1760 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (6), 1760—1764 (1979) [Vol. 52, No. 6

A Highly Stereoselective Synthesis of Trisubstituted Ethylenes from α-Trialkylsilyl Ketones[1,2]

Michio Obayashi, Kiitiro Utimoto,* and Hitosi Nozaki
Department of Industrial Chemistry, Kyoto University, Yoshida, Kyoto 606

(Received February 19, 1979)

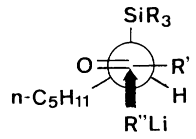
A novel procedure for preparing trisubstituted ethylenes stereoselectively is based on the reaction of α-trialkylsilyl-substituted ketones with alkyllithium reagents and on the following highly discriminative elimination of the silyl and oxido (or hydroxyl) groups from the resulting adducts. The *syn*-elimination of both groups is observed under basic conditions, while the reaction proceeds in *anti*-fashion on acid treatment. Furthermore α-trimethylsilylated ketones are shown to be readily obtained from 2-trimethylsilyl-2,3-dialkyloxiranes. The reaction sequence is applied to the stereoselective synthesis of tetrahomonerol which has been obtained from the codling moth.

Synthesis of trisubstituted ethylenes[3,4] has received considerable attention because of the widespread occurrence of these olefin units in many classes of naturally occurring compounds. Furthermore, recent progress in organic synthesis *via* silicon compounds[5] has disclosed novel methods for the synthesis of 1,2-disubstituted ethylenes with rigorous stereochemistry.[6] This paper describes a facile procedure for the stereoselective synthesis of trisubstituted ethylenes *via* reaction of α-trialkylsilyl ketones with alkyllithium reagents followed by *syn*-elimination under basic conditions or by *anti*-elimination on acid treatment.[7,8]

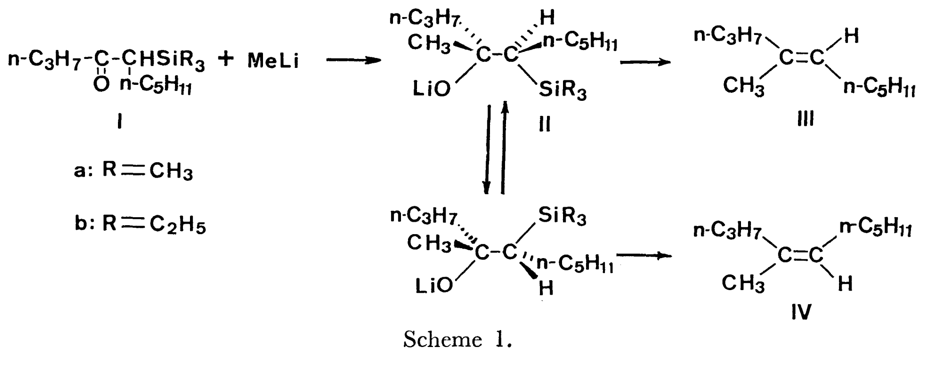
Reaction of 5-trimethylsilyl-4-decanone (Ia)[1] with MeLi in THF at −78 °C afforded a reaction mixture containing IIa.[9] Treatment of the reaction mixture directly with $\mathrm{KO}^t\mathrm{Bu}$ (Run 1 in Table 1) afforded (*E*)-4-methyl-4-decene (III)[10] in 76% overall yield as shown in Scheme 1. When the reaction mixture was treated with glacial acetic acid saturated with sodium acetate (Run 5), the (*Z*)-isomer IV was obtained with *E*/*Z* ratio of 12/88.[11] On the contrary the elimination with concentrated sulfuric acid (Run 7) gave less the stereoselectivity. Similar results were obtained in the case of 5-triethylsilyl-4-decanone (Ib). These and other data are summarized in Table 1.[12,13]

Further information about the stereoselectivity of this olefin synthesis was obtained from the reaction of 3-trimethylsilyl-2-octanone with *n*-PrLi. Treatment of the reaction mixture with $\mathrm{KO}^t\mathrm{Bu}$ gave IV in 21% yield ($E/Z=4/96$) *via* the diastereomer of II.[15]

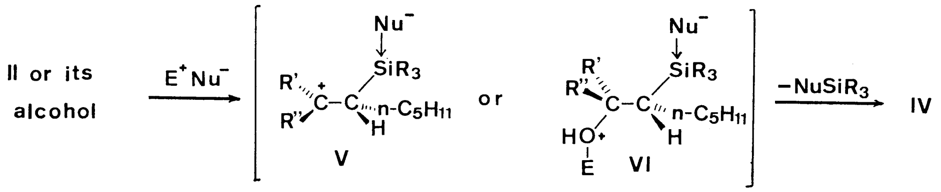
Clearly β-trialkylsilyl alcoholates II are produced from α-trialkylsilyl ketones and alkyllithium reagents with high stereoselectivity. Although it was unsuccessful to directly determine the diastereomeric composition of the alcoholate II or the respective alcohol, the composition was inferred from the *E*/*Z* ratios of the olefins obtained in the elimination reactions. The high selectivity of this carbonyl addition is explained formally by the Felkin model,[16] in which the separation between the trialkylsilyl group and the incoming alkyllithium is the greatest.



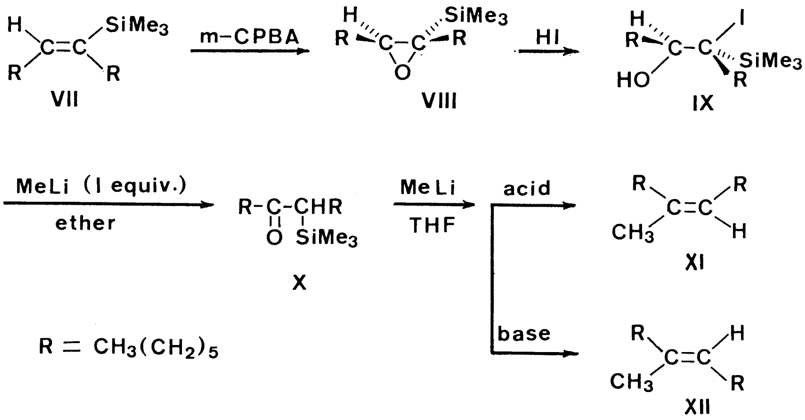
The lithium salt or the potassium salt of the alcohol produces a trisubstituted ethylene by *syn*-elimination of trialkylsilyl and oxido groups. Comparison of Runs 1 and 2, or Runs 3 and 4 as well, indicates that the *syn*-elimination from the lithium salt is slower than that from the potassium salt. On the other hand, acidic treatment of the alcoholates II directly or of the isolated alcohols induces *anti*-elimination of trialkylsilyl and hydroxyl groups as shown in Scheme 2.[6a–c] Poor stereoselectivity is observed when such nucleophiles having weak affinity to silicon as $\mathrm{HSO_4^-}$ or H_2O are present (Runs 7 and 8). Meanwhile, nucleophiles with strong affinity to silicon such as $\mathrm{AcO^-}$ and $\mathrm{F^-}$ give much improved selectivity data (Runs 5, 9—12). Probably in the absence of suitable nucleophiles, C–C bond rotation of the β-silyl carbocation V competes with the *anti*-elimination. The effective nucleophiles obviously favor the concerted *anti*-elimination of the intermediate VI without the loss of stereochemistry. Runs 11 and 12, indicate that the acid strength is an additional factor influencing the *E*/*Z* ratio.



Scheme 1.



Scheme 2.



Scheme 3.

Furthermore as shown in Scheme 3, both isomers (XI and XII) of a trisubstituted ethylene have been obtained from the silylated olefin (VII) *via* the trialkylsilyloxirane (VIII) and the iodohydrin (IX). Treatment of IX with 1 equivalent of MeLi in ether afforded α-trimethylsilyl ketone (X). The resulting mixture was further treated with MeLi (3 equiv.) at −78 °C affording (*Z*)-7-methyl-7-tetradecene (XI) after acidic work-up (Scheme 3 and Table 2). Reaction of IX with 4 equivalents of MeLi in ether at −78 °C gave the same result. The stereoselectivity of the olefin formation is rather low as compared with the previous reaction (for example, Run 5 in Table 1). Remarkably, the *E*/*Z* selectivity of olefin formation is much improved by the coexistence of THF in the MeLi-treatment of X.

Table 1. Transformation of 5-trialkylsilyl-4-decanone (Ia and Ib) to 4-methyl-4-decene (III and IV)

Run No.	I	Addition[a] condition	Elimination condition (temp)	Olefin %[b]	III/IV[c] (*E*/*Z*)
1	a	A	KO^{t}Bu (refl.)	76	91/9
2	a	B	— (refl.)	53	86/14
3	b	B	KO^{t}Bu (refl.)	76	91/9
4	b	B	— (refl.)	30	—[e]
5	a	A	AcONa/AcOH (−20 °C)	69	12/88
6	a	0 °C-r.t./ 0.5 h	AcONa/AcOH (−20 °C)	—[e]	20/80
7	a	A	H_2SO_4 (r.t.)[d]	69	24/76
8	a	B	H_2SO_4 (r.t.)[d]	80	50/50
9	b	B	AcONa/AcOH (−20 °C)	57	10/90
10	b	B	AcONa/AcOH (−20 °C)[d]	46	10/90
11	b	B	KF/AcOH (r.t.)[d]	72	12/88
12	b	B	KF/H_2SO_4 (r.t.)[d]	84	18/82

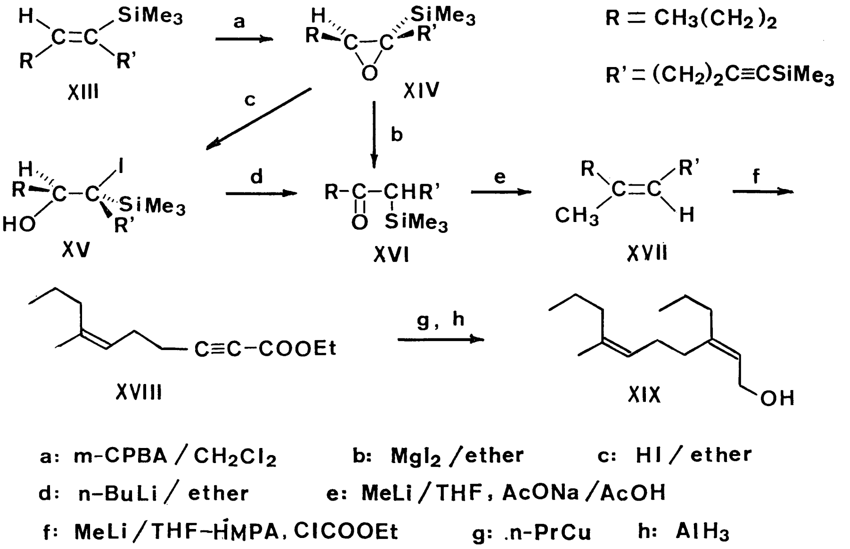
a) A: Addition of MeLi was carried out at −78 °C and then the mixture was allowed to stand at a room-temperature for 1—1.5 h. B: The addition occurred at −78 °C and then the reaction completed at a room-temperature overnight. b) Yield determined by GLPC using dodecane as an internal standard. c) Determined by GLPC. d) Carried out after hydrolytic work-up of II. e) Not determined.

An application of these stereoselective olefin formations has provided (2*Z*,6*Z*)-7-methyl-3-propyl-2,6-decadien-1-ol (XIX), which is known to be a tetrahomonerol obtained from the codling moth (Scheme 4).[17] Silyloxirane (XIV) prepared from XIII[6k] was converted to XVII by the following two ways. Isomerization of silyloxirane XIV[1b] in the presence of MgI_2 gave α-trimethylsilyl ketone (XVI). Further treatment

Table 2. Conversion of iodohydrin (IX) to trisubstituted ethylenes (XI and XII)

MeLi[a] Equiv.	MeLi[a] Temp	MeLi[b] Equiv.	Elimination condition	Olefin %[d]	XI/XII[c] (*Z*/*E*)
1	−20 °C	3[e]	AcONa/AcOH	84	86/14
4	−78 °C	—	AcONa/AcOH	85	84/16
1	−20 °C	3	AcONa/AcOH	74	91/9
4	−78 °C	—	KO^{t}Bu	78	15/85
1	−20 °C	3	KO^{t}Bu	79	9/91

a) The amount of MeLi (ether) admixed initially. b) The amount of MeLi (ether) added (at −78 °C) to the isomerization mixture, which was diluted with THF in advance. c) Without dilution with THF, the reaction was carried out in ether. d) Overall yield from VIII. e) Determined by GLPC.



Scheme 4.

of XVI with MeLi, AcONa/AcOH afforded XVII. Secondly, iodohydrin (XV) obtained from XIV was treated with *n*-BuLi (1 equiv.) followed by MeLi giving XVII after acidic work-up. Direct ethoxycarbonylation of XVII to acetylenic ester XVIII was effected by treatment with MeLi/THF–HMPA[18] and then with ClCOOEt. The acetylenic ester was finally transformed into XIX by the reported procedure.[17]

Experimental

GLPC was performed on Shimadzu GC-4BPT with 3 m × 3 mm glass column packed with 20 % polyethylene glycol and 20 % HVSG on Chromosorb W-AW (80—100 mesh). Mass spectra were obtained on Hitachi RMU-6L with 70 V chamber voltage. NMR were measured on Varian EM-360, JEOL JNM-PMX 60, and Varian EM-390 with Me_4Si as internal standard and CCl_4 as solvent. IR on Shimadzu IR-27G spectrometer. Elemental microanalyses were performed by Elemental Analyses Center of Kyoto University. All the reactions were carried out under an atmosphere of dry argon.

*Reaction of α-Trialkylsilyl Ketones (I) with Alkyllithium Reagents. (*E*)-4-Methyl-4-decene (III, Run 1)*: To a solution of 5-trimethylsilyl-4-decanone (Ia, 0.23 g, 1 mmol) in 5 ml of THF was added MeLi (3 mmol, 3.5 ml of 0.87 M ethereal solution) at −78 °C. The mixture was stirred at a room-temperature for 1 h and treated with KO^{t}Bu (1.0 g, 9 mmol) at reflux for 1 h. The resulting mixture was poured into aq NH_4Cl overlaid with hexane, washed (aq NH_4Cl, sat. NaCl), and dried (Na_2SO_4). GLPC analysis indicated that III was formed in 76 % overall yield (*E*/*Z*=91/9). Bp 93—96 °C/21 mmHg; IR (neat) 1380 cm^{-1}; MS *m*/*e* (rel. %), 154 (M$^+$, 11), 111 (13), 97 (22), 84 (16), 69 (52), 55 (100); NMR (CCl_4) δ=0.60—1.03 (6H, m), 1.03—1.70 (8H, m), 1.55 (3H, br-s), 1.70—2.20 (4H, m), 5.03 (1H, t, *J*=7 Hz).

Found: C, 85.50; H, 14.45 %. Calcd for $C_{11}H_{22}$: C, 85.63; H, 14.37 %.

(Z)-4-Methyl-4-decene (IV, Run 5): The reaction mixture from Ia (1 mmol) and MeLi (3 mmol) was treated with 10 ml of glacial acetic acid saturated with sodium acetate under stirring at −20 °C for 30 min and at a room-temperature overnight. The resulting mixture was poured into sat. NaCl overlaid with hexane, washed (sat. $NaHCO_3$, sat. NaCl), and dried (Na_2SO_4). GLPC analysis indicated that IV was formed in 69 % overall yield (*E*/*Z*=12/88). Bp 90—95 °C/21 mmHg; IR (neat) 1380 cm^{-1}; MS *m*/*e* (rel. %), 154 (M$^+$, 15), 111 (15), 97 (23), 84 (19), 69 (57), 55 (100); NMR (CCl_4) δ=0.60—1.03 (6H, m), 1.03—1.70 (8H, m), 1.63 (3H, br-s), 1.70—2.15 (4H, m), 5.01 (1H, t, *J*=7 Hz).

Found: C, 85.77; H, 14.40 %. Calcd for $C_{11}H_{22}$: C, 85.63; H, 14.37 %.

4-Phenyl-4-decene: To a solution of Ia (0.23 g, 1 mmol) in 5 ml of THF was added PhLi (3 mmol, 3.5 ml of 0.87 M ethereal solution) at −78 °C. The mixture was stirred at a room-temperature for 1 h and poured into aq NH_4Cl overlaid with ether. The ether layer was washed (aq NH_4Cl, sat. NaCl) and dried (Na_2SO_4). The concentrate was dissolved in 5 ml of THF and treated with a few drops of concentrated H_2SO_4 at a room-temperature for 1 h. The reaction mixture was poured into sat. $NaHCO_3$ overlaid with hexane, washed (sat. $NaHCO_3$, sat. NaCl), and dried (Na_2SO_4). Chromatography of the concentrate on silica-gel column (hexane) afforded 0.11 g (52 %) of 4-phenyl-4-decene (*E*/*Z*=39/61). The mixture formed an oil; IR (neat) 1601, 1492, 1380, 705 cm^{-1}; NMR (CCl_4) δ=0.65—1.10 (6H, m), 1.10—1.67 (8H, m), 1.67—2.60 (4H, m), 6.90—7.70 (5H, m) and two olefinic signals at 5.35 (br-t, *J*=7 Hz, C=CH of (4*Z*)-isomer) and 5.58 (br-t, *J*=7 Hz, C=CH of (4*E*)-isomer). The sum of these olefinic signals was equal to 1H. GLPC gave each isomer in pure form.

(4E)-Isomer: MS *m*/*e* (rel. %), 216 (M$^+$, 19), 173 (31), 159 (16), 131 (20), 118 (33), 117 (100), 105 (14), 91 (49), 77 (7), 55 (5), 41 (12), 40 (48), 29 (32).

Found: C, 88.80; H, 11.44 %. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18 %.

(4Z)-Isomer: The mass spectrum was very similar to that of (4*E*)-isomer.

Found: C, 88.55; H, 11.24 %. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18 %.

Reaction of (7S,8S*)-8-Iodo-8-trimethylsilyl-7-tetradecanol (IX) with MeLi.* Iodohydrin (IX) was prepared according to the reported procedure from (2*S**,3*S**)-2-trimethylsilyl-2,3-dihexyloxirane (VIII).[1c]

(Z)-7-Methyl-7-tetradecene (XI): To a solution of IX (0.41

g, 0.98 mmol) in 5 ml of ether was added MeLi (0.98 mmol, 0.61 ml of 1.63 M ethereal solution) at −20 °C. The mixture was stirred at a room-temperature for 1 h and treated with 5 ml of THF and MeLi (3 mmol, 1.84 ml of 1.63 M ethereal solution) at −78 °C. The resulting mixture was stirred at a room-temperature for 1 h and treated with 5 ml of glacial acetic acid saturated with sodium acetate under stirring at −20 °C for 0.5 h and at a room-temperature overnight. The mixture was poured into sat. NaCl overlaid with hexane, washed (sat. $NaHCO_3$, sat. NaCl), and dried ($MgSO_4$). Chromatography of the concentrate on silica-gel column (hexane) afforded 0.16 g of XI (yield, 74 % based on 1 mmol of VIII, $E/Z=9/91$). Bp 115—120 °C/4 mmHg; IR (neat) 1368 cm^{-1}; MS m/e (rel. %) 210 (M$^+$, 12), 181 (0.6), 140 (10), 125 (16), 112 (14), 111 (17), 97 (26), 84 (25), 83 (65), 71 (17), 70 (100), 43 (33), 41 (50), 29 (23); NMR (CCl_4) δ=0.88 (6H, t, J=6 Hz), 1.05—1.50 (16H, m), 1.62 (3H, s), 1.70—2.10 (4H, m).

Found: C, 85.22; H, 14.33 %. Calcd for $C_{15}H_{30}$: C, 85.63; H, 14.37 %.

(E)-7-Methyl-7-tetradecene (XII): The reaction mixture from IX (0.39 g, 0.94 mmol) and MeLi (0.94 mmol, 0.58 ml of 1.63 M ethereal solution) was treated with 5 ml of THF and MeLi (3 mmol) at −78 °C. The resulting mixture was stirred at a room-temperature for 1 h and poured into sat. $NaHCO_3$ overlaid with ether. The ether layer was washed (sat. $NaHCO_3$, sat. NaCl) and dried ($MgSO_4$). The concentrate was dissolved in 5 ml of THF and treated with KO^{t}Bu (1.0 g, 8 mmol) at a room-temperature for 1 h. The resulting mixture was poured into aq. NH_4Cl overlaid with hexane, washed (aq NH_4Cl, sat. NaCl) and dried ($MgSO_4$). Chromatography of the concentrate on silica-gel column (hexane) afforded 0.17 g of XI (yield, 79 % based on 1 mmol of VIII, $E/Z=91/9$). Bp 115—120 °C/4 mmHg; IR (neat) 1368 cm^{-1}; NMR (CCl_4) δ=0.88 (6H, t, J=6 Hz), 1.05—1.50 (16H, m), 1.53 (3H, s), 1.75—2.10 (4H, m). The mass spectrum was very similar to that of (7Z)-isomer.

Found: C, 86.27; H, 14.47 %. Calcd for $C_{15}H_{30}$: C, 85.63; H, 14.37 %.

(2Z,6Z)-7-Methyl-3-propyl-2,6-decadien-1-ol (XIX). (2S,3S*)-2-Trimethylsilyl-2-(4-trimethylsilyl-3-butynyl)-3-propyloxirane (XIV)*: Treatment of (E)-1,5-bis(trimethylsilyl)-5-nonen-1-yne (XIII, 1.0 g, 3.9 mmol) with m-chloroperbenzoic acid (85 % purity, 1.0 g, 5 mmol) in CH_2Cl_2 at 0 °C overnight gave 1.1 g (quantitative yield) of XIV. IR (neat) 2200, 1245, 837, 758, 696, 640 cm^{-1}; MS m/e (rel. %), 282 (M$^+$, 0.2), 267 (0.2), 253 (2), 239 (3), 225 (8), 171 (9), 169 (5), 147 (15), 133 (5), 91 (5), 83 (4), 75 (13), 74 (9), 73 (100), 59 (8), 43 (5); NMR (CCl_4) δ=0.03 (9H, s), 0.10 (9H, s), 0.75—1.15 (3H, m), 1.15—2.50 (8H, m), 2.61 (1H, br-t, J=6 Hz).

Found: C, 63.82; H, 10.88 %. Calcd for $C_{15}H_{30}OSi$: C, 63.76; H, 10.70 %.

Conversion of XIV to (Z)-1-Trimethylsilyl-6-methyl-5-nonen-1-yne (XVII) Involving the Isomerization of XIV to 5,9-Bis(trimethylsilyl)-8-nonyn-4-one (XVI) in the Presence of MgI_2: To a solution of MgI_2 (10 mmol) in 10 ml of ether was added XIV (0.28 g, 1 mmol dissolved in 10 ml of ether). The resulting mixture was stirred at reflux for 2 h and then treated with 6 ml of 1,4-dioxane at 0 °C overnight. The solution was freed from solids by filtration. The solids were washed with hexane several times and the combined organic layer was washed (sat. $NaHCO_3$, sat. NaCl), dried ($MgSO_4$), and concentrated affording 0.28 g (98 %) of XVI. Oil; IR (neat) 2200, 1686, 1246, 840, 761, 700, 642 cm^{-1}; MS m/e (rel. %), 282 (M$^+$, 1), 267 (2) 253 (3), 239 (2), 225 (2), 209 (5), 172 (10), 171 (61), 147 (11), 143 (12), 130 (32), 115 (5), 75 (22), 74 (9), 73 (100), 59 (7), 45 (16), 43 (7). To a solution of XVI (0.28 g, 0.98 mmol) in 2 ml of THF was added MeLi (3 mmol, 2.9 ml of 1.04 M ethereal solution) at −78 °C. The mixture was stirred at 0 °C for 1 h and treated with 3 ml of glacial acetic acid saturated with sodium acetate under stirring at −20 °C for 30 min and at a room-temperature overnight. The resulting mixture was poured into sat. NaCl overlaid with hexane, washed (sat. $NaHCO_3$, sat. NaCl), and dried (Na_2SO_4). Chromatography of the concentrate on silica-gel column (hexane) afforded XVII (0.11 g, yield, 51 % based on XIV, $E/Z=5/95$). Bp 104—108 °C/17 mmHg; IR (neat) 2210, 1247, 844, 763, 701, 645 cm^{-1}; MS m/e (rel. %), 208 (M$^+$, 0.6), 193 (3), 179 (4), 165 (2), 149 (5), 144 (12), 119 (6), 105 (5), 97 (37), 96 (15), 83 (7), 81 (16), 75 (3), 74 (7), 73 (65), 69 (10), 59 (22), 55 (100), 43 (12); NMR (CCl_4) δ=0.10 (9H, s), 0.90 (3H, t, J=6 Hz), 1.10—1.65 (2H, m), 1.67 (3H, br-s), 1.80—2.40 (6H, m), 5.14 (1H, br-t, J=6 Hz).

Found: C, 75.05; H, 11.74 %. Calcd for $C_{13}H_{24}Si$: C, 74.92; H, 11.61 %.

Conversion of XIV to XVII via (4S,5S*)-5,9-Bis(trimethylsilyl)-5-iodo-8-nonyn-4-ol (XV)*: To a solution of XIV (0.37 g, 1.3 mmol) in 5 ml of ether was added 0.6 ml of 57 % HI at −20 °C. After 20 min the mixture was poured into sat. $NaHCO_3$ overlaid with ether. The ether layer was washed (10 % $Na_2S_2O_3$, sat. $NaHCO_3$, sat. NaCl), dried ($MgSO_4$), and concentrated, affording 0.50 g (29 %) of XV. To a solution of XV (0.50 g, 1.2 mmol) in 5 ml of ether was added n-BuLi (1.2 mmol, 1.5 ml of 0.82 M hexane solution) at −20 °C. The mixture was stirred at room temperature for 0.5 h and treated with 5 ml of THF and MeLi (3.7 mmol, 2.2 ml of 1.63 M ethereal solution) at −78 °C. Work-up gave XVII (0.16 g, yield, 57 % based on XIV, $E/Z=5/95$).

Transformation of XVII into (2Z,6Z)-7-Methyl-3-propyl-2,6-decadien-1-ol (XIX): To a solution of XVII (0.10 g, 0.48 mmol) in 2 ml of THF and 1 ml of HMPA was added MeLi (0.6 mmol, 0.58 ml of 1.04 M ethereal solution) at −78 °C. The mixture was stirred at −30 °C for 1 h and treated with ClCOOEt (0.06 ml, 0.6 mmol) at −78 °C. The resulting mixture was stirred at a room-temperature for 0.5 h and poured into sat. $NaHCO_3$ overlaid with ether. The ether layer was washed (sat. $NaHCO_3$, sat. NaCl) and dried ($MgSO_4$). Chromatography of the concentrate on silica-gel column (benzene) gave 70 mg (70 %) of ethyl (Z)-7-methyl-6-decen-2-ynoate (XVIII, $E/Z=4/96$). IR (neat) 2265, 1709, 1371, 1360, 1243, 1070, 757 cm^{-1}; MS m/e (rel. %), 208 (M$^+$, 0.5), 193 (1), 180 (16), 151 (7), 149 (5), 135 (8), 134 (7), 121 (7), 112 (15), 111 (7), 97 (26), 84 (16), 69 (11), 56 (8), 55 (100), 43 (8), 41 (13); NMR (CCl_4) δ=0.88 (3H, t, J=6 Hz), 1.25 (3H, t, J=7 Hz), 1.10—1.53 (2H, m), 1.65 (3H, br-s), 1.75—2.15 (2H, m), 2.15—2.40 (4H, m), 4.04 (2H, q, J=7 Hz), 4.80—5.25 (1H, m). The product XVIII was transformed into the tetrahomonerol XIX according to the reported procedure.[16] IR (neat) 3300, 1659, 1366, 1239, 1002, 833, 750 cm^{-1}; MS (as trimethylsilyl ether) m/e (rel. %), 282 (M$^+$, 10), 267 (3), 239 (12), 197 (13), 192 (10), 171 (11), 169 (15), 161 (25), 156 (15), 155 (11), 149 (48), 143 (10), 129 (12), 121 (24), 119 (25), 97 (38), 93 (18), 91 (20), 81 (20), 79 (22), 75 (59), 73 (81), 55 (100), 43 (23), 41 (22); NMR (CCl_4) δ=0.90 (6H, t, J=6 Hz), 1.10—1.77 (4H, m), 1.67 (3H, br-s), 1.77—2.40 (9H, m), 4.02 (2H, br-d, J=7 Hz), 5.10 (1H, m), 5.33 (1H, t, J=7 Hz).

The authors wish to thank the Ministry of Education, Science and Culture, Japan, for the Grant-in-Aid (911506, 011010, 110309, 203014, 303023).

References

1) Preliminary reports dealing with certain aspects of this

work have appeared: (a) K. Utimoto, M. Obayashi, and H Nozaki, *J. Org. Chem.*, **41**, 2940 (1976); (b) M. Obayashi, K. Utimoto, and H. Nozaki, *Tetrahedron Lett.*, **1977**, 1807; (c) M. Obayashi, K. Utimoto. and H. Nozaki, *ibid.*, **1978**, 1383.

2) α-Trialkylsilyl ketone means α-trialkylsilyl-substituted ketone in this paper.

3) For reviews of olefin synthesis see (a) I. Reucroft and P. G. Sammes, *Q. Rev. Chem. Soc.*, **25**, 135 (1971); (b) A. S, Arora and I. K. Ugi, "Methoden der Organischen Chemie (Houben-Weyl)," 4th ed, ed by E. Müller, G. Thieme Verlag, Stuttgart (1972), Vol. V/1b, pp. 728—945.

4) For recent methods for the synthesis of trisubstituted ethylenes see (a) A. Marfat, P. R. McGuirk, and P. Helquist, *Tetrahedron Lett.*, **1978**, 1363; (b) D. E. van Horn and E. Negishi, *J. Am. Chem. Soc.*, **100**, 2252 2254 (1978) and references cited therein.

5) For recent reviews see (a) I. Fleming, *Chem. Ind. (London)*, **1975**, 449; (b) P. F. Hudrlik, "New Application of Organometallic Reagents in Organic Synthesis," J. Organomet. Chem. Library, ed by D. Seyferth, Elsevier, Amsterdam (1976), Vol. 1, p. 127; (c) E. W. Colvin, *Chem. Soc. Rev.*, **7**, 15 (1978).

6) (a) P. F. Hudrlik and D. Peterson, *Tetrahedron Lett.*, **1974**, 1133; (b) P. F. Hudrlik and D. Peterson, *J. Am. Chem. Soc.*, **97**, 1464 (1975); (c) P. F. Hudrlik, D. Peterson, and R. J. Rona, *J. Org. Chem.*, **40**, 2263 (1975); (d) K. Utimoto, M. Kitai, and H. Nozaki, *Tetrahedron Lett.*, **1975**, 2825; (e) P. B. Dervan and M. A. Shippey, *J. Am. Chem. Soc.*, **98**, 1265 (1976); (f) J. J. Eisch and G. A. Damasevitz, *J. Org. Chem.*, **41**, 2214 (1976); (g) K. Uchida, K. Utimoto, and H. Nozaki, *ibid.*, **41**, 2215 (1976); (h) K. Uchida, K. Utimoto, and H. Nozaki, *ibid.*, **41**, 2941 (1976); (i) K. Uchida, K. Utimoto and H. Nozaki, *Tetrahedron*, **33**, 2987 (1977); (j) T. H. Chan, W. Michajlowskij, B. S. Ong, and D. N. Harpp, *J. Organomet. Chem.*, **107**, Cl (1976); (k) M. Obayashi, K. Utimoto, and H. Nozaki, *Tetrahedron Lett.*, **1977**, 1805; (l) W. Michajl owskij and T. H. Chan, *ibid.*, **1976**, 4439.

7) Stereochemistry of olefin-forming reaction from β-trialkylsilyl alcohols was studied in ref. 6a—c and 6e.

8) 1,1-Disubstituted ethylenes were prepared by analogous procedures: (a) P. F. Hudrlik and D. Peterson, *Tetrahedron Lett.*, **1972**, 1785; (b) R. A. Ruden and B. L. Gaffney, *Synth. Commun.*, **5**, 15 (1975).

9) The corresponding alcohol was obtained in 80 % yield by hydrolytic work-up.

10) The structures of III and IV are based on NMR analysis.

11) This mixture did not contain other isomers. We could not detect (*E*)- and (*Z*)-4-methyl-3-decene from the product mixture.

12) In further attempts for preparation of IV treatment of IIb with $HSCH_2COOH$ gave IV in 61 % yield, $E/Z=46/54$; with BF_3-OEt_2, 82 %, 37/63.

13) When α-trimethylsilylketone (Ia) was treated with MeMgBr in place of MeLi, IV was obtained in 22 % yield ($E/Z=23/77$) after acidic work-up (AcONa/AcOH). Reaction of Ia with PhLi gave 4-phenyl-4-decene in 52 % yield ($E/Z=39/61$) after treatment of the reaction mixture with H_2SO_4.14)

14) Treatment of the reaction mixture with KO^tBu or AcONa/AcOH gave no olefinic products. Sulfuric acid produces a benzyl-type cation which gives 4-phenyl-4-decene by the elimination of Me_3Si group.

15) Propyllithium may abstract proton from methyl ketone in 3-trimethylsilyl-2-octanone. This side reaction may be responsible for the decreased overall yield of IV.

16) M. Cherst, H. Felkin, and N. Prudent, *Tetrahedron Lett.*, **1968**, 2199.

17) (a) S. B. Bowlus and J. A. Katzenellenbogen, *Tetrahedron Lett.*, **1973**, 1277; (b) S. B. Bowlus and J. A. Katzenellenbogen, *J. Org. Chem.*, **38**, 2733 (1973); (c) M. P. Cooke, *Tetrahedron Lett.*, **1973**, 1281.

18) This procedure is, to the best of our knowledge, the first, direct,19) and irreversible transformation of silylacetylene to the acetylide. The same treatment of n-$C_6H_{13}C{\equiv}CSiMe_3$ gave n-$C_6H_{13}C{\equiv}CCOOEt$ in 93 % yield.

19) For stepwise transformation of silylacetylene to the acetylide see E. J. Corey, J. A. Katzenellenbogen, N. W. Gilman, S. A. Roman, and B. W. Erickson, *J. Am. Chem. Soc.*, **90**, 5618 (1968).