1-Bromo-2-ethoxycyclopropyllithium: A Synthetic Equivalent of 2-Lithio- or 3-Lithiopropenal. Application to the Synthesis of Juvenile Hormone (JH-II), β-Sinensal, and Jasmonoids

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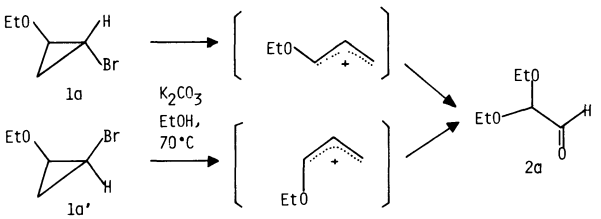
The ethyl vinyl ether-dibromocarbene adduct was lithiated with butyllithium at −95 °C in tetrahydrofuran. The resulting lithium carbenoid **3** was allowed to react with various electrophiles to give 1-substituted *trans*-1-bromo-2-ethoxycyclopropanes (**1**) in good yields. The trans relationship of Br and OEt groups was found particularly pertinent to the ethanolysis of **1** producing 2-substituted propenal diethyl acetal derivatives. The reaction has been applied to 1-methoxycyclohexene–dibromocarbene adducts, giving rise hereby 2-substituted 2-cyclohepten-1-one dimethyl acetals under ring enlargement. The transformation has been utilized in the synthesis of a homoterpenoid (JH-II) or a terpenoid (β-sinensal) structure by S_N2' substitution of allylic acetates with lithium dimethylcuprate(I) or iron pentacarbonyl respectively. The reaction products of **3** with aldehydes are oxidized with dimethyl sulfoxide to give cyclopropyl ketones whose ethanolysis in the presence of boron trifluoride ether complex gives β-bromo γ-keto aldehyde acetals. Debromination followed by acidic hydrolysis produces γ-keto aldehydes serving as precursors of dihydrojasmone and *cis*-jasmone.

Cyclopropane ring cleavage provides highly efficient methods for stereoselective and often stereospecific transformation.[1] The synthetic application heavily depends on the accessibility of appropriately substituted cyclopropanes, which are often prepared *via* lithium carbenoids.[2] Lithium-halogen exchange reaction of *gem*- dihalocyclopropanes at low temperature provides the requisite carbenoids. The present paper deals with the chemistry of a lithium carbenoid derived from the ethyl vinyl ether-dibromocarbene adduct as applied to the synthesis of some terpenoids and related compounds.[3]

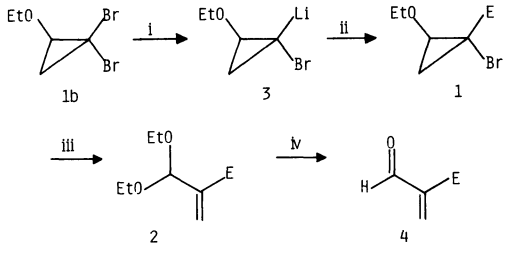
Reaction of 1-Bromo-2-ethoxycyclopropyllithium. Thermal rearrangement of 1,1-dihalo-2-alkoxycyclopropanes to 2-halopropenal derivatives is well-documented,[4] although the stereo-electronic aspect of the ring opening still remains unsolved. *trans*- and *cis*-1-Bromo-2-ethoxycyclopropanes (**1a**), (**1a'**) are prepared by reducing 1,1-dibromo-2-ethoxycyclopropane (**1b**) with tributyltin hydride.[5] As shown in Scheme 1 each isomer (1 mol dm^{-3}) was dissolved in ethanol and heated at 70 °C in the presence of potassium carbonate. The reaction was monitored by GLC assay. Pseudo first order rate constant for the trans isomer (**1a**) was 9.2×10^{-2} min^{-1}, whereas that for the cis isomer (**1a'**) was 7.8×10^{-4} min^{-1}. Thus, the transformation of **1a** to propenal diethyl acetal (**2a**) (93% GLC yield) proceeded about 100 times faster than the cis isomer (**1a'**). The difference of the reaction rate is attributed to the one of the energy-barrier of the ring-opening to give ethoxyallyl cation of W-form and sickle one, since the cyclopropyl halide-allyl cation transformation proceeds under orbital control.[11]



Scheme 1.

The favored isomers **1**[6] (Scheme 2) are prepared by means of the carbenoid **3** obtained by bromine–lithium exchange reaction of 1,1-dibromo-2-ethoxycyclopropane[7] **1b** with butyllithium. Treatment of the resulting carbenoid **3** at −95 °C with an electrophile gave the corresponding adduct **1**, which was successively heated in ethanol in the presence of potassium carbonate to afford a diethyl acetal **2**. Acidic hydrolysis gave the aldehyde **4**. The results are summarized in Table 1. According to the present two-step procedure, the carbenoid **3** is synthetically equivalent to 2-lithiopropenal[8] and provides 2-substituted propenal derivatives which themselves are potentially useful synthetic intermediates.[9]

The methodology described herein has been applicable to cyclic enol ether-dibromocarbene adducts (Scheme 3). For example, lithiation of 1-methoxy-7,7-dibromonorcarane **5** with butyllithium at −95 °C and treatment of the resulting carbenoid **6**[10] with an electro-



Scheme 2.

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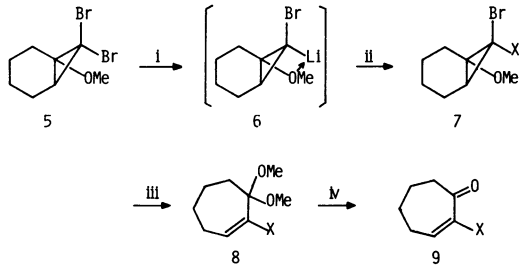
Table 1. Synthesis of 2-substituted propenal diethyl acetals and 2-substituted propenals

Entry	Electrophile	Yield (%)[a] of 2		Yield (%)[a] of 4	
1	H_2O	**2a**	93[b]		—
2	Br_2[c]	**2b**	93		—
3	Me_3SiCl	**2c**	87	**4c**	80[d]
4	PhSSPh	**2d**	74		—
5	n-$C_6H_{13}CHO$	**2e**	77[e]	**4e**	100

a) Isolated yield. b) GLC yield (5% Apieson L, 6% KOH). c) **2b** was prepared from **1b** under the ethanolysis conditions. d) Transformed into its 2,4-dinitrophenylhydrazone. e) Based on the consumed heptanal.



a: X = $SiMe_3$
b: X = CH(OH)n-C_6H_{13}
c: X = $CH_2CH{=}CMe_2$
d: X = n-C_5H_{11}
e: X = Me

i: n-BuLi, THF, -95°C, ii : Electrophile,
iii: MeOH, K_2CO_3, reflux, iv : H_3O^+.

Scheme 3.

phile afforded **7** whose substituents were appropriately disposed for the subsequent rearrangement.[11] Solvolysis of **7** in methanol in the presence of potassium carbonate gave cycloheptenone dimethyl acetal (**8**) under ring-enlargement. Although the reaction of **6** with trimethylsilyl chloride and heptanal took place with no difficulty, alkylation of the carbenoid turned out rather arduous. By employing hexamethylphosphoric triamide (HMPA) as the cosolvent,[1b] the alkylated products **9c—9e** were obtained. The results are shown in Table 2.

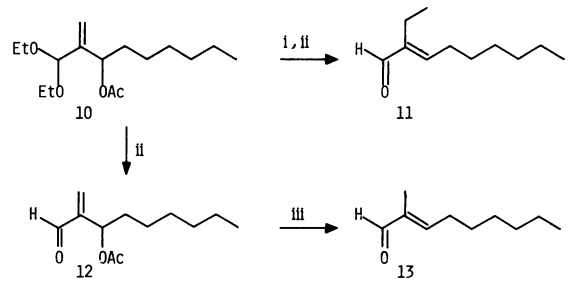
Synthesis of JH-II and β-Sinensal. The allylic acetate of type **10** is useful for the synthesis of α, β-unsaturated aldehyde moiety of homoterpenoid and terpenoid structure, such as **11** and **13** as shown in Scheme 4. For example, the allylic acetate **10** derived from **2e** was treated with lithium dimethylcuprate(I) in ether at −18 °C[12] to give, after acid-hydrolysis, (*E*)-2-ethyl-2-nonenal (**11**).[13] Selective S_N2' type methyl introduction is the key of the present synthesis.

As shown in Scheme 5, this result has been successfully applied to the synthesis of juvenile hormone (JH-II).[14] The aldehyde **20** (Scheme 6) was allowed to react with the carbenoid **3**, and the adduct was subjected to the two-step transformation of Scheme 2 to afford the acetal which was isolated as the acetate **14** in 84% overall

Table 2. Transformation of 1-methoxycyclohexene-dibromocarbene adducts into 2-substituted 2-cycloheptenones

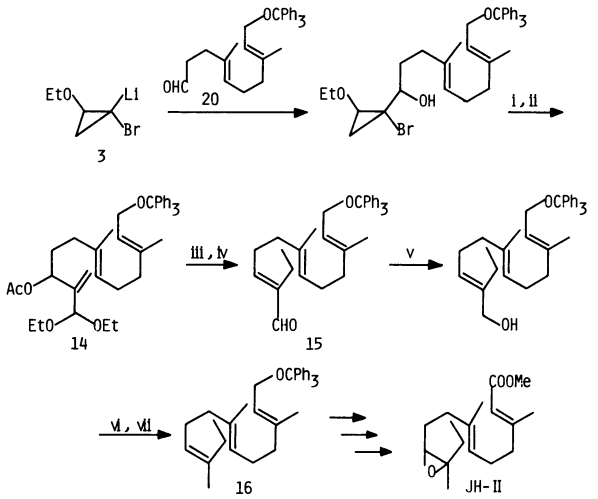
Entry	Electrophile	Yield (%)	
1	$ClSiMe_3$	**9a**	57
2	n-$C_6H_{13}CHO$	**9b**	57
3	$Me_2C{=}CHCH_2Br$	**9c**	46[a]
4	n-$C_5H_{11}I$	**9d**	40[a]
5	MeI	**9e**	41[a]

a) HMPA : THF = 10 : 1 was used as a solvent for the alkylation step.



i: Me_2CuLi, ii: H_3O^+, iii: $NaBCNH_3$ or $Fe(CO)_5$-DABCO-DMF.

Scheme 4.

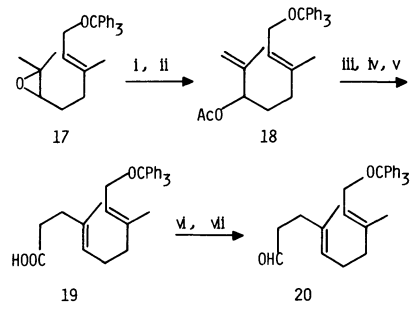


i: K_2CO_3, EtOH, 70°C, ii: Ac_2O, pyr., iii: Me_2CuLi,
iv: H_3O^+, v: $NaBH_4$, vi: SO_3-pyr., vii: $LiAlH_4$, reflux.

Scheme 5.

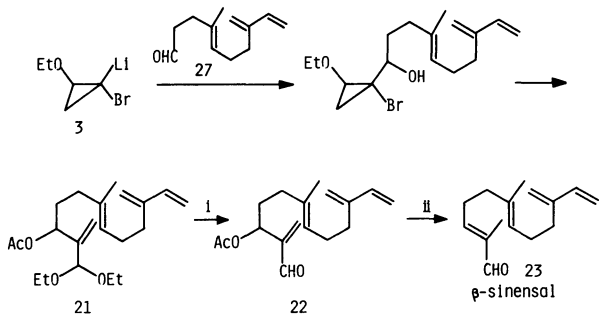
yield. Treatment of **14** with lithium dimethylcuprate(I) and then with 5% aq sulfuric acid in THF gave an aldehyde **15** in 83% yield. Deoxygenation of **15** was accomplished by sodium borohydride reduction followed by removal of the produced allylic hydroxyl group[15] to afford **16** (78% yield). Cleavage of the protecting trityl group[14c] and the subsequent route[14a] to the target molecule are already established.

As Shown in Scheme 4, the aldehyde **12** is also transformed into (*E*)-α,β-unsaturated aldehyde **13** by a formal S_N2' type introduction of hydride and elimination of acetoxyl group. For example, when **12** was mixed with 0.5 mol of sodium cyanotrihydroborate in metha-



i: $LiNEt_2$, ii: Ac_2O-Py, iii: $LiN(i\text{-}Pr)(C_6H_{11})$, t-$BuMe_2SiCl$, iv: 70°C, v: AcOH, vi: $LiAlH_4$, vii, PCC.

Scheme 6.

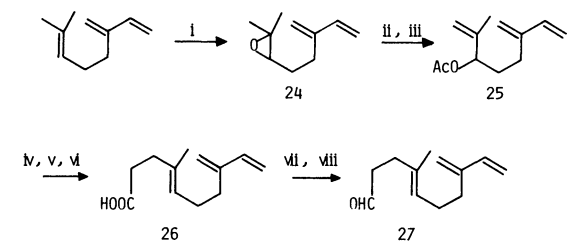


Scheme 7.

nol–acetic acid 10:1 at 0 °C, saturation of the olefinic bond occurred preferentially to afford the aldehyde **13** in 61% yield. The reduction is much more efficiently performed by means of iron pentacarbonyl and 1,4-diazabicyclo[2.2.2]octane (DABCO) in wet *N,N*-dimethylformamide (DMF) (96% yield).[16] It should be noted that the incipient 1,1-disubstituted ethylenic linkage is reduced to produce a new, triply substituted one which remains intact under the conditions.

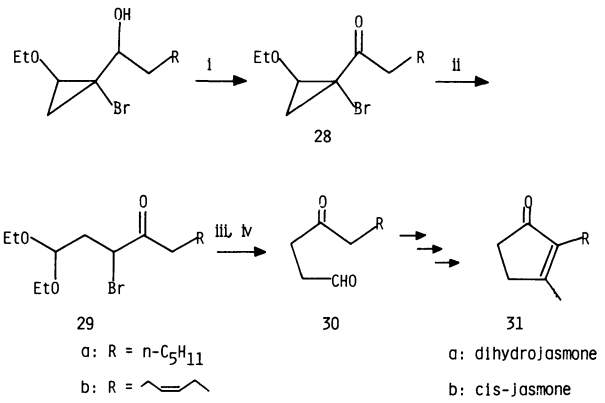
The applicability of the new method has been demonstrated in the synthesis of β-sinensal (**23**) (Scheme 7), an important constituent of the odor and taste of Chinese orange oil (*Citrus sinensus L.*).[17] A triene aldehyde **27** (Scheme 8) was subjected to the carbenoid reaction as described in Scheme 2 to give the acetal acetate **21**. Deprotection of the aldehyde group with 5% aq sulfuric acid in THF resulted in polymerization of the large part of the product due to the acid-sensitive 1,3-diene moiety. The hydrolysis with silica gel-10% aq oxalic acid (10:1) suspended in dichloromethane[18] at room temperature gave the aldehyde **22** in 87% yield. Reductive removal of the acetoxyl group was selectively attained with iron pentacarbonyl–DABCO in wet DMF and β-sinensal (**23**) was produced in 95% yield.

Transformation of the Adducts of the Carbenoid 3 with Aldehydes into γ-Keto Aldehydes. Synthesis of Dihydrojasmone and cis*-Jasmone.* Ring-cleavage reaction of cyclopropyl ketone derivatives[19] has been also applicable to the homologation of carbon skeleton as shown in Scheme 9. Oxidation of **1e** type adducts of Scheme 2 was best carried out to give acid-lable *r*-1-bromo-*t*-2-ethoxy-1-heptanoyl-cyclopropane (**28a**) by the Swern's method.[20] Without isolation, **28a** was treated with



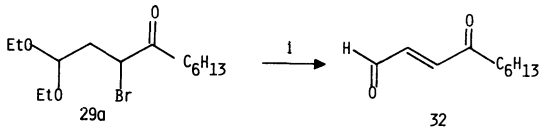
i: MCPBA, ii: $LiNi\text{-}Pr_2$, iii: Ac_2O-pyr., iv: $LiNi\text{-}Pr_2$, t-$BuMe_2SiCl$, v: 70°C, vi: $PhCH_2NMe_3F$, aq MeOH, vii: $LiAlH_4$, viii: PCC.

Scheme 8.



i: DMSO, $(CF_3CO)_2O$, Et_3N, ii: EtOH, BF_3:OEt_2 or AcOH, iii: $CrCl_3$-$LiAlH_4$, iv: H_3O^+

Scheme 9.



i: 15% H_2SO_4-THF

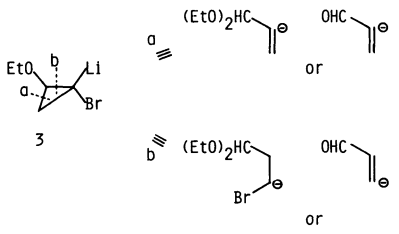
Scheme 10.

catalytic amount of boron trifluoride ether complex at room temperature to give a bromo acetal ketone **29a**. Reductive debromination with $CrCl_3$–$LiAlH_4$[21] followed by hydrolysis gave 4-oxodecanal (**30a**)[22], which was readily transformed into dihydrojasmone (**31a**)[23].

Starting with (*Z*)-4-heptenal,[24] *cis*-jasmone was prepared by the similar sequence of reactions. The ring-opening of the cyclopropyl ketone **28b** with BF_3–OEt_2 proceeded very slowly and gave complex mixture. On treatment with a catalytic amount of acetic acid, however, **28b** was converted to a bromo acetal ketone **29b** at room temperature in fairly good yield. The compound **29b** was reduced to give the γ-keto aldehyde **30b**,[22] a key precursor of *cis*-jasmone (**31b**).[25]

Acid hydrolysis of **29a** resulted in the formation of an α, β-unsaturated γ-keto aldehyde **32** (56% yield) (Scheme 10).

In conclusion, 1-bromo-2-ethoxycyclopropyllithium (**3**) is found to be a useful C_3 homologation reagent. The sequence shown in Scheme 2 clearly demonstrates that the lithium carbenoid **3** is a synthetic equivalent of 2-lithiopropenal or its acetal. In contrast, Scheme 9



together with Scheme 10 shows that **3** is attached to an aldehyde at the carbon (3) of propenal or 3-bromopropanal. This ambient reactivity of **3** is controlled by the ring-opening operation (*a* or *b*) of **1** derived from **3**, and the applicability of the reagent has been illustrated in the synthesis of terpenoids and jasmonoids.

Experimental

All temperatures recorded are uncorrected. Distillation of small amount of samples (less than 1 g) was carried out with Kugelrohr. ^{1}H-NMR spectra (tetramethylsilane as an internal standard unless otherwise noted) were obtained on a Varian EM 390 spectrometer or JOEL PMX-60 spectrometer, chemical shifts being given in ppm unit. IR spectra of neat liquid film samples (unless otherwise noted) on a Shimadzu IR-27G spectrometer, MS on a Hitachi RMU-6L spectrometer, and exact mass on a Hitachi M-80 spectrometer, Gas-liquid phase chromatography (GLC) analyses were performed with a Yanagimoto GCG-550F chromatograph. Preparative TLC plates were prepared with Merck Kiesel-gel PF_{254}. Column chromatography was carried out with silica gel (Wakogel C-100) at atmospheric pressure.

*Synthesis of 2-(Diethoxymethyl)-1-nonen-3-ol (**2e**) and 3-Hydroxy-2-methylenenonanal (**4e**). A Typical Procedure for the Reaction of 1-Bromo-2-ethoxycyclopropyllithium (**3**) with an Electrophile*: Butyllithium (1.67 M† hexane solution, 7.2 ml, 12.0 mmol) was added to a THF (50 ml) solution of 1,1-dibromo-2-ethoxycyclopropane (2.93 g, 12.0 mmol) at −95 °C over a period of 5 min. After stirring for 10 min heptanal (1.12 g, 9.8 mmol) was added at −95 °C, and the reaction mixture was stirred at −95 °C for 30 min, then at room temperature for 20 min. Workup gave **1e** which was dissolved in ethanol (15 ml), and the mixture was stirred with potassium carbonate (6.90 g, 50 mmol) for 1 h under reflux. Workup and purification by column chromatography (hexane–ether=3:1) gave **2e** (1.84 g, 77% yield): bp 100—105 °C (bath temperature)/14 Torr**; ^{1}H-NMR (CCl_4) δ= 0.6—1.6 (m+t, 19 H), 2.20 (br s, 1H), 3.2—3.8 (m, 4H, $CH_3C\underline{H}_2O$), 4.05 (t, *J*=5 Hz, 1H, C<u>H</u>–OH), 4.80 (br s, 1H), 5.17 (br s, 2H, =C<u>H</u>$_2$); IR 3450, 2940, 2870, 1460, 1365, 1105, 1050, 923 cm^{-1}; MS *m/z* (rel intensity) 199 (9), 154 (4), 115 (56), 103 (53), 85 (100), 55 (47), 43 (69).

A mixture of the acetal **2e** in THF (5 ml) and 5% aq sulfuric acid (5 ml) was stirred at room temperature for 5 min. Workup followed by purification by column chromatography gave **4e** (1.32 g, quantitative yield): bp 115—120 °C (bath temperature)/20 Torr; ^{1}H-NMR δ=0.7—1.6 (m. 13H), 2.20 (br s, 1H), 4.37 (t, *J*=6 Hz, 1H), 5.95 (d, *J*=1 Hz, 1H), 6.38 (d, *J*=1 Hz, 1H), 9.52 (s, 1H); IR 3450, 1685, 955, 908, 790 cm^{-1}; MS *m/z* (rel intensity) 170 (M$^+$, 2), 123 (7), 100 (13), 85 (100), 55 (40), 43 (80). Found: C, 70.63; H, 10.86%. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66%.

*r-1-Bromo-t-2-ethoxy-1-trimethylsilylcyclopropane (**1c**)*: Bp 61—63 °C (bath temperature)/2 Torr; ^{1}H-NMR (CCl_4, internal standard CH_2Cl_2) δ=0.15 (s, 9H), 1.04—1.26 (m+t(δ=1.15, *J*=7.1 Hz), 5H), 3.52 (q, *J*=7.1 Hz, 2H), 3.68 (dd, *J*=6.5, 4.5 Hz, 1H); IR 2980, 2890, 1335, 1240, 1120. 1050, 840 cm^{-1}; MS *m/z* (rel intensity) 209 (4), 207 (4), 157 (24), 139 (10), 137 (10), 113 (45), 75 (24), 73 (100).

*2-Bromo-3,3-diethoxypropene (**2b**)*[26]: Bp 120—130 °C (bath temperature)/20 Torr; ^{1}H-NMR (CCl_4, internal standard, $CHCl_3$) δ=0.95 (t, *J*=7 Hz, 6H), 3.1—3.5 (m, 4H), 4.57 (br, s, 1H), 5.43 (br, s, 1H), 5.87 (br, s, 1H); IR 2980, 2880, 1630, 1370, 1050, 905 cm^{-1}; MS *m/z* (rel intensity) 165 (32), 163 (34), 137 (88), 135 (99), 109 (21), 108 (26), 103 (100), 75 (52).

*2-Trimethylsilyl-3,3-diethoxypropene (**2c**)*: Bp 88—90 °C/26 Torr; ^{1}H-NMR (CCl_4, $CHCl_3$ internal standard) δ=0.03 (s, 9H), 1.10 (t, *J*=6.5 Hz, 6H), 3.2—3.7 (m, 4H), 4.80 (br s, 1H), 5.45 (m, 1H), 5.80 (m, 1H); IR 2980, 2880, 1240, 1110, 940, 840 cm^{-1}; MS *m/z* (rel intensity) 157 (17), 113 (28), 103 (100), 75 (51), 73 (44). Hydrolysis of **2c** with aq sulfuric acid gave 2-trimethylsilylpropenal (*4c*) which was characterized as the 2,4-dinitrophenylhydrazone: mp 153.5—154 °C (orange needle, 95% ethanol–ethyl acetate); ^{1}H-NMR ($CDCl_3$, $CHCl_3$ internal standard); δ=0.12 (s, 9H), 5.88 (d, *J*=1.8 Hz, 1H), 6.03 (d, *J*=1.8 Hz, 1H), 7.70 (d, *J*=10 Hz, 1H), 7.79 (br s, 1H), 8.21 (dd, *J*=10, 3 Hz, 1H), 9.00 (d, *J*=3 Hz, 1H), 11.0 (br s, 1H); IR 3280, 2930, 2850, 1615, 1595, 1510, 1315, 1130, 1080, 840 cm^{-1}; MS *m/z* (rel intensity) 308 (M$^+$, 1), 148 (17), 147 (100), 75 (24), 73 (26), 66 (12). Found: C, 46.94; H, 5.23, N, 18.36%. Calcd for $C_{12}H_{16}N_4O_4$: C, 46.74; H, 5.23; N, 18.17%.

*2-Phenylthio-3,3-diethoxypropene (**2d**)*: Bp 115—125 °C (bath temperature)/0.06 Torr; ^{1}H-NMR (CCl_4) δ=1.16 (t, *J*=7 Hz, 6H), 3.3—3.7 (m, 4H), 4.85 (s, 2H), 5.51 (s, 1H), 7.2—7.5 (m, 5H); IR 3060, 2980, 2880, 1610, 1480, 1445, 1380, 1110, 1010, 880, 750 cm^{-1}; MS *m/z* (rel intensity) 238 (M$^+$, 11), 194 (25), 147 (25), 185 (31), 103 (100), 91 (29), 75 (74); Found: C, 65.54; H, 7.50%. Calcd for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61%.

*2-Trimethylsilyl-2-cyclohepten-1-one (**9a**)*. A hexane solution (1.7 M) of butyllithium (1.64 ml, 2.8 mmol) was added drop by drop to 7,7-dibromo-1-methoxynorcarane[27] (0.71 g, 2.5 mmol) in THF (10 ml) at −95 °C. After 10 min's aging chlorotrimethylsilane (1 ml, *ca.* 8 mmol) was added and the reaction mixture was stirred for 2 h at −95 °C, allowed to warm up to room temperature and treated with water. The organic layer was extracted with ether, dried (sodium sulfate) and concentrated *in vacuo*. The residue was heated in methanol (7 ml) to reflux with potassium carbonate (2.1 g, 15 mmol) for 2 h. Usual workup gave **8a**, which was dissolved in a mixture of THF (5 ml) and 5% aq sulfuric acid (5 ml) and stirred at room temperature for 20 min. Workup followed by purification by column chromatography gave **9a** (0.31 g, 57% yield): bp 147—150 °C (bath temperature)/15 Torr; ^{1}H-NMR (CCl_4, CH_2Cl_2 internal standard) δ=0.07 (s, 9H), 1.6—1.8 (m, 4H), 2.4—2.6 (m, 4H), 6.58 (t, *J*=6 Hz, 1H); IR 2940, 2865, 1660, 1595, 1450, 1235, 945, 840 cm^{-1}; MS *m/z* (rel intensity) 182 (M$^+$, 82), 167 (1), 155 (4), 137 (3), 75 (11), 73 (8), 40 (100). Found: C, 65.93; H, 10.09%. Calcd for $C_{10}H_{18}OSi$: C, 65.87; H, 9.95%.

*2-(1-Hydroxyheptyl)-2-cyclohepten-1-one (**9b**)*: Bp 90—110 °C (bath temperature)/1 Torr; ^{1}H-NMR (CCl_4) δ=0.88 (t, *J*=6 Hz, 3H), 1.1—1.6 (m, 10H), 1.6—2.0 (m. 4H), 2.3—3.0 (m, 5H), 4.0—4.3 (m, 1H), 6.52 (t, *J*=6 Hz, 1H); IR 3450, 2930, 2860, 1660, 1460, 1370, 900 cm^{-1}; MS *m/z* (rel intensity) 224 (M$^+$, 2), 206 (9), 149 (16), 139 (100), 121 (10), 111 (13), 97 (17), 93 (15), 83 (14), 79 (16). Found: C, 74.78; H, 10.86%. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78%.

*2-(3-Methyl-2-butenyl)-2-cyclohepten-1-one (**9c**)*: Bp 115—125 °C (bath temperature)/0.15 Torr; ^{1}H-NMR (CCl_4) δ=1.6—1.9 (m+s (δ=1.60)+s (δ=1.70), 10H), 2.2—2.6 (m, 4H), 2.83 (d, *J*=7.8 Hz, 2H), 5.02 (t, *J*=7.8 Hz, 1H), 6.30 (t,

† 1 M=1 mol dm^{-3}; ** Torr=133.322 Pa.

J=6.3 Hz, 1H); IR 2920, 2850, 1665, 1455, 1370, 850 cm^{-1}; MS m/z (rel intensity) 178 (M^+, 33), 163 (100), 135 (53), 107 (33), 95 (40), 93 (45), 79 (47). Found: C, 81.05; H, 10.44%. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18%.

*2-Pentyl-2-cyclohepten-1-one (**9d**)*: Bp 160—170 °C (bath temperature)/0.3 Torr; ^{1}H-NMR (CCl_4) δ=0.90 (t, J=6 Hz, 3H), 1.0—1.5 (m, 6H), 1.5—2.0 (m, 4H), 2.0—2.6 (m, 6H), 6.33 (t, J=6 Hz, 1H); IR 2970, 1665, 1270, 885 cm^{-1}; MS m/z (rel intensity) 180 (M^+, 14), 151 (40), 133 (30), 112 (40), 95 (100), 81 (37), 67 (100). Found: C, 79.89; H, 11.44%. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18%.

*2-Methyl-2-cyclohepten-1-one (**9e**)*[28]: Bp 135—140 °C (bath temperature)/12 Torr; ^{1}H-NMR (CCl_4) δ=1.6—1.8 (m+d (δ=1.76, J=1.5 Hz), 7H), 2.2—2.6 (m, 4H), 6.44 (tq, J=1.5, 6 Hz, 1H); IR 2950, 1660, 1050, 850, 790 cm^{-1}; MS m/z (rel intensity) 125 (M^++1, 7), 124 (M^+, 53), 95 (58), 81 (46), 67 (100), 55 (31).

*3-Acetoxy-2-diethoxymethyl-1-nonene (**10**).* Acetal alcohol **2e** was acetylated with excess acetic anhydride and pyridine at room temperature for 12 h: bp 110—116 °C (bath temperature)/0.5 Torr; ^{1}H-NMR (CCl_4) δ=0.7—1.8 (m, 19H), 1.98 (s, 3H), 3.2—3.6 (m, 4H), 4.80 (br s, 1H), 5.0—5.3 (m, 3H); IR 2950, 2880, 1740, 1360, 1226, 1050 cm^{-1}; MS m/z (rel intensity) 181 (52), 103 (100), 85 (20), 75 (45), 43 (82). Found: C, 67.09; H, 10.51%. Calcd for $C_{16}H_{30}O_4$: C, 67.09; H, 10.56%.

*(E)-2-Ethyl-2-nonenal (**11**).* To lithium dimethylcuprate(I) (1.2 mmol) in ether (5 ml), **10** dissolved in ether (1 ml) was added at −18 °C and stirred for 30 min. The reaction mixture was poured into aq ammonium chloride and extracted with ether. The organic layer was concentrated and treated with aq 5% sulfuric acid (5 ml)–THF (5 ml) at room temperature for 5 min. Workup and purification by preparative TLC (hexane–ether=5:1) gave (*E*)-2-ethyl-2-nonenal (**11**) (82 mg, 61% yield) along with the (*Z*)-isomer (less than 5%). **11** gave: bp 118—120 °C (bath temperature)/18 Torr; ^{1}H-NMR (CCl_4) δ=0.90 (t, J=6.0 Hz, 3H), 0.94 (t, J=7.6 Hz, 3H), 1.1—1.8 (m, 7H), 2.0—2.6 (m, 4H), 6.28 (t, J=7.6 Hz, 1H), 9.28 (s, 1H); IR 2950, 2875, 2730, 1685, 1640, 1460, 1080, 792 cm^{-1}; MS m/z (rel intensity) 168 (M^+, 8), 149 (6), 139 (12), 111 (33), 85 (37), 79 (33), 55 (74), 41 (100). Found: m/z 168.1540. Calcd for $C_{11}H_{20}O$: M^+ 168.1514. (*Z*)-2-Ethyl-2-nonenal gave ^{1}H-NMR (CCl_4) δ=0.6—1.8 (m, 13H), 1.9—2.8 (m, 4H), 6.30 (t, J=8.0 Hz, 1H), 10.06 (s, 1H).

*Hydrolysis of **10** to 3-Acetoxy-2-methylenenonenal (**12**).* Diethyl acetal **10** (1.43 g, 5.0 mmol) was treated with THF (15 ml)-aq 5% sulfuric acid (15 ml) at room temperature for 80 min. Workup gave pure aldehyde **12** (1.06 g, quantitative yield): ^{1}H-NMR (CCl_4) δ=0.87 (t, J=5.9 Hz, 3H), 1.1—1.8 (m, 10H), 2.00 (s, 3H), 5.47 (t, J=7.5 Hz, 1H), 5.98 (s, 1H), 6.25 (s, 1H), 9.48 (s, 1H).

*Synthesis of (E)-2-Methyl-2-nonenal (**13**).*[29] *Procedure A*: To the compound **12** (50 mg, 0.23 mmol) dissolved in methanol (1 ml)–acetic acid (0.1 ml), sodium cyanotrihydroborate (11 mg, 0.18 mmol) was added at room temperature for 2 h. Workup with brine and purification by preparative TLC gave **13** (22 mg, 61% yield).

Procedure B: Iron pentacarbonyl (0.25 ml, 1.9 mmol) was added to DABCO (0.11 g, 0.94 mmol) in wet *N*,*N*-dimethylformamide (DMF:H_2O=98:2) (1 ml). To the resulting dark-brown solution, the compound **12** (0.10 g, 0.46 mmol) was added and allowed to react for 1 h. Quenching was effected by addition of satd ethereal solution of iodine and water. Workup and purification by preparative TLC (hexane–ether=7:1, R_f 0.40—0.55) gave **13** (67 mg, 96% yield): ^{1}H-NMR (CCl_4) δ=0.90 (t, J=6.0 Hz, 3H), 1.2—1.7 (m, 8H), 1.71 (s, 3H), 2.32 (q, J=7.0 Hz, 2H), 6.34 (t, J=7.5 Hz, 1H), 9.31 (s, 1H), IR 2940, 2730, 1685, 1640, 1465, 1225, 1070, 820, 790, 725 cm^{-1}; MS m/z (rel intensity) 154 (M^+, 5), 135 (5), 97 (50), 84 (46), 71 (68), 55 (75), 43 (100).

*Synthesis of (E)-4-Methyl-8-methylene-4,9-decadienal (**27**).* Myrcene (10.0 g, 73 mmol) was transformed with *m*-chloroperbenzoic acid (15.9 g, 73.5 mmol) in chloroform (150 ml) at 0 °C for 5 h into 6,7-epoxy-7-methyl-3-methylene-1-octene (**24**) (6.7 g, 60% yield): bp 79—81 °C/9 Torr; ^{1}H-NMR (CCl_4) δ=1.22 (s, 3H), 1.26 (s, 3H), 1.63 (dt, J=6.0, 7.6 Hz, 2H), 2.34 (dt, J=4.5, 7.6 Hz, 2H), 2.57 (t, J=6.0 Hz, 1H), 4.9—5.4 (m, 4H), 6.33 (dd, J=11.4, 18.0 Hz, 1H); IR 3090, 2930, 1595, 1465, 1240, 1115, 990, 895 cm^{-1}; MS m/z (rel intensity) 152 (M^+, 5), 137 (8), 134 (8), 119 (16), 109 (18), 93 (29), 79 (100), 71 (57), 59 (57). Found: C, 78.99; H, 10.76%. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59%. The epoxide **24** (0.16 g, 1.05 mmol) was added to lithium diisopropylamide (1.5 mmol) in ether (4 ml) at 0 °C, and the reaction mixture was stirred for 15 h. To this solution, acetic anhydride (1 ml) and pyridine (0.5 ml) were added and stirred at room temperature for 2 h. Workup and purification by preparative TLC (hexane–ethyl acetate=5:1, R_f 0.55—0.65) gave an acetate **25** (0.13 g, 70% yield): bp 75—85 °C (bath temperature)/11 Torr; ^{1}H-NMR (CCl_4) δ=1.6—2.3 (m+d (δ=1.72, J=0.9 Hz), 7H), 1.99 (s, 3H), 4.8—5.3 (m, 7H), 6.27 (dd, J=11.4, 17.4 Hz, 1H); IR 3030, 2935, 1735, 1650, 1595, 1225, 1020, 900 cm^{-1}; MS m/z (rel intensity) 194 (M^+, 0.3), 152 (4), 134 (8), 119 (17), 105 (11), 93 (14), 91 (16), 79 (17), 43 (100). Found: C, 74.30; H, 9.45. Calcd for $C_{12}H_{18}O_2$: C, 74.19: H, 9.34%.

The acetate **25** (3.37 g, 17.3 mmol) was added to lithium diisopropylamide (34.7 mmol) at −78 °C and stirred for 1 h at −78 °C. To this solution, *t*-butylchlorodimethylsilane (5.22 g, 34.7 mmol) dissolved in THF (10 ml)–hexamethylphosphoric triamide (3 ml) was added, and the reaction mixture was warmed up gradually to room temperature, then heated at 70 °C for 2.5 h, after cooling poured into water and extracted with ether. The organic layer was concentrated. The residue was dissolved in methanol (20 ml) and treated with aq trimethylbenzylammonium fluoride (*ca.* 0.5 ml). Workup and purification by column chromatography gave a carboxylic acid **26** (2.76 g, 82% yield): bp 70—80 °C (bath temperature)/1 Torr; ^{1}H-NMR (CCl_4) δ=1.62 (br s, 3H), 2.1—2.5 (m, 8H), 4.9—5.3 (m, 5H), 6.27 (dd, J=11.4, 17.4 Hz, 1H), 11.10 (br s, 1H); IR 3100, 2650, 1710, 1595, 1450, 990, 895 cm^{-1}; MS m/z (rel intensity) 194 (M^+, 4), 134 (7), 121 (9), 109 (12), 93 (100), 81 (46), 67 (24). Found: C, 73.93; H, 9.49%. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34%.

The carboxylic acid **26** (0.075 g, 0.38 mmol) was reduced with lithium aluminum hydride (0.026 g, 0.67 mmol) in ether. Workup and purification by preparative TLC (hexane–ether=1:2, R_f 0.40—0.50) gave an alcohol (0.058 g, 84% yield): bp 70—80 °C (bath temperature)/1 Torr; ^{1}H-NMR (CCl_4) δ=1.60 (br s, 3H), 1.9—2.3 (m, 8H), 2.70 (br s, 1H), 3.50 (t, J=6.5 Hz, 2H), 4.8—5.3 (m, 5H), 6.27 (dd, J=11.4, 17.4 Hz, 1H); IR 3350, 3090, 2980, 1595, 1445, 1060, 990 cm^{-1}; MS m/z (rel intensity) 180 (M^+, 3), 121 (9), 119 (9), 93 (100), 75 (100).

The alcohol (1.57 g, 8.7 mmol) was converted into the aldehyde **27** with pyridinium chlorochromate (PCC)[30] (5.65 g, 17.5 mmol) in 77% yield. Bp 95—105 °C (bath temperature)/15 Torr; ^{1}H-NMR (CCl_4) δ=1.61 (br s, 3H), 2.1—2.5 (m, 8H), 4.8—5.3 (m, 5H), 6.27 (dd, J=11.4, 17.4 Hz, 1H), 9.65 (s, 1H); IR 3090, 2910, 2730, 1725, 1595, 990, 895 cm^{-1}; MS m/z (rel intensity) 178 (M^+, 2), 160 (2), 145 (4), 134 (10), 119 (16), 93 (100), 85 (37). Found: C, 81.13; H, 10.33%. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18%.

*(E)-3-Acetoxy-2-diethoxymethyl-6-methyl-10-methylene-1,6,11-dodecatriene (**21**).* The lithium carbenoid was produced from 1,1-dibromocyclopropane (0.85 g, 3.5 mmol) and allowed to react with the aldehyde **27** (0.36 g, 2.0 mmol) to give cyclopropylmethanol, which was without purification treated with ethanol (10 ml) in the presence of potassium carbonate (1.4 g, 10 mmol). The resulting alcohol was directly acetylated to give **21** (0.59 g, 83% yield): bp 132—134

°C (bath temperature)/1 Torr; ^{1}H-NMR (CCl_4) δ=1.18 (t, J=7.4 Hz, 6H), 1.60 (br s, 3H), 1.7—2.2 (m+s (δ=1.99), 11H), 3.2—3.7 (m, 4H), 4.7—5.3 (m, 7H), 6.27 (dd, J=11.4, 17.4 Hz, 1H); IR 2990, 1740, 1595, 1450, 1230, 1115, 1050, 890 cm^{-1}; MS m/z (rel intensity) 244 (21), 217 (23), 198 (14), 183 (11), 151 (22), 149 (23), 131 (28), 123 (31), 105 (33), 93 (75), 79 (38), 43 (100). Found: C, 71.88; H, 9.96%. Calcd for $C_{21}H_{34}O_4$: C, 71.96; H, 9.78%.

(E)-3-Acetoxy-2,10-dimethylene-6-methyl-6,11-dodecadienal (22). The diethyl acetal (**21**) (0.45 g, 1.29 mmol) dissolved in dichloromethane (1 ml) was treated with silica gel (Wakogel C-100) (1.36 g) and 10% aq oxalic acid (0.14 ml) in dichloromethane (3 ml) at room temperature for 1 h. The reaction mixture was neutralized with sodium hydrogencarbonate (0.045 g), and then filtered. Concentration of the filtrate and purification by column chromatography gave the desired aldehyde (**22**) (0.31 g, 87% yield): bp 120 °C (bath temperature)/1 Torr; ^{1}H-NMR (CCl_4) δ=1.60 (br s, 3H), 1.6—2.3 (m+s (δ=2.03), 11H), 4.9—5.6 (m, 6H), 5.97 (br s, 1H), 6.21 (dd, J=11.4, 17.4 Hz, 1H), 6.24 (br s, 1H), 9.50 (s, 1H); IR 3080, 2700, 1740, 1690, 1595, 1440, 1220, 1050, 1020, 895 cm^{-1}; MS m/z (rel intensity) 221 (5), 188 (6), 173 (5), 145 (8), 133 (19), 119 (19), 105 (20), 93 (100), 79 (37). Found: C, 73.99; H, 8.84%. Calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75%.

Transformation of 22 into β-Sinensal (23). Iron pentacarbonyl (0.91 ml, 1.45 mmol) was added to **22** (90 mg, 0.33 mmol) dissolved in a mixture of DABCO (81 mg, 0.72 mmol) and DMF-water (98:2, 1 ml), and the whole was stirred at room temperature for 1 h. Workup gave **23**[17] in 95% yield: ^{1}H-NMR (CCl_4) δ=1.63 (br s, 3H), 1.71 (br s, 3H), 1.9—2.6 (m, 8H), 4.8—5.3 (m, 5H), 6.1—6.5 (m, 2H), 9.28 (s, 3H); IR 2940, 2740, 1680, 1655, 1595, 990, 893 cm^{-1}; MS m/z (rel intensity) 218 (M^+, 5), 203 (3), 190 (10), 133 (26), 93 (100), 81 (39).

Preparation of (4E,8E)-4,8-Dimethyl-10-triphenylmethoxy-4,8-decadienal (20). A pyridine (100 ml) solution of geraniol (15.4 g, 0.10 mol) and triphenylmethyl chloride (35.0 g, 0.12 mol) was refluxed for 15 h. Evaporation of the pyridine under reduced pressure followed by column chromatography gave the geranyl triphenylmethyl ether in 33% yield: ^{1}H-NMR (CCl_4) δ=1.46 (s, 3H), 1.61 (s, 3H), 1.67 (s, 3H), 1.9—2.1 (m, 4H), 3.52 (d, J=6 Hz, 2H), 4.9—5.1 (m, 1H), 5.2—5.5 (m, 1H), 7.0—7.5 (m, 15H); IR 3080, 3050, 2950, 1670, 1600, 1495, 1455, 1050, 900, 765, 748, 710 cm^{-1}.

The geranyl triphenylmethyl ether (13.0 g, 32.7 mmol) was treated with *m*-chloroperbenzoic acid (7.1 g, 32.7 mmol) in chloroform (30 ml) at 0 °C for 2.5 h. Purification by column chromatography gave the epoxide **17** (7.9 g, 58% yield): ^{1}H-NMR (CCl_4) δ=1.22 (s, 3H), 1.25 (s, 3H), 1.47 (s, 3H), 1.5—1.6 (m, 2H), 2.13 (d, J=8 Hz, 2H), 2.50 (t, J=6 Hz, 1H), 3.53 (d, J=6 Hz, 2H), 5.42 (t, J=7 Hz, 1H), 7.0—7.5 (m, 15H); IR 3080, 2980, 1672, 1598, 1495, 1454, 1050, 900, 765, 750, 710 cm^{-1}.

The epoxide **17** (8.0 g, 19 mmol) was isomerized with lithium diethylamide (20 mmol) in ether for 48 h to an allylic alcohol (4.5 g, 57% yield) which showed: ^{1}H-NMR (CCl_4) δ=1.3—1.8 (m+s (δ=1.47, 3H)+d (δ=1.70, J=1.2 Hz, 3H), totally 9H), 1.9—2.2 (m, 2H), 3.53 (d, J=6 Hz, 2H), 3.93 (t, J=6 Hz, 1H), 4.74 (t, J=2 Hz, 1H), 4.87 (quintet, J=1.2 Hz, 1H), 5.41 (t, J=6 Hz, 1H), 7.0—7.5 (m, 15H); IR 3400, 3080, 1650, 1600, 1495, 1453, 1045, 900, 765, 712 cm^{-1}.

The alcohol (4.0 g, 9.8 mmol) was treated with acetic anhydride (10 ml) and pyridine (10 ml) at room temperature for 12 h to give **18** in 93% yield: ^{1}H-NMR (CCl_4) δ=1.47 (s, 3H), 1.5—1.8 (m+d (δ=1.72, J=1.2 Hz), 5H), 1.8—2.1 (m+s (δ=1.97), 5H), 3.53 (d, J=6 Hz, 2H), 4.83 (t, J=2 Hz, 1H), 4.91 (quintet, J=1.2 Hz, 1H), 5.09 (t, J=6 Hz, 1H), 5.39 (t, J=6 Hz, 1H), 7.0—7.5 (m, 15H); IR 3070, 2940, 1738, 1649, 1595, 1490, 1450, 1225, 1042, 895, 763 cm^{-1}.

The acetate **18** was converted into a carboxylic acid **19** in 85% yield as described for the transformation of **25** into **26**. ^{1}H-NMR ($CDCl_3$) δ=1.45 (s, 3H), 1.61 (s, 3H), 1.9—2.1 (m, 4H), 2.2—2.5 (m, 4H), 3.53 (d, J=6 Hz, 2H), 5.0—5.2 (m, 1H), 5.33 (t, J=6 Hz, 1H), 7.0—7.5 (m, 15H), 10.0—10.2 (m, 1H); IR 3080, 2950, 1710, 1598, 1494, 1453, 1045, 765, 710 cm^{-1}.

The carboxylic acid **19** was reduced with lithium aluminum hydride to give an alcohol, which was converted into the aldehyde **20** with pyridinium chlorochromate in 80% yield: ^{1}H-NMR (CCl_4) δ=1.43 (s, 3H), 1.61 (s, 3H), 1.9—2.0 (m, 4H), 2.1—2.4 (m, 4H), 3.56 (d, J=6 Hz, 2H), 5.0—5.2 (m, 1H), 5.40 (t, J=6 Hz, 1H), 7.0—7.5 (m, 15H), 9.53 (t, J=0.6 Hz, 1H); IR 3080, 2940, 2740, 1725, 1672, 1596, 1492, 1450, 1048, 900, 765, 750, 710 cm^{-1}. Found: C, 85.02; H, 7.96%. Calcd for $C_{31}H_{34}O_2$: C, 84.89; H, 7.81%.

(6E,10E)-3-Acetoxy-2-diethoxymethyl-6,10-dimethyl-12-triphenylmethoxy-1,6,10-dodecatriene (14): ^{1}H-NMR (CCl_4) δ=1.17 (t, J=7.2 Hz, 6H), 1.46 (s, 3H), 1.5—2.1 (m+s (δ=1.60, 3H)+s (δ=1.93, 3H), totally 14H), 3.2—3.6 (m, 6H), 4.78 (s, 1H), 5.0—5.5 (m, 5H), 7.0—7.5 (m, 15H); IR 2990, 1740, 1452, 1230, 1115, 1050, 765, 710 cm^{-1}.

(2E,6E,10E)-2-Ethyl-6,10-dimethyl-12-triphenylmethoxy-2,6,10-dodecatrienal (15). To lithium dimethylcuprate(I) (0.6 mmol) in ether (3 ml), allylic acetate (**14**) (0.12 g, 0.20 mmol) was added at −18 °C and the resulting mixture was stirred for 30 min at −18 °C. Workup followed by hydrolysis with aq 5% sulfuric acid-THF (1:1) and isomerization with potassium carbonate (8 mg) in methanol (12 ml) at 40 °C for 15 h gave **15** (0.072 g, 73% yield): ^{1}H-NMR (CCl_4) δ= 0.92 (t, J=7.5 Hz, 3H), 1.47 (s, 3H), 1.63 (s, 3H), 2.0—2.5 (m, 10H), 3.52, (d, J=7.2 Hz, 2H), 5.0—5.2 (m, 1H), 5.37 (t, J=7.0 Hz, 1H), 6.22 (t, J=7.2 Hz, 1H), 7.0—7.5 (m, 15H), 9.23 (s, 1H); IR 3080, 3000, 2950, 2740, 1688, 1644, 1598, 1494, 1453, 1046 710 cm^{-1}.

(2E,6E,10E)-2-Ethyl-6,10-dimethyl-12-triphenylmethoxy-2,6,10-dodecatrien-1-ol. The aldehyde **15** was reduced with sodium borohydride (quantitative yield): ^{1}H-NMR (CCl_4) δ= 0.97 (t, J=7 Hz, 3H), 1.47 (s, 3H), 1.62 (s, 3H), 1.8—2.2 (m, 10H), 3.52 (d, J=6 Hz, 2H), 3.88 (s, 2H), 5.0—5.5 (m, 3H), 7.0—7.5 (m, 15H); IR 3320, 3080, 2930, 1665, 1596, 1494, 1452, 1050, 900, 750, 710 cm^{-1}. Found: C, 85.15; H. 8.72%. Calcd for $C_{35}H_{42}O_2$: C, 84.97; H, 8.56%.

(2E,6E,10Z)-3,7,11-Trimethyl-2,6,10-tridecatriene-1-ol triphenyl methyl Ether (16). To the above alcohol (77 mg, 0.16 mmol) dissolved in THF (2 ml), sulfur trioxide-pyridine complex (49 mg, 0.31 mmol) was added at 0 °C. After 3 h, lithium aluminum hydride (*ca.* 50 mg) was added and the reaction was heated to reflux for 3 h. Workup and purification by preparative TLC (hexane-ether=5:1, R_f 0.80) gave **16**[31] 58 mg, 78% yield): ^{1}H-NMR (CCl_4) δ=0.94 (t, J=7.5 Hz, 3H), 1.48 (s, 3H), 1.61 (s, 3H), 1.64 (s, 3H), 1.7—2.1 (m, 10H), 3.52 (d, J=6.0 Hz, 2H), 4.9—5.1 (m, 2H), 5.39 (d, J=6.0 Hz, 1H), 7.0—7.5 (m, 15H); IR 3080, 2990, 2940, 1665, 1596, 1494, 1453, 1050, 900, 745, 710 cm^{-1}.

Preparation of 3-Bromo-1,1-diethoxy-4-decanone (29a). To dimethyl sulfoxide (DMSO) (1.56 g, 20.0 mmol) dissolved in dichloromethane (20 ml), trifluoroacetic anhydride (3.15 g, 15.0 mmol) in dichloromethane (5 ml) was added over 10 min at −78 °C. After 10 min, a dichloromethane solution (5 ml) of the alcohol **1e** (prepared from **3** (15 mmol) and heptanal (9.65 mmol), and used without purification) was added over a period of 10 min at −78 °C, and the resulting solution was stirred for 70 min before quenching with triethylamine (4 ml), then warmed up and stirred for 70 min at room temperature. Workup gave a crude cyclopropyl ketone **28a** which was dissolved in ethanol (15 ml) containing a catalytic amount of boron trifluoride ether complex (*ca.* 50 mg) for 2 h at room temperature. Workup and purification by column chromatography (hexane-ether=10:1) gave **29a** (2.32g, 74% yield): ^{1}H-NMR (CCl_4) δ=0.89 (t, J=5.6 Hz, 3H), 1.13 (t,

J=7.1 Hz, 3H), 1.17 (t, J=7.1 Hz, 3H), 1.3—1.8 (m, 8H), 1.9—2.9 (m, 4H), 3.2—4.1 (m, 4H), 4.27 (t, J=7.4 Hz, 1H), 4.47 (dd, J=4.7, 6.3 Hz, 1H); IR 2940, 1715, 1460, 1360, 1120, 1155 cm^{-1}; MS m/z (rel intensity) 280 (5), 279 (4), 278 (5), 277 (5), 197 (24), 113 (17), 103 (100), 97 (33), 85 (70), 75 (43).

Synthesis of 4-Oxodecanal (30a). Lithium aluminum hydride (48 mg, 1.25 mmol) was added to the suspension of chromium(III) chloride (0.40 g, 2.50 mmol) in THF (2 ml) at 0 °C. To the resulting dark brown reagent[21], the α-bromo ketone **29a** (0.17 g, 0.52 mmol) was added, and the whole was stirred for 1 h at room temperature. Workup gave a crude keto acetal (0.13 g) which was stirred in a mixture of THF (3 ml) and aq 15% sulfuric acid (1 ml) at room temperature for 1.5 h. Workup and purification by column chromatography (hexane–ether=3:1) gave **30a**[22] (70 mg, 80% yield): ^{1}H-NMR (CCl_4) δ=0.7—1.1 (m, 3H), 1.1—1.8 (m, 8H), 2.38 (t, J=7.4 Hz, 2H), 2.63 (s, 4H), 9.72 (s, 1H); IR 2940, 2740, 1705, 1460, 1405, 1125, 865 cm^{-1}; MS m/z (rel intensity) 170 (M^+, 1), 113 (35), 100 (24), 85 (79), 72 (52), 57 (47), 43 (100).

Preparation of (Z)-3-Bromo-1,1-diethoxy-7-decen-4-one (29b). The lithium carbenoid **3** was prepared from 1,1-dibromo-2-ethoxycyclopropane (0.44 g, 1.79 mmol), butyllithium (1.98 M hexane solution, 0.88 ml, 1.75 mmol) and allowed to react with (*Z*)-heptenal (0.12 g, 1.04 mmol). The produced alcohol was oxidized without purification by the Swern's method as described for the oxidation of **1e** to give **28b** which was stirred in ethanol (5 ml) containing acetic acid (*ca.* 15 mg) at room temperature for 4 h. Workup gave **29b** (0.26 g, 77% yield): ^{1}H-NMR (CCl_4) δ=0.98 (t, J=8.4 Hz, 3H), 1.16 (t, J=6.6 Hz, 3H), 1.19 (t, J=6.6 Hz, 3H), 1.9—3.0 (m, 8H), 3.3—3.8 (m, 4H), 4.33 (t, J=6.6 Hz, 1H), 4.52 (dd, J=9.6, 15.6 Hz, 1H), 5.1—5.5 (m, 2H); IR 2980, 1720, 1450, 1380, 1125, 1160, 790 cm^{-1}; MS m/z (rel intensity) 277 (8), 275 (8), 195 (66), 167 (22), 149 (22), 103 (98), 85 (61), 75 (88), 55 (88), 47 (100). Found: m/z 275.0616. Calcd for $C_{12}H_{20}O_2Br$ (M–OEt): M 275.0646.

Synthesis of (Z)-4-Oxo-7-decenal (30b). Reduction of **29b** with the $CrCl_3$–$LiAlH_4$ reagent[21] gave **30b** in 91% yield: ^{1}H-NMR (CCl_4) δ=0.97 (t, J=7.2 Hz, 3H), 1.7—2.8 (m+s (δ=2.65, 4H), totally 10H), 5.0—5.5 (m, 2H), 9.73 (s, 1H); IR 3055, 2960, 1720, 1415, 1095, 1020, 865, 720 cm^{-1}; MS m/z (rel intensity) 168 (M^+, 3), 149 (7), 123 (35), 95 (37), 85 (91), 69 (51), 68 (53), 55 (86), 41 (100).

(E)-4-Oxo-2-decenal (32). The bromo acetal **29a** (0.17 g, 0.52 mmol) was treated with THF (3 ml)-aq 15% sulfuric acid (2 ml) at room temperature for 5 h. Workup and purification by preparative TLC (hexane–ethyl acetate=10:1, double development) gave **32** (56 mg, 64% yield): ^{1}H-NMR (CCl_4) δ=0.91 (t, J=5.7 Hz, 3H), 1.1—1.9 (m, 8H), 2.65 (t, J=6.9 Hz, 2H), 6.7—6.9 (m, 2H), 9.75 (dd, J=1.8, 5.4 Hz, 1H); IR 2950, 2750, 1700, 1625, 1115, 1080, 980 cm^{-1}; MS m/z (rel intensity) 168 (M^+, 6), 139 (47), 125 (15), 111 (20), 98 (83), 83 (77), 70 (58), 55 (94), 43 (100). Found: m/z 168.1158. Calcd for $C_{10}H_{16}O_2$: M 168.1149.

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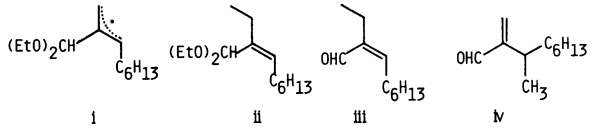

i ii iii iv

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