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ORGANOALUMINIUM ASSISTED REARRANGEMENTS OF FIVE-MEMBERED RING ENOL ETHERS WITH VINYL SUBSTITUENTS

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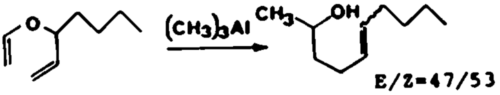
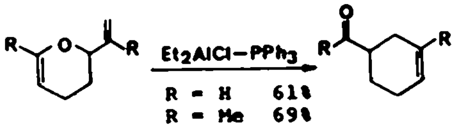
Abstract: Such organoaluminium reagents as $^{i}Bu_3Al$, $PhC{\equiv}CAlEt_2$, and Et_2AlSPh mediate the title reactions in three different directions. (1) [3,3] sigmatropic rearrangement producing 7-membered rings. (2) isomerization to form vinylcyclopropane derivatives and (3) S_N2' type reaction with phenylthio anion via oxolane ring opening.

Previously[1] recorded reaction of 1-butyl-2-propenyl vinyl ether with trimethylaluminium affords 5-decen-2-ol as a result of [3,3]sigmatropic rearrangement and successive methylation. Reaction with Et_2AlSPh or $Et_2AlCl-PPh_3$ gives the regular Claisen rearrangement products.[2]

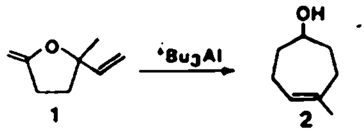




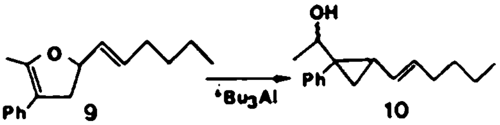
R = H 61%
R = Me 69%

In further extension of this technique,[3] we have examined the reaction of 2-vinyloxolane enol ethers[4] with organoaluminium reagents to observe rather unexpected transformations proceeding in three different directions as summarized in Scheme 1.

Scheme 1. **Three types of transformations of 2-vinyloxolane enol ethers with organoaluminium reagents.**
(1) Claisen Rearrangement to Form a Seven-Membered Carbocycle

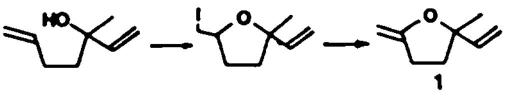


(2) Vinylcyclopropane Formation

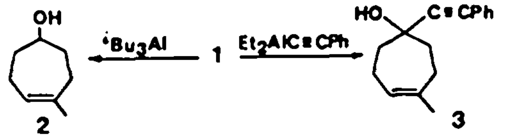


(3) S_N2' Type Reaction with Phenylthio Anion via Oxolane Ring Opening.

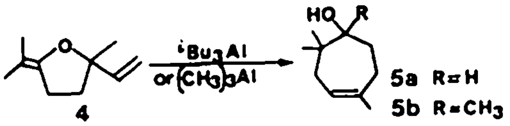
The seven-membered ring formation has provided a synthetic route to a cycloheptenol from an open-chain alcohol which is readily accessible. Iodoetherification[5] of 3-methyl-1,6-heptadien-3-ol followed by dehydroiodination with potassium *t*-butoxide gave vinyloxolane 1. Treatment of 1 with triisobutylaluminium in dichloromethane at 25°C for 15 min gave 4-methyl-4-cyclohepten-1-ol (2) via Claisen rearrangement and successive reduction of the resulting carbonyl moiety with aluminium hydride generated from triisobutylaluminium.[1] Alkynyl group was introduced in preference to an alkyl group. Thus, the use of $PhC{\equiv}CAlEt_2$ instead of



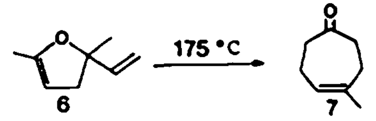
$^{i}Bu_3Al$ provided the corresponding phenylethynylated compound (**3**).

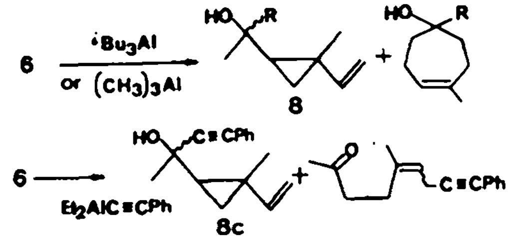


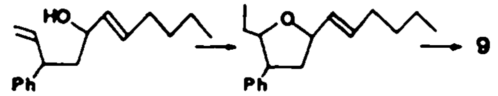
Similarly, a vinyloxolane (**4**) afforded the corresponding hydrogenated or methylated alcohol (**5a** or **5b**) upon treatment with triisobutylaluminium or trimethylaluminium.



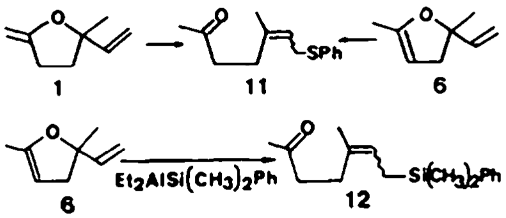
The isomerization to vinylcyclopropane derivatives is rather unexpected. As shown in the following equation, reductive rearrangement of vinyloxolene **6** has provided vinylcyclopropane **8a** (R = H) in sharp contrast to the thermally proceeding isomerization-[3,3]sigmatropy sequence[6] affording **7**. Thus, treatment of **6** with 2.5 equivalents of triisobutylaluminium in dichloromethane at 25°C for 10 h gave 2-(1-hydroxyethyl)-1-methyl-1-vinylcyclopropane **8a** in 51% yield in addition to 4-methyl-4-cyclohepten-1-ol **2** (17%). Oxidation of cyclopropane **8a** with pyridinium chlorochromate (PCC) gave a mixture of trans-1-methyl-1-vinyl-2-acetylcyclopropane and its cis isomer (trans:cis = 86:14). The addition of Me_3Al to the compound **6** produced the corresponding cyclopropane derivative **8b** (R = Me) almost exclusively. Only a trace amount of 1,4-dimethyl-4-cyclohepten-1-ol was observed in a reaction mixture (<3%). The reaction with $PhC{\equiv}CAlEt_2$ gave a mixture of cyclopropane derivative **8c** (R = PhC≡C, 48% yield) and 5-methyl-9-phenyl-5-nonen-8-yn-2-one (28%). The latter compound is a third type reaction product (*vide infra*). Further example shown in Scheme 1-(2) has provided trans-cyclopropane **10** as a threo and erythro isomeric mixture. Oxidation with PCC gave trans-cyclopropane as a single isomer. The starting material **9** was prepared in a similar fashion as the oxolane **1**. Treatment of iodomethyloxolane with potassium *t*-butoxide in DMF, however, produced endo-double bond in conjugation of phenyl group via the exo methylene isomer.







The third S_N2' type attack by phenylthio anion finds its analogy in the reactions of organoaluminium reagents with allylic systems.[7] The oxolane **1** or **6** gave allylic sulfide **11** on treatment with $PhSAlEt_2$ in dichloroethane. Allylic silane **12** was also obtained starting from **6** with $Et_2AlSiMe_2Ph$.[8] Possibly the strong nucleophilicity of these anions and the ready opening of the oxolane ring explain the observed results.



Experimental

Melting points and boiling points are uncorrected. Bulb-to-bulb distillation is carried out by use of Kugelrohr (Büchi) and bps were determined by measuring the bath temperature. ^1H-NMR spectra (tetramethylsilane as an internal standard) were obtained on a Varian EM-390. The chemical shifts are given in δ, IR spectra of neat liquid film samples (unless otherwise noted) were recorded on a Shimadzu IR-27-G spectrometer, MS on a Hitachi M-80 spectrometer. The analyses were carried out by the staff at the Elemental Analyses Centre of

Kyoto University. Gas-liquid phase chromatography (GLC) analyses were performed with a Yanagimoto GCG-550-F and Shimadzu GC-4CPT. All the experiments were carried out under nitrogen atmosphere. Purification of products were performed by preparative thin layer chromatography (TLC, Merck Kiesel-gel PF_{254}) or silica gel column chromatography (Wakogel C-100).

2-Methyl-5-methylene-2-vinyloxolane (1)

To a mixture of 3-methyl-1,6-heptadien-3-ol (0.13 g, 1.0 mmol) and potassium carbonate (0.42 g, 3.0 mmol) in acetonitrile (5.0 ml) was added iodine (0.25 g, 2.0 mmol) in three portions at 0°C. After 1 h, the mixture was poured into 10% sodium thiosulfate (5.0 ml) and extracted with ether and the organic phase was dried (Na_2SO_4). Purification by silica gel column chromatography (hexane : ethyl acetate = 20:1) gave 5-iodomethyl-2-methyl-2-vinyloxolane quantitatively. A solution of iodomethylvinyloxolane (0.25 g, 1.0 mmol) in dimethylformamide (1.0 ml) was added to a solution of potassium t-butoxide[9] (0.22 g, 2.0 mmol) in dimethylformamide (5.0 ml) at 0°C. After 30 min, the mixture was poured into water and extraced with ether. The combined organic layer was washed with water (2 x 10 ml) and brine, and dried over potassium carbonate. Concentration in vacuo gave the title compound 1[5] (0.12 g) quantitatively which was distilled: Bp 76°C/90 Torr; IR 2940, 1660, 1230, 980, 925, 790 cm^{-1}; ^1H-NMR (CCl_4) δ 1.35 (s, 3H), 1.7-1.9 (m, 2H), 2.4-2.6 (m, 2H), 3.59 (s, 1H), 4.03 (s, 1H), 4.93 (dd, *J* = 2, 10 Hz, 1H), 5.15 (dd, *J* = 2, 16 Hz, 1H), 5.77 (dd, *J* = 10, 16 Hz, 1H).

4-Methyl-4-cyclohepten-1-ol (2)

A solution of triisobutylaluminium (1.0 M in hexane, 4.0 ml, 4.0 mmol) was added to a solution of 2-methyl-5-methylene-2-vinyloxolane 1 (0.25 g, 2.0 mmol) in dichloromethane (4.0 ml) at 25°C under nitrogen atmosphere and the mixture was stirred for 15 min. The resulting mixture was poured into 1 N HCl (30 ml) and extracted with ethyl acetate. The combined organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated. Purification of the residue by silica gel column chromatography (hexane : ethyl acetate = 1:5) gave 4-methyl-4-cyclohepten-1-ol 2 (0.21 g, 82% yield) as colorless oil: Bp 85-88°C (bath temperature)/14 Torr; ^1H-NMR (CCl_4) δ 1.1-1.5 (m, 2H), 1.6-2.5 (m, 7H), 1.68 (s, 3H), 3.5-3.8 (m, 1H), 5.43 (t, *J* = 6 Hz, 1H); IR 3350, 2950, 1450, 1040, 815 cm^{-1}; MS m/z (rel intensity) 126 (M^+, 5), 108 (10), 98 (17), 93 (100), 81 (12), 80 (34), 79 (23), 77 (12), 69 (17), 67 (42). Found: C, 76.16; H, 11.40%. Calcd for $C_8H_{14}O$: C, 76.16; H,11.18%.

4-Methyl-1-(phenylethynyl)-4-cyclohepten-1-ol (3)

Butyllithium (1.65 M in hexane, 2.4 ml, 4.0 mmol) was added to a solution of phenylacetylene (0.41 g, 4.0 mmol) in hexane (2.0 ml) at 0°C. A solution of Et_2AlCl (1.0 M in hexane, 4.0 ml, 4.0 mmol) was added to the resulting suspension and the whole was stirred for 30 min at 25°C. A solution of oxolane 1 (0.25 g, 2.0 mmol) in dichloromethane (6.0 ml) was added dropwise and the mixture was stirred for another 2 h at 25°C. The mixture was poured into 1 N HCl (30 ml) and extracted with ethyl acetate. The combined organic layer was washed with water and brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was submitted to silica gel column chromatography (hexane : ethyl acetate = 5:1) to give cycloheptenol 3 (0.38 g, 83% yield) as white crystals: Mp 87°C (recrystallization from hexane); ^1H-NMR (CCl_4) δ 1.4-2.9 (m, 9H), 1.70 (s, 3H), 5.50 (t, *J* = 6 Hz, 1H), 7.2-7.5 (m, 5H); IR ($CHCl_3$) 3450, 2950, 1600, 1495, 1450 cm^{-1}; MS m/z (rel intensity) 226 (M^+, 28), 208 (99), 193 (100), 192 (48), 178 (35), 169 (49), 131 (33), 129 (52), 102 (48), 73 (38). Found: C, 84.76; H, 8.03%. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02%.

Preparation of 2-Dimethylmethylene-5-methyl-5-vinyloxolane (4)

Bromoetherification of 3,7-dimethyl-1,6-octadien-3-ol[10] followed by treatment with potassium t-butoxide provided the oxolane 4 in 68% overall yield: Bp 42-49°C/16 Torr; ^1H-NMR (CCl_4) δ 1.31 (s, 3H), 1.48 (s, 3H), 1.54 (s, 3H), 1.6-1.9 (m, 2H), 2.2-2.5 (m, 2H), 4.90 (dd, *J* = 2, 10 Hz, 1H), 5.07 (dd, *J* = 2, 18 Hz, 1H), 5.76 (dd, *J* = 10, 18 Hz, 1H); IR (neat) 1700, 1635, 1130, 990, 920 cm^{-1}. Found: C, 78.94; H, 10.77%. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59%.

2,2,5-Trimethyl-4-cyclohepten-1-ol

(5a)

A solution of 4 (0.15 g, 1.0 mmol) in dichloromethane (2.0 ml) was added to a solution of triisobutylaluminium (1.0 M in hexane, 2.0 ml, 2.0 mmol) at 25°C and the resulting mixture was stirred for 1 h. Workup and purification gave **5a** (94 mg, 61% yield): ^{1}H-NMR (CCl$_4$) δ 0.85 (s, 3H), 0.95 (s, 3H), 1.2-2.6 (m, 7H), 1.70 (s, 3H), 3.25 (dd, J = 3, 8 Hz, 1H), 5.25 (t, J = 7, 1H); IR 3450, 2960, 1460, 1030, 785 cm^{-1}; MS m/z (rel intensity) 154 (M$^+$, 7), 146 (25), 126 (100), 121 (96), 95 (64), 93 (98), 86 (76), 71 (88). Oxidation of **5a** with PCC in dichloromethane gave 2,2,5-trimethyl-4-cyclopentenone whose spectra (^{1}H-NMR and IR) were identical with the reported data of karahanaenone.[10]

1,2,2,5-Tetramethyl-4-cyclohepten-1-ol (5b)

A solution of the oxolane **4** (0.30 g, 2.0 mmol) in dichloromethane (6.0 ml) was added to a solution of trimethylaluminium (1.0 M in hexane, 6.0 ml, 6.0 mmol) at 25°C. The mixture was stirred for 1h. Extractive workup furnished a liquid which was chromatographed on silica gel to afford methylated product **5b** (0.16 g) in 48% yield: Bp 58-62°C/1.0 Torr; ^{1}H-NMR (CCl$_4$) δ 0.85 (s, 3H), 0.88 (s, 3H), 1.10 (s, 3H), 1.15-1.25 (bs, 1H), 1.4-1.9(m, 4H), 1.68 (s, 3H), 2.0-2.5 (m, 2H), 5.28 (t, J = 7Hz, 1H); IR 3450, 2930, 2890, 1440, 1370, 1100, 890, 830 cm^{-1}; MS m/z (rel intensity) 168 (M$^+$, 4), 150 (49), 135 (62), 110 (32), 107 (47), 95 (100), 86 (40), 69 (49), 43 (68). Found: C, 78.52; H, 12.20%. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98%.

2,5-Dimethyl-5-vinyl-2-oxolene(6) The title compound was prepared according to the reported procedure.[11]

2-(1-Hydroxyethyl)-1-methyl-1-vinylcyclopropane (8a)

A solution of triisobutylaluminium (1.0 M in hexane, 5.0 ml, 5.0 mmol) was added to a solution of **6** (0.25 g, 2.0 mmol) in dichloromethane (10 ml) at 25°C and the mixtutre was stirred for 10 h. The mixture was poured into 1 N HCl (40 ml) and extracted with ethyl acetate. The combined organic layer was washed with water and brine, and dried (Na_2SO_4). Purification by silica gel column chromatography (hexane : ethyl acetate = 5:1) gave **8a** (0.13 g) in 51% yield along with 2 (43 mg, 17% yield). **8a**: Bp 55-58°C/12 Torr; ^{1}H-NMR (CCl$_4$) δ 0.2-0.3 (m, 1H), 0.65-1.1 (m, 2H), 1.1-1.3 (m, 6H), 2.65 (bs, 1H), 3.1-3.5 (m, 1H), 4.7-5.1 (m, 2H), 5.35 (dd, J = 18, 12 Hz, 0.8H), 5.73 (dd, J = 18, 12Hz, 0.2H); IR 3300, 2940, 1630, 1080, 990, 965, 940, 910, 885 cm^{-1}; MS m/z (rel intensity) 126 (M$^+$, 1), 111 (9), 108 (7), 82 (31), 71 (100), 68 (36), 67 (69), 58 (56), 45 (40). Found: C, 75.89; H, 11.46%. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18%. Oxidation of **8a** with PCC gave the corresponding cyclopropyl ketone whose ^{1}H-NMR spectrum showed signals of methyl group on cyclopropane ring at δ 1.14 and 1.29 in a ratio of 5:1.[10]

2-(2-Hydroxy-2-propyl)-1-methyl-1-vinylcyclopropane (8b)

To a solution of trimethylaluminium (1.0 M in hexane, 15 ml, 15 mmol) was added a solution of **6** (0.62 g, 5.0 mmol) in dichloromethane at 25°C and the mixture was stirred for 15 h. The resulting mixture was poured into 1 N HCl (30 ml) and extracted with ethyl acetate. Concentration of the dried organic layer and preparative TLC purification gave **8b** (0.41 g, 58% yield): Bp 58-60°C/12 Torr; ^{1}H-NMR (CCl$_4$) δ 0.6-0.9 (m, 2H), 1.1-1.5 (m, 11H), 4.6-5.1 (m, 2H), 5.31 (dd, J = 10, 18 Hz, 0.8H), 6.06 (dd, J = 10, 18 Hz, 0.2H); IR 3400, 2940, 1720, 1610, 1450, 1370, 990, 940 cm^{-1}; MS m/z (rel intensity) 122 (M$^+$-H$_2$O, 4), 119 (16), 117 (16), 72 (57), 71 (47), 70 (26), 59 (31), 57 (16), 43 (100). Found: C, 77.07; H, 11.76%. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50%.

2-(3-Hydroxy-1-phenyl-1-butyn-3-yl)-1-methyl-1-vinylcyclopropane (8c)

A solution of **6** in 1,2-dichloroethane (3.0 ml) was added to a solution of diethylphenylethynylaluminium (1.0 mmol) in hexane (2.0 ml) at 25°C. The mixture was stirred for 5 h at 60°C. Workup and purification by TLC (hexane : ethyl acetate = 5:1) gave **8c** (54 mg, 48% yield) and 5-methyl-9-phenyl-5-nonen-8-yn-2-one (32 mg, 28% yield). The product **8c** consists of two diastereoisomers **A** and **B** in ca. 1 : 2 ratio. **A**: Bp 83-88°C/0.3 Torr ^{1}H-NMR (CCl$_4$) δ 0.7-1.0 (m, 2H), 1.1-1.4 (m+s (δ 1.23), 4H), 1.61 (s, 3H), 1.9-2.1 (m, 1H), 5.05 (dd, J = 11, 18 Hz, 2H), 6.88 (dd, J = 11, 18 Hz, 1 H), 7.1-7.4 (m, 5H); IR 3450, 2950, 2230, 1640, 1600, 1500, 1450, 1000, 920, 755 cm^{-1}; MS m/z (rel intensity) 211 (M$^+$-CH$_3$, 2), 208 (M$^+$-H$_2$O, 3), 193 (13), 178 (10), 158 (100), 145 (19), 115 (32), 43 (86). Found: C, 84.67; H, 8.13%. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02%. **B**: Bp 78-81°C/0.3 Torr ^{1}H-NMR (CCl$_4$) δ 0.7-1.3 (m, 3H), 1.52 (s, 3H), 1.70 (s, 3 H), 1.90 (bs, 1 H), 4.75 (dd, *J* = 1.5, 16 Hz, 1H), 4.86 (dd, *J* = 1.5, 11 Hz, 1H), 5.37 (dd, *J* = 11, 16 Hz, 1H), 7.1-7.4 (m, 5H); IR 3440, 3000, 1640, 1600, 1500, 1450, 990, 820, 755 cm^{-1}; MS m/z (rel intensity) 211 (M$^+$-CH$_3$, 2), 208 (M$^+$-H$_2$O, 3), 193 (13), 178 (10), 158 (100), 145 (19), 115 (32), Found: C, 84.73; H, 8.16%. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02%. 5-Methyl-9-phenyl-5-nonen-8-yn-2-one: Bp 102-106°C/0.2 Torr; ^{1}H-NMR (CCl$_4$) δ 1.66 (s, 3H), 2.04 (s, 3H), 2.1-2.6 (m, 4H), 3.03 (d, *J* = 6 Hz, 2H), 5.21 (t, *J* = 6 Hz, 1H), 7.3-7.5 (m, 5H); IR 2890, 1710, 1590, 1490, 1440, 760 cm^{-1}; MS m/z (rel intensity) 226 (M$^+$, 2), 193 (26), 183 (24), 169 (27), 168 (100), 167 (64), 153 (27), 115 (23), 91 (33), 43 (34). Found: C, 84.84; H, 8.04%. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02%.

3-Phenyl-1,6-undecadien-5-ol

Reduction of ethyl 3-phenyl-4-pentenoate with lithium aluminium hydride followed by oxidation with PCC gave 3-phenyl-4-pentenal in 55% yield. Butyllithium (1.56 M hexane solution, 2.6 ml, 4.0 mmol) was added to a solution of 1-hexyne (0.39 g, 4.2 mmol) in THF (10 ml) at -78°C. After 30 min, 3-phenyl-4-pentenal (0.61 g, 3.8 mmol) in THF (5.0 ml) was added dropwise over 10 min and the whole was stirred for 1 h. Workup and purification gave 3-phenylundec-1-en-6-yn-5-ol (0.68 g, 74% yield) which was reduced with lithium aluminium hydride[12] to give the title compound (0.65 g, 95% yield).

5-(1-Hexenyl)-2-methyl-3-phenyl-2-oxolene (9)

Iodine (1.0 g, 4.0 mmol) was added to a mixture of 3-phenyl-1,6-undecadien-5-ol (0.49 g, 2.0 mmol) and potassium carbonate (1.1 g, 8.0 mmol) in acetonitrile (5.0 ml) at 0°C. After 1 h, workup and purification gave 2-iodomethyl-5-(1-hexenyl)-3-phenyloxolane (0.68 g, 92% yield). A solution of oxolane (0.37 g, 1.0 mmol) in dimethylformamide (2.0 ml) was added to a solution of potassium t-butoxide (0.61 g, 5.0 mmol) in dimethylformamide (3.0 ml). Workup gave the compound **9** (0.26 g) which was pure enough and used directly for further reaction without purification: Bp 105-112°C/0.3 Torr; ^{1}H-NMR (CCl$_4$) δ 0.93 (d, *J* = 3 Hz, 3H), 1.2-1.5 (m, 4H), 1.8-2.2 (m, 5H), 2.6-3.3 (m, 2H), 4.8-5.0 (m, 1H), 5.5-5.7 (m, 2H), 6.9-7.3 (m, 5H); IR 2920, 1660, 1600, 1500, 1210, 945, 965, 750, 685, cm^{-1}; MS m/z (rel intensity) 242 (M$^+$,25), 157 (54), 128 (91), 43 (100), 41 (41). Found: C, 84.37; H,9.24%. Calcd for $C_{17}H_{22}O$: C,84.25; H,9.15%.

2-(1-Hexenyl)-1-(1-hydroxyethyl)-1-phenylcyclopropane (10)

A solution of (9) (0.12 g, 0.50 mmol) in 1,2-dichloroethane (3.0 ml) was added to a solution of triisobutylaluminium (1.0 M in hexane, 2.5 ml, 2.5 mmol) at 25°C. The mixture was heated to reflux for 3 h. Workup and successive purification by preparative TLC (hexane : ethyl acetate = 10:1) gave cyclopropane **10** (87 mg, 71% yield): Bp 80-83°C/0.08 Torr; ^{1}H-NMR (CCl$_4$) δ 0.6-1.5 (m, 13H), 1.5-2.1 (m, 3H), 3.1-3.6 (m, 1H) 4.45 (dd, *J* = 7, 15 Hz, 1H), 5.2-5.6 (m, 1H), 7.17 (bs, 5H); IR 3430, 2940, 1600, 1500, 1450, 965 cm^{-1}; MS m/z (rel intensity) 244 (M$^+$, 0.4), 226 (1.0), 143 (67), 134 (68), 132 (100), 91 (89), 57 (29). Found: C, 83.66; H, 10.12%. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90%.

5-Methyl-7-phenylthio-5-hepten-2-one (11)

A solution of benzenethiol (0.22 g, 2.0 mmol) in hexane (1.0 ml) was added to a solution of triethylaluminium (1.0 M in hexane, 2.0 ml, 2.0 mmol) at 0°C and the mixture was stirred at 25°C for 30 min. A solution of 1 (0.12 g, 1.0 mmol) in dichloromethane (3.0 ml) was added dropwise and the resulting mixture was stirred at 25°C. After 8 h, workup followed by TLC purification (hexane : ethyl acetate = 5:1) gave 11 (Rf = 0.5-0.6, 176 mg) in 75% yield: Bp 106-109°C/0.4 Torr; ^{1}H-NMR (CCl$_4$) δ 1.51 (s, 2.4H), 1.65 (s, 0.6H), 2.00 (s, 3H), 2.1-2.5 (m, 4H), 3.40 (d, *J* = 7 Hz, 1.6H), 3.45 (d, *J* = 7 Hz, 0.4H), 5.20 (t, *J* = 7 Hz, 1H), 7.0-7.3 (m, 5H); IR 2870, 1700, 1570, 1470, 1430, 1150, 735, 685 cm^{-1}; MS m/e (rel intensity) 234 (M$^+$, 3), 168 (7), 167 (5), 126 (6), 125 (53), 110 (6), 109

(6), 107 (6), 81 (15), 43 (100). Found: C, 71.86; H, 7.93%. Calcd for $C_{14}H_{18}OS$: C, 71.75; H, 7.74%.

5-Methyl-7-dimethylphenylsilyl-5-hepen-2-one (12)
To a solution of dimethylphenylsilyllithium in THF (0.47 M, 8.5 ml, 4.0 mmol) was added diethylaluminium chloride (1.0 M in hexane, 4.0 ml, 4.0 mmol) at 0°C. After stirred at 25°C for 25 min, a solution of **6** (0.25 g, 2.0 mmol) in THF (2.0 ml) was added and the mixture was stirred for 10 h. Workup followed by TLC purification gave 12 (0.23 g, 47% yield): ^{1}H-NMR (CCl_4) δ 0.24 (s, 6H), 1.1-1.7 (m, 5H), 1.8-2.4 (m+s (δ 1.97), 7H), 5.1 (t, J = 8 Hz, 1H), 7.1-7.8 (m, 5H); IR 2920, 1700, 1420, 1240, 1150, 1105, 830 cm^{-1}; MS m/z (rel intensity) 260 (M^+, 22), 245 (11), 192 (22), 177 (45), 137 (17), 135 (100), 75 (97). Found: C, 74.01; H, 9.57%. Calcd for $C_{16}H_{24}OSi$: C, 73.78; H, 9.28%.

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