **^1H NMR** (δ ppm) : 5.09 (1H, s, C<u>H</u>), 4.51 (2H, s, C<u>H</u>$_2$Br), 4.18 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 3.89 (2H, q, J 7.0, $OC\underline{H}_2CH_3$), 1.38 (3H, t, J 7.0, $OCH_2C\underline{H}_3$), 1.29 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$). **IR** (CH_2Cl_2) (υ_{max}): 1705 (C=O), 1685, 1620 (C=C), 1370, 1350, 1130, 1050 cm^{-1}. **MS** (CI, NH_3): 256 (98), 254 ($M^{+\cdot}$+NH_3, 100), 239 ($M^{+\cdot}$+2, 80), ($M^{+\cdot}$, 79), 210 (6), 208 ($M^{+\cdot}$-C_2H_5, 7), 159 (39), 130 (6), 78 (9) and **3b** (130 mg, 46%) : **^1H NMR** (δ ppm) : 4.13 (4H, q, J 7.1, 2 x $CO_2C\underline{H}_2CH_3$), 4.03 (1H, sept, J 6.1, $CH_3C\underline{H}CH_3$), 2.86 (1H, dd, J 11.4, 16.8, $CHC\underline{H}_aH_b$), 2.58 (1H, dd, J 3.2, 11.4, $C\underline{H}CH_aH_b$), 2.47 (1H, dd, J 3.2, 16.8, $CHCH_a\underline{H}_b$), 1.25 (6H, t, J 7.1, 2 x $CO_2CH_2C\underline{H}_3$), 1.16 (3H, d, J 6.1, $C\underline{H}_3CHCH_3$), 1.14 (3H, d, J 6.1, $CH_3CHC\underline{H}_3$), 0.23 (3H, s, $SiCH_3$), 0.18 (3H, s, $SiCH_3$). **IR** (CH_2Cl_2) (υ_{max}): 1730 (C=O), 1710 (C=O), 1630, 1370, 1200, 1030 (Si-O) cm^{-1}. **MS** (CI, NH_3): 275 ($M^{+\cdot}$-CH_3, 2), 245 ($M^{+\cdot}$-C_2H_5O, 11), 231 ($M^{+\cdot}$-*i*-PrO, 100), 217 ($M^{+\cdot}$-$CO_2C_2H_5$, 12), 203 ($M^{+\cdot}$-$CH_2CO_2C_2H_5$, 41), 129 (12). **Anal.** Calcd for $C_{13}H_{26}O_5Si$: C, 53.76; H, 9.02. Found : C, 53.88; H, 9.04.

4(*Z*). **^1H NMR** (δ ppm) : 5.80 (1H, m, C<u>H</u>), 4.68 (2H, d, J 0.4, C<u>H</u>$_2$Cl), 4.18 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 2.03 (3H, d, J 1.4, CH_3), 1.29 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$). **IR** (CH_2Cl_2) (υ_{max}) : 1710 (C=O), 1650 (C=C), 1380, 1350, 1170, 1050, 1020 cm^{-1}. **MS** (CI, NH_3) : 119(1), 117 ($M^{+\cdot}$-C_2H_5O, 2), 98 (2), 85 (55), 83 (100), 82 (9), 73 ($CO_2C_2H_5^{+\cdot}$, 7), 71 ($C_3H_3O_2^{+\cdot}$, 9).

4(*E*). **^1H NMR** (δ ppm) : 5.97 (1H, m, C<u>H</u>), 4.18 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 4.04 (2H, d, J 1.0, C<u>H</u>$_2$Cl), 2.24 (3H, d, J 1.3, CH_3), 1.29 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$). **IR** (CH_2Cl_2) (υ_{max}) : 1710 (C=O), 1660 (C=C), 1370, 1230, 1040 cm^{-1}. **MS** (CI, NH_3) : 162 ($M^{+\cdot}$, 19), 128 (8), 119(12), 117 ($M^{+\cdot}$-C_2H_5O, 34), 98 (23), 95 (21), 85 (85), 83 (100), 82 (40), 71 ($C_3H_3O_2^{+\cdot}$, 62).

General procedure for the preparation of radical precursors 6. A 1.6M solution of n-BuLi in hexane (3.37 ml, 5.4 mmol) was added at -20°C to a solution of hexamethyldisilazane (1.22 ml, 5.85 mmol) in dry THF (5

ml). The solution was stirred at -5°C for 15 minutes then cooled to -60°C and a solution of the ester **1a** (1 g, 4.5 mmol) in dry THF (5 ml) was added dropwise. The mixture was stirred at -60°C for one hour, then a solution of PhSeCl (0.86 g, 4.5 mmol) in dry THF (4 ml) was added dropwise. The mixture was stirred at -60°C for 30 minutes then treated with a saturated solution of $NaHCO_3$ and the organic layer was decanted. The aqueous layer was extracted with ether and the combined extracts were washed with brine, dried ($MgSO_4$) and evaporated in vacuo to give an oil which was purified using flash chromatography (Petroleum ether/AcOEt/NEt_3 98.5:1:0.5) to afford the ester **6c** as a colorless oil (1.49 g, 87%). **^{1}H NMR** (δ ppm) : 7.55-7.49 (2H, m, aromatic H), 7.31-7.21 (3H, m, aromatic H), 4.15 (1H, dq, J 7.1, 10.8, $CO_2C\underline{H}_aH_bCH_3$), 4.08 (1H, dq, J 7.1, 10.8, $CO_2CH_a\underline{H}_bCH_3$), 3.33 (1H, s, $SiC\underline{H}SePh$), 1.28 (9H, s, *t*-Bu), 1.21 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 0.36 (3H, s, $SiCH_3$), 0.34 (3H, s, $SiCH_3$). **IR** (CH_2Cl_2) (υ_{max}) : 2970, 2930 (C-H), 2900, 1705 (C=O), 1470, 1360, 1190, 1125, 1050 (Si-O), 850 cm^{-1}. **MS** (CI, NH_3) : 374 (M^++1, 17), 299 (4), 198 (8), 131 (M^+-CH(SePh)$CO_2C_2H_5$, 4), 105 (13), 103 (10), 77 (34), 75 ($Si(CH_3)_2OH^+$, 100), 74 ($Si(CH_3)_2O^+$, 24). **Anal.** Calcd for $C_{16}H_{26}O_3SiSe$: C, 51.46; H, 7.02; Si, 7.52. Found : C, 51.41; H, 6.97; Si, 7.49.

Following the same procedure, and changing PhSeCl for CBr_4 and CCl_4 when required, the precursors **6a**, **6b**, **6d** and **6e** were obtained as oily compounds, used in the next step without further purification.

General procedure for the radical allylation. A solution of **6c** (373 mg; 1 mmol), allyltributylstannane (0.46 ml; 1.5 mmol) and AIBN (16 mg; 0.1 mmol) in dry benzene (10 ml) was stirred under reflux for 2 hours. After evaporation under vacuum, flash chromatography (Petroleum ether/AcOEt/NEt_3 98.5:1:0.5) gave **8a** as a colorless oil (245 mg ; 95%). **^{1}H NMR** (δ ppm) : 5.86-5.73 (1H, m, CH_2=C$\underline{H}$), 5.06-4.89 (2H, m, C$\underline{H}_2$=CH), 4.08 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 2.60-2.45 (1H, m, $CHC\underline{H}_aH_b$), 2.27-2.19 (1H, m, $CHCH_a\underline{H}_b$), 2.13 (1H, dd, J 3.1, 11.6, $SiC\underline{H}CH_2$), 1.24 (9H, s, *t*-Bu), 1.22 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 0.20 (3H, s, $SiCH_3$), 0.18 (3H, s, $SiCH_3$). **IR** (CH_2Cl_2)(υ_{max}) : 1705 (C=O), 1630 (C=C), 1365, 1180, 1050 (Si-O), 910 cm^{-1}. **MS** (CI, NH_3) : 259 (M^++1, 69), 258 (M^+, 17), 243 (M^+-CH_3, 11), 203 (38), 201 (M^+-*t*-Bu, 11), 185(M^+-$CO_2C_2H_5$ or *t*-BuO, 10), 92 (23), 82 (23), 81 (22), 75 ($Si(CH_3)_2OH^+$, 100), 74 ($Si(CH_3)_2O^+$, 25). **Anal.** Calcd for $C_{13}H_{26}O_3Si$: C, 60.42; H, 10.14; Si, 10.87. Found : C, 60.26; H, 9.98; Si, 10.29.

8b. **^{1}H NMR** (δ ppm) : 7.55-7.49 (2H, m, aromatic H), 7.43-7.33 (3H, m, aromatic H), 5.83-5.67 (1H, m, C$\underline{H}$=CH_2), 5.02-4.89 (2H, m, CH=C$\underline{H}_2$), 4.05 (1H, dq, J 7.1, 10.1, $CO_2C\underline{H}_aH_bCH_3$), 3.99 (1H, q, J 7.1, 10.1, $CO_2CH_a\underline{H}_bCH_3$), 2.59-2.48 (1H, m, $SiCHC\underline{H}_cH_d$), 2.30 (1H, dd, J 3.0, 11.7, $SiC\underline{H}CH_2$), 2.18-2.04 (1H, m, $SiCHCH_c\underline{H}_d$), 1.13 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 0.40 (3H, s, $SiCH_3$), 0.39 (3H, s, $SiCH_3$). **IR** (film) (υ_{max}) : 3070, 3000, 2950 (C-H), 2870, 1710 (C=O), 1640 (C=C), 1430, 1330, 1250 (Si-C), 1240, 1170, 1110, 1040, 840, 810 cm^{-1}. **MS** (CI, NH_3): 235 (13), 185 (M^+-C_6H_5, 37), 174 (22), 170 (29), 157 (16), 135 ($Ph(CH_3)_2Si^+$, 19), 103 (14), 78 (10), 77 ($C_6H_5^+$, 9). **Anal.** Calcd for $C_{15}H_{22}O_2Si$: C, 68.65; H, 8.45; Si, 10.70. Found : C, 68.74; H, 8.47; Si, 10.56.

8c. **^{1}H NMR** (δ ppm) : 6.15 (1H, d, J 0.6, Vinylic H), 5.62 (1H, d, J 1.0, Vinylic H), 4.09 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 4.08 (1H, sept, J 6.1, $CH_3C\underline{H}CH_3$), 3.75 (3H, s, CO_2CH_3), 2.81-2.55 (2H, m, $SiCHC\underline{H}_2$), 2.40 (1H, dd, J 2.6, 12.1, $SiC\underline{H}CH_2$), 1.23 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 1.18 (3H, d, J 6.1, $C\underline{H}_3CHCH_3$), 1.17 (3H, d, J 6.1, $CH_3CHC\underline{H}_3$), 0.23 (6H, s, $Si(CH_3)_2$). **IR** ($CHCl_3$) (υ_{max}) : 2960 (C-H), 1720 (C=O), 1710 (C=O), 1630 (C=C), 1440, 1370, 1300, 1255 (Si-C), 1145, 1115, 1015 (Si-O), 885 cm^{-1}. **MS** (CI, NH_3) : 319 (M^++NH_3, 8), 295 (18), 257 (M^+-C_2H_5O, 8), 243 (M^+-*i*-PrO, 15), 229 (M^+-$CO_2C_2H_5$, 8), 215 (M^+-$CH_2CO_2C_2H_5$, 34), 158 (100), 135 (64), 117 (29), 91 (98). **Anal.** calcd for $C_{14}H_{26}O_5Si$: C, 55.60; H, 8.66. Found : C, 55.48; H, 8.56.

8d. **^{1}H NMR** (δ ppm) : 5.57 (1H, m, Vinylic H), 5.30 (1H, m, Vinylic H), 4.15-4.0 (3H, m, $CO_2C\underline{H}_2CH_3$ and $CH_3C\underline{H}CH_3$), 2.72-2.60 (1H, m, $SiCHC\underline{H}_aH_b$), 2.39-2.28 (2H, m, $SiC\underline{H}CH_a\underline{H}_b$), 1.22 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 1.18 (3H, d, J 6.3, $C\underline{H}_3CHCH_3$), 1.15 (3H, d, J 6.3, $CH_3CHC\underline{H}_3$), 0.21 (6H, s, $Si(CH_3)_2$), 0.10 (9H, s, $Si(CH_3)_3$). **IR** ($CHCl_3$) (υ_{max}) : 2960, 2920 (C-H), 1705 (C=O), 1450, 1365, 1250 (Si-C), 1140, 1120, 1030 (Si-O), 1015, 910, 885, 840 cm^{-1}. **MS** (CI, NH_3) : 316 (M^+, 3), 301 (M^+-CH_3, 44), 271 (M^+-C_2H_5O, 10), 257 (6), 243 (5), 217 (23), 191 (7), 149 (17), 133 (12), 129 (20), 117 (22), 85 (20), 81 (22), 75 ($Si(CH_3)_2OH^+$, 100), 73 (55). **Anal.** calcd for $C_{15}H_{32}O_3Si_2$: C, 56.91; H, 10.19; Si, 17.74. Found : C, 56.78; H, 10.23; Si, 17.70.

8f ***(Z+E)***. **^{1}H NMR** (δ ppm) : 6.39-6.01 (4H, m, Vinylic H), 5.80-5.63 (2H, m, Vinylic H), 5.22-4.94 (4H, m, Vinylic H), 4.14 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 4.11 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 4.04 (2H, sept, J 6.0, 2 x

$CH_3C\underline{H}CH_3$), 2.66-2.24 (4H, m, $SiCHC\underline{H}_2$), 2.17 (2H, dd, J 3.2, 11.6, $SiC\underline{H}CH_2$), 1.26 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 1.24 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 1.17 (6H, d, J 6.0, $C\underline{H}_3CHC\underline{H}_3$), 1.15 (6H, d, J 6.0, $C\underline{H}_3CHC\underline{H}_3$), 0.20 (6H, s, $Si(CH_3)_2$), 0.19 (6H, s, $Si(CH_3)_2$). **IR** ($CHCl_3$) (υ_{max}) : 2950 (C-H), 2880, 1720 (C=O), 1660, 1615 (C=C), 1475, 1460, 1380, 1340, 1260 (Si-C), 1180, 1150, 1015 (Si-O), 960, 855 cm^{-1}. **MS** (CI, NH_3) : 270 (M^+, 2), 256 (M^+-CH_2, 5), 213 (8), 191 (11), 181 (11), 169 (84), 145 (13), 117 ((*i*-PrO)$(CH_3)_2Si^+$, 18), 109 (16), 97 (41), 95 (53), 85 (74), 83 (80), 81 (67), 75 ($Si(CH_3)_2OH^+$, 52), 71 (100).

8g. **^{1}H NMR** (δ ppm) : 4.71 (2H, s, Vinylic H), 4.13 (1H, dq, J 7.1, 10.1, $CO_2C\underline{H}_aH_bCH_3$), 4.08 (1H, dq, J 7.1, 10.1, $CO_2CH_a\underline{H}_bCH_3$), 4.05 (1H, sept, J 6.0, $CH_3C\underline{H}CH_3$), 2.57 (1H, dd, J 2.0, 15.2, $SiCHC\underline{H}_cH_d$), 2.34 (1H, dd, J 2.2, 11.9, $SiC\underline{H}CH_aH_b$), 2.17 (1H, d, J 15.1, $SiCHCH_a\underline{H}_b$), 1.72 (3H, s, CH_3), 1.24 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 1.17 (3H, d, J 5.9, $C\underline{H}_3CHCH_3$), 1.15 (3H, d, J 5.9, $CH_3CHC\underline{H}_3$), 0.20 (6H, s, $Si(CH_3)_2$). **IR** (film) (υ_{max}) : 2980, 2960 (C-H), 1720 (C=O), 1640 (C=C), 1440, 1370, 1250 (Si-C), 1150, 1120, 1030 (Si-O), 890 cm^{-1}. **MS** (CI, NH_3) : 212 (M^+-C_2H_5OH, 9), 198 (6), 191 (10), 169 (30), 123 (25), 111 (39), 109 (31), 97 (77), 95 (57), 85 (84), 71 (100). **Anal.** Calcd for $C_{13}H_{26}O_3Si$: C, 60.42; H, 10.14; Si, 10.87. Found : C, 60.29; H, 10.10; Si, 10.72.

Competitive allylation of ester 6d. Typically, A mixture of **6d** (40 mg, 0.11 mmol), **7f** (58 mg, 0.16 mmol), **7c** (67 mg, 0.16 mmol), and AIBN (2 mg, 0.01 mmol) in anhydrous benzene (4 ml) was stirred under reflux for 15 hours. The solvent was then evaporated in vacuo and the mixture analyzed without further purifications using 360 MHz ^{1}H NMR. Integration of the signal corresponding to the vinylic CH_2 led to a 37:63 **8g/8d** ratio. The other competitive allylations were carried out using the same procedure.

9a. To a solution of **6d** (300 mg; 0.83 mmol) and methyl acrylate (0.37 ml; 4.15 mmol) in dry benzene (2 ml) was added, over a period of 4 hours (syringe pump), under reflux, a solution of n-Bu_3SnH (0.24 ml ; 0.91 mmol) and AIBN (7 mg ; 0.04 mmol) in dry benzene (2 ml). The mixture was refluxed for 1 hour then evaporated under vacuum. Flash chromatography of the residue (Petroleum ether/AcOEt/NEt_3 98:1.5:0.5) afforded **9a** as a colorless oil (36 mg; 15%). **^{1}H NMR** (δ ppm) : 4.12 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 4.04 (1H, sept, J 6.0, $CH_3C\underline{H}CH_3$), 3.67 (3H, s, $CO_2C\underline{H}_3$), 2.53-1.84 (5H, m, Aliphatic H), 1.25 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 1.16 (3H, d, J 6.0, $C\underline{H}_3CHCH_3$), 1.15 (3H, d, J 6.0, $CH_3CHC\underline{H}_3$), 0.20 (3H, s, $SiCH_3$), 0.19 (3H, s, $SiCH_3$). **IR** ($CHCl_3$) (υ_{max}) : 3010, 2970 (C-H), 1725 (C=O), 1710 (C=O), 1510, 1435, 1365, 1250 (Si-C), 1210, 1030 (Si-O), 930 cm^{-1}. **MS** (CI, NH_3): 290 (M^+, 3), 259 (M^+-CH_3O, 7), 245 (M^+-C_2H_5O, 14), 232 (17), 231 (M^+-CO_2CH_3, 100), 219 (11), 217 (M^+-$CO_2C_2H_5$, 46), 203 (M^+-$CH_2CO_2C_2H_5$, 31), 190 (16), 129 (24), 117 (25), 85 (12), 75 ($Si(CH_3)_2OH^+$, 45). **Anal.** Calcd for $C_{13}H_{26}O_5Si$: C, 53.76; H, 9.02. Found : C, 53.83; H, 9.01.

9b. **^{1}H NMR** (δ ppm) : 7.53-7.48 (2H, m, Aromatic H), 7.43-7.32 (3H, m, Aromatic H), 4.03 (1H, dq, J 7.1, 10.7, $CO_2C\underline{H}_aH_bCH_3$), 3.98 (1H, dq, J 7.1, 10.7, $CO_2CH_a\underline{H}_bCH_3$), 3.63 (3H, s, $CO_2C\underline{H}_3$), 2.45-1.63 (5H, m, Aliphatic H), 1.12 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 0.40 (3H, s, $SiCH_3$), 0.38 (3H, s, $SiCH_3$). **IR** ($CHCl_3$) (υ_{max}) : 2980, 2950 (C-H), 1725 (C=O), 1705 (C=O), 1460, 1435, 1425, 1370, 1250 (Si-CH_3), 1210, 1150, 835 cm^{-1}. **MS** (CI, NH_3): 308 (M^+, 2), 293 (M^+-CH_3, 10), 263 (M^+-C_2H_5O, 6), 236 (8), 235 (M^+-$CH_2CO_2CH_3$ or $CO_2C_2H_5$, 40), 231 (33), 207 (9), 177 (9), 165 (9), 137 (22), 135 ($Ph(CH_3)_2Si^+$, 100), 129 (27), 121 (14), 105 ($PhSi^+$, 14), 100 (26), 91 ($C_7H_7^+$, 21), 85 (44), 78 (42), 77 ($C_6H_5^+$, 13), 74 (41), 71 (36). **Anal.** Calcd for $C_{16}H_{24}O_4Si$: C, 62.30; H, 7.84. Found : C, 62.38; H, 7.84.

General procedure for the preparation of homoallylic-1,2-diols. 10a. To a solution of ester **8d** (0.26 g, 0.82 mmol) in dry ether (10ml) was added dropwise at 0°C a 1M solution of $LiAlH_4$ in ether (0.45 ml, 0.45 mmol). The mixture was stirred at 0°C for 10 minutes then treated with a 1M solution of HCl and the organic layer was decanted. The aqueous layer was extracted with ether and the combined extracts were washed with brine, dried ($MgSO_4$) and evaporated in vacuo to give the alcohol as a colorless oil, which was used in the next step without further purifications. To a solution of β-hydroxysilane (0.21 g, 0.77 mmol) in a 1:1 mixture of MeOH:THF (4 ml), was added at room temperature, $KHCO_3$ (0.23g, 2.3 mmol), KF (0.133 g, 2.3 mmol) then a solution of 30% wt H_2O_2 (1.53 ml, 14.9 mmol). The mixture was stirred for 15 hours then treated cautiously at 0°C with $Na_2S_2O_3$ (1.5 g). The solution was stirred at room temperature for 30 minutes, diluted with ether, filtered through a plug of celite and evaporated in vacuo. The residue was diluted in ether, dried ($MgSO_4$) and evaporated to give a yellow oil which was purified by chromatography over silica gel (CH_2Cl_2/MeOH 98:2) to afford the expected diol **10a** as a colorless oil (0.103 g, 72%): **^{1}H NMR** (δ ppm) : 5.69 (1H, m, Vinylic H), 5.51 (1H, d, J 2.9, Vinylic H), 3.90-3.77 (1H, m, $C\underline{H}OH$), 3.69 (1H, dd, J 3.1, 11.2, $C\underline{H}_aH_bOH$), 3.48 (1H, dd, J 6.9,

11.2, $CH_a\underline{H}_bOH$), 2.41-2.22 (2H, m, $CHC\underline{H}_2$), 2.15 (2H, broad s, 2 x OH), 0.12 (9H, s, $Si(CH_3)_3$). **IR** ($CHCl_3$) (υ_{max}) : 3580, 3420 (O-H), 2950 (C-H), 1400, 1250 (Si-C), 1080, 1020, 940, 855, cm^{-1}. **MS** (CI, NH_3) : 159 (M^+-CH_3, 4), 142 (M^+-CH_3OH, 8), 141 (60), 127 (6), 117 (7), 111 (13), 101 (M^+-$Si(CH_3)_3$, 23), 99 (H_2C=$CSi(CH_3)_3^+$, 23), 85 (11), 83 (11), 75 ($CH_2CH(OH)CHOH^+$, 100). **Anal.** Calcd for $C_8H_{18}O_2Si$: C, 55.12; H, 10.41; Si, 16.11. Found : C, 54.96; H, 10.39; Si, 16.03.

10b. **^{1}H NMR** (δ ppm) : 4.87 (1H, s, Vinylic H), 4.80 (1H, s, Vinylic H), 3.91-3.82 (1H, m, C<u>H</u>OH), 3.66 (1H, dd, J 3.0, 11.3, $C\underline{H}_aH_bOH$), 3.46 (1H, dd, J 7.0, 11.3, $CH_a\underline{H}_bOH$), 2.75 (2H, s, 2 x OH), 2.24-2.15 (2H, m, $CHC\underline{H}_2$), 1.77 (3H, s, $C\underline{H}_3$). **IR** (film) (υ_{max}) : 3400 (O-H), 3100, 2950 (C-H), 1700, 1640 (C=C), 1440, 1250 (Si-C), 1100, 1040, 880 cm^{-1}. **Anal.** Calcd for $C_6H_{12}O_2$: C, 62.04; H, 10.41. Found : C, 62.03; H, 10.42.

10c (***Z+E***). **^{1}H NMR** (δ ppm) : 6.39-6.08 (4H, m, Vinylic H), 5.75-5.63 (2H, m, Vinylic H), 5.17-5.0 (4H, m, vinylic H), 3.81-3.72 (2H, m, 2 x $CH_2C\underline{H}CH_2$), 3.66 (2H, dd, J 3.0, 11.3, 2 $C\underline{H}_aH_bOH$), 3.47 (2H, dd, J 7.2, 11.3, 2 x $CH_a\underline{H}_bOH$), 2.78 (4H, broad s, 4 x OH), 2.29-2.24 (4H, m, 2 x $CHC\underline{H}_2CHOH$). **IR** ($CHCl_3$) (υ_{max}): 3600, 3400 (O-H), 3000, 2940 (C-H), 1640 (C=C), 1600 (C=C), 1410, 1035, 1000, 950, 900 cm^{-1}.

11. To a solution of dimethylchlorosilane (1 ml, 9.2 mmol) and $Rh_2(OAc)_4$ (14 mg, 0.03 mmol) in dry CH_2Cl_2 (3 ml) was added slowly at room temperature (syringe pump (2 mmol/h)), a solution of ethyl diazoacetate (0.9 ml, 8.7 mmol) in CH_2Cl_2 (2 ml). The mixture was cooled to 0°C and a solution of triethylamine (1.55 ml, 11 mmol) in CH_2Cl_2 (1 ml) was added, followed by 2,2-dimethylpent-3-en-2-ol (0.85 ml, 11 mmol) in CH_2Cl_2 (1 ml). The suspension was stirred for 3 hours then treated at 0°C with a saturated solution of $NaHCO_3$ and the organic layer was decanted. The aqueous layer was extracted with CH_2Cl_2 and the combined extracts were washed with brine, dried ($MgSO_4$) and evaporated in vacuo to give a brown oil which was purified by filtration over Florisil® (Petroleum ether/ethyl acetate/NEt_3 98.5/1/0.5) to afford the ester **11** as a colorless oil (1.60 g, 71%): **^{1}H NMR** (δ ppm) : 5.26 (1H, sept, J 1.3, C=C<u>H</u>), 4.08 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 1.99 (2H, s, $SiCH_2$), 1.79 (3H, d, J 1.3, $C\underline{H}_3C$=CH), 1.67 (3H, d, J 1.3, $C\underline{H}_3C$=CH), 1.36 (6H, s, 2 x CH_3), 1.24 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 0.23 (6H, s, $Si(CH_3)_2$). **IR** ($CHCl_3$) (υ_{max}) : 2990, 2980 (C-H), 2900, 1700 (C=O), 1440, 1400, 1360, 1255 (Si-C), 1210, 1140, 1030 (Si-O), 830 cm^{-1}. **MS** (CI, NH_3) : 241 (M^+-CH_3, 9), 219 (8), 163 (12), 145 ($(CH_3)_2SiCH_2CO_2C_2H_5^+$, 51), 117 (12), 103 (67), 97 ($(CH_3)_2C$=$CHC(CH_3)_2^+$, 100), 96 (80), 75 ($(CH_3)_2SiOH^+$, 57). **Anal.** Calcd for $C_{13}H_{26}O_3Si$: C, 60.42; H, 10.14; Si, 10.87. Found : C, 60.07; H, 10.20; Si, 10.74.

12. Following the general procedure, **12** was obtained as a yellow oil (75%) and used in the next step without further purifications: **^{1}H NMR** (δ ppm) : 7.53-7.49 (2H, m, Aromatic H), 7.33-7.23 (3H, m, Aromatic H), 5.28 (1H, m, C=C<u>H</u>), 4.12 (1H, dq, J 7.1, 10.8, $CO_2C\underline{H}_aH_bCH_3$), 4.09 (1H, dq, J 7.1, 10.8, $CO_2CH_a\underline{H}_bCH_3$), 3.35 (1H, s, C<u>H</u>SePh), 1.79 (3H, s, $C\underline{H}_3C$=CH), 1.67 (3H, s, $C\underline{H}_3C$=CH), 1.39 (6H, s, 2 x CH_3), 1.20 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 0.34 (3H, s, $SiCH_3$), 0.32 (3H, s, $SiCH_3$). **IR** ($CHCl_3$) (υ_{max}) : 2985, 2920 (C-H), 1705 (C=O), 1575, 1470, 1360, 1255 (Si-C), 1165, 1125, 1030 (Si-O), 840 cm^{-1}. **MS** (CI, NH_3) : 414 (M^++1, 7), 301 (M^+-$C_7H_{12}O$, 5), 257 (M^+-PhSe, 8), 244 (11), 198 (23), 171 (M^+-$PhSeCHCO_2C_2H_5$, 11), 170 (13), 157 (8), 103 (29), 97 ($(CH_3)_2C$=$CHC(CH_3)_2^+$, 64), 75 ($(CH_3)_2SiOH^+$, 100). **Anal.** Calcd for $C_{19}H_{30}O_3SiSe$: C, 55.19; H, 7.31; Si, 6.79. Found : C, 55.35; H, 7.15; Si, 6.73

13. To a solution of the ester **12** (1.05 g; 2.54 mmol) in dry benzene (100 ml), was added, under reflux, over a period of 6 hours, a solution of Ph_3SnH (0.93 g; 2.67 mmol) and AIBN (0.083 g; 0.5 mmol) in dry benzene (8 ml). The mixture was refluxed for 1 hour, then evaporated under vacuum. The mixture was dissolved in pentane (10 ml), then allowed to stand at - 20°C for a night and filtered. After evaporation of the solvents under vacuum, the resulting oil was dissolved in dry ether (30 ml) and cooled at - 65°C. A 1<u>M</u> solution of DIBAH in toluene (4 ml; 4 mmol) was then added dropwise and the mixture was stirred at - 65°C for 1 hour. The reaction mixture was treated with a 1<u>M</u> solution of HCl at room temperature, then stirred 30 minutes and the organic layer was decanted. The aqueous layer was extracted with ether and the combined extracts were washed successively with 1<u>M</u> HCl, a saturated solution of $NaHCO_3$, brine then dried ($MgSO_4$) and evaporated under vacuum to give a yellow oil which was purified by flash chromatography (CH_2Cl_2/MeOH 98:2) to afford **13** as a colorless oil (0.36 g; 65%). **^{1}H NMR** (δ ppm) : 4.13 (1H, dd, J 6.6, 9.5, $C\underline{H}_aH_bOH$), 3.56 (1H, dd, J 9.9, 9.9, $CH_a\underline{H}_bOH$), 1.77-1.47 (3H, m, Aliphatic H), 1.28 (3H, s, CH_3), 1.08 (3H, s, CH_3), 0.95 (3H, d, J 7.0, $C\underline{H}_3CHCH_3$), 0.93 (3H, d, J 7.0, $CH_3CHC\underline{H}_3$), 0.27 (3H, s, $SiCH_3$), 0.20 (3H, s, $SiCH_3$). **^{13}C NMR** (δ ppm): 82.3 (s, CO), 64.4 (t, J 141, CH_2O), 56.4 (d, J 129, SiCH), 30.4 (q, J 126, CH_3), 30.3 (d, J 126, CH), 27.7 (d, J 124, CH), 25.5 (q, J

126, CH_3), 25.1 (q, J 126, CH_3), 18.1 (q, J 129, CH_3), 1.2 (q, J 120, $SiCH_3$), -2.0 (q, J 120, $SiCH_3$). **IR** ($CHCl_3$) (υ_{max}) : 3605, 3400 (O-H), 2960, 2930 (C-H), 2870, 1460, 1380, 1370, 1250 (Si-C), 1210, 1110, 1065 (Si-O), 1010, 975, 845 cm^{-1}. **MS** (CI, NH_3) : 217 ($M^{+\cdot}$+1, 6), 216 ($M^{+\cdot}$, 3), 207 (5), 169 (6), 133 (32), 119 (5), 100 (6), 97 (7), 92 (23), 91 (10), 83 (19), 77 (20), 75 ($(CH_3)_2SiOH^{+\cdot}$, 100), 74 ($(CH_3)_2SiO^{+\cdot}$, 54), 73 (10), 71 ($CH_2CHSiO^{+\cdot}$, 11). **Anal.** Calcd for $C_{11}H_{24}O_2Si$: C, 61.06; H, 11.18; Si, 12.98. Found : C, 61.18; H, 11.19; Si, 12.88.

14. Following the general procedure, **14** was obtained after purification using flash chromatography (CH_2Cl_2/MeOH 95:5) as a colorless oil (46%): **^{1}H NMR** (δ ppm) : 3.99 (1H dt, J 5.8, 6.0, $CH_2\underline{C}\underline{H}OH$), 3.62 (2H, d, J 6.0, $C\underline{H}_2OH$), 1.95 (1H, sept, J 6.9, $CH_3C\underline{H}CH_3$), 1.35 (1H, d, J 5.8, $CHC\underline{H}CHOH$), 1.32 (3H, s, CH_3), 1.31 (3H, s, CH_3), 1.01 (3H, d, J 6.9, $C\underline{H}_3CHCH_3$), 0.93 (3H, d, J 6.9, $CH_3CHC\underline{H}_3$). **^{13}C NMR** (δ ppm): 75.5 (s, CO), 72.0 (d, J 140, CHOH), 67.9 (t, J 137, CH_2OH), 53.1 (d, J 124, $\underline{C}HCHOH$), 31.9 (q, J 124, CH_3), 27.6 (d, J 123, CH), 27.2 (q, J 130, CH_3), 24.2 (q, J 124, CH_3), 18.3 (q, J 123, CH_3). **IR** ($CHCl_3$) (υ_{max}) : 3400 (O-H), 2970 (C-H), 2870, 1460, 1210, 1160, 1180, 905 cm^{-1}. **MS** (CI, NH_3) : 159 ($M^{+\cdot}$-OH, 5), 143 (3), 127 (7), 109 (9), 98 (27), 96 (17), 85 (50), 83 ($C_4H_3O_2^{+\cdot}$, 100), 73 (21). **Anal.** Calcd for $C_9H_{20}O_3$: C, 61.33; H, 11.44. Found : C, 61.37; H, 11.31.

15. To a solution of **14** (105 mg; 0.59 mmol) and DMAP (218 mg; 1.77 mmol) in dry CH_2Cl_2 (2 ml) was added at 0°C a solution of *t*-butyldiphenylchlorosilane (0.17 ml; 0.65 mmol) in dry CH_2Cl_2 (1 ml). The solution was stirred overnight then treated with water and the organic layer was decanted. The aqueous layer was extracted with CH_2Cl_2 and the combined extracts were washed successively with 1M HCl, a saturated solution of $NaHCO_3$, H_2O, brine then dried ($MgSO_4$) and evaporated under vacuum to give a yellow oil which was dissolved in 2,2-dimethoxypropane (3 ml) and treated with p-toluenesulfonic acid (20 mg). The mixture was stirred at room temperature for 2 hours then poured into a saturated solution of $NaHCO_3$. The solution was extracted with ether and the combined extracts were washed with brine, dried ($MgSO_4$) and evaporated under vacuum to give a yellow oil which was purified by flash chromatography (Petroleum ether/AcOEt/NEt_3 98:1.5:0.5) to afford **15** as a colorless oil (0.23 g; 85%). **^{1}H NMR** (δ ppm) : 7.83-7.73 (4H, m, Aromatic H), 7.47-7.34 (6H, m, Aromatic H), 3.87 (1H, ddd, J 2.2, 6.3, 8.4, $OC\underline{H}CH_aH_b$), 3.79 (1H, dd, J 2.2, 11.1, $C\underline{H}_aH_bO$), 3.71 (1H, dd, J 6.3, 11.1, $CH_a\underline{H}_bO$), 1.91-1.86 (1H, m, $CH_3C\underline{H}CH_3$), 1.46-1.43 (1H, m, CH), 1.43 (3H, s, CH_3), 1.40 (3H, s, CH_3), 1.36 (3H, s, CH_3), 1.23 (3H, s, CH_3), 1.07 (9H, s, *t*-Bu), 0.96 (3H, d, J 7.0, $C\underline{H}_3CHCH_3$), 0.79 (3H, d, J 7.2, $CH_3CHC\underline{H}_3$). **^{13}C NMR** (δ ppm): 135.8 (d, J 158, Aromatic C), 134.1 (s, Aromatic C), 133.9 (s, Aromatic C), 129.5 (d, J 160, Aromatic C), 127.5 (d, J 160, Aromatic C), 98.3 (s, OCO), 74.2 (s, CO), 68.9 (d, J 140, CHO), 68.1 (t, J 140, CH_2O), 47.2 (d, J 125, $CH_3\underline{C}HCH_3$), 32.4 (q, J 130, CH_3), 31.3 (q, J 128, CH_3), 27.0 (q, J 127, CH_3), 26.8 (q, J 130, $C(\underline{C}H_3)_3$), 26.4 (q, J 128, CH_3), 25.3 (q, J 128, CH_3), 23.5 (d, J 126, CH), 19.3 (s, $\underline{C}(CH_3)_3$), 18.0 (q, J 125, CH_3). **IR** (film) (υ_{max}) : 2960 (C-H), 2870, 1580 (C=C), 1450, 1420, 1250 (Si-C), 1220, 1190, 1100 (Si-O), 1010, 820 cm^{-1}. **MS** (CI, NH_3) : 411 ($M^{+\cdot}$-*i*-Pr, 3), 339 (2), 281 (5), 241 (100), 223 (9), 221 (13), 199 ($M^{+\cdot}$-$OSiPh_2t$-Bu, 13), 163 (8), 123 (10). **Anal.** Calcd for $C_{28}H_{42}O_3Si$: C, 73.96; H, 9.31; Si, 6.18. Found : C, 73.87; H, 9.23; Si, 6.17.

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Mechanism of Photochemical Rearrangements of 3-Substituted Cyclopropenes to Cyclopentadienes

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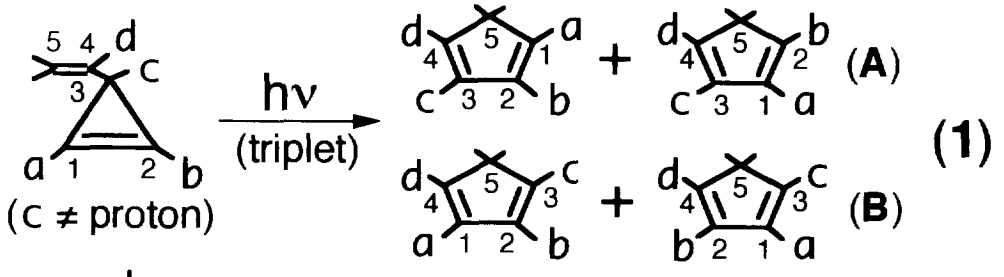
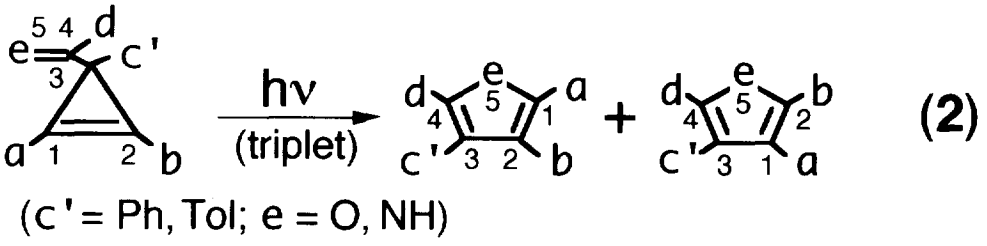
Abstract: The spin-orbit coupling parts in the effective one-electron Hamiltonian operators, with inclusion of symmetry, have been used to formulate mechanism of spin inversion in triplet photoreactions for the radiationless decay of triplet complexes to singlet ground state products. This has been applied to investigate the photochemical behavior of 3-vinyl, acyl, and iminocyclopropenes. Two competing reaction mechanisms are suggested and the results obtained agree with the available experimental results.

INTRODUCTION

3-substituted cyclopropenes have been shown to be astonishingly versatile substrates which can serve as useful precursors for the synthesis of cyclopentadienes as well as other heterocyclic rings[1,2]. Upon irradiation with ultraviolet light, this system undergoes intramolecular rearrangement during the photocycle reaction, producing products considerably more complex than the reactant itself as illustrated typically in (**1**) and (**2**).





Four popular reaction mechanisms, including diradicals and carbenes[1(e)] suggested by Zimmerman and coworkers, have been adopted to explain this behavior. These mechanisms, however, are subtly different and their predictions are not consistent with experimentally observed behavior[3]. Additionally, one intriguing feature of these rearrangements is that they are known to originate from triplet excited states, which should be

exclusively responsible for the variety of those above photoproducts[1,2]. In the case of a triplet reaction, a spin inversion process is required for decay to either the ground singlet state reactants or products in a radiationless way. We therefore report our investigation of the photochemical behavior of the 3-substituted cyclopropenes from a unified point of view and delineate the significant role played by spin-orbit (SO) coupling and symmetry in controlling the mode of cycloaddition.

THEORY

The efficiency of spin inversion is proportional to the SO coupling matrix element $< T_1 \mid \hat{H}_{SO} \mid S_0 >$, and inversely proportional to the energy gap separating the singlet (S_0) and triplet (T_1) states[4]. Moreover, efficient spin inversion can be enhanced by motions, Q_k , which maximize the SO coupling matrix element and minimize the T_1-S_0 separation[5]. We then use group theory to search for potentially efficient spin inversion motions (Q_k)[5], thus

$$\Gamma(Q_k) = \Gamma(T_1^{\nu}) \times \Gamma(\mathbf{R_k}) \times \Gamma(S_0) \qquad (k = x, y, z) \tag{1}$$

where $\Gamma(T_1^{\nu})$ and $\Gamma(S_0)$ are the representations of the spatial part (ν) of T_1^{ν} and S_0, respectively, and the $\Gamma(\mathbf{R_k})$ are the representations of the spin wave functions which transform as the rotation vectors $\mathbf{R_k}$ ($k = x, y, z$) in the point group of the triplet complex[4]. It should be pointed out that the concept of spin-inversion mechanisms in such photoreactions was expressed for the first time by Shaik and Epiotis[5(c)].

RESULTS AND DISCUSSIONS

We now use this principle to discover the motions that induce spin inversion in the triplet state of 3-substituted cyclopropenes. Since, as seen in (**1**) and (**2**), there are basically two competing reaction pathways in such a cycloaddition, we shall firstly investigate the mechanism, which leads to the (**1**-(**A**)) product which we will call case-(A)[6]. A system (**3**) consisting only of the reacting π and σ bonds will serve as a model to describe the stereochemical features of spin-inversion mechanism[7]. For simplicity, symmetries will be designed with respect to the molecular plane (xy) which bisects the π bond (the nodal plane)[5(g)]. Using eq(1), we thus obtain the symmetries of the Q_k 's in the C_s group as follows, $\Gamma(Q_x) = \Gamma(Q_y) = A' \times A'' \times A' = A''$ and $\Gamma(Q_z) = A' \times A' \times A' = A'$. Therefore, in order to maximize the y component of a two-centre SO coupling interaction, orthogonal $p_x - p_z$ atomic orbitals (AOs) are required[8]. A motion that meets the above requirement is (**4**) which consists of a rotation of the C-5 $p\pi$ orbital (γ) and a cleavage rotation of the C-1 $p\sigma$ orbital (ϕ) as well as C-3 $p\sigma$ orbital (θ). It has to be pointed out that the rotation direction of angle θ is along the y axis, while that of angle ϕ is along the z axis and that of angle γ is along the x axis[9(b)].