Carbocyclic Ring Formation by the Intramolecular Reaction between Enol Silyl Ether and Allylic Acetate Moieties

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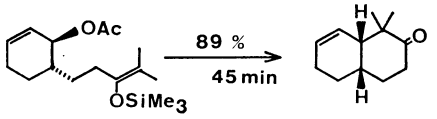
The title reaction of *trans*-3-acetoxy-4-(4-methyl-3-trimethylsiloxy-3-pentenyl)cyclohexene proceeds in the presence of Et_2AlOAr, where Ar=2,6-di-*t*-butyl-4-methylphenyl, affording stereospecifically the *cis* isomer of 2,2-dimethylbicyclo[4.4.0]dec-9-en-3-one. In contrast, the *cis*-disubstituted cyclohexene compound reacts only sluggishly to produce a mixture of the *cis*- and *trans*-fused octalones. Similar stereospecific effect of the allylic double bond configuration on the ease of cyclization has been observed in the synthesis of karahanaenone from 3,7-dimethyl-6-trimethylsiloxy-2,6-octadienyl acetate and related reactions.

We report a remarkable case of stereochemically controlled cyclization reaction proceeding intramolecularly among trimethylsiloxyethenyl group and allylic acetate moiety as shown in Eqs. 1 and 2.



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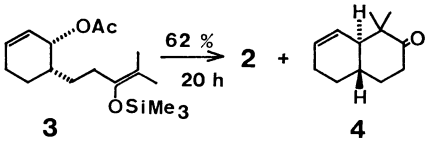
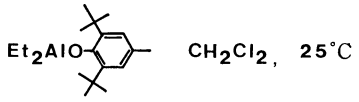


3 4 (2)

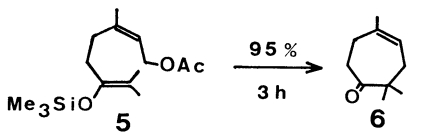
66 : 34



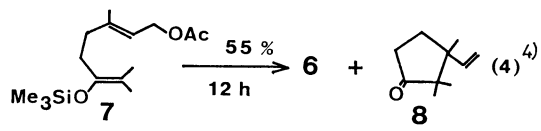
Obviously, the *trans*-substituted cyclohexenyl acetate (**1**) reacts smoothly in the presence of diethylaluminum 2,6-di-*t*-butyl-4-methylphenoxide as prepared from diethylaluminum chloride and the sterically hindered sodium phenoxide.[1] The resulting product is isomerically homogeneous *cis*-octalone (**2**). In sharp contrast, however, the *cis*-substituted cyclohexene (**3**) is transformed very sluggishly into a mixture of *cis*- and *trans*-octalone (**2** and **4**) only with inferior yields. This observation clearly excludes anticipated, possible intermediacy of the same, "free", allylic carbonium ion from both **1** and **3** which should be further cyclized into the trimethylsiloxy-stabilized cation presumably.

This type of cyclization has originally been described as a means of constructing the skeleton of karahanaenone (**6**) biomimetically (Eq. 3)[2] in the sense that neryl cation "equivalent" cyclizes in the *anti*-Markovnikov manner[3] to form a seven-membered ring. Extention of the same reaction to an isomeric system is shown in Eqs. 4, 5, and 6.

These equations impressively indicate that the (*E*), (*Z*) stereochemistry of the allylic double bond determines the rates of cyclization as well as the yields and distributions of the resulting products. Here again

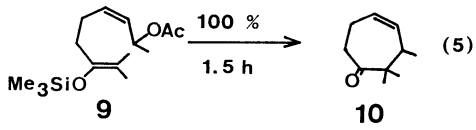


5 6 (3)

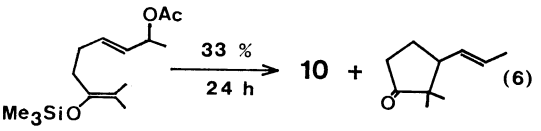


7 8

82 : 18



9 10



11 12

53 : 47

$MeAl(OCOCF_3)_2$, hexane-CH_2Cl_2, 25°C

the "free" allylic cation does not account for the observed dependence of the reaction on the allylic olefinic bond configuration of the substrates. Under comparable reaction conditions, diethyl geranyl phosphate does react quite analogously as the neryl isomer to afford limonene and terpinolene mixture in the presence of $(Bu^i_2Al)_2O$ in tetrahydrofuran (THF).[5,6] The $(Bu^i_2Al)_2O$–THF combination might increase the life-time of allylic carbonium ion so that (*E*)-allylic carbonium ion can be converted into (*Z*)-isomer which cyclizes with ease.[9]

The aluminum reagent in Eq. 3 through 6, methylaluminum bis(trifluoroacetate) or dimethylaluminum trifluoroacetate, was prepared from trimethylaluminum and calculated amount of trifluoroacetic acid in hexane and was used *in situ*. These proved to give less satisfactory results in the reaction of Eqs. 1 and 2.

Further examples of analogous cyclization are given in Eqs. 7, 8, and 9. For the allylic acetate unequally substituted at α and γ position, the silyl enol ether attacks the less substituted end of the allylic system

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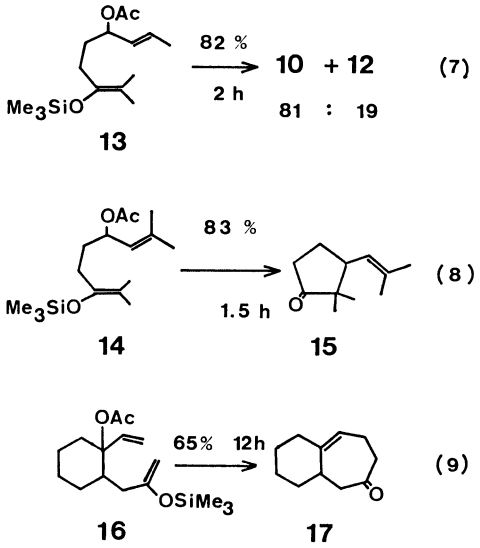
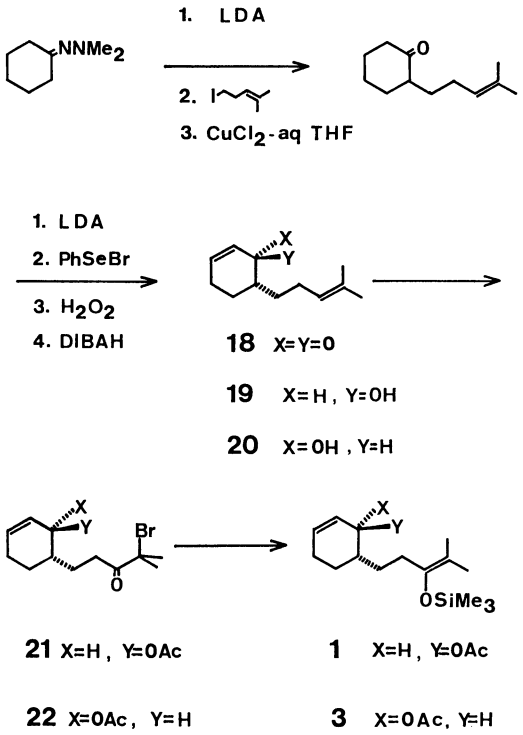
preferentially.

The preparation of cyclization substrates merits brief descriptions. The acetates **1** and **3** are obtained through the sequence in Scheme 1.



Scheme 1.



Experimental

The infrared spectra were determined on a Shimadzu IR-27-G spectrometer; the mass spectra on a Hitachi RMU-6L machine; the GLPC analyses on a Yanagimoto GCG-550F; and the NMR spectra on a JNM-PMX 60 or Varian EM-390H spectrometer. The chemical shifts are given in δ in ppm with TMS as the internal standard. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. The microanalyses were carried out by the staffs at the Elemental Analyses Center of Kyoto University. All experiments were carried under an atmosphere of dry argon. Tetrahydrofuran was dried by distillation from sodium-benzophenone. Thin layer or thick layer plates were made of E. Merck PF-254, and preparative column chromatography on silica gel E. Merck Art. 7734.

cis-2,2-Dimethylbicyclo[4.4.0]dec-9-en-3-one (2). A mixture of sodium hydride (50%, 50 mg, 1.0 mmol) and 2,6-di-*t*-butyl-4-methylphenol (0.22 g, 1.0 mmol) in hexane (5.0 ml) was stirred for 5 min at 0 °C. After stirring for an additional 15 min at 25 °C, a hexane solution of diethylaluminum chloride (1.0 M, 1.0 ml) was added. After 10 min, the solvent was removed *in vacuo* and the residue was diluted with dichloromethane (7.0 ml). A solution of **1** (157 mg, 0.51 mmol) in dichloromethane (3.0 ml) was added at −23 °C. After 3 h at −23 °C and 45 min at 25 °C, the mixture was poured into 1 mol dm^{-3} HCl and extracted with ethyl acetate (2×20 ml). The combined organic layers were washed with water and saturated aqueous sodium chloride solution and dried over anhydrous sodium sulfate. Removal of solvent *in vacuo* gave an oil which was purified by column chromatography on silica gel (5:1 hexane–ether) to give **2** (80 mg, 89%): IR (neat) 1710, 1382, 1070, 1010, 860, 755, 690 cm^{-1}; NMR (CCl_4) δ 1.06 (s, 3H), 1.24 (s, 3H), 5.63 (bs, 2H); MS *m/e* (%) 179 (9), 178 (M^+, 46), 93 (92), 92 (100), 79 (85). Hydrogenation (PtO_2) of **2** gave *cis*-2,2-dimethylbicyclo[4.4.0]decan-3-one which was spectrometrically identical with an authentic sample.[10]

trans-2,2-Dimethylbicyclo[4.4.0]dec-9-en-3-one (4). A solution of **3** (154 mg, 0.50 mmol) in dichloromethane (3.0 ml) was treated with the aluminum reagent (1.0 mmol) prepared as described above at 25 °C for 20 h. Purification by column chromatography afforded a mixture of **2** and **4** in 62% yield in a ratio of 66:34 as determined by GLPC (10% PEG, 2 m, 122 °C). Careful purification by preparative thick layer chromatography (PLC) on silica gel (5:1 hexane–ether) gave pure sample of **4**: IR (neat) 1708, 1180, 1110 cm^{-1}; NMR (CCl_4) δ 0.97 (s, 3H), 1.09 (s, 3H), 5.62 (m, 2H); MS *m/e* (%) 179 (11), 178 (M^+, 66), 79 (100). The compound **4** was hydrogenated to provide *trans*-2,2-dimethylbicyclo[4.4.0]decan-3-one.[10]

Karahanaenone (6). A solution of trifluoroacetic acid (0.91 g, 8.0 mmol) in hexane (4.0 ml) was added slowly at 0 °C to a solution of trimethylaluminum in hexane (1.0 M, 4.0 ml, 4.0 mmol) to give a white slurry. The mixture was stirred at 25 °C for 15 min and cooled to 0 °C. A solution of **5** (0.28 g, 1.0 mmol) in dichloromethane (8.0 ml) was added and stirring continued at 0 °C for 10 min and 25 °C for 3 h. After the usual workup, PLC (10:1 hexane–ether) gave **6** (130 mg, 85%): bp 160 °C (760 Torr); IR (neat) 1698, 1660, 1398, 1358 cm^{-1}; NMR (CCl_4) δ 1.05 (s, 6H), 1.70 (s, 3H), 2.03—2.30 (m, 4H), 2.55—2.80 (m, 2H), 5.42 (t, 1H, J=5.8 Hz); MS *m/e* (%) 152 (M^+, 100), 109 (66), 95 (94). The compound was identical with the authentic sample.[11] The yield determined by GLPC using 4-*t*-butylcyclohexanone as an internal standard was 95%.

2,2,3-Trimethyl-3-vinylcyclopentanone (8). The above procedure using **7** (142 mg, 0.5 mmol) and dimethylaluminum trifluoroacetate derived from trimethylaluminum (2.0 mmol) and trifluoroacetic acid (2.2 mmol) in dichloromethane (4.0 ml) afforded after usual workup and purification by PLC (10:1 hexane–ether) a mixture of **6** and **8** in 55% (42 mg) yield in a ratio of 82:18 as determined by GLPC (5% PEG 20 M, 1.5 m, 130 °C). Pure sample of **8** was obtained by preparative GLPC and its identity with an authentic sample[12] was established by IR and NMR. **8**: bp 110 °C (bath temp,

50 Torr); IR (neat) 1735, 1640, 1380, 1275, 1000, 915 cm^{-1}; NMR ($CDCl_3$) δ 0.88 (s, 3H), 0.93 (s, 3H), 1.06 (s, 3H), 1.80—2.05 (m, 2H), 2.32 (bd, 2H), 4.87—5.17 (m, 2H), 5.90 (dd, 1H, J=16, 12 Hz); MS *m/e* (%) 152 (M^+, 38), 137 (28), 109 (44), 96 (66), 81 (56), 70 (44), 67 (62), 55 (44), 43 (100), 41 (90).

*2,2,3-Trimethyl-3-cycloheptenone (**10**).* Following the procedure for the preparation of **6**, a solution of **9** (22 mg, 0.08 mmol) was treated with methylaluminum bis(trifluoroacetate) (0.5 mmol) in hexane (0.5 ml) to give **10** (12 mg, 100%): bp 80 °C (bath temp, 20 Torr); IR (neat) 1704, 1655, 1084, 780, 730 cm^{-1}; NMR (CCl_4) δ 1.01 (s, 3H), 1.05 (d, 3H, J=9 Hz), 1.10 (s, 3H), 5.45 (m, 2H); MS *m/e* (%), 153 (11), 152 (M^+, 73), 137 (18), 124 (16), 109 (60), 95 (100), 84 (60); Found: C, 78.97; H, 10.75%. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59%.

*2,2-Dimethyl-3-(1-propenyl)cyclopentanone (**12**)*: IR (neat) 1740, 1090, 1056, 975 cm^{-1}; NMR (CCl_4) δ 0.81 (s, 3H), 0.98 (s, 3H), 1.70 (d, 3H, J=5 Hz), 5.40 (m, 2H); MS *m/e* (%) 153 (12), 152 (M^+, 69), 137 (18), 109 (40), 95 (47), 81 (100); Found: *m/e* 152.1208. Calcd for $C_{10}H_{16}O$: M, 152.1202.

*2,2-Dimethyl-3-(2-methyl-1-propenyl)cyclopentanone (**15**)*: Bp 96 °C (bath temp, 19 Torr); IR (neat) 1745, 1671, 1090, 848, 802 cm^{-1}; NMR (CCl_4) δ 0.82 (s, 3H), 0.94 (s, 3H), 1.60 (s, 3H), 1.70 (s, 3H), 4.87 (bd, 1H, J=9 Hz); MS *m/e* (%) 167 (25), 166 (M^+, 48), 151 (34), 133 (21), 123 (99), 95 (69), 82 (100); Found: C, 79.23; H, 10.62%. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91%.

*Bicyclo[5.4.0]undec-5-en-2-one (**17**)*: IR (neat) 1707, 1225, 1150, 825 cm^{-1}; NMR (CCl_4) δ 2.40 (m, 2H), 2.67 (d, 1H, J=5.3 Hz), 2.70 (d, 1H, J=8.1 Hz), 5.50 (t, 1H, J=4.5 Hz); MS *m/e* (%) 164 (M^+, 61), 108 (52), 107 (52), 93 (71), 79 (100); Found: *m/e* 164.1189. Calcd for $C_{11}H_{16}O$: M, 164.1199.

*6-(4-Methyl-3-pentenyl)-2-cyclohexenone (**18**).* The title compound was prepared from 2-(4-methyl-3-pentenyl)cyclohexanone[13] as described by Reich[14] in 54% yield.

trans- *and* cis-*6-(4-Methyl-3-pentenyl)-2-cyclohexenol (**19** and **20**).* A solution of **18** (2.6 g, 14.6 mmol) and diisobutylaluminum hydride (0.5 M solution in hexane, 35 ml, 17.5 mmol) in benzene (50 ml) was stirred at 0 °C for 1.5 h. The resulting mixture was poured into 1 mol dm^{-3} HCl and extracted with ethyl acetate (2×100 ml). The combined extracts were washed with saturated sodium hydrogencarbonate and water, dried, and concentrated *in vacuo*. Trimethylsilylation (Et_3N, Me_3SiCl) of the crude mixture of **19** and **20** gave separable two bands by PLC (5:1 hexane–benzene). Hydrolysis of the slower moving band (R_f= 0.17) with 1 mol dm^{-3} HCl in tetrahydrofuran afforded **19**: IR (neat) 3330, 1650 cm^{-1}; NMR (CCl_4) δ 0.8—2.2 (m, 10H), 1.60 (s, 3H), 1.67 (s, 3H), 3.71 (m, 1H), 5.06 (t, 1H, J=7.5 Hz), 5.47—5.76 (m, 2H). Faster moving band (R_f= 0.37) gave **20**: IR (neat) 3350, 1650 cm^{-1}; NMR (CCl_4) δ 0.8—2.2 (m, 10H), 1.60 (s, 3H), 1.67 (s, 3H), 3.90 (bs, 1H), 5.07 (t, 1H, J=7.5 Hz), 5.74—5.82 (m, 2H). Hydrogenation of **19** or **20** provided *trans*- or *cis*-2-(4-methylpentyl)cyclohexanol, respectively, whose IR and NMR spectra agree with the published data.[15]

trans-*3-Acetoxy-4-(4-methyl-3-trimethylsiloxy-3-pentenyl)cyclohexene (**1**).* *m*-Chloroperbenzoic acid (70%, 1.47 g, 6.0 mmol) was added portionwise over a period of 30 min at 0 °C to a solution of *trans*-acetate (1.2 g, 5.4 mmol) derived from **19** in dichloromethane (25 ml). After 30 min, the reaction mixture was filtered through a pad of Celite 545 and the filtrate was washed with saturated sodium hydrogencarbonate, dried, and concentrated *in vacuo*. The crude epoxide (1.1 g) was dissolved in toluene (20 ml) and treated with 47% HBr (2.7 ml) at −78 °C. After 2 h, the mixture was poured into water and extracted with ether (2×20 ml). The combined ether layers were washed with brine and dried, and freed of the solvent. Purification of the residual oil by column chromatography on silica gel (10:1 benzene–ethyl acetate) gave *trans*-3-acetoxy-4-(4-bromo-4-methyl-3-hydroxypentyl)cyclohexene (1.1 g) as a pale yellow oil. Oxidation of bromohydrin by the method of Corey and Kim[16] afforded **21** (0.80 g, 74%). A solution of **21** (0.80 g, 2.5 mmol) in THF (5.5 ml) was added to a mixture of zinc–silver couple (0.51 g), chlorotrimethylsilane (0.97 ml, 7.7 mmol), and THF (10 ml) over a period of 30 min at 25 °C.[17] After 30 min, pyridine (2.1 ml, 25 mmol) was added[18] and the reaction mixture was poured into saturated sodium hydrogencarbonate and extracted with ether. After removal of solvent *in vacuo*, the resultant oil was purified by precooled (below 0 °C) silica gel column chromatography (10:1 hexane–ether) to give **1** (0.64 g, 82%): bp 145 °C (bath temp, 3 Torr); IR (neat) 1735, 1680, 1240, 750, 685 cm^{-1}; NMR (CCl_4) δ 0.13 (s, 9H), 1.52 (s, 3H), 1.55 (s, 3H), 1.96 (s, 3H), 4.96 (bs, 1H), 5.65 (m, 2H); MS *m/e* (%) 312 (1), 311 (3), 310 (M^+, 10), 251 (3), 250 (8), 249 (4), 207 (14), 171 (78), 170 (57), 73 (100); Found: C, 66.06; H, 9.97%. Calcd for $C_{17}H_{30}O_3Si$: C, 65.76; H, 9.74%.

cis-*3-Acetoxy-4-(4-methyl-3-trimethylsiloxy-3-pentenyl)cyclohexene (**3**).* In similar fashion, **20** was converted to **3** in 36% overall yield. **3**: bp 145 °C (bath temp, 3 Torr); IR (neat) 1733, 1680, 1248, 750, 682 cm^{-1}; NMR (CCl_4) δ 0.15 (s, 9H), 1.53 (s, 3H), 1.56 (s, 3H), 1.92 (s, 3H), 5.12 (bs, 1H), 5.80 (m, 2H); MS *m/e* (%) 312 (2), 311 (3), 310 (M^+, 11), 251 (4), 250 (10), 249 (4), 207 (16), 171 (54), 170 (88), 73 (100); Found: C, 65.54; H, 9.86%. Calcd for $C_{17}H_{30}O_3Si$: C, 65.76; H, 9.74%.

*6-Trimethylsiloxyneryl Acetate (**5**) and 6-Trimethylsiloxygeranyl Acetate (**7**).* As outlined for the preparation of **1**, the title acetates were obtained from neryl and geranyl acetate, respectively. **5**: bp 130 °C (bath temp, 0.5 Torr); IR (neat) 1740, 1682, 1374, 1250—1225, 1020, 950, 860—840 cm^{-1}; NMR (CCl_4) δ 0.17 (s, 9H), 1.53 (s, 3H), 1.58 (s, 3H), 1.74 (s, 3H), 1.95 (s, 3H), 2.17 (bs, 4H), 4.30 (d, 2H, J=7 Hz); MS *m/e* (%) 284 (3), 220 (6), 206 (4), 180 (17), 157 (35), 116 (23), 90 (69), 75 (72), 73 (100), 43 (59); Found: C, 63.33; H, 10.10%. Calcd for $C_{15}H_{28}O_3Si$: C, 63.33; H, 9.92%. **7**: bp 125 °C (bath temp, 0.5 Torr); IR (neat) 1740, 1677, 1380, 1362, 1240, 1190—1160, 1020, 965, 865, 840, 750 cm^{-1}; NMR ($CDCl_3$) δ 0.16 (s, 9H), 1.53 (s, 3H), 1.59 (s, 3H), 1.72 (s, 3H), 1.97 (s, 3H), 2.16 (bs, 4H), 4.48 (d, 2H, J=7 Hz), 5.31 (t, 1H, J=7 Hz); MS *m/e* (%) 284 (6), 181 (20), 158 (46), 117 (24), 91 (94), 75 (68), 73 (100), 43 (56); Found: C, 63.15; H, 10.06%. Calcd for $C_{15}H_{28}O_3Si$: C, 63.33; H, 9.92%.

*(3Z)-2-Acetoxy-8-methyl-7-trimethylsiloxy-3,7-nonadiene (**9**).* A solution of 6-methyl-5-hepten-2-one (21.4 g, 0.17 mol) in 2,6-lutidine (172 ml, 1.48 mol) was added at 0 °C over 40 min to a suspension of phosphorus pentachloride (89.6 g, 0.42 mol). The precipitate was removed by filtration through a pad of Celite 545 and the filtrate was washed with water, dried, and concentrated *in vacuo*. The crude product and lithium diisopropylamide, prepared from diisopropylamine (42.5 ml, 0.30 mol) and butyllithium (1.6 M hexane solution, 174 ml, 0.28 mol) in THF (300 ml) were reacted at 0 °C for 10 min and acetaldehyde (11.6 ml, 0.21 mol) was added. After usual workup, 8-methyl-7-nonen-3-yn-2-ol (4.7 g, 31 mmol) was obtained in 18% yield based on the heptenone. A mixture of the alcohol (3.1 g, 20.5 mmol), sodium borohydride (0.33 g, 8.5 mmol), and nickel acetate (1.8 g, 7.3

mmol) in ethanol (190 ml) was stirred at 25 °C for 1 h under hydrogen atmosphere. The black precipitate was removed by filtration and the filtrate was concentrated *in vacuo*. Acetylation followed by distillation under reduced pressure (bp 72—73 °C, 0.5 Torr) gave (3*Z*)-2-acetoxy-8-methyl-3,7-nonadiene (2.86 g, 47%). According to the procedure described for the preparation of **1**, the acetate was converted to **9**: IR (neat) 1735, 1678, 1240, 693 cm^{-1}; NMR (CCl_4) δ 0.16 (s, 9H), 1.23 (d, 3H, J=5.8 Hz), 1.56 (s, 3H), 1.58 (s, 3H), 1.96 (s, 3H), 2.16 (m, 4H), 5.2—5.7 (m, 3H); MS *m/e* (%) 286 (5), 285 (3), 284 (M^+, 12), 225 (15), 224 (10), 209 (9), 195 (4), 181 (10), 169 (9), 158 (20), 141 (34), 91 (69), 75 (61), 73 (100); Found: *m/e* 284.1805. Calcd for $C_{15}H_{28}O_3Si$: M, 284.1806.

*(3E)-2-Acetoxy-8-methyl-7-trimethylsiloxy-3,7-nonadiene (**11**).* Reduction of 8-methyl-7-nonen-3-yn-2-ol with lithium aluminum hydride in ether gave (3*E*)-8-methyl-3,7-nonadien-2-ol in 80% yield. As described previously, the alcohol was transformed to **11**: bp 118 °C (bath temp, 2 Torr); IR (neat) 1735, 1677, 1240, 965 cm^{-1}; NMR (CCl_4) δ 0.15 (s, 9H), 1.23 (d, 3H, J=6.3 Hz), 1.52 (s, 3H), 1.56 (s, 3H), 1.92 (s, 3H), 2.13 (m, 4H), 5.1—5.6 (m, 3H); MS *m/e* (%) 286 (2), 285 (5), 284 (M^+, 17), 225 (21), 224 (13), 209 (10), 195 (6), 181 (12), 156 (24), 141 (47), 91 (87), 75 (63), 73 (100); Found: C, 63.18; H, 10.21%. Calcd for $C_{15}H_{28}O_3Si$: C, 63.33; H, 9.92%.

*(2E)-4-Acetoxy-8-methyl-7-trimethylsiloxy-2,7-nonadiene (**13**).* Bp 100 °C (bath temp, 2.5 Torr); IR (neat) 1735, 1678, 1240, 962 cm^{-1}; NMR (CCl_4) δ 0.14 (s, 9H), 1.53 (s, 6H), 1.65 (d, 3H, J=6.3 Hz), 1.7 (m, 2H), 1.90 (s, 3H), 2.0 (m, 2H), 5.07 (m, 1H), 5.27 (dd, 1H, J=15, 7.5 Hz), 5.69 (dq, 1H, J=15, 6.3 Hz); MS *m/e* (%) 286 (2), 285 (2), 284 (M^+, 6), 224 (11), 209 (11), 181 (24), 158 (34), 143 (26), 141 (24), 119 (13), 117 (17), 75 (56), 73 (100); Found: C, 63.46; H, 9.75%. Calcd for $C_{15}H_{28}O_3Si$: C, 63.33; H, 9.92%.

*4-Acetoxy-2,8-dimethyl-7-trimethylsiloxy-2,7-nonadiene (**14**).* A solution of 6-methyl-5-hepten-2-one (6.0 g, 48 mmol) in THF (20 ml) was added at −78 °C over a period of 1 h by means of mechanically driven syringe to a solution of lithium diisopropylamide (53 mmol) generated from diisopropylamine and butyllithium in THF (100 ml). After 20 min, acetone (39 ml, 0.53 mol) was added in one portion and the mixture was stirred for an additional 20 min. The reaction was quenched by addition of acetic acid (3.6 ml, 63 mmol) and the resulting mixture was poured into water and extracted with ethyl acetate. The combined extracts were washed with saturated sodium hydrogencarbonate and brine, dried and concentrated *in vacuo*. The resultant crude oil was purified by column chromatography on silica gel to give 2,8-dimethyl-2-hydroxy-7-nonen-4-one (8.5 g, 97%). A mixture of this β-hydroxy ketone (8.5 g, 46 mmol) triethylamine (32 ml, 0.23 mol), and methanesulfonyl chloride (8.0 ml, 0.10 mol) in dichloromethane (200 ml) was stirred at 25 °C for 15 h. The suspension was diluted with ether and water. After extracting with ether and drying (Na_2SO_4), distillation (bp 49—52 °C, 0.5 Torr) gave 2,8-dimethyl-2,7-nonadien-4-one (7.1 g, 93%). The dienone (5.8 g, 35 mmol) was reduced with sodium borohydride (1.35 g, 35 mmol) in ethanol (35 ml) at 25 °C for 17 h to give an alcohol which was converted to 4-acetoxy-2,8-dimethyl-2,7-nonadiene (bp 75—76 °C, 10.5 Torr, 6.0 g, 82%) by the successive treatment with pyridine (20 ml) and acetic anhydride (20 ml) at 0 °C. Following the procedure for the preparation of **1**, the acetate gave **14** (30% overall yield): bp 139 °C (bath temp, 2 Torr); IR (neat) 1736, 1680, 1252 cm^{-1}; NMR (CCl_4) δ 0.15 (s, 9H), 1.53 (s, 6H), 1.68 (s, 6H), 1.94 (s, 3H), 4.93 (d, 1H, J=8.6 Hz), 5.28 (td, 1H, J=5.8, 8.6 Hz); MS *m/e* (%) 299 (3), 298 (M^+, 9), 239 (11), 238 (32), 223 (26), 195 (27), 158 (26), 141 (33), 91 (29), 75 (52), 73 (100); Found: *m/e* 298.1957. Calcd for $C_{16}H_{30}O_3Si$: M, 298.1963.

*1-Acetoxy-2-(2-trimethylsiloxy-2-propenyl)-1-vinylcyclohexane (**16**).* Vinylmagnesium bromide (0.27 mol) and 2-allylcyclohexanone (14.4 g, 104 mmol) were stirred in THF (200 ml) at 25 °C for 30 min. The reaction mixture was poured into aqueous ammonium chloride and extracted with ether. Distillation under reduced pressure (bp 95—105 °C, 10 Torr) afforded 2-allyl-1-vinylcyclohexanol (14.5 g, 87.7 mmol) in 84% yield. A mixture of this alcohol (6.2 g, 37.5 mmol) and sodium hydride (37.5 mmol) in benzene was refluxed for 1.5 h and diethylene glycol diacetate (6.5 g, 37.5 mmol) was added.[19] The mixture was stirred at 25 °C for 16 h, poured into water, and extracted with ether. Purification by column chromatography on silica gel gave 1-acetoxy-2-allyl-1-vinylcyclohexane (4.0 g, 52%) which was further converted in similar way to silyl enol ether **16** (2.5 g, 65% overall yield): IR (neat) 1736, 1678, 1671, 1010, 908 cm^{-1}; NMR (CCl_4) δ 0.18 (s, 9H), 1.95 (s, 3H), 3.90 (s, 2H), 4.89 (d, 1H, J=17 Hz), 5.03 (d, 1H, J=11 Hz), 5.94 (dd, 1H, J=11, 17 Hz); MS *m/e* (%) 253 (8), 237 (14), 236 (28), 223 (5), 222 (8), 221 (28), 195 (8), 193 (8), 182 (16), 147 (34), 117 (33), 91 (36), 75 (43), 73 (100); Found: *m/e* 296.1810. Calcd for $C_{16}H_{28}O_3Si$: M, 296.1808.

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4) $Me_2Al(OCOCF_3)$ was used instead of $MeAl(OCOCF_3)_2$. See experimental part.

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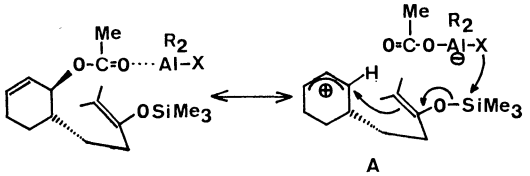
6) The most economical assumption to account for the observations as mentioned here would be as follows. Coordination of the aluminum reagent R_2AlX on the allyl acetate moiety of the substrate **1** in Eq. 1 produces the adduct **A**:



A

The very tight ion-pair lying slightly above the level of such an adduct may experience the attack on silicon atom either by X or by acetoxyl oxygen. This will result in "almost concerted" cyclization proceeding in the stereospecific manner as observed to afford completely homogeneous *cis*-octalone (**2**). Molecular models show such a process can not be expected with the *cis*-substrate (**3**). Similar explanation applies to Eq. 3 through 6. The importance of this kind of combined acid-base attack in the reactions of R_2AlX

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