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THE REACTION OF LITHIUM TRIALKYLALKYNYLBORATES WITH OXIRANES

γ-HYDROXYKETONE SYNTHESIS AND STEREOSELECTIVE PREPARATION OF TRISUBSTITUTED ETHYLENES

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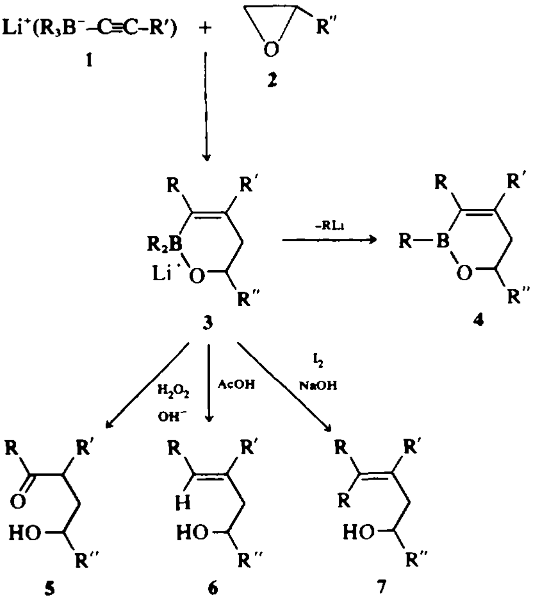
Abstract—Lithium trialkylalkynylborates (**1**) react with oxiranes (**2**) to give non-isolable intermediates **3** which subsequently afford either γ-hydroxyketones **5**, trisubstituted ethylenes of homoallylic alcohol type **6** or a tetrasubstituted ethylene **7** upon appropriate treatment with $NaOH/H_2O_2$, AcOH or $NaOH/I_2$, respectively. The reaction of oxiranes with **1** proceeds in high regioselectivity and the resulting homoallylic alcohols **6** are of nearly 100% (E) configuration. A straight chain γ-hydroxyketone **16** is obtained in the reaction of methyloxirane with the ate-complex (**1**), which has been prepared from lithium acetylide ethylenediamine complex and trihexylborane.

In continuation of the studies on synthetic applications of lithium trialkyl-1-alkynylborates (**1**),[1,2] the reaction with oxiranes **2** has been investigated in anticipation of two kinds of selectivity: one is the regioselective reaction at the methylene carbon of a monosubstituted oxirane **2** to afford γ-hydroxyketone and the other is stereoselective formation of a homoallylic alcohols **6** of (E) configuration.

This paper describes the reaction of the ate-complexes **1** with oxiranes proceeding through non-isolable intermediates **3**, which produce subsequently upon the appropriate work-up γ-hydroxyketones **5**, trisubstituted ethylene type homoallylic alcohols **6** and a tetrasubstituted ethylene **7**, respectively.

To a THF-hexane solution of lithium tributyl-1-heptynylborate **1** (R = Bu, R′ = Am) prepared from 1-lithio-1-heptyne and tributylborane, ethyloxirane **2** (R″=Et) was added at room temperature and the whole was heated at reflux for 10 h. When the mixture was directly subjected to GLC, only one product peak was detected. Heating of the concentrated mixture at 150–200° under reduced pressure gave the same product (45% yield), which was shown to be an oxaborinene **4a** (R = Bu, R′ = Am, R″ = Et) by the following data: the IR spectrum showed strong absorptions at 1610 and 1320 cm^{-1} suggesting the existence of C═C and B—O linkages, respectively. The NMR spectrum (Fig 1) showed the presence of 6 allylic protons and nonexistence of an olefinic proton, while the mass spectrum (Fig 2) was explained by the fragmentation scheme shown in Fig 3. The first fragmentation affording *m/e* 208 peak was ascribed to the loss of Bu—B═O fragment in analogy to the similar one of the reported 1,6,6-trialkyl-2-oxa-4-borinene.[3]

When the original mixture was directly treated with 1,2-dibromoethane, no gas evolution was observed. If the liberated butyllithium is present among the products, ethylene should hereby be evolved. GLC analysis of a mixture of lithium ethoxide and tributylborane showed the generation of ethyl dibutylborinate. These observations as well as the comparison of the mixture with the above isolated borinate **4a** strongly suggested that the



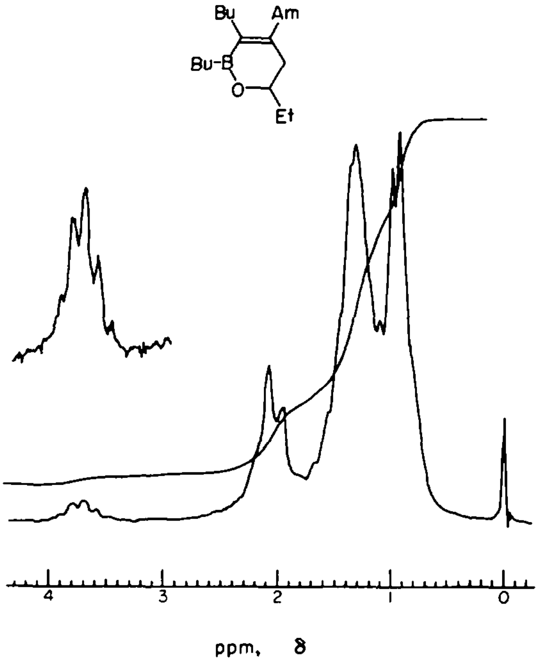


Fig 1. NMR spectrum of 4a (60 MHz in CCl_4).

initial reaction mixture contained the borates 3 instead of the borinates 4.

Appropriate work-up of the borates 3 led to the production of the following title compounds to indicate the synthetic utility of the organoboron reactions.

Preparation of γ-hydroxyketones 5. The above described mixture containing 3 gave 5 upon usual oxidative work-up with alkaline hydrogen peroxide as listed in Table 1. The yields are based on terminal acetylenes initially added. The γ-hydroxyketones 5 obtained in this way were easily cyclized and dehydrated to give 2,3-dihydrofurans and 2-alkylidenetetrahydrofurans under GLC condition analogous to the reported case of γ-hydroxyaldehyde.[4] GLC and MS analyses were performed with trimethylsilyl ethers of 5.

The C—O cleavage of alkyloxirane 2 thus occurred regioselectively at the unsubstituted C-3 side to afford the corresponding single isomer of 5. Cyclohexene oxide as a typical symmetrically disubstituted oxirane gave only 19% yield of 6-(2-hydroxycyclohexyl)-undecan-5-one (**5h**). The low yield is ascribed to the steric hindrance at the reaction site. As a by-product, 2-(1-heptynyl)-cyclohexanol (**8**) was obtained and was attributed to the reaction of cyclohexene oxide and 1-lithio-1-heptyne which was produced under the reaction condition.

Table 1. γ-Hydroxyketones 5

	R	R′	R″	Yield (%)	bp °(mm)
a	n-Bu	Am	Et	70	112–115 (5)
b	i-Pr	Am	Et	95	162–163 (26)
c	i-Pr	Ph	Et	59	136–140 (4)
d	i-Pr	Am	Ph	65	150–152 (5)
e	i-Pr	Am	Me	75	102–104 (6)
f	i-Pr	Am	H	82	127–131 (5)
g	n-Bu	Am	H	74	142–145 (5)

In this way, C-1 of the substrate acetylene is transformed into an acyl group containing the R of the borane and C-2 joins the oxirane 2 at the unsubstituted site to form the γ-hydroxyketones 5.

Trisubstituted ethylenes 6 *with rigorous stereochemistry*. Reported stereospecific protonolysis of a C—B bond by means of carboxylic acids[5] prompted us to examine the possibility of the

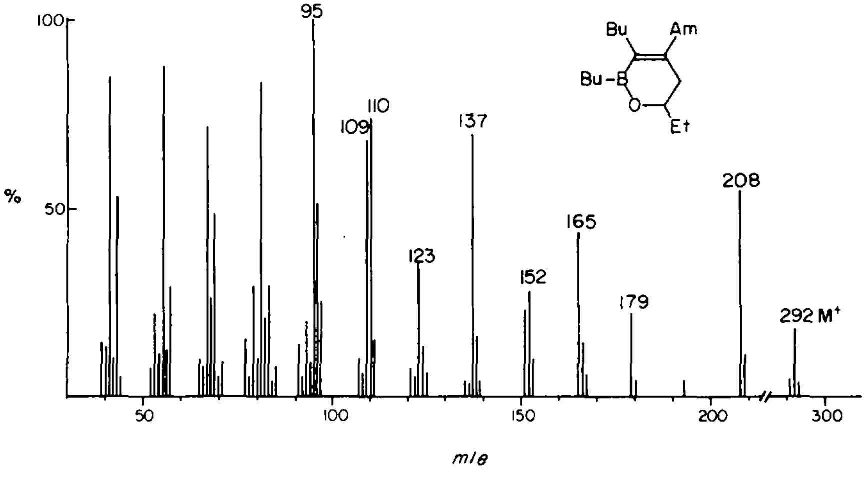


Fig 2. Mass spectrum of 4a (70 eV ionization potential).

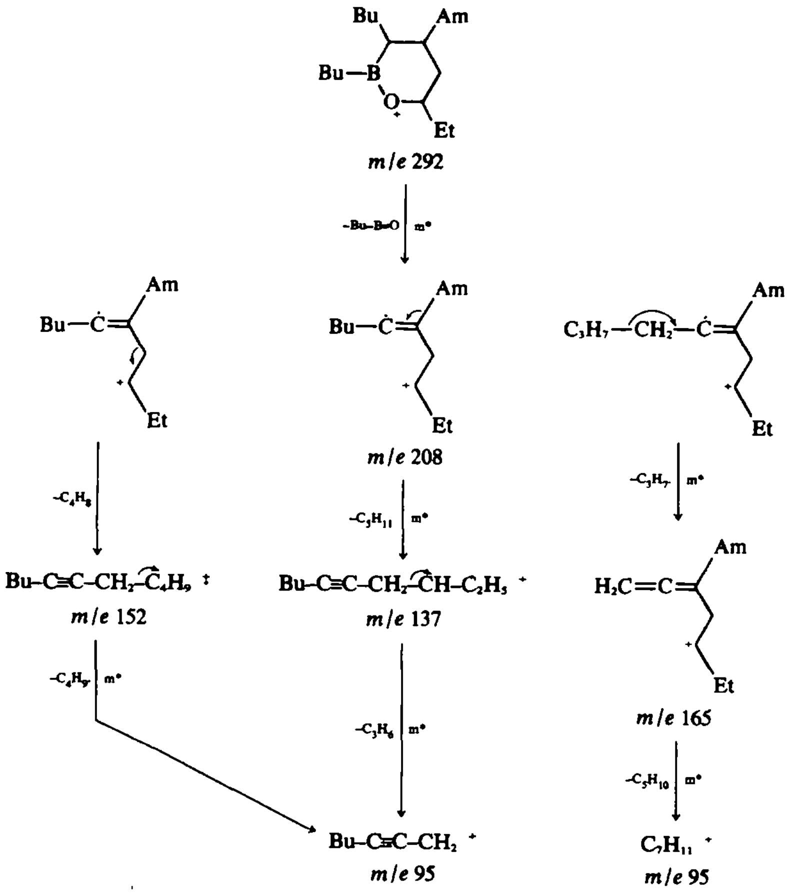
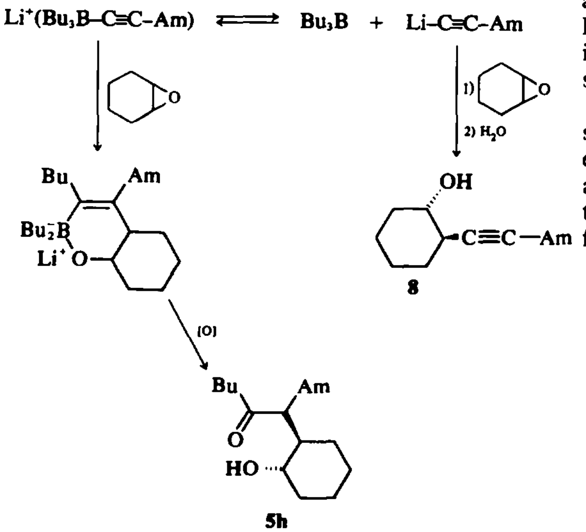


Fig 3.

intermediates 3 serving as a useful precursor for trisubstituted ethylenes with rigorous stereochemistry. The stereochemistry of the intermediates 3 reflects on that of the resulting olefins 6. The above-described mixture containing 3 was treated with glacial acetic acid under reflux for 5 h and treated with aqueous sodium hydroxide. Distillation gave γ,δ-unsaturated alcohols 6 as listed in Table 2. Structures of 6 were consistent with the spectra.



This sequence is a novel addition to the stereoselective synthesis of trisubstituted ethylenes[6] and schematically involves monoalkylation at C-1 and 2-hydroxyalkylation at C-2 of the acetylenes, both occurring selectively in a *trans* fashion.

A Tetrasubstituted olefin 7 and vinyl iodide

Table 2. Trisubstituted ethylenes 6

	R	R′	R″	Yield (%)	bp °(mm)
a	n-Bu	Am	Et	75	117–120 (5)
b	i-Pr	Am	Et	98	119–121 (6)
c	i-Pr	Am	Me	70	81–83 (6)
d	i-Pr	Am	H	80	90–91 (6)
e	n-Bu	Am	H	74	102–105 (4)

9. Treatment of the above-described mixture containing **3a** (R = Bu, R′ = Am, R″ = Et) with aqueous sodium hydroxide and then with iodine[7] gave 6-butyl-5-pentyl-5-decen-3-ol (**7**) in 39% yield. The reaction schematically consists of gem-dialkylation at C-1 and 2-hydroxyalkylation at C-2 of 1-heptyne. The low yield of **7** is due to a side reaction affording an olefinic iodide **9** in 25% yield.

The structure of **9** was identified by the spectra and the following transformation. Treatment of the tetrahydropyranyl ether of **9** with magnesium, followed by hydrolysis, gave the known homoallylic alcohol **6a**, to show that the configuration of **9** was (Z).

Two pathways leading to **9** are possible: one involving the *trans* addition of iodine to the olefinic linkage of **3a** to form **10** and the subsequent *cis* elimination of boron and β-iodine would give **9**. The other is a direct cleavage of the C—B bond of either **3a** or **4a** with iodine.[8]

The reaction of **4a** with iodine in the presence of base (3N NaOH) at −10° gave **9** as a major product (**9**: 73%, **7**: 11%). Treatment of the isolated **4a** first with an equimolar amount of butyllithium to form **3a** and then with iodine gave a mixture of **7** and **9** in a ratio of 14:3. Treatment of **4a** with iodine alone gave neither **7** or **9**.

These observations support that the vinyl iodide **9** originates from **4a** possibly via the direct C—B bond cleavage, while **7** from **3a** according to the established scheme.[7]

A Straight-chain γ-hydroxyketone 16

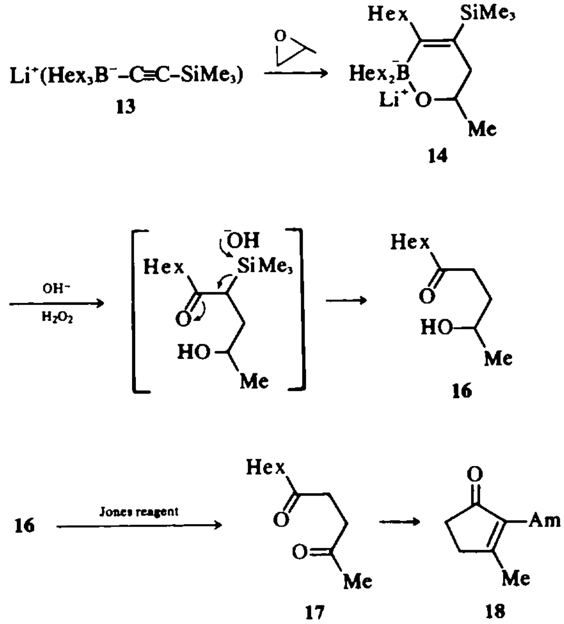
Convenient synthesis of dihydrojasmone. Most of the γ-hydroxyketones listed in Table 1 are secondary alcohols to be easily oxidized to γ-diketones which are useful precursors for cyclopentenone synthesis. Application of the present reaction to jasmone synthesis requires that R′ is hydrogen or hydrogen equivalent. Preparation of undecan-2-ol-5-one (**16**) was achieved in the following way.

As lithium trialkylethynylborate (**11**) was known to be disproportionated to the diborate **12**,[9] we first tried trimethylsilylacetylene[10] for this synthesis to obtain undecan-2-ol-5-one (**16**) in only 21% yield.

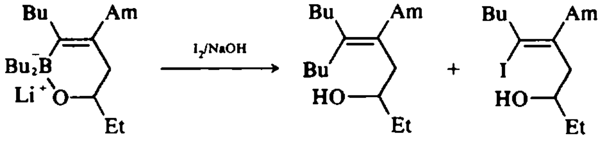
Another trial was based on the ate-complex **1** prepared from trihexylborane and lithioacetylene ethylenediamine complex.[11] The resulting mixture was treated with methyloxirane at 40°. Oxidative work-up gave **16** in 65% yield. Jones oxidation[12] of the hydroxyketone gave undecane-2,5-dione (**17**) in 95% yield, which was converted to dihydrojasmone (**18**) in 93% yield.[13]

$Li^+(R_3B^-{—}C{\equiv}C{—}H)$ $Li_2^+(R_3B^-{—}C{\equiv}C{—}^-BR_3)$

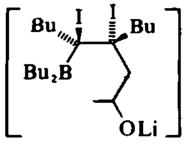
11 **12**



13 **14** **16** **17** **18**



3a **7** **9**



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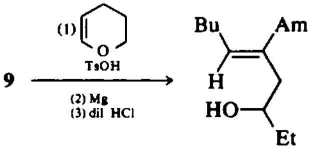

6a

EXPERIMENTAL

All b.ps were uncorrected. GLC was performed on Shimadzu GC-4BPT with 3 m × 3 mm column packed with 20% polyethyleneglycol and 25% HVSG on Chromosorb W-AW (80–100 mesh). MS were obtained on a Hitachi RMU-6L with 70 eV ionization potential, NMR with Me_4Si internal standard and CCl_4 solvent on Jeol C-60-H, Varian T-60 and Varian EM-360, UV on Hitachi EPS-2 and IR on Shimadzu IR-27G spectrometer.

Reaction of the Ate-complex (1) *with oxiranes*

General procedure. To a stirred soln of 1-alkyne (5·0 mmol) in THF (5·0 ml) at 0° maintained under N_2, a hexane soln of BuLi (5·0 mmol in 5·0 ml) was added and the mixture stirred at room temp for 30 min. The mixture was cooled to 0° and trialkylborane (5·0 mmol) was added, then the whole was stirred at room temp for 1 hr. To the soln, oxirane (6·0 mmol) was added and worked up as follows.

(1) The reaction of lithium triisopropyl (2-phenylethynyl) borate with ethyloxirane was performed by heating the mixture at reflux for 30 h.

(2) The following oxiranes were heated under reflux with lithium trialkylalkynylborate for the period shown in parentheses: cyclohexene oxide (30 h), ethyl- and phenyloxirane (15 h) and methyloxirane (5 h).

(3) With ethylene oxide, the gas was bubbled into the solution of **1** at room temp, then the resulting mixture was stirred at room temp for 3 h.

The mixture, thus obtained, was immediately subjected to the following treatment.

1, 6 *Dibutyl-3-ethyl-5-pentyl-2-oxa-5-borinene* (**4a**). The reaction of **1a** (20 mmol) with ethyloxirane (22 mmol) was performed by the general procedure. The mixture was transferred to a round-bottomed Claisen flask with a stirring bar in it. The solvent was distilled off under argon with stirring. Then the residue was heated at 150–200° under reduced pressure (3 mm) with continued stirring. Heavy foaming subsided at about 150° and colourless liquid was distilled off. The crude yield was 3·8 g, and GLC analysis revealed that the liquid contained 69% of **4a** (45% from 1-heptyne). Redistillation under partial decomposition gave **4a**: bp 142–147° (6 mm); IR (neat) 2940, 2855, 1610 ($\nu_{C=C}$), 1463, 1380, 1320 ($\nu_{B—O}$); NMR (CCl_4) δ 0·7–1·7 (26H, m), 2·1 (6H, m), 3·73 (7H, m). (High resolution MS. Found: *m/e* 292.1662. Calcd for $C_{19}H_{33}BO$: *m/e* 292.1671).

γ-*Hydroxyketones* (5)

General procedure. To the above described mixture containing **3**, 3N NaOH (5 ml) was added and then 30% H_2O_2 (5 ml) was added dropwise at room temp. The resulting mixture was heated at 50° for 3 h. The mixture was extracted with hexane, dried (Na_2SO_4), and concentrated. Chromatographic separation (silica gel-benzene, ether 9:1) gave **5** as listed in Table 1.

6-(2-*Hydroxybutyl*)*undecan*-5-*one* (**5a**). The yield was 0·85 g (70%); bp 112–115° (5 mm); IR (neat) 3430, 1703, 1470, 1384, 1023 cm^{-1}; MS of TMS ether *m/e* (rel. intensity %) 314 (M$^+$, 0·5), 299 (10), 285 (25), 145 (30), 131 (76), 85 (27), 75 (48), 73 (100). (Found: C, 74·15; H, 12·57. Calcd for $C_{15}H_{30}O_2$: C, 74·32; H, 12·48%).

2-*Methyl*-4-(2-*hydroxybutyl*)*nonan*-3-*one* (**5b**). The yield was 1·08 g (95%); bp 162–163° (26 mm); IR (neat) 3450, 1706, 1464, 1384, 1091 cm^{-1}; MS of TMS ether *m/e* (rel. intensity %) 300 (M$^+$, 0·5), 285 (5), 271 (16), 257 (22), 145 (22), 131 (47), 75 (43), 73 (100). (Found: C, 73·35; H, 12·40. Calcd for $C_{14}H_{28}O_2$: C, 73·63; H, 12·36%).

2-*Methyl*-4-*phenyloctan*-6-*ol*-3-*one* (**5c**). The yield was 0·69 g (59%); bp 136–140° (4 mm); IR (neat) 3450, 1709, 1602, 1495, 1469, 1390, 1383, 1123, 749, 700 cm^{-1}; MS of TMS ether, *m/e* (rel. intensity %) 306 (M$^+$, 0·2), 291 (3), 277 (7), 234 (16), 162 (36), 145 (39), 131 (98), 75 (39), 73 (100), 71 (67), 43 (71). (Found: C, 76·20; H, 9·54. Calcd for $C_{15}H_{22}O_2$: C, 76·88; H, 9·46%).

2-*Methyl*-4-*pentyl*-6-*phenylhexan*-6-*ol*-3-*one* (**5d**). The yield was 0·90 g (65%); bp 150–152° (5 mm); IR (neat) 3475, 1706, 1605, 1494, 1469, 1454, 1385, 1060, 759, 700 cm^{-1}; MS of TMS ether, *m/e* (rel. intensity %) 348 (M$^+$, 0·4), 333 (2), 305 (5), 193 (36), 179 (100), 91 (20), 75 (30), 73 (85), 43 (52). (Found: C, 78·11; H, 9·95. Calcd for $C_{18}H_{28}O_2$: C, 78·21; H, 10·12%).

2-*Methyl*-4-(2-*hydroxypropyl*)*nonan*-3-*one* (**5e**). The yield was 0·70 g (65%); bp 102–104° (6 mm); IR (neat) 3475, 1709, 1468, 1383, 1130 cm^{-1}; MS of TMS ether, *m/e* (rel. intensity %) 286 (M$^+$, 0·5), 271 (6), 243 (33), 131 (36), 117 (42), 75 (35), 73 (100). (Found: C, 72·61; H, 12·13. Calcd for $C_{13}H_{26}O_2$; C, 72·84; H, 12·23%).

2-*Methyl*-4-(2-*hydroxyethyl*)*nonan*-3-*one* (**5f**). The yield was 0·82 g (82%); b.p. 127–131° (5 mm); IR (neat) 3440, 1708, 1469, 1386, 1370, 1051 cm^{-1}; MS of TMS ether, *m/e* (rel. intensity %) 272 (M$^+$, 0·2), 257 (7), 229 (88), 113 (45), 103 (41), 75 (40), 73 (100), 69 (63), 43 (74). (Found: C, 72·14; H, 11·88. Calcd for $C_{12}H_{24}O_2$: C, 71·95; H, 12·08%).

6-(2-*Hydroxyethyl*)*undecan*-5-*one* (**5g**). The yield was 0·79 g (74%); bp 142–145° (5 mm); IR (neat) 3430, 1710, 1469, 1383, 1050 cm^{-1}; MS of TMS ether, *m/e* (rel. intensity %) 286 (M$^+$, 0·3), 271 (20), 229 (33), 139 (49), 117 (45), 113 (100), 103 (33), 85 (59), 75 (75), 73 (100). (Found: C, 72·63; H, 12·05. Calcd for $C_{14}H_{28}O_2$: C, 72·84; H, 12·23%).

6-(2-*Hydroxycyclohexyl*)*undecan*-5-*one* (**5h**), 2-(1-*heptynyl*)*cyclohexanol* (**8**) *and* 6-(2-*hydroxycyclohexyl*)-5-(*E*)-*undecene* (**6g**). The yield of **5h** was 0·25 g (19%), the yield of **8** was 0·10 g (10%) and the yield of **6g** was 1·51 g (12%). **5h**: bp 135–138° (3 mm); IR (neat) 3450, 1706, 1468, 1452, 1383, 1061 cm^{-1}; MS of TMS ether, *m/e* (rel. intensity %) 340 (M$^+$, 1), 325 (6), 283 (11), 228 (14), 193 (16), 170 (100), 75 (42), 73 (97). (Found: C, 76·22; H, 12·23. Calcd for $C_{17}H_{32}O_2$: C, 76·06; H, 12·02%). **8**; bp 133–135° (9 mm); IR (neat) 3410, 1452, 1383, 1068 cm^{-1}; MS of TMS ether, *m/e* (rel. intensity %) 266 (M$^+$, 16), 209 (26), 195 (29), 75 (43), 73 (100). (Found: C, 80·23; H, 11·49. Calcd for $C_{13}H_{22}O$: C, 80·35; H, 11·41%). **6g**: bp 111–114° (3 mm); IR (neat) 3475, 1465, 1450, 1382, 1036 cm^{-1}; MS *m/e* (rel. intensity %) 252 (M$^+$, 2), 234 (10), 191 (30), 163 (36), 110 (37), 55 (100), 41 (92). (Found: C, 80·60; H, 12·80. Calcd for $C_{17}H_{32}O$: C, 80·88; H, 12·78%).

Trisubstituted ethylene (6)

General procedure. To the above described mixture containing **3**, AcOH (4 ml) was added at room temp and the resulting mixture was heated at reflux for 10 h. The mixture was treated with 6N NaOH (10 ml) and was extracted with hexane, dried (Na_2SO_4), and concentrated under reduced pressure. Distillation in *vacuo* gave **6** as listed in Table 2.

5-*Pentyl*-5-(*E*)-*decen*-3-*ol* (**6a**). The yield was 0·85 g (75%); bp 117–120° (5 mm); IR (neat) 3400, 1469, 1383, 1111, 971 cm^{-1}; MS *m/e* (rel. intensity %) 226 (M$^+$, 1), 208 (4), 165 (15), 137 (20), 113 (29), 97 (48), 83 (63), 69 (76), 55

(100). (Found: C, 79·86; H, 13·51. Calcd for $C_{15}H_{30}O$: C, 79·57; H, 13·36%).

7-*Methyl*-5-*pentyl*-5-(*E*)-*octen*-3-*ol* (**6b**). The yield was 1·04 g (98%); bp 118–120° (6 mm); IR (neat) 3420, 1468, 1383, 1101 cm^{-1}; MS *m*/*e* (rel. intensity %) 212 (M^+, 2), 194 (3), 131 (28), 83 (100), 73 (62), 69 (36), 59 (48), 55 (70). (Found: C, 79·41; H, 13·26. Calcd for $C_{14}H_{28}O$: C, 79·18; H, 13·29%).

6-*Methyl*-4-*pentyl*-4-(*E*)-*hepten*-2-*ol* (**6c**). The yield was 0·69 g (70%) bp 81–83° (6 mm); IR (neat) 3380, 1468, 1383, 1121, 939 cm^{-1}; MS *m*/*e* (rel. intensity %) 198 (M^+, 4), 180 (2), 109 (26), 83 (100), 69 (45), 55 (54); NMR (CCl_4) δ 0·90 (3H, m), 0·96 (6H, d, J = 7 Hz), 1·14 (3H, d, J = 7 Hz), 1·31 (6H, m), 2·0 (2H, m) 2·02 (2H, d, J = 8 Hz), 2·38 (1H, s), 2·6 (1H, m), 5·07 (1H, d, J = 9 Hz). (Found: C, 78·43; H, 13·30. Calcd for $C_{13}H_{26}O$: C, 78·72; H, 13·21%).

5-*Methyl*-3-*pentyl*-3-(*E*)-*hexen*-1-*ol* (**6d**). The yield was 0·74 g (80%); bp 90–91° (6 mm); IR (neat) 3350, 1468, 1385, 1365, 1047 cm^{-1}; MS *m*/*e* (rel. intensity%) 184 (M^+, 3) 166 (2), 95 (26), 69 (34), 59 (37), 55 (36), 45 (37), 41 (37), 31 (100); NMR (CCl_4) δ 0·90 (3H, m), 0·95 (6H, d, J = 7 Hz), 1·27 (6H, m), 1·95 (2H, m), 2·26 (2H, t, J = 8 Hz), 2·50 (1H, m), 3·10 (1H, s), 3·53 (2H, t, J = 8 Hz), 5·50 (1H, d, J = 10 Hz). (Found: C, 77·93; H, 12·89. Calcd for $C_{12}H_{24}O$: C, 78·19; H, 13·13%).

3-*Pentyl*-3-(*E*)-*octen*-1-*ol* (**6e**). The yield was 0·75 g (74%); bp 102–105° (4 mm); IR (neat) 3440, 1469, 1461, 1382, 1110, 1048 cm^{-1}; MS *m*/*e* (rel. intensity %) 198 (M^+, 4), 180 (3) 139 (19), 137 (18), 109 (27), 55 (73), 45 (46), 43 (56), 41 (73), 31 (100). (Found: C, 78·51; H, 13·29. Calcd for $C_{13}H_{26}O$: C, 78·72; H, 13·21%).

6-*Butyl*-5-*pentyl*-5-*decen*-3-*ol* (**7**) *and* 6-*iodo*-5-*pentyl*-5-(*Z*)-*decen*-3-*ol* (**9**). To the above described mixture containing **3**, 3N NaOH (3 ml) was added and the resulting mixture was cooled at −10°. To the soln, I_2 (1·27 g 5 mmol) in THF (5 ml) was added. The resulting mixture was stirred at room temp for 30 min, extracted with hexane, dried (Na_2SO_4) and concentrated under reduced pressure. Chromatographic separation (silica gel-benzene) afforded 0·55 g (39%) of **7** and 0·43 g (25%) of **9**. The homoallylic alcohol **7**: bp 134–136° (4 mm); IR (neat) 3360, 1466, 1383, 1111, 972 cm^{-1}; MS of TMS ether, *m*/*e* (rel. intensity %) 354 (M^+, 0·3), 339 (0·7), 325 (0·8), 169·5 (double charge of *m*/*e* 339 fragment, 0·2), 131 (100), 73 (34). (Found: C, 80·96; H, 13·29. Calcd for $C_{19}H_{38}O$: C, 80·78; H, 13·56%). The vinyl iodide **9**: IR (neat) 3380, 1612, 1469, 1384, 1107, 972, 687 cm^{-1}; MS of TMS ether *m*/*e* (rel. intensity %) 424 (M^+, 0·04), 409 (0·5), 395 (0·3), 297 (0·9), 204, 5 (double charge of *m*/*e* 409 fragment, 0·08), 131 (100), 73 (38). (Found: C, 51·32; H, 8·55. Calcd for $C_{15}H_{29}IO$: C, 51·14; H, 8·30%).

Reaction of **4a** *first with butyllithium, and then with iodine*. To the ice-cooled soln of **4a** (0·107 g, 0·36 mmol) in THF (1·0 ml), a hexane soln of BuLi (0·36 mmol in 0·26 ml) was added under argon. The mixture was stirred for 30 min at room temp. To the soln, a THF soln of I_2 (0·10 g, in 0·3 ml) was added at −10°. The resulting mixture was stirred for 30 min at room temp, 3N NaOH (0·5 ml) was added and the mixture was stirred for 2 h. The resulting mixture was extracted with ether, dried (Na_2SO_4) and the solvents were evaporated. Preparative TLC gave 0·085 g of the mixture of **7** and **9**. GLC analysis of the mixture showed that the ratio of **7** to **9** was 4·7 : 1.

Reaction of **4a** *with* (1) *aq*. NaOH, (2) *iodine*. To an ice-cooled soln of **4a** (0·076 g, 0·26 mmol) in THF (1·0 ml), 0·2 ml of 3N NaOH was added under argon. Then THF (0·2 ml) soln of iodine (0·075 g, 0·29 mmol) was added at the same temp. The resulting mixture was stirred overnight at room temp, extracted with ether, dried (Na_2SO_4) and the solvents were evaporated. Preparative TLC gave 0·073 g of the mixture of **7** and **9**. GLC analysis showed that the ratio of **7** to **9** was 1 : 9.

Undecan-2-*ol*-5-*one* (**16**) *from lithium trihexyl*(2-*trimethylsilylethylyl*)*borate* (**13**). To an ice-cooled soln of trimethylsilylacetylene (0·98 g, 10 mmol) in THF (10 ml) maintained under N_2, a hexane soln of BuLi (10 mmol in 10 ml) was added. The mixture was stirred for 15 min at the same temp, then a THF soln of trihexylborane (10 mmol in 12 ml), which had been prepared by hydroboration of 1-hexene (2·5 g, 30 mmol), was added. The resulting mixture was stirred for 1 h at room temp. After exchange of the solvent to THF (10 ml), methyloxirane (1·08 g, 20 mmol) was added to the soln and the mixture was heated under reflux for 20 h. The resulting soln was oxidized with 3N NaOH (10 ml) and 30% H_2O_2 (10 ml). The resulting mixture was extracted with hexane, dried (Na_2SO_4) and concentrated under reduced pressure. Distillation *in vacuo* gave 0·39 g of **16**; bp 89–95° (7 mm); IR (neat) 3450, 1715, 1459, 1380, 1064 cm^{-1}; MS of TMS ether *m*/*e* (rel. intensity %) 258 (M^+, 3), 243 (49), 188 (10), 130 (74), 117 (100), 75 (68), 73 (93). (Found: C, 70·65; H, 11·69. Calcd for $C_{11}H_{22}O_2$: C, 70·92; H, 11·90%).

Undecan-2-*ol*-5-*one* (**16**) *from lithium acetylide ethylenediamine complex*. To a soln of lithium acetylide ethylenediamine complex (0·92 g, 10 mmol) in dioxane (40 ml) maintained under argon, trihexylborane (2·66 g, 10 mmol) was added at 0°. The resulting mixture was stirred for 1 h at room temp, then methyloxirane (0·59 g, 12 mmol) was added at room temp and the resulting mixture was heated under reflux for 10 h. The mixture was oxidized as described above, extracted with hexane, dried (Na_2SO_4) and concentrated under reduced pressure. Chromatographic separation (silica gel-benzene) gave 1·21 g (65%) of **16**.

Undecane-2,5-*dione* (**17**).[13] To an acetone soln of **16** (0·56 g, 3 mmol in 10 ml), Jones reagent was added until the reddish brown colour remained at 0°. The resulting mixture was stirred for additional 30 min and acetone was evaporated. The residual aqueous layer was made basic, extracted with ether, dried (Na_2SO_4) and concentrated under reduced pressure. The residue was chromatographed (silica gel-benzene) to give 0·52 g of **17** (95%); IR (neat) 1711, 1468, 1460, 1405, 1368, 1162, 1128, 1083 cm^{-1}; MS *m*/*e* (rel. intensity %) 184 (M^+, 3) 114 (62), 99 (40), 85 (15), 71 (54), 43 (100).

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