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SILICON IN ORGANIC SYNTHESIS. STEREOSELECTIVE SYNTHESIS OF SOME INSECT SEX PHEROMONES *

T.H. CHAN * and K. KOUMAGLO

Department of Chemistry, McGill University, Montreal, Quebec, H3A 2K6 (Canada)

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Summary

Trialkylsilylallyl anion is alkylated by alkyl halides to give regio- and stereo-selectively the γ-product with *trans*-stereochemistry at the double bond. The *trans*-vinylsilanes are transformed stereoselectively to *Z*-vinyl iodides. Coupling of the vinyl iodides with organometallic reagents gives *Z*-alkenes. This approach has been applied to the synthesis of several insect sex pheromones.

Introduction

Many insect sex pheromones [2] have the general structure **1** where X is an oxygen functional group. For some of the lepidopterous pheromones, the effective attractant is often a precise mixture of the *Z* and *E* isomers of the double bond.

$$CH_3(CH_2)_nCH{=}CH(CH_2)_mX$$
(1)

There are a number of methods for the synthesis of this type of compounds. The Wittig reaction, which has been used extensively in this area, usually gives rise to the *Z*-olefin selectively. The other method of choice is to proceed by the alkylation of acetylenic compounds followed by reduction. This route offers the advantage that either the *Z* or the *E* isomer can be obtained stereoselectively [2]. We want to demonstrate that a synthetic methodology based on organosilicon compounds can be developed for the effective syntheses of these compounds.

Regioselection in the alkylation of trialkylsilylallyl anion

α-Trimethylsilylallyl lithium (**2**, M = Li^+), generated readily from the reaction of trimethylallylsilane and n-butyllithium in TMEDA/THF, was reported [3] to react with methyl iodide to give exclusively the γ-product **3** (R′ = Me) (Scheme 1) with

* For a preliminary account of part of this work see ref. 1.

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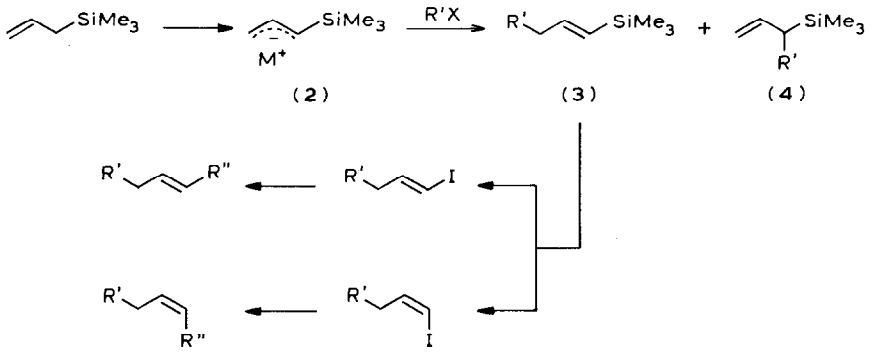
trans-geometry at the double bond. If this regioselective alkylation can be extended to other alkyl halides, this reaction may offer a general stereoselective synthesis of terminal vinylsilanes. The silyl group may then be further replaced, and the overall scheme (Scheme 1) would represent a stereoselective synthesis of olefins.



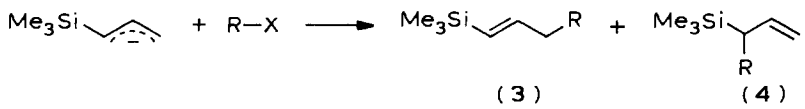
SCHEME 1

However, the alkylation of the anion **2** with a number of alkyl halides was found to give a mixture of γ- and α-products (**3** and **4**, Table 1). The presence of two regioisomers were verified by GC, GC-MS, ^{1}H NMR and in some case ^{29}Si NMR. Furthermore, the ratio of α/γ products did not seem to vary significantly with the solvent system used (HMPA/THF), by the addition of DABCO or 12-crown-4 or by the addition of various metal salts (MgX_2, ZnX_2 and CuX).

When Schlosser's base (KO-t-Bu/n-BuLi in hexane) [4] was used as the proton abstracting system to generate **2**, alkylation with alkyl halides gave predominantly the γ-adduct **3** (Table 2). It is of interest to try to understand the origin of this improved regioselectivity. Recently, Schlosser has provided evidence to suggest that KO-t-Bu/n-BuLi is not the same as n-BuK [5]. The change in regioselection cannot be due to a change in the counter ion in **2** from Li^+ to K^+. Nor can we ascribe the change to a greater dissociation of the ion pair **2** since DABCO or 12-crown-4 had no effect on the regioselection. We suspect that a possible role is the association of

TABLE 1

RELATIVE AMOUNTS OF γ- AND α-PRODUCTS IN THE ALKYLATION OF TRIMETHYLSILYLALLYLLITHIUM IN TMEDA/THF



Alkyl halide (R–X)	γ-Products (3) (%)	α-Products (4) (%)
$CH_3CH_2CH_2I$	65	33
$CH_3(CH_2)_8CH_2I$	65	35
$CH_3(CH_2)_8CH_2Br$	57	42

the t-butoxide anion with the silicon moiety, thus giving greater steric hindrance to α-alkylation. To verify this idea, we prepared a series of silylallyl anions where the substituent on silicon is varied. When the substituent changes from methyl to ethyl to propyl with increasing bulk, the ratio of γ/α alkylation increases (Table 2). With tripropylsilylallyl anion prepared from KO-t-Bu/n-BuLi, alkylation with alkyl chloride can give γ/α ratio as high as 40.

In terms of a practical synthesis, the trimethylsilylallyl anion is still preferred since the starting material is commercially available. Furthermore, we found that the minor α-adduct **4** can be readily removed by treating the crude mixture with a catalytic amount of hydroiodic acid (57%) in benzene at room temperature. We have thus been able to obtain the pure γ-adduct **3** consistently in about ~ 80% yield by simple distillation.

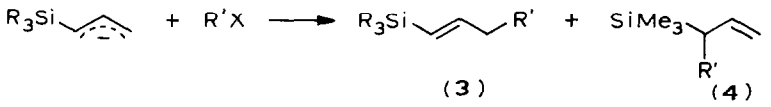
In all cases, the γ-products **3** have the double bond in the *trans*-stereochemistry (no detectable amount of *Z* isomer according to ^{1}H NMR). Since vinylsilanes can react with electrophiles often with high stereospecificity [6], the present regio- and stereoselective synthesis of *E*-vinylsilanes **3** from readily available trimethylallylsilane offers a facile method for the stereoselective synthesis of disubstituted alkenes.

Synthesis of *Z*-9-tricosene (5, muscalure) and the Gypsy moth sex pheromone (6, disparlure)

The house fly (Musca domestica) pheromone, *Z*-9-tricosene (**5**), is commercially used to increase the effectiveness of fly bait containing insecticides [2]. Compound **3a** can serve as the precursor to **5** (Scheme 2). When the vinylsilane **3a** was treated with ICl/KF [6], it gave in high yield the *Z*-vinyliodide **7a**. (Table 3). From ^{1}H NMR, **7a** contained less than 2% of the *E* isomer which was prepared independently for comparison.

TABLE 2

RELATIVE AMOUNTS OF α- AND γ-PRODUCTS ACCORDING TO THE SUBSTITUTION ON SILICON IN THE ALKYLATION OF TRIALKYLALLYLSILANE WITH SCHLOSSER'S BASE

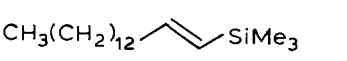
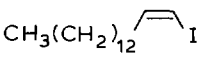
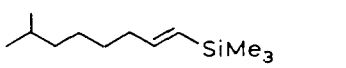
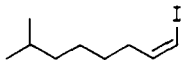
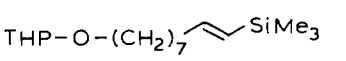
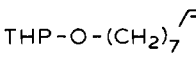
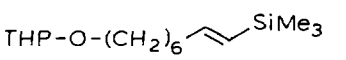
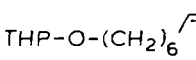


(3) (4)

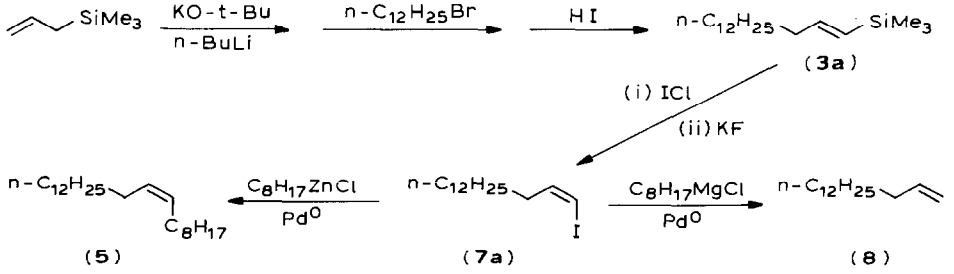
Silylallyl anion	Alkyl halide R'X	γ/α ratio (3/4)	
$^-SiMe_3$	$CH_3(CH_2)_{11}Br$	11/2	**3a**
	$(CH_3)_2CH(CH_2)_3Br$	4/1	**3b**
	THP-O-$(CH_2)_6Br$	9/1	**3c**
	THP-O-$(CH_2)_5Br$	7/1	**3d**
$^-SiEt_3$	$CH_3(CH_2)_{11}Br$	18/1	**3e**
	$CH_3CH_2CH_2I$	16/1	**3f**
	$(CH_3)_2CH(CH_2)_3Br$	20/1	**3g**
	THP-O-$(CH_2)_6Br$	22/1	**3h**
$^-SiPr_3$	$CH_3CH_2CH_2Br$	46/1	**3i**
	THP-O-$(CH_2)_6Br$	36/1	**3j**
$^-SiPh_3$	$CH_3CH_2CH_2Br$	16/1	**3k**

TABLE 3

STEREOSELECTIVE IODODESILYLATION OF VINYLSILANE

Vinylsilane	Vinyl iodide		Yield (%)
		(7a)	83
		(7b)	85
		(7c)	96
		(7a)	84

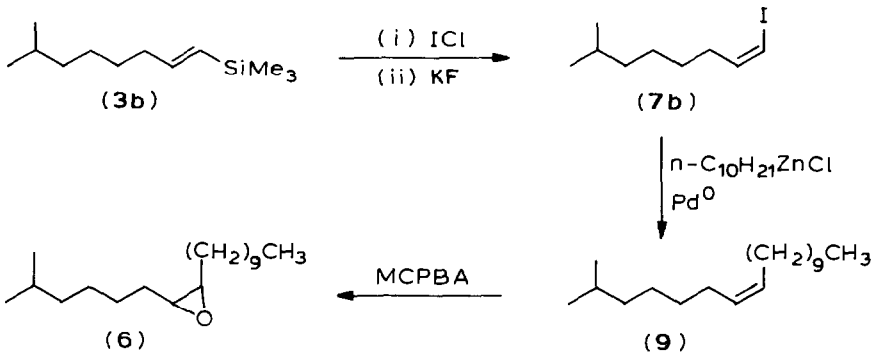
A number of methods are available to couple vinyl halides with organometallic reagents to give alkenes. We found that when the octylcopper reagent, prepared from octylmagnesium bromide and lithium copper chloride [7], was allowed to react with **7a**, the coupled product, *Z*-(9)-tricosene, was obtained quantitatively. Equally effective is the coupling of **7a** with octylzinc chloride with $(Ph_3P)_4Pd$ as catalyst [8]. Interestingly, when octylmagnesium chloride was used in place of the zinc reagent, no coupled product was obtained. Instead the vinyl compound **8** was found as the product. Similar observations on the difference in reactivity between organozinc and organomagnesium compounds have been noted in the literature [9,11]. Coupling also occurred with organozinc reagent and palladium(0) catalyst generated in situ from $(Ph_3P)_2PdCl_2$/i-Bu_2AlH [10].



SCHEME 2

Using the same approach, the sex pheromone of the Gypsy moth, (Porthetria (Lymantria) dispar), *cis*-7,8-epoxy-2-methyloctadecane (**6**), was synthesized from the vinylsilane **3b** (Scheme 3). The Gypsy moth is a serious pest of forest in northeastern USA and in Europe. The synthetic racemic disparlure has been used extensively in traps for the monitoring of the Gypsy moth.

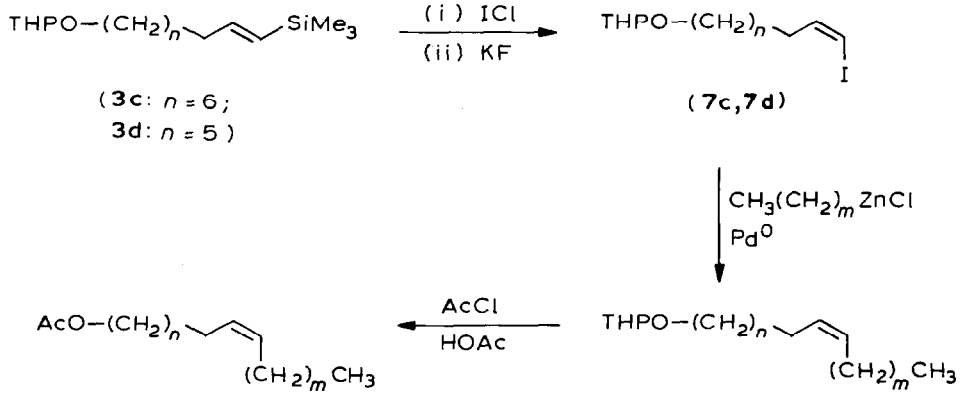
Compound **3b** was treated with ICl/KF to give *Z*-vinyl iodide **7b** in 83% yield. Coupling of **7b** with n-$C_{10}H_{21}ZnCl$ and catalytic amount of $(Ph_3P)_4Pd$ gave the *Z*-olefin **9** in 90% yield. Epoxidation of **9** with *m*-chloroperbenzoic acid (MCPBA) gave the epoxide **6**. The *cis/trans* ratio of **6** could be determined easily by GC or by ^1H NMR to be 94/6. The methine protons on the epoxide ring are clearly distinguishable between the *cis*- and the *trans*-isomers. Similarly, the *Z/E* ratio of **5** was deduced by conversion to the corresponding epoxide followed by ^1H NMR determination.



SCHEME 3

Synthesis of *Z*-8-dodecen-1-yl acetate (10) and *Z*-7-dodecen-1-yl acetate (11)

The two sex pheromones of oriental fruit moth (**10**) and cabbage looper moth (**11**) can be synthesized by the silicon route (Scheme 3). The vinylsilane **3c** ($n = 6$) was iododesilylated by ICl/KF to give **7c** without cleavage of the tetrahydropyranyl protecting group. It is interesting to note that, in contrast, when **3c** was treated with HCl/methanol, the tetrahydropyranyl ether could be cleaved with the vinylsilane intact. Coupling of the vinyliodide **7c** with C_3H_7ZnCl using $(Ph_3P)_4Pd$ catalyst gave



SCHEME 4

the alkene **12** in 88% yield. Compound **12** was converted to the sex pheromone **10** by reaction with acetyl chloride in acetic acid. The ratio of *Z*/*E* in **10** was determined to be 96/4 by capillary GC as well by the epoxidation method used for **5**.

Using the same scheme, the insect sex pheromone **11** was prepared in an overall yield of 57% starting from the vinylsilane **3d**. The ratio of *Z*/*E* in **11** was 92/8 as determined by ^{1}H NMR of the epoxide of **11**.

Conclusion

These syntheses demonstrate that the silicon methodology can be applied as a general approach for the synthesis of *Z*-alkenes. In principle, the vinylsilane **3** can be converted to the *E*-vinyl iodide. We are now in the process of developing the vinylsilane route as a method for *E*-alkenes as well.

Experimental

Boiling points and melting points are reported uncorrected. Nuclear magnetic resonance spectra were recorded on Varian XL-200 and T-60A spectrometers. Low and high resolution mass spectra were determined on Dupont 21-492B or Hewlett–Packard 5980A instruments. Infrared spectra were recorded on Perkin–Elmer 297 or Nicolet 7002 MC spectrophotometers. Analytical gas-chromatography was performed on a Hewlett–Packard 5730A instrument equipped with a flame ionization detector using helium carrier gas flow. The column used was a 10 ft X 0.125 in. 6% OV-101 on Chromosorb W/HP, 80/100.

Potassium t-butoxide and n-butyllithium were supplied by Aldrich company. A standard solution of dilithium tetrachlorocuprate [7] (0.1 *M*) was prepared by treating lithium chloride (2 mmol) with copper(II) chloride (1 mmol) in 10 ml of tetrahydrofuran. Tetrakis(triphenylphosphine)palladium [8] was prepared according to literature procedure [8]. The palladium(0) catalyst was also prepared in situ by treating dichlorobis(triphenylphosphine)palladium with 2 equivalents of diisobutylaluminum hydride in tetrahydrofuran [10]. The amount of catalyst used in each coupling reaction was 5 mole%. The organozinc chloride was prepared in the following manner [11]. A suspension of alkyl halide, magnesium (1.5 equiv.) and anhydrous zinc chloride in tetrahydrofuran was refluxed for 3–4 h.

5-Bromopentan-1-yl acetate was prepared according to literature method [12]. It had b.p. 101°C/0.5 torr.

5-Bromopentanol was prepared by the hydrolysis of 5-bromopentan-1-yl acetate according to literature report [12]. The yield was 98%.

1-(2-Tetrahydropyranyloxy)-5-bromopentane (**15**) was prepared from 5-bromopentanol using literature procedure [12]. It had b.p. 110°C/2 torr.

6-Bromo-1-hexanol was prepared by literature procedure [14a]. It had b.p. 100–104°C/9 torr.

1-(2-Tetrahydropyranyloxy)-6-bromohexane (**14**) was prepared from 6-bromo-1-hexanol using literature method [14b]. It was purified by flash chromatography (hexane/ethyl acetate 9/1). ^{1}H NMR ($CDCl_3$): δ 4.5(br.s, 1H), 3.7(m, 2H), 3.4(m, 3H), 3.37(t, 2H, *J* 6.8 Hz), 1.83(m, 2H), 1.51(m, 1.2H); MS(EI): *m*/*z* 265(100%), 263(92), 208(10), 193(21), 191(19), 165(69), 163(69), 137(9), 135(10), 123(33), 121(33).

Preparation of allyltrialkylsilanes. These silanes were prepared according to literature procedure [15]. Allyltriethylsilane: b.p. 48°C/20 torr (lit. [15] b.p. 44–48°C/8 torr); allyltripropylsilane: b.p. 80°C/20 torr (lit. [15] b.p. 216–217°C/748 torr).

Synthesis of E-vinylsilanes; Alkylation of trialkylsilylallyl anion with alkyl halides

General procedure. A suspension of KO-t-Bu (2.47 g, 22 mmol) in dried hexane (15 ml) was cooled in ice bath and n-BuLi (13.8 ml, 1.6 *M*) was added dropwise. The ice bath was removed and the mixture was stirred for 30 min then cooled down to −78°C. Freshly distilled ether (10 ml) was added followed with allyltrialkylsilane (22 mmol) in 10 ml ether. The solution was allowed to warm to room temperature for 3.5 h and cooled back to −78°C before addition of the appropriate alkyl halide (10 mmol) in 10 ml ether. The reaction mixture was stirred from −78°C to room temperature for 17 h then washed with brine, dried over $MgSO_4$, (or K_2CO_3) and evaporated. The residue was dissolved in pentane and filtered through a 2 in. layer silica gel or purified by flash chromatography. The yield was quantitative. The ratio of γ to α products was determined by GC, ^{1}H NMR, or INEPT ^{29}Si NMR ((with decoupling experiment), δ ~ 1 ppm (allylic Si), −8 ppm (vinylic Si)).

Selective desilylation. The mixture obtained from the alkylation reaction was diluted with benzene (100 ml) and 0.10 ml of hydroiodic acid (57%) was added. The solution was stirred for 4–6 h and the reaction was followed by GC or ^{1}H NMR. The reaction mixture was washed with $Na_2S_2O_3$ (10%), dried and evaporated. The residue was purified by fractional distillation or by flash chromatography.

1-Trimethylsilyl-1-(E)-pentadecene (3a). The reaction was performed as described above (γ/α 11/2). Compound **3a** was obtained after desilylation and fractional distillation, b.p. 170°C/4 torr. ^{1}H NMR ($CDCl_3$): δ 6.0(dt *J* 18.5 Hz, 6Hz, 1H), 5.6(dt, *J* 18.5 Hz, 1.4 Hz, 1H), 2.06(m, 2H), 1.24(b, 22H), 0.86(t, *J* 6.5Hz, 3H), 0.00(s, 9H); IR: 2950, 2920, 2890, 1620, 1410, 1245, 980, 830–860 cm^{-1}; MS(EI): $m/z = 282$ (5%), 267(68), 114(48), 111(16), 99(26), 73(100), 67(15), 59(54); Exact Mass: calcd. for $C_{18}H_{38}Si$ 282.2743, found 282.2738.

1-Trimethylsilyl-7-methyl-1-(E)-octene (3b). Compound **3b** was obtained after desilylation and fractional distillation, b.p. 98°C/760 torr. ^{1}H NMR ($CDCl_3$): δ 6.0(dt, *J* 18.5 Hz, 6Hz, 1H), 5.54(dt, *J* 18.5 Hz, 1.4 Hz, 1H), 2.05 (m, 2H), 1.28(m, 7H), 0.82(d, *J* 7.2 Hz, 6H), 0.01(s, 9H).

9-Trimethylsilyl-1-(2-tetrahydropyranyloxy)-8-(E)-nonene (3c). The vinylsilane **3c** was obtained after desilylation and chromatography (hexane/ethyl acetate 9/1). ^{1}H NMR ($CDCl_3$): δ 6.1(dt, *J* 18.5 Hz, 6Hz, 1H), 5.6(d, *J* 18.5 Hz, 1H), 4.5(br.s, 1H), 3.7(m, 2H), 3.2(m, 2H), 2.1(m, 2H), 1.5–1.28(m, 16H), 0.01(s, 9H); MS(EI): $m/z =$ 298 (M^+, 2%), 297(7), 213(11), 197(28), 173(28), 159(100), 156(74), 141(77), 129(51), 123(35).

8-Trimethylsilyl-1-(2-tetrahydropyranyloxy)-7-(E)-octene (3d). Reaction time: 36 h, γ/α 9/1. A yield of 88% of pure **3d** was obtained after desilylation and chromatography. ^{1}H NMR ($CDCl_3$): δ 6.0(dt, *J* 18 Hz, 6Hz, 1H), 5.5(d, *J* 18 Hz, 1H), 4.6(br.s; 1H), 3.6(m, 4H), 2.0(m, 2H), 1.6–1.25(m, 14H), 0.00(s, 9H). MS(EI): $m/z = 284(M^+$, 3%), 211(10), 200(22), 167(49), 159(84), 156(28), 143(28), 141(100), 129(67), 126(14), 125(37).

1-Triethylsilyl-1-(E)-pentadecene (3e). The γ/α ratio was 18/1. A yield of 91% of **3e** was obtained after desilyation and fractional distillation, bp. 168°C/0.4 torr. ^{1}H

NMR ($CDCl_3$): δ 6.0(dt, *J* 18.5 Hz, 6.5 Hz, 1H), 5.5(dt, *J* 18.5, 1.4 Hz, 1H), 2.1(m, 2H), 1.29(br, 22H), 0.9(t, *J* 7.5 Hz, 9H), 0.86(t, *J* 6.5 Hz, 3H), 0.5(q, *J* 7.8 Hz, 6H); MS(EI): $m/z = 324(1.5\%)$, 296(62), 295(100); Exact mass: calcd. for $C_{12}H_{44}Si$: 324.3212, found 324.3212.

*1-Triethylsilyl-7-methyl-1-(E)-octene (**3g**).* The γ/α ratio was 20/1. A yield of 92% of *E*-vinylsilane **3g** was obtained after desilylation and distillation, b.p. 78–81°C/0.1 torr. ^1H NMR ($CDCl_3$): δ 6.0(dt, *J* 18.7 Hz, 6.2 Hz, 1H), 5.5(dt, *J* 18.7 Hz, 1.4 Hz, 1H), 2.1(m, 2H), 0.9(m, 22H), 0.5(q, *J* 7.8 Hz, 6H). MS(EI): *m/z* 219(25%), 218(36), 217(100), 190(30), 189(64), 161(39), 105(47), 94(24), 87(24), 80(35), 59(46).

*1-Triethylsilyl-1-(E)-hexene (**3f**).* The γ/α was 16/1. A yield of 92% of **3f** was obtained after desilylation and distillation, b.p. 81°C/20 torr. ^1H NMR: δ 6.0 (dt, *J* 18.5 Hz, 6Hz, 1H), 5.4(d, *J* 18.5 Hz, 1H), 2.0(m, 2H), 1.2–0.9(m, 16H), 0.5(m, 6H).

*9-Triethylsilyl-1-(2-tetrahydropyranyloxy)-8-(E)-nonene (**3h**).* The alkylation reaction was performed for 36 h (γ/α 22/1). The residue obtained after desilylation was purified by flash chromatography (hexane/ethyl acetate 9/1) to give a colourless oil of **3h** (91%). ^1H NMR ($CDCl_3$): δ 6.0(dt, *J* 18.6 Hz, 6.5 Hz, 1H), 5.5(d, *J* 18.6 Hz, 1H), 4.5(br.s, 1H), 3.7(m, 2H), 3.3(m, 2H), 2.04(m, 2H), 1.5–1.28(m, 16H), 0.86(t, *J* 6 Hz, 9H), 0.5(q, *J* 6 Hz, 6H). MS(EI): $m/z = 340(M^+, 4\%)$, 339(3), 311(19), 255(11), 225(81), 227(85), 187(32), 169(19), 159(41), 131(100).

*1-Tripropylsilyl-1-(E)-hexene (**3i**).* The γ/α ratio was 46/1. A yield of 90% of pure vinylsilane **3i** was obtained after desilylation and distillation, b.p. 90–92°C/1 torr. ^1H NMR ($CDCl_3$): δ 6.0(dt, *J* 18.6 Hz, 6 Hz, 1H), 5.58(d, *J* 18.5 Hz, 1H), 2.07(m, 2H), 1.28(m, 9H), 0.9(m, 22H), 0.53(m, 6H); MS(EI): *m/z* 240(2.3%), 197(85), 155(100), 113(56), 99(35), 97(221), 85(59), 57(34); Exact mass calcd. for $C_{15}H_{32}Si$ 240.2273, found 240.2286.

*9-Tripropylsilyl-1-(2-tetrahydropyranyloxy)-8-(E)-nonene (**3j**).* The alkylation reaction was performed as described above for 36h (γ/α 36/1). Compound **3j** (83%) was obtained after desilylation and chromatography. ^1H NMR ($CDCl_3$): δ 6.0(dt, *J* 18.5 Hz, 6 Hz, 1H), 5.5(dt, *J* 18.5 Hz, 1.4 Hz, 1H), 4.5(br.s, 1H), 3.7(m, 2H), 3.37(m, 2H), 2.04(m, 2H), 1.52–1.3(m, 16H), 0.92(t, *J* 7.1 Hz, 9H), 0.51(m, 6H). MS(EI): $m/z = 382(M^+, 4\%)$, 339(6), 255(56), 213(31), 211(79), 173(100), 169(17), 159(25), 157(29), 131(88).

*1-Triphenylsilyl-1-(E)-hexene (**3k**).* Reaction time was 36 h (γ/α 16/1) and 77% of **3k** was obtained after desilylation and chromatography (hexane). The final product was recrystallized from petroleum ether, m.p. 60–61°C. ^1H NMR ($CDCl_3$): δ 7.47(m, 18H), 6.1(s, 2H), 2.2(br.s, 2H), 1.3(m, 4H), 0.87(t, *J* 6.6 Hz, 3H); MS(EI): $m/z = 324(25\%)$, 285(56), 259(61), 207(38), 183(100), 105(56), 53(221); Exact mass calcd. for $C_{24}H_{26}Si$, 342.1804, found 342.1786.

Iododesilylation of vinylsilanes with iodine monochloride

General procedure. A solution of vinylsilane in CCl_4(~ 5 mmol/10 ml) was cooled to 0°C. Iodine monochloride (1.1 equiv) in CCl_4 was added dropwise. Fifteen min after the addition, the reaction mixture was washed with $Na_2S_2O_4$ (10%). The organic solution was dried ($MgSO_4$ or K_2CO_3) and evaporated. A mixture of DMSO (10 ml) and 1.5 equiv. of $KF/2H_2O$ was added to the residue and the mixture was stirred at room temperature for 4 h, then extracted three times with ether/water. The ethereal solution was dried, evaporated and the final product purified by flash chromatography.

(Z)-1-Iodo-1-pentadecene (7a). By the procedure described above, 3.38 g (12 mmol) of **3a** was treated with ICl and $KF \cdot 2H_2O$ to give 3.36 g (83%) of vinyl iodide **7a** after chromatography (hexane). ^1H NMR ($CDCl_3$): δ 6.1(s, 2H), 1.54(m, 2H), 1.23(br.s, 22H), 0.86(t, J 6.5 Hz, 3H), MS(EI): $m/z = 336$ (12), 128(11), 154(23), 97(77), 83(86), 71(83), 55(100); Exact mass calcd. for $C_{15}H_{29}I$: 336.1316, found 336.1306.

(Z)-1-Iodo-7-methyl-1-octene (7b). By the same procedure, 1.51 g (6.28 mmol) of vinylsilane **3b** was treated with ICl and $KF \cdot 2H_2O$ and 1.35 g (85%) of **7b** was obtained. ^1H NMR ($CDCl_3$): δ J 6.15(s, 2H), 2.1(m, 2H), 1.3(m, 7H), 0.84(d, J 6.5 Hz, 6H); IR: 3075, 2795, 1604, 1446, 1371, 1356, 1280, 1170, 1070, 1007, 935, 680 cm^{-1}; MS(EI), $m/z = 252$ (3%), 167(36), 83(72), 81(26), 68(84), 55(100). Exact mass calcd. for $C_9H_{17}I$: 252.0377, found 252.0332.

(Z)-9-Iodo-1-(2-tetrahydropyranyloxy)non-8-ene (7c). By the same procedure, 3.57 g (12 mmol) of **3c** was allowed to react with ICl and $KF \cdot 2H_2O$ and 3.65 g (86%) of **7c** was obtained. ^1H NMR ($CDCl_3$): δ 6.14(s, 2H), 4.53(br.s, 1H), 3.40(m, 2H), 3.74(m, 2H), 2.10(m, 2H), 1.53–1.2(m, 16H); MS(EI): $m/z = 352$ (0.7%), 180(46), 167(270), 124(3), 123(22), 85(100), 84(21), 56(60), 55(95).

(Z)-8-Iodo-1-(2-tetrahydropyranyloxy)oct-7-ene (7d). By the general procedure described above, **3d** (4.55 g, 15.3 mmol) was converted into 4.33 g (84%) of vinyl iodide **7d**. ^1H NMR ($CDCl_3$): δ 6.14(s, 2H), 4.52(br.s, 1H), 3.74(m, 2H), 3.37(m, 2H), 2.08(m, 2H), 1.52–1.34(m, 14H); ^{13}C NMR: 141.30, 98.79, 82.12, 67.50, 62.21, 34.54, 30.76, 29.76, 29.56, 28.87, 27.85, 26.02, 25.48, 19.65. MS(EI): $m/z = 338(M^+, 2\%)$, 337(5), 211(140), 180(80), 167(100).

(Z)-9-Tricosene (5) [16]. To a solution of (*Z*)-1-iodo-1-pentadecene **7a** (1.41 g, 4.2 mmol) in THF (10 ml), $(Ph_3P)_4Pd$ (242 mg) was added followed with n-octylzinc chloride (10 ml, ~ 1*M* in THF). The mixture was kept at room temperature for overnight, then diluted with ether, washed with saturated solution of NH_4Cl. The organic layer was dried over $MgSO_4$ and evaporated. Compound **5** was obtained quantitatively ($\geq$ 96% from GC analysis). Fractional distillation of the residue gives 1.1 g (81%) of pure compound **5** (*Z/E* 96/4) [14], b.p. 136–140°C/0.1 torr. ^1H NMR ($CDCl_3$): δ 5.31(t, J 4.6 Hz, 2H), 2.0(m, 4H), 1.22(br, 34H), 0.85(t, J 6.5 Hz, 6H); ^{13}C NMR ($CDCl_3$): δ 129.92, 31.95, 29.74, 29.58, 29.36, 28.44, 27.26, 22.72, 14.04; MS(EI): $m/z = 322(M^+, 2.8\%)$, 111(12), 97(31), 84(16), 83(43), 69(53), 57(81), 56(44), 55(79), 43(100); Exact mass calcd. for $C_{23}H_{46}$: 322.3599, found 322.3566. Determination of *Z/E* ratio: An aliquot of **5** was epoxidized in CH_2Cl_2 solution using 1.2 equiv. of MCPBA. The reaction mixture was washed with sodium bicarbonate solution, dried over $MgSO_4$ and evaporated. The product was purified by flash chromatography. ^1H NMR ($CDCl_3$): δ 2.89 (methines, *cis*, 96%), 2.59(methines, *trans*, 4%).

(Z)-2-Methyl-7-octadecene (9) [17]. To a solution of (*Z*)-vinyliodide **7b** (1.33 g, 5.2 mmol) in THF (10 ml), $(Ph_3P)_4Pd$ (300 mg) was added followed with n-decylzinc chloride (11 ml, ~ 1*M* in THF) and the mixture was stirred at room temperature for overnight. Ether (30 ml) was added before extraction with saturated solution of NH_4Cl. The ethereal solution was dried over $MgSO_4$, evaporated and the residue purified by fractional distillation to give 1.32 g (95%) of **9**, b.p. 102°C/01. torr. ^1H NMR ($CDCl_3$): δ 5.34(t, J 4.5 Hz, 2H), 2.0(m, 4H), 1.25(s, 23H), 0.85(m, 9H). ^{13}C NMR ($CDCl_3$): δ 19.92, 38.96, 31.95, 30.06, 29.68, 29.36, 28.08, 27.26, 27.09, 22.67, 14.09; MS(EI): $m/z = 267$ (20%), 2.66(25), 111(35), 97(44), 96(18), 95(20), 85(50),

84(25), 83(63), 82(28), 69(66), 67(37), 57(100), 55(59); Exact mass calcd. for $C_{19}H_{38}$: 266.2973, found 266.2935.

cis-7–8-epoxy-2-methyloctadecane (6) (dispalure) [17]. A solution of **9** (266 mg, 1 mmol) in CH_2Cl_2 (10 ml) was cooled in ice bath. MCPBA (1.2 equiv.) in 10 ml CH_2Cl_2 was added. The mixture was stirred for 4–6 h; then washed with sodium bicarbonate solution. The organic layer was dried over $MgSO_4$ and evaporated. The residue was purified by flash chromatography (pentane) to give **6** (253 mg, 89%, *cis/trans* 94/6). ^1H NMR ($CDCl_3$): δ 2.85(br.s, 2H methines *cis* 94%), 2.6(m, 2H, methines *trans* 6%), 1.4–1.21(m, 27H), 0.81(m, 9H). IR: 2938, 1379, 1360, 1260, 1165, 1073, 1012, 916, 794 cm^{-1}; MS(EI): $m/z = 264(1\%)$, 260(3), 128(4), 105(24), 92(25), 78(43), 70(22), 69(23), 56(35), 55(41), 44(100).

(Z)-1-(2-Tetrahydropyranyloxy)dodec-8-ene (12). A solution of **7c** (841 mg, 2.4 mmol) in 10 ml THF was treated with n-propylzinc chloride (9 ml, ~ 1 *M* in THF) in presence of $(Ph_3P)_4Pd$ (0.05 equiv.) as described above for compound **9**. Compound **12** (565 mg, 88%) was obtained after flash chromatography (hexane/ethyl acetate, 9/1). ^1H NMR ($CDCl_3$): δ 5.3(t, *J* 5 Hz, 2H), 4.56(br.s, 1H), 3.7(m, 2H), 3.4(m, 2H), 1.98(m, 4H), 1.56–1.3(m, 18H), 0.88(t, *J* 6.5 Hz, 3H); MS(EI): $m/z =$ 268(M^+, 1.8%), 267(2), 101(36), 97(20), 95(33), 85(100), 69(87), 67(57).

(Z)-8-Dodecen-1-yl acetate (10) [18]. A mixture of **12** (426 mg, 1.6 mmol), acetic acid (15 ml) and acetyl chloride (0.5 ml) was kept at 60°C for 6 h. The reaction mixture was then diluted with CH_2Cl_2, washed with H_2O and a solution of Na_2CO_3 (10%). The organic layer was dried over $MgSO_4$, evaporated and the residue purified by flash chromatography (hexane/ethyl acetate, 10/0.5). (*Z*)-8-Dodecen-1-yl acetate (**10**, 240 mg, 77%) was obtained. ^1H NMR ($CDCl_3$): δ 5.3(t, *J* 5 Hz, 2H), 4.0(t, *J* 6.7 Hz, 2H), 2.01 (s, 3H), 1.97 (m, 4H), 1.5–1.3(m, 12H), 0.85(t, *J* 7 Hz, 3H); MS(EI): $m/z = 205(1\%)$, 166(24), 110(30), 108(24), 96(85), 95(68), 82(90), 68(87), 55(100); Exact mass of $M^+ -$ AcOH ion calcd. for $C_{12}H_{22}$ 166.1721, found 166.1750.

(Z)-1-(2-Tetrahydropyranyloxy)dodec-7-ene (13). (*Z*)-8-Iodo-1-(2-tetrahydropyranyloxy)oct-7-ene (**7d**), (651 mg, 1.9 mmol) was allowed to react with butylzinc chloride (4 ml, ~ 1 *M* in THF) in the presence of $(Ph_3P)_4Pd$ in the same way as described above for compound **9**. The final residue was purified by chromatography (hexane/ethyl acetate 9/1) and 426 mg (82%) of **13** was obtained. ^1H NMR ($CDCl_3$): δ 5.33(t, *J* 5Hz, 2H), 4.53(br.s, 1H), 3.7–3.4(m, 4H), 1.96(m, 7H), 1.5–1.3(m, 18H), 0.83(t, *J* 6 Hz, 3H); MS(EI): $m/z = 205$ (11%). 154(17), 152(18), 128(18), 91(28), 84(53), 83(63), 78(66), 55(96), 41(47), 28(100).

(Z)-7-Dodecen-1-yl acetate (11) [19]. The reaction was performed as described above for compound **10**. (*Z*)-1-(2-Tetrahydropyranyloxy)dodec-7-ene (**13**), (367 mg, 1.4 mmol) was treated with ACOH/AcCl at 60°C for 6 h and 2.48 mg (82%) of **11** was obtained after chromatography (hexane/ethyl acetate 20/1). ^1H NMR ($CDCl_3$): δ 5.3(t, *J* 5.6 Hz, 2H), 4.0(t, *J* 6.7 Hz, 2H), 1.97(s, 3H), 1.96(m, 4H), 1.5–1.3(m, 12H), 0.8(t, *J* 7 Hz, 3H). MS(EI): $m/z = 225(1)$, 166(37), 154(3), 138(8), 123(23), 110(47), 109(51), 95(75), 82(67), 67(100); Exact mass of M^+–AcOH, calcd. for $C_{12}H_{22}$: 166.1721, found 166.1765. The ratio of *Z/E* in **11** was determined by epoxidation with MCPBA using the same procedure developed for **5**. ^1H NMR ($CDCl_3$): δ 2.89 (methine, *cis*, 92%), 2.60 (methine, *trans*, 8%).

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