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CLEAVAGE OF VINYL CARBON-SILICON BOND WITH TETRABUTYLAMMONIUM FLUORIDE

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Abstract Dimethylphenylsilyl group is removed from a vinyl carbon with tetrabutylammonium fluoride The presence of phenyl group on silicon atom plays a critical role The cleavage of allyldimethylsilyl- and alkoxydimethylsilyl groups also proceeds very easily

Protodesilylation of vinylsilanes is usually performed with HI[1] or p-TsOH[2] and proceeds with retention of the alkene geometry The method, however, cannot be applied to the substrates which are acid-sensitive Further limitation is the possibility of acid-catalyzed isomerization of the alkene product Meanwhile, the affinity of fluoride ion for silicon has been well recognized and widely used for desilylation [3] Chan has reported[4] that the cleavage of vinyl carbon-trimethylsilyl bond is difficult or even impossible under ordinary conditions In connection with our new synthesis of vinylsilanes,[5,6] we have reexamined the reaction of vinylsilanes with tetrabutylammonium fluoride in detail [7]

The results are summarized as follows (1) The presence of phenyl, allyl, or alkoxyl group on the silicon atom facilitates the cleavage of vinylsilanes (2) The cleavage of vinyl carbon-silicon bond can proceed stepwise Substitution of allyl, alkoxyl, or phenyl group[8] by fluoride ion provides a fluorosilane which is transformed into a silanol by the action of contaminated water Further attack of fluoride ion on the silanol causes the cleavage of sp^2C-Si bond (3) Suitably located hydroxyl group facilitates the cleavage of C-Si bonds possibly by intramolecular participation For instance, the reaction of (Z)-6-dimethylphenylsilyl-6-tridecen-5-ol (**31**) proceeds at 25°C

<u>(1) Cleavage of olefinic carbon-dimethylphenylsilyl bond</u>

The desilylation of 1-silylalkyne with fluoride ion is relatively facile,[9] whereas the cleavage of sp^2C-Si bond is rather difficult Only a few exceptional examples[10,11] are known Surprisingly, tetrabutylammonium fluoride effectively cleaves the vinyl carbon-dimethylphenylsilyl bonds The presence of phenyl substituent on silicon atom plays an important role for the reaction For example, treatment of (E)-1-dimethylphenylsilyl-2-methyl-1-dodecene (**1**) with tetrabutylammonium fluoride in DMSO at 80°C gave 2-methyl-1-dodecene (**2**) in 88% yield, whereas the corresponding trimethylsilylated olefin is recovered completely unchanged under the same reaction conditions The results are summarized in Table 1 The reaction proceeded in aprotic polar solvents such as HMPA, DMSO, or DMF Prolonged heating of the reaction mixture was needed in THF (entry 1 in Table 1) The use of KF, CsF, or KF/18-Crown-6 instead of tetrabutylammonium fluoride gave no cleavage product

High stereospecificity of the reactions is shown in the transformation of (Z) and (E)-2-dimethylphenylsilyl-2-tridecene (**3** and **5**) into (E) and (Z)-tridecene, respectively (entry 2 and 3 in Table 1) Desilylation proceeds with retention of configuration Remarkably, this new method is quite effective by application to the substrates sensitive under acidic conditions For instance, treatment of dimethyl acetal **15** with tetrabutylammonium fluoride in DMSO provided the corresponding desilylated acetal in 91% yield Desilylation of 1-dimethylphenylsilyl-6,10-dimethyl-2-vinyl-1,5,9-undecatriene (**21**) by this technique gave β-farnesene (**22**) in 85% yield, whereas the treatment with HI provided a complex mixture containing no desired tetraene (entry 11 in Table 1) The conversion of (E)-1-bromo-1-dimethylphenylsilyl-1-dodecene (**17**) into 1-bromo-1-dodecene (**18**) proceeded in excellent yield, but 1-dimethylphenylsilyl-2-iodo-1-dodecene (**19**) gave 1-dodecyne under elimination of $PhMe_2SiI$

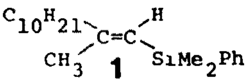
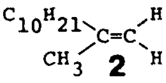
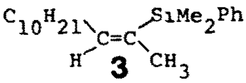
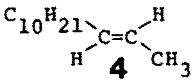
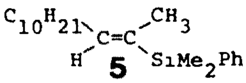
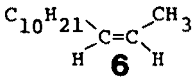
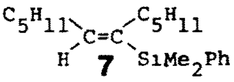
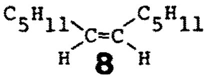
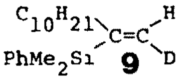
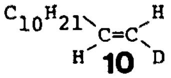
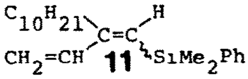
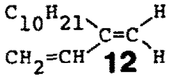
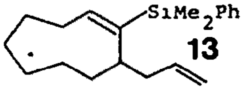
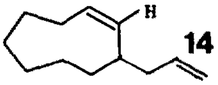
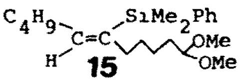
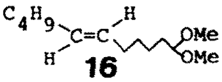
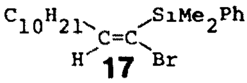
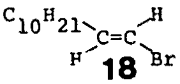
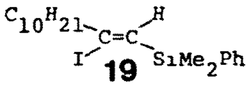
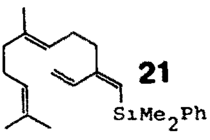
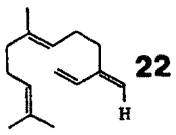
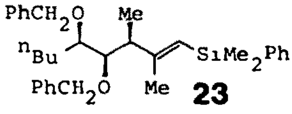
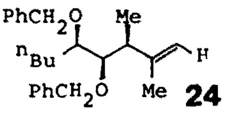
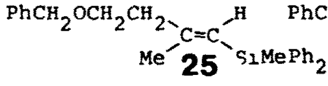
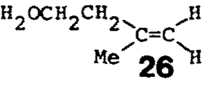
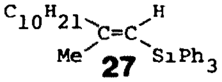
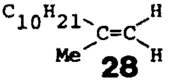
(Diphenylmethylsilyl)alkenes and triphenylsilylalkenes also are susceptible to this procedure but less effectively[12] For instance, desilylation of 4-diphenylmethylsilyl-3-methyl-3-buten-1-ol benzyl ether (**25**), or 1-triphenylsilyl-2-methyl-1-dodecene (**27**) with tetrabutylammonium fluoride in HMPA (80°C, 1 h) gave the desired product in 80% or 52% yield, respectively

(2) Reaction of a vinylsilane containing hydroxyl group

The intramolecular assistance of a hydroxyl group is noticed by data in Table 2 The reaction of compound **29** required heating of the reaction mixture at 90°C for 4 h after the Chan's method[4] In contrast, the reaction of vinylsilane **31** proceeded at 25°C in 15 min (entry 1 and 2 in Table 2) Both (Z)-6-trimethylsilyl-6-tridecen-4-ol and 1-trimethylsilyl-9-(1-hydroxypentyl)-1-cyclononene were completely stable upon treatment with tetrabutylammonium fluoride in THF-DMSO at 80°C, whereas the corresponding dimethylphenylsilyl-carbon bond of the hydroxy compounds **33** and **35** was cleaved under the same reaction conditions Thus, it is obvious that the presence of phenyl group on silicon facilitates the cleavage of vinyl carbon-silicon bond in these hydroxy substrates as well as prosaic vinylsilanes described above

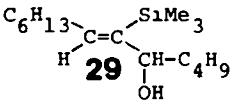
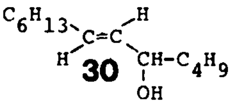
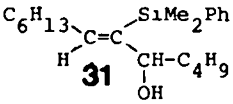
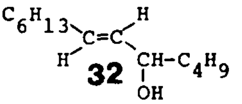
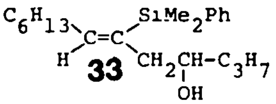
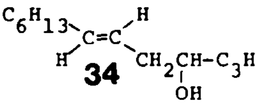
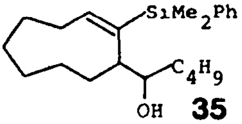
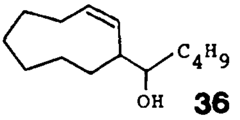
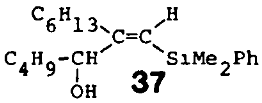
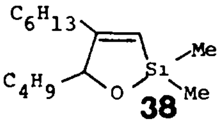
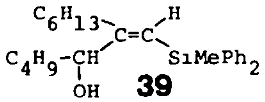
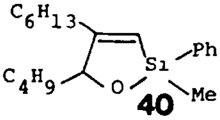
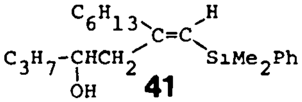
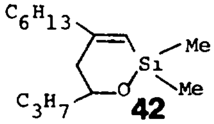
Surprisingly, γ-hydroxy compound such as **37** or **39** reacted with tetrabutylammonium fluoride easily to give cyclic silyl ether **38** or **40** Similarly, δ-hydroxy substrate **41** provided six-membered silyl ether **42**, although heating of the reaction mixture was needed The formation of silyl ether is explained by Scheme 1 Substitution of phenyl group on silicon atom by fluoride ion provides an intermediate **43** which is transformed into **38** by the internal attack of hydroxyl group on silicon and fluoride ion is reproduced Thus, the reaction should proceed in the presence of a catalytic amount of tetrabutylammonium fluoride This was indeed the case and treatment of vinylsilane **37** with 0 2 equiv of tetrabutylammonium fluoride in THF at 25°C for 6 h gave silyl ether **38** in 70% yield All attempts to isolate fluorosilane **43** resulted in failure The cyclized silyl ether **38**, **40**, or **42** could be converted into the corresponding

Table 1 Stereospecific cleavage of vinyl carbon-$PhMe_2Si$ bond with $^nBu_4NF$[a]

Entry	Substrate	Product	Reaction Solvent	Conditions		Yield[b] (%)
				Temp (°C)	Time (h)	
1	 **1**	 **2**	THF-HMPA (1:2)	80	0.5	91
			THF-DMSO (1.2)	80	0.5	88
			THF-DMF (1:2)	80	0.5	89
			THF	80	10	66 (28)[c]
2	 **3**	 **4**	THF-DMSO (2:1)	80	0.5	99
3	 **5**	 **6**	THF-HMPA (1:4)	80	0.5	60
4	 **7**	 **8**	THF-DMSO (1:2)	80	2.0	55
5	 **9**	 **10**	THF-DMSO (1:2)	80	0.5	80
6	 **11**	 **12**	THF	80	0.5	89
			THF-HMPA (1:2)	25	0.5	82
7	 **13**	 **14**	THF-HMPA (2:1)	80	2.0	68
8	 **15**	 **16**	THF-DMSO (1:2)	80	0.25	91
9	 **17**	 **18**	THF-HMPA (2:1)	80	0.3	95
10	 **19**	$C_{10}H_{21}C{\equiv}CH$ **20**	THF-DMSO (1:2)	80	0.25	95
11	 **21**	 **22**	THF-DMSO (1:1)	80	0.5	85
12	 **23**	 **24**	THF-DMSO (1:2)	100	2.0	95
13	 **25**	 **26**	THF	80	1.0	80
14	 **27**	 **28**	THF-HMPA (1:2)	80	1.0	52

a) One mmol of vinylsilane and five mmol of $^nBu_4NF$ (THF solution) were employed. b) Yields represent isolated products after purification. c) The starting material was recovered in 28% yield.

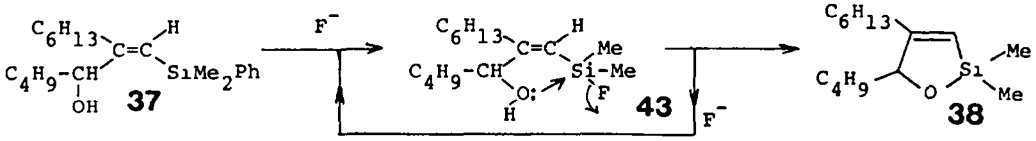
Table 2 Reaction of vinylsilane carrying hydroxyl group with $^{n}Bu_4NF^{a}$

Entry	Substrate	Product	Reaction Solvent	Conditions Temp (°C)	Conditions Time (h)	Yield^{b} (%)
1	 **29**	 **30**	THF-MeCN (1 2)	90	4 0	72
2	 **31**	 **32**	THF-DMSO (2 1)	25	0 25	100
3	 **33**	 **34**	THF-DMSO (2 1)	80	1 0	82
4	 **35**	 **36**	THF-DMSO (2 1)	80	1 0	93
5	 **37**	 **38**	THF	25	0 5	81
6	 **39**	 **40**	THF	25	0 3	54
7	 **41**	 **42**	THF	70	0 5	65

a) One mmol of vinylsilane and three mmol of $^{n}Bu_4NF$ (THF solution) were employed
b) Yields represent isolated products after purification

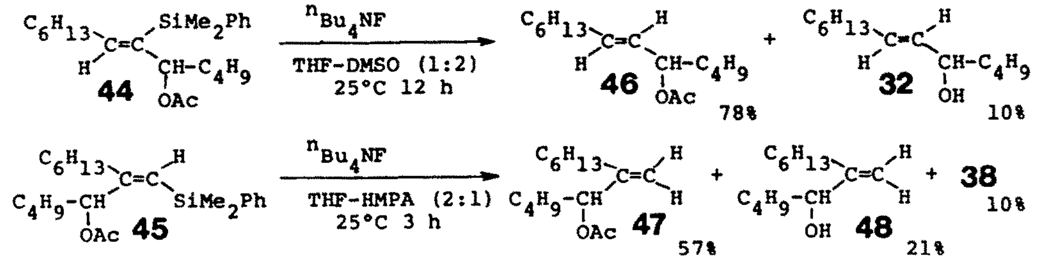
allylic or homoallylic alcohol on further treatment with tetrabutylammonium fluoride in THF-DMSO at 80°C for 1 h Heating a mixture of vinylsilanes **37**, **39**, or **41** and tetrabutylammonium fluoride in THF-DMSO gave desilylated allylic or homoallylic alcohols directly and no intermediary silyl ethers

Scheme 1



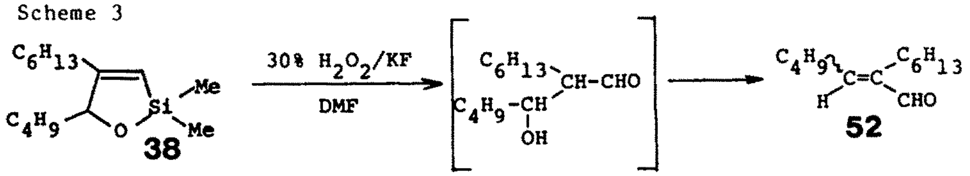
In order to check the role of hydroxyl group, hydroxy compounds **31** and **37** were converted into acetates **44** and **45** The acetate **44** reacted much sluggishly with tetrabutylammonium fluoride to give a mixture of desilylated product **46** and **32** In contrast, Si-C bond in substrate **45** was cleaved as easily as the hydroxy compound **37** to afford allylic acetate **47** along with allylic alcohol **48** and cyclic silyl ether **38** (Scheme 2) [13]

Scheme 2



Incidentally, a crude product **38** derived from **37** was treated with 30% H_2O_2-KF-DMF system according to Kumada and Tamao procedure[14] to give enal **52** in 33% overall yield from **37** (Scheme 3) Various attempts of improving the yield of **52** failed[15] The six-membered silyl ether **42** (Table 2) was not oxidized by this technique

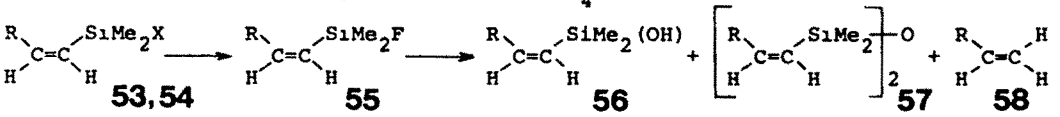
Scheme 3



(3) Reaction of allylvinylsilane and 1-disilanyl-1-alkene

Treatment of allyldimethylvinylsilane (**53**) or 1-(1,1,2,2-tetramethylphenyldisilanyl)-1-dodecene (**54**) with tetrabutylammonium fluoride in THF-DMSO at 80°C for 30 min gave 1-dodecene in 92% or 100% yield, respectively Such highly reactive silanes supposedly react with fluoride ion[16,17] to give a fluorosilane **55** first, which is hydrolyzed at room temperature Thus, a mixture of silanol **56** and disiloxane **57** was obtained under mild conditions (in THF, 25°C, 30 min) The ratios of these two products (**56** and **57**) varied from 22 68 to 68 16 (Table 3) and are hardly reproducible On the other hand, less reactive dimethylphenylvinylsilane or dimethylmethoxyvinylsilane (**59**) requires heating at 80°C in THF-DMSO and gave the hydrocarbon **58** and no fluorosilane or silanol

Table 3. Reaction of vinylsilanes with $^nBu_4NF$



Substrate R = $C_{10}H_{21}$	F^- (equiv)	Reaction Solvent	Conditions Temp (°C)	Conditions Time (min)	Yield (%) **56**	Yield (%) **57**	Yield (%) **58**
X: $CH_2CH=CH_2$ **53**	2-3	THF	25	5-30	22-68	16-68	trace
	3	THF-DMSO (1:2)	80	30	0	0	92
X: $SiMe_2Ph$ **54**	3	THF	25	30	67	9	trace
	3	THF-DMSO (1:2)	80	30	0	0	100

EXPERIMENTAL

Melting points and boiling points are uncorrected Bulb-to-bulb distillation was carried out by use of Kugelrohr (Büchi) and bp was determined by measuring the bath temperature ^{1}H-NMR spectra (tetramethylsilane as an internal standard unless otherwise noted) were obtained on a Varian EM-390, JEOL PMX-60, or XL-200 spectrometer, chemical shifts being given in ppm units IR data of neat liquid film samples (unless otherwise noted) were recorded on a Shimadzu IR-27G spectrometer, MS on a Hitachi M 80 spectrometer Thin-layer chromatograph (TLC) analyses were performed on commercial glass plates bearing 0 25 mm layer of Merck silica-gel 60 F_{254} Preparative TLC plates were prepared with Merck Kiesel-gel PF_{254} Column chromatography was carried out with silica-gel (Wakogel C-200) at atmospheric pressure

Materials Tetrahydrofuran (THF) was purified by distillation from sodium benzophenone ketyl Hexamethylphosphoric triamide (HMPA) was distilled on CaH_2 and stored over 4-Å molecular sieves Other solvents, DMSO, DMF, and CH_3CN were purchased from Wako and used without further purification Tetrabutylammonium fluoride (THF solution) was purchased from Aldrich

Preparation of vinylsilanes 1, 9, 11, 19, 25, and 27 The compounds were prepared according to the method previously described[5] The compounds 5 and 7 were prepared following the method reported by Fleming[18]

(E)-1-dimethylphenylsilyl-2-methyl-1-dodecene (1) Bp 129°C (bath temp, 0 5 Torr), IR (neat) 2890, 2820, 1600, 1420, 1245, 1105, 825, 725, 695 cm^{-1}, ^{1}H-NMR (CCl_4, 90 MHz) δ0 31 (s, 6H), 0 73-0 97 (m, 3H), 1 07-1 53 (bm, 16H), 1 62 (s, 3H), 1 93-2 23 (m, 2H), 5 25 (s, 1H), 7 10-7 49 (m, 5H), MS m/z (rel intensity) 317 (0 6), 316 (M^+, 2), 301 (12), 190 (17), 148 (22), 135 (100) Found C, 79 91, H, 11 54% Calcd for $C_{21}H_{36}$ C, 79 67, H, 11 46%

(Z)-1-Deuterio-2-dimethylphenylsilyl-1-dodecene (9) Bp 104°C (bath temp, 0 1 Torr), IR (neat) 2890, 2820, 1460, 1420, 1245, 1110, 830, 810, 770, 725 cm^{-1}, ^{1}H-NMR (CCl_4, 90 MHz) δ0 33 (s, 6H), 0 69-1 01 (m, 3H), 1 06-1 50 (bm, 16H), 1 93-2 18 (m, 2H), 5 54 (m, 1H), 7 10-7 49 (m, 5H), MS m/z (rel intensity) 304 (2), 303 (M^+, 8), 302 (1), 288 (11), 177 (15), 162 (23), 135 (100), 121 (27) Found C, 78 98, H, 11 79% Calcd for $C_{20}H_{33}DSi$ C, 79 13, H, 11 62%

1-Dimethylphenylsilyl-2-vinyl-1-dodecene (11) Silylmagnesation of 1-octyne followed by $NiCl_2(PPh_3)_2$ catalyzed coupling reaction with vinyl bromide[19] gave the title compound in 91% yield as a mixture of stereoisomer (37 63) IR (neat) 2900, 2825, 1420, 1245, 1105, 840, 725, 695 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 200 MHz) δ0 39 (s, 3 78H), 0 40 (s, 2 22H), 1 15-1 69 (bm, 8H), 2 21-2 45 (m, 2H), 5 06 (d, J = 10 8 Hz, 1H), 5 22 (d, J = 17 5 Hz, 0 37H), 5 28 (d, J = 17 5 Hz, 0 63H), 5 64 (s, 0 37H), 5 67 (s, 0 63H), 6 32 (dd, J = 17 5, 10 8 Hz, 0 37H), 6 52 (dd, J = 17 5, 10 8 Hz, 0 37H), 7 37-7 70 (m, 5H) Found 272 1966 Calcd for $C_{18}H_{28}Si$ M^+ 272 1960

(E)-3-Allyl-2-dimethylphenylsilyl-1-cyclononene (13) The compound was prepared according to the reported procedure from 1,2-cyclononadiene[6] Bp 110°C (bath temp, 1 0 Torr), IR (neat) 3080, 1645, 1620, 1595, 1430, 1250, 1105 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 200 MHz) δ0 37 (s, 3H), 0 40 (s, 3H), 1 21-1 71 (bm, 10H), 1 95-2 41 (m, 4H), 2 63-2 82 (m, 1H), 4 84-5 01 (m, 2H), 5 58-5 93 (m, 1H), 5 98 (t, J = 8 4 Hz, 1H), 7 23-7 65 (m, 5H), MS m/z (rel intensity) 298 (M^+, 0 2), 283 (0 2), 257 (0 6), 220 (3), 135 (100) Found C, 80 24, H, 10 35% Calcd for $C_{20}H_{30}Si$ C, 80 46, H, 10 13%

(Z)-6-Dimethylphenylsilyl-6-undecenal dimethylacetal (15) Bp 117°C (bath temp, 0 05 Torr), IR (neat) 2920, 1425, 1250, 1125, 1110, 1070, 1050, 830, 815, 770, 730, 700 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 200 MHz) δ0 37 (s, 6H), 0 73-0 86 (m, 3H), 1 06-1 66 (m, 10H), 1 87-2 03 (m, 2H), 2 03-2 20 (m, 2H), 3 30 (s, 6H), 4 33 (t, J = 5 7 Hz, 1H), 6 06 (t, J = 7 5 Hz, 1H), 7 30-7 61 (m, 5H), MS m/z (rel intensity) 348 (M^+, 0 1), 302 (11), 240 (25), 223 (40), 151 (39), 150 (38), 135 (100), 111 (37), 89 (33), 84 (41) Found C, 72 14, H, 10 67% Calcd for $C_{21}H_{36}O_2Si$ C, 72 35, H, 10 41%

(Z)-2-Iodo-1-dimethylphenylsilyl-1-dodecene (19) Bp 136°C (bath temp, 0 07

Torr), IR (neat) 2890, 2825, 1585, 1420, 1245, 1110, 835, 725, 695 cm^{-1}, ^{1}H-NMR (CCl_4, 90 MHz) δ0 45 (s, 6H), 0 72-0 98 (m, 3H), 1 09-1 47 (bm, 16H), 2 42-2 63 (m, 2H), 6 43 (s, 1H), 7 13-7 52 (m, 5H), MS m/z (rel intensity) 301 (M$^+$-I, 36), 135 (100) Found C, 56 32, H, 7 91% Calcd for $C_{20}H_{33}ISi$ C, 56 06, H, 7 76%

23 bp 162°C (bath temp, 0 06 Torr), IR (neat) 2960, 1615, 1250, 1110, 1065, 840, 725, 695 cm^{-1}, ^{1}H-NMR (CCl_4, 90 MHz) δ0 30 (s,6H), 0 76-1 60 (m, 9H), 1 10 (d, J = 6 3 Hz, 3H), 1 69 (s, 3H), 2 44 (m, 1H), 3 21-3 54 (m, 2H), 4 44 (d, J = 10 5 Hz, 1H), 4 47 (bs, 2H), 4 61 (d, J = 10 5 Hz, 1H), 5 44 (bs, 1H), 7 01-7 46 (m, 15H) Found C, 79 18, H, 8 94% Calcd for $C_{33}H_{44}O_2Si$ C, 79 14, H, 8 86%

General procedure for the cleavage of dimethylphenylsilyl-vinyl carbon bond A THF solution of tetrabutylammonium fluoride (1 0 M, 2 5 ml, 2 5 mmol) was added to a solution of (E)-1-dimethylphenylsilyl-2-methyl-1-dodecene (1) (0 16 g, 0 5 mmol) in HMPA (5 0 ml) under an argon atmosphere and the whole was stirred for 0 5 h at 80°C The reulting mixture was diluted with ethyl acetate (25 ml) and washed with water (10 ml x4) Purification by preparative thin-layer chromatography on silica-gel gave 2-methyl-1-dodecene (2) (83 mg) in 91% yield

2-Vinyl-1-dodecene (12) Bp 132°C (bath temp, 20 Torr), IR (neat) 2880, 2820, 1585, 1460, 985, 885 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 200 MHz) δ0 80-0 95 (m, 3H), 1 16-1 40 (bs, 16H), 2 13-2 28 (m, 2H), 4 99 (bs, 2H), 5 04 (d, J = 10 8 Hz, 1H), 5 23 (d, J = 17 7 Hz, 1H), 6 38 (dd, J = 17 7, 10 8 Hz, 1H), MS m/z (rel intensity) 195 (0 2), 194 (M$^+$, 2), 166 (2), 95 (25), 81 (17), 68 (100) Found C, 86 62, H, 13 65% Calcd for $C_{14}H_{26}$ C, 86 52, H, 13 48%

(Z)-3-Allyl-1-cyclononene (14) Bp 113°C (bath temp, 20 Torr), IR (neat) 2900, 2830, 1630, 1445, 990, 735 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 200 MHz) δ1 13-1 95 (m, 10H), 2 07-2 48 (m, 4H), 2 64-2 88 (m, 1H), 5 23-5 44 (m, 3H), 5 44-5 62 (m, 1H), 5 86-6 05 (m, 1H), 6 07-6 33 (m, 1H), MS m/z (rel intensity) 164 (M$^+$, 2), 123 (56), 81 (100), 79 (34), 67 (95), 55 (34) Found C, 87 69, H, 12 53% Calkcd for $C_{12}H_{20}$ C, 87 73, H, 12 27%

(E)-6-Undecenal dimethyl acetal (16) Bp 77°C (bath temp, 1 0 Torr), IR (neat) 2890, 1460, 1120, 1050, 960 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 200 MHz) δ0 83-0 98 (m, 3H), 1 20-1 48 (m, 8H), 1 53-1 67 (m, 2H), 1 90-2 08 (m, 4H), 3 31 (s, 6H), 4 36 (t, J = 5 7 Hz, 1H), 5 37-5 46 (m, 2H), MS m/z (rel intensity) 214 (M$^+$, 0 1), 183 (0 8), 150 (20), 114 (30), 75 (100), 71 (41) Found C, 72 96, H, 12 41% Calcd for $C_{13}H_{26}O_2$ C, 72 85, H, 12 23%

24 Bp 132°C (bath temp, 0 06 Torr), IR (neat) 2950, 1645, 1455, 1380, 1210, 885 cm^{-1}, ^{1}H-NMR (CCl_4, 90 MHz) δ0 88 (m, 3H), 1 07 (d, J = 7 2 Hz, 3H), 1 16-1 63 (m, 6H), 1 71 (s, 3H), 2 18-2 56 (m, 1H), 3 26-3 53 (m, 2H), 4 33-4 83 (m, 6H), 7 19 (m, 10H) Found C, 82 14, H, 9 47% Calcd for $C_{25}H_{34}O_2$ C, 81 92, H, 9 35%

4-Benzyloxy-2-methyl-1-butene (26) Bp 67°C (bath temp, 1 0 Torr), IR (neat) 2830, 1450, 1100, 890, 735, 695 cm^{-1}, ^{1}H-NMR (CCl_4, 90 MHz) δ1 71 (s, 3H), 2 24 (m, 2H), 3 46 (t, J = 7 2 Hz, 2H), 4 39 (m 2H), 4 55-4 73 (bs, 2H), 7 03-7 29 (bs, 5H), MS m/z (rel intensity) 177 (0 6), 176 (M$^+$, 4), 175 (4), 161 (6), 107 (24), 91 (100), 70 (62) Found C, 81 98, H, 9 30% Calcd for $C_{12}H_{16}O$ C, 81 77, H, 9 15%

Preparation of vinylsilanes containing hydroxyl group (Z)-6-Dimethylphenylsilyl-6-tridecen-5-ol (31) Butyllithium (hexane solution, 1 65 M, 6 1 ml, 10 0 mmol) was added dropwise to a mixture of (E)-1-iodo-1-dimethylphenylsilyl-1-octene (1 86 g, 5 0 mmol)^{20} and pentanal (1 6 ml, 15 0 mmol) in THF (40 ml) at -78°C The resulting mixture was stirred at -78°C for 45 min, then at 0°C for additional 30 min Workup (H_2O, AcOEt) and purification by silica-gel column chromatography (hexane AcOEt = 20 1) gave the title compound **31** (1 31 g, 85% yield) as an oil Bp 110°C (bath temp, 0 03 Torr), IR (neat) 3325, 2900, 2830, 1465, 1425, 1250, 1110, 815, 770, 725, 700 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 200 MHz) δ0 43 (s, 6H), 0 80-0 96 (m, 6H), 1 06-1 68 (bm, 15H), 1 92-2 07 (m, 2H), 4 15-4 27 (bm, 1H), 6 30 (dt, J = 1 1, 7 6 Hz, 1H), 7 32-7 63 (m, 5H), MS m/z (rel intensity) 314 (M^+-H_2O, 9), 197 (59), 137 (45), 135 (100), 75 (58)

(Z)-6-Dimethylphenylsilyl-6-tridecen-4-ol (**33**) Diisobutylaluminium hydride (hexane solution, 1 5 M, 5 5 ml, 8 3 mmol) was added to a solution of 1-dimethylphenylsilyl-1-octyne (1 69 g, 6 9 mmol) in hexane (10 ml)-ether (5 ml)[20] After stirring for 1 h at 0°C, butyllithium (hexane solution, 1 6 M, 5 2 ml, 8 3 mmol) was added and the whole was stirred for 5 min The resulting mixture was treated with 1-pentene oxide (0 86 g, 10 0 mmol) and heated at reflux for 3 h The mixture was poured into 1N HCl and extracted with ethyl acetate The combined organic layer was washed with brine, dried (Na_2SO_4), and concentrated in vacuo The residual oil was submitted to silica-gel column chromatography (hexane AcOEt = 20 1) to provide the allylic alcohol **33** (0 51 g, 22% yield) as a colourless oil Bp 112°C (bath temp, 0 03 Torr), IR (neat) 3360, 2890, 2820, 1420, 1245, 1105, 830, 810, 770, 725, 700 cm^{-1}, ^1H-NMR (CCl_4, 90 MHz) δ0 37 (s, 6H), 0 72-1 00 (m, 6H), 1 00-1 52 (bm, 13H), 1 79-2 48 (m, 4H), 3 20-3 51 (bm, 1H), 5 92-6 15 (m, 1H), 7 13-7 52 (m, 5H), MS m/z (rel intensity) 317 (M^+-CH_3,5), 245 (19), 182 (26), 137 (66), 135 (100), 75 (91) Found C, 75 99, H, 11 00% Calcd for $C_{21}H_{36}OSi$ 75 84, H, 10 91%

(Z)-1-Dimethylphenylsilyl-2-hexyl-1-hepten-3-ol (**37**) Bp 115°C (bath temp, 0 03 Torr), IR (neat) 3400, 2900, 2830, 1420, 1250, 1110, 835, 700 cm^{-1}, ^1H-NMR ($CDCl_3$, 200 MHz) δ0 38 (s, 6H), 0 80-0 98 (m, 6H), 1 13-1 64 (bm, 15H), 1 96-2 30 (m, 2H), 4 18-4 28 (bm, 1H), 5 45 (m, 1H), 7 34-7 64 (100), MS m/z (rel intensity) 319 (1), 318 (4), 317 (M^+-CH_3, 22), 237 (14), 137 (56), 135 (55), 75 (100)

(Z)-1-Methyldiphenylsilyl-2-hexyl-1-hepten-3-ol (**39**) Bp 140°C (bath temp, 0 03 Torr), IR (neat) 3400, 2890, 2825, 1600, 1420, 1105, 785, 695 cm^{-1}, ^1H-NMR ($CDCl_3$, 200 MHz) δ0 67 (s, 3H), 0 75-0 85 (m, 3H), 0 85-1 00 (m, 3H), 1 05-1 65 (bm, 15H), 2 01-2 36 (m, 2H), 4 13-4 25 (m, 1H), 5 72 (m, 1H), 7 32-7 66 (m, 10H), MS m/z (rel intensity) 379 (M^+-CH_3, 5), 317 (33), 197 (33), 137 (100) Found C, 79 30, H, 9 83% Calcd for $C_{26}H_{38}OSi$ C, 79 12, H, 9 71%

(Z)-1-Dimethylphenylsilyl-2-hexyl-1-hepten-4-ol (**41**) The compound was prepared according to silylcupration method reported by Fleming[18] Dimethylphenylsilyllithium (THF solution, 0 63 M, 15 9 ml, 10 0 mmol) was added to a suspension of CuCN (0 45 g, 5 0 mmol) in THF (5 0 ml) at 0°C A THF solution of 1-octyne (0 55 g, 5 0 mmol) was added and the whole was stirred for 30 min at 0°C In another flask, 1-pentene oxide (0 86 g, 10 0 mmol) and BF_3 OEt_2[21] (1 3 ml, 10 0 mmol) were combined at -78°C To this flask, a reaction mixture of the silylcupration was added via syringe at -78°C The resulting mixture was stirred for 10 min at -78°C and warmed up to room temperature Workup (NH_4Cl, AcOEt) and purification by silica-gel column chromatography gave homoallylic alcohol **41** (0 78 g, 47% yield) Bp 115°C (bath temp, 0 03 Torr), IR (neat) 3380, 2900, 2830, 1600, 1420, 1250, 1110, 835, 695 cm^{-1}, ^1H-NMR (CCl_4, 90 MHz) δ0 36 (s, 6H), 0 74-1 04 (m, 6H), 1 10-1 62 (bm, 13H), 1 89-2 31 (m, 4H), 3 33-3 68 (bm, 1H), 5 43 (bs, 1H), 7 12-7 54 (m, 5H), MS m/z (rel intensity) 332 (M^+, 0 09), 317 (2), 299 (2 5), 207 (17), 135 (100), 75 (40) Found C, 75 87, H, 11 17% Calcd for $C_{21}H_{36}OSi$ C, 75 84, H, 10 91%

General Procedure for the Desilylation of Vinylsilane Having Hydroxyl Group Tetrabutylammonium fluoride (THF solution, 1 3 M, 2 3 ml, 3 0 mmol) was added to a solution of vinylsilane **29** (0 27 g, 1 0 mmol) in CH_3CN (4 6 ml) and the whole was heated at reflux for 4 h The resulting mixture was poured into water and extracted with AcOEt Purification by preparative TLC on silica-gel gave (E)-6-tridecen-5-ol (**30**) (142 mg, 71% yield) as an oil Bp 75°C (bath temp, 1 0 Torr), IR (neat) 3280, 2880, 2820, 1460, 960 cm^{-1}, ^1H-NMR ($CDCl_3$, 200 MHz) δ0 80-1 01 (m, 6H), 1 07-1 72 (bm, 15H), 1 93-2 12 (m, 2H), 3 97-4 13 (m, 1H), 5 45 (ddt, *J* = 15 5, 6 5, 1 1 Hz, 1H), 5 64 (dt, *J* = 15 5, 6 5 Hz, 1H), MS m/z (rel intensity) 180 (M^+-H_2O, 7), 141 (55), 113 (47), 81 (67), 67 (44), 57 (100)

(E)-6-Tridecen-4-ol (**34**) Bp 74°C (bath temp, 1 0 Torr), IR (neat) 3300, 2890, 2830, 1460, 965 cm^{-1}, ^1H-NMR (CCl_4, 90 MHz) δ0 72-1 07 (m, 6H), 1 12-1 50 (bm, 12H), 1 54-1 72 (bs, 1H), 1 81-2 30 (m, 4H), 3 30-3 61 (bm, 1H), 5 10-5 62 (m, 2H), MS m/z (rel intensity) 126 (M^+-C_3H_7CHO, 40), 97 (29), 84 (31), 73 (42), 70

(42), 56 (39), 55 (100) Found C, 78 63, H, 13 42% Calcd for $C_{13}H_{26}O$ C, 78 72, H, 13 21%

1-((Z)-2'-Cyclononenyl)-1-pentanol (**36**) Bp 90°C (bath temp, 0 05 Torr), IR (neat) 3300, 2880, 2820, 1460, 735 cm^{-1}, ^{1}H-NMR (CCl_4, 90 MHz) δ0 74-1 03 (m, 3H), 1 07-1 87 (bm, 16H), 1 95-2 64 (m, 4H), 3 07-3 41 (bm, 1H), 4 98-5 68 (m, 2H), MS m/z (rel intensity) 124 (M^+-C_4H_9CHO, 43), 96 (100), 82 (61), 81 (49), 69 (60), 67 (41) Found C, 79 66, H, 12 70% Calcd for $C_{14}H_{26}O$ C, 79 94, H, 12 46%

General Procedure for the Preparation of Cyclic Silyl Ether Tetrabutylammonium fluoride (THF solution, 1 0 M, 3 0 ml, 3 0 mmol) was added to a solution of allylic alcohol **37** (0 33 g, 1 0 mmol) in THF (5 0 ml) at 25°C and the mixture was stirred for 30 min The resulting mixture was poured into water and extracted with ether (20 mlx2) The combined ethereal layer was washed with brine, dried (Na_2SO_4), and concentrated *in vacuo* The product was purified by preparative TLC on silica-gel (hexane AcOEt = 10 1) gave cyclized silyl ether **38** (0 21 g, 81% yield) Bp 66°C (bath temp, 1 0 Torr), IR (neat) 2900, 2830, 1580, 1465, 1250, 1080, 920, 860, 775 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 200 MHz) δ0 20 (s, 3H), 0 22 (s, 3H), 0 82-1 04 (m, 6H), 1 17-1 87 (bm, 14H), 1 93-2 24 (m, 2H), 4 55-4 66 (bs, 1H), 5 64 (m, 1H), MS m/z (rel intensity) 256 (1), 255 (5), 254 (M^+, 20), 239 (17), 197 (100), 183 (96), 169 (79), 127 (79), 75 (25) Found C, 70 95, H, 12 11% Calcd for $C_{15}H_{30}OSi$ C, 70 79, H, 11 88%

40 Bp 105°C (bath temp, 0 03 Torr), IR (neat) 2900, 2825, 1580, 1425, 1250, 1115, 830, 695 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 200 MHz) δ0 52 and 0 56 (s, total 3H), 0 81-1 04 (m, 6H), 1 18-1 95 (bm, 14H), 2 00-2 31 (m, 2H), 4 62-4 80 (bm, 1H), 5 73 (m, 1H), 7 32-7 68 (m, 5H), MS m/z (rel intensity) 318 (1), 317 (8), 316 (M^+, 35), 259 (100), 245 (89), 231 (73), 190 (35), 189 (68), 137 (38) Found C, 75 94, H, 10 33% Calcd for $C_{20}H_{32}OSi$ C, 75 88, H, 10 19%

42 Bp 72°C (bath temp, 1 0 Torr), IR (neat) 2890, 2830, 1590, 1460, 1245, 1030, 925, 845, 770 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 200 HMz) δ0 14 (s, 3H), 0 15 (s, 3H), 0 84-1 05 (m, 6H), 1 20-1 70 (bm, 12H), 1 93-2 23 (m, 4H), 3 81-3 96 (bm, 1H), 5 38 (m, 1H), MS m/z (rel intensity) 255 (1 5), 254 (M^+, 6), 253 (1), 239 (88), 211 (100), 169 (30), 75 (20) Found C, 70 95, H, 12 15% Calcd for $C_{15}H_{30}OSi$ C, 70 79, H, 11 88%

Desilylation of Cyclic Silyl Ether **38** Tetrabutylammonium fluoride (THF solution, 1 0 M, 3 4 ml, 3 4 mmol) was added to a solution of **38** (175 mg, 0 69 mmol) in DMSO (6 8 ml) and the mixture was heated at 80°C for 1 h Workup and purification by preparative TLC on silica-gel (hexane AcOEt = 10 1) provided desilylated alkene, 2-hexyl-1-hepten-3-ol (0 13 g, 92% yield) Bp 84°C (bath temp, 1 0 Torr), IR (neat) 3300, 2900, 2830, 1460, 1010, 895 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 200 HMz) δ0 81-1 03 (m, 6H), 1 18-1 71 (bm, 15H), 1 87-2 20 (m, 2H), 4 00-4 14 (bm, 1H), 4 84 (m, 1H), 5 00 (m, 1H), MS m/z (rel intensity) 198 (M^+, 1), 141 (13), 113 (43), 71 (100) Found C, 78 78, H, 13 46% Calcd for $C_{13}H_{26}O$ C, 78 72, H, 13 21%

2-Hexyl-1-hepten-4-ol Bp 76°C (bath temp, 1 0 Torr), IR (neat) 3320, 2890, 2830, 1635, 1460, 885 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 200 MHz) δ0 80-1 06 (m, 6H), 1 17-1 61 (bm, 12H), 1 76 (bs, 1H), 1 94-2 34 (m, 4H), 3 63-3 83 (bm, 1H), 4 83 (m, 1H), 4 89 (m, 1H), MS m/z (rel intensity) 180 (M^+-H_2O, 1), 126 (29), 73 (47), 69 (50), 57 (74), 56 (100), 55 (88) Found C, 78 99, H, 13 46% Calcd for $C_{13}H_{26}O$ C, 78 72, H, 13 21%

(Z)-5-Acetoxy-6-dimethylphenylsilyl-6-tridecene (**44**) IR (neat) 2960, 2930, 2860, 1740, 1370, 1250, 1110, 1020, 820, 775, 730, 700 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 200 MHz) δ0 42 (s, 3H), 0 43 (s, 3H), 0 78-0 95 (m, 6H), 1 01-1 72 (bm, 14H), 1 83-2 00 (m, 2H), 2 02 (s, 3H), 5 22 (t, *J* = 6 5 Hz, 1H), 6 25 (dt, *J* = 0 8, 7 5 Hz, 1H), 7 32-7 63 (m, 5H), MS m/z (rel intensity) 374 (M^+, 0 1), 297 (2), 179 (40), 135 (27), 117 (100)

(Z)-3-Acetoxy-1-dimethylphenylsilyl-2-hexyl-1-heptene (**45**) IR (neat) 2960, 2930, 2860, 1740, 1235, 1115, 1020, 840, 700 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 0 38 (s, 3H), 0 48 (s, 3H), 0 74-0 98 (m, 6H), 1 02-1 76 (bm, 14H), 1 94 (s, 3H), 2 01-2 14 (m, 2H), 5 38 (dd, *J* = 9 1, 4 6 Hz, 1H), 5 53 (t, *J* = 1 2 Hz, 1H), 7 32-7 65 (m, 5H), MS m/z (rel intensity) 376 (1), 375 (4), 374 (M^+, 16), 345 (20), 331 (45) 179 (35), 135 (100), 117 (96), 75 (24)

Desilylation of Allylic Acetates **44** or **45** Tetrabutylammonium fluoride (THF solution, 1 0 M, 2 7 ml, 2 7 mmol) and allylic acetate **44** (0 20 g, 0 53 mmol) were combined in DMSO (5 4 ml) The mixture was stirred for 12 h at 25°C Workup (AcOEt, water) and purification by silica-gel column chromatography gave a mixture of desilylated allylic acetate **46** (0 10 g, 78% yield) and allylic alcohol **32** (10 mg, 10% yield) Desilylation of **45** (0 35 g, 0 93 mmol) was performed in a similar fashion to give a mixture of allylic acetate **47** (0 13 g, 57% yield), cyclic silyl ether (24 mg, 10% yield), and allylic alcohol **48** (39 mg, 21% yield)

Oxidation of Cyclic Silyl Ether **38** Crude product derived from allylic alcohol **37** (0 33 g, 1 0 mmol) and tetrabutylammonium fluoride (3 0 mmol) was dissolved in DMF (3 0 ml) Potassium fluoride (0 29 g, 5 0 mmol) and 30% H_2O_2 (0 6 ml) were added to the solution and the resulting mixture was heated at 60°C for 1 h Workup ($NaHSO_3$, ether) and purification by silica-gel column chromatography (hexane AcOEt = 10 1) gave 2-hexyl-2-heptenal **52** (46 mg, 33% overall yield from **37**) IR (neat) 2900, 2830, 1720, 1680, 1465 cm^{-1}, ^1H-NMR (CCl_4, 90 MHz) 0 73-1 13 (m, 6H), 1 13-1 73 (bm, 12H), 2 04-2 49 (m, 4H), 6 32 (t, *J* = 7 5 Hz, 1H), 9 32 (s, 1H), MS m/z (rel intensity) 197 (12), 196 (M^+, 69), 167 (41), 139 (70), 111 (52), 97 (51), 95 (65), 83 (65), 81 (57), 71 (58), 69 (58), 55 (100), 43 (75)

(Z)-1-Allyldimethylsilyl-1-dodecene (**53**) A solution of 1-lithio-1-dodecyne derived from butyllithium (hexane solution, 1 72 M, 14 5 ml, 25 mmol), 1-dodecyne (4 16 g, 25 mmol), and THF (30 ml), was added to a solution of allylmethyldichlorosilane (3 6 ml, 25 mmol) in THF (120 ml) at 0°C The resulting mixture was stirred for 2 h at 25°C, then cooled to 0°C Methylmagnesium iodide (ether solution, 35 mmol) was added and the whole was stirred at 25°C overnight Workup and purification provided 1-allyldimethylsilyl-1-dodecyne (2 93 g, 44% yield) The silane (2 93 g, 11 1 mmol) was dissolved in a mixture of hexane (15 ml) and ether (5 ml), and treated with diisobutylaluminium hydride (hexane solution, 1 5 M, 11 3 ml, 17 0 mmol) After stirring for 1 h, the resulting mixture was diluted with CH_2Cl_2 and treated with NaF (7 g) and water (3 4 ml) Stirring was continued until white precipitate came out The organic layer was collected by decantation, dried (Na_2SO_4), and concentrated Purification by silica-gel column chromatography (hexane) gave the title allylsilane **53** (2 68 g, 91% yield) Bp 95°C (bath temp, 1 0 Torr), IR (neat) 2920, 2850, 1605, 1250, 990, 930, 890, 835 cm^{-1}, ^1H-NMR ($CDCl_3$, 200 MHz) δ 0 12 (s, 6H), 0 83-0 94 (m, 3H), 1 20-1 46 (bm, 16H), 1 60 (dt, *J* = 8 0, 1 1 Hz, 2H), 2 06-2 19 (m, 2H), 4 80-4 92 (m, 2H), 5 44 (dt, *J* = 14 0, 1 3 Hz, 1H), 5 80 (*J* = 16 8, 10 2, 8 0 Hz, 1H), 6 35 (dt, *J* = 14 0, 7 4 Hz, 1H), MS m/z (rel intensity) 266 (M^+, 0 5), 225 (81), 99 (50), 59 (100) Found C, 76 56, H, 12 86% Calcd for $C_{17}H_{34}Si$ C, 76 61, H, 12 81%

1,1,2,2-Tetramethyl-1-((Z)-1'-dodecenyl)-2-phenyldisilane (**54**) The compound was prepared according to the same procedure for **53** Dimethylphenylsilyllithium was used instead of methylmagnesium iodide **54** Bp 140°C (bath temp, 1 0 Torr), IR (neat) 2925 2860, 1605, 1245, 1110, 830, 795, 730, 700 cm^{-1}, ^1H-NMR ($CDCl_3$,200 MHz) δ 0 16 (s, 6H), 0 35 (s, 6H), 0 81-0 96 (m, 3H), 1 13-1 39 (bm, 16H), 1 87-2 04 (m, 2H), 5 44 (dt, *J* = 13 7, 1 2 Hz, 1H), 6 31 (dt, *J* = 13 7, 7 2 Hz, 1H), 7 29-7 53 (m, 5H), MS m/z (rel intensity) 362 (1), 361 (3), 360 (M^+, 9), 287 (66), 225 (43), 135 (100), 121 (23), 59 (27) Found C, 73 19, H, 11 38% Calcd for $C_{22}H_{40}Si_2$ C, 73 25, H, 11 18%

Desilylation of Allylvinylsilane **53** Tetrabutylammonium fluoride (THF solution, 1 0 M, 3 0 ml, 3 0 mmol) was added to a solution of allylvinylsilane **53** (0 40 g, 1 5 mmol) in THF (5 0 ml) at 25°C After stirring for 5 min, the mixture was poured into water and extracted with ether Ethereal layer was dried (Na_2SO_4) and concentrated The residual oil was submitted to preparative TLC on silica-gel to provide a mixture of dimethyl silanol **56** (0 25 g, 68% yield) and disiloxane **57** (57 mg, 16% yield) Treatment of **53** (0 20 g, 0 75 mmol) with tetrabutylammonium fluoride (THF solution, 1 0 M, 3 0 ml, 3 0 mmol) in DMSO (6 0 ml) at 80°C for 1 h gave 1-dodecene (0 17 g) quantitatively **56** Bp 98°C (bath temp, 1 0 Torr), IR (neat) 3275, 2920, 2850, 1605, 1250, 865, 780 cm^{-1}, ^1H-NMR ($CDCl_3$, 200 MHz) δ0 25 (s, 6H), 0 81-0 94 (m, 3H), 1 15-1 48 (bm, 16H), 1 69-1 79 (bs, 1H), 2 11-2 26 (m, 2H), 5 47 (dt, *J* = 14 2, 1 2 Hz, 1H), 6 37 (dt, *J* = 14 2, 7 4 Hz, 1H), MS m/z (rel intensity) 242 (M^+, 0 5), 241 (0 4), 227 (24), 75 (100) Found C, 69 52, H, 12 70% Calcd for $C_{14}H_{30}OSi$ C, 69 35, H, 12 47% **57** Bp 146°C (bath temp, 1 0 Torr) IR (neat) 2925, 2860, 1610, 1470, 1255, 1055, 840, 790 cm^{-1}, ^1H-NMR ($CDCl_3$, 200 MHz) δ0 17 (s, 12H), 0 81-0 93 (m, 6H), 1 17-1 44 (bm, 32H), 2 07-2 21 (m, 4H), 5 44 (dt, *J* = 14 2, 1 2 Hz, 2H), 6 29 (dt, *J* = 14 2, 7 4 Hz, 2H) Found C, 72 03, H, 12 76% Calcd for $C_{28}H_{58}OSi_2$ C, 72 02, H, 12 52%

Desilylation of 56 and 57 Tetrabutylammonium fluoride (1 0 M, 0 13 ml, 0 13 mmol) was added to a solution of **56** (0 16 g, 0 66 mmol) or **57** (0 16 g, 0 33 mmol) in THF (2 0 ml)-DMSO (4 0 ml) and the resulting mixture was stirred at 80°C for 2 h Workup and purification afforded 1-dodecene in 94% or 84% yield, respectively

(E)-1-Dimethylmethoxysilyl-1-dodecene (59) Dimethylchlorosilane (0 67 ml, 6 0 mmol), 1-dodecyne (0 83 g, 5 0 mmol), and H_2PtCl_6 $6H_2O$ (isopropyl alcohol solution, 0 05 M, one drop) were combined and the mixture was heated at 70°C for 2 h The resulting mixture was cooled, and treated with methanol (2 0 ml) and pyridine (0 57 ml, 7 0 mmol) Workup (ether, water) and purification by silica-gel column chromatography (hexane AcOEt = 20 1) gave **59** (1 12 g, 87% yield) Bp 92°C (bath temp, 1 0 Torr), IR (neat) 2925, 2850, 1250, 1090, 840 cm^{-1}, ^1H-NMR ($CDCl_3$, 200 MHz) δ 0 16 (s, 6H), 0 83-0 96 (m, 3H), 1 12-1 50 (bm, 16H), 2 07-2 21 (m, 2H), 3 42 (s, 3H), 5 61 (dt, *J* = 18 7, 1 5 Hz, 1H), 6 19 (dt, *J* = 18 7, 6 2 Hz, 1H), MS m/z (rel intensity) 257 (0 2), 256 (M^+, 0 7), 241 (68), 89 (100), 75 (42) Found C, 70 15, H, 12 76% Calcd for $C_{15}H_{32}OSi$ C, 70 24, H, 12 58%

Desilylation of 59 Treatment of **59** with tetrabutylammonium fluoride in THF-DMSO (1 2) at 80°C for 0 5 h according to the general procedure for the cleavage of vinyl carbon-dimethylphenylsilyl bond to give 1-dodecene in 98% yield

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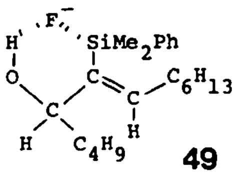
ammonium fluoride at room temperature to give excellent yields of the corresponding hydrocarbons This is ascribed to the acceleration given in 51



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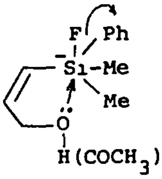

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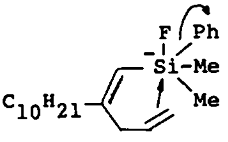

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