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Improved Synthesis of Three Methyl-Branched Pheromone Components Produced by the Female Lichen Moth

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Female moths of *Lyclene dharma dharma* (Arctiidae, Lithosiinae) produce a novel sex pheromone composed of three methyl-branched ketones: 6-methyl-2-octadecanone (I), 14-methyl-2-octadecanone (II), and 6,14-dimethyl-2-octadecanone (III). Their structures were confirmed by syntheses accomplished by a different route for each component. In order to obtain a sufficient amount of the synthetic pheromone, we developed new routes *via* methyl-branched 1-alkenes: 6-methyl-1-octadecene (1), 14-methyl-1-octadecene (2), and 6,14-dimethyl-1-octadecene (3). Compound 1 was synthesized by coupling between a C_{10}-chain bromide and a 3-methyl-branched C_8 unit (A) prepared from 3-methyl-1,5-pentanediol, 2, by coupling between a C_{11}-chain bromide and a 3-methyl-branched C_7 unit (B) prepared from 2-hexanone, and 3, by connecting A and B, using propargyl alcohol as a C_3 linchpin. The use of 3-chloro-1-propanol and *tert*-butyl acetoacetate as the linchpin was also examined to connect the two synthetic blocks in the synthesis of 3. Components I–III were obtained by Wacker oxidation of the corresponding 1-alkenes 1–3 in good yields.

Key words: Lepidoptera; female sex pheromone; methyl-branched 2-ketone; methyl-branched 1-alkene; Wacker oxidation

Lepidopteran sex pheromones have been identified from adult females of more than 600 species. In addition to Type I and II pheromones with a straight chain, there are a considerable number of miscellaneous chemicals,[1–3] and we have recently identified novel methyl-branched ketones from *Lyclene dharma dharma*. The *L. d. dharma* females, which were caught on the Iriomote Islands, produced 6-methyl-2-octadecanone (**I**), 14-methyl-2-octadecanone (**II**), and 6,14-dimethyl-2-octadecanone (**III**). The structures were estimated by GC-MS analyses of the pheromone gland extracts before and after Wollf-Kishner reduction.[4] Although the absolute configurations of their chiral centers could not be determined because of the difficulty collecting a sufficient amount of the pheromone extract, the planar structures of **I–III** were confirmed by the synthesis regardless of their stereochemistry. The mass spectrum of each synthetic ketone coincided well with that of the corresponding natural component.[4,5] Furthermore, lures baited with the optically inactive synthetic ketones successfully attracted many *L. d. dharma* males in the field.[5]

L. d. dharma belongs to Lithosiinae in the family of Arctiidae and is the first species whose sex pheromone has been revealed among the species in this subfamily. The Lithosiinae species, called lichen moths, are commonly found throughout the world, and about 80 species inhabit Japan. The larvae mainly feed on the lichen in forests and contribute to the ecosystem of the forest. While information on the ecological aspects of the Lithosiinae species is very limited, the pheromone, which can be easily synthesized with achiral materials, is utilized as a good monitoring tool for the adults. In our previous study, three components were separately synthesized by routes that started from diols of different chain length and involved no common synthetic units.[4,5] To obtain a sufficient amount of the synthetic pheromone, we investigated methods for increasing the yields of the three components. This report presents new synthetic routes for **I–III** *via* Wacker oxidation of the terminal alkenes which were constructed with common synthetic units.

Results and Discussion

Wacker oxidation[6] might enable **I–III** to be directly synthesized from the corresponding 1-alkenes: 6-methyl-1-octadecene (**1**), 14-methyl-1-octadecene (**2**), and 6,14-dimethyl-1-octadecene (**3**). Since both **1** and **2** bear a structure common to **3**, we made a synthetic plan for **1–3** which involved mutual synthetic blocks, as shown in Fig. 1. If **1** and **2** could be prepared from methyl-branched C_8 and C_7 units (**A** and **B**), **3** could be synthesized by coupling **A** and **B**, using a C_3-chain compound as the linchpin.

Scheme I in Fig. 2 summarizes the synthesis of the key building block ($\mathbf{A_1}$; **A**, X = OTs) and its conversion to **I**. 3-Methyl-1,5-pentanediol was introduced to silanyloxy tosylate (**4**) by treating tosyl chloride (TsCl) after mono sililating by *tert*-butyldimethylsilyl chloride (TBDMSCl). Tosylate **4** was coupled with allylmagnesium bromide by employing the Schlosser's copper-catalyzed Grignard reaction,[7] and its TBDMS group

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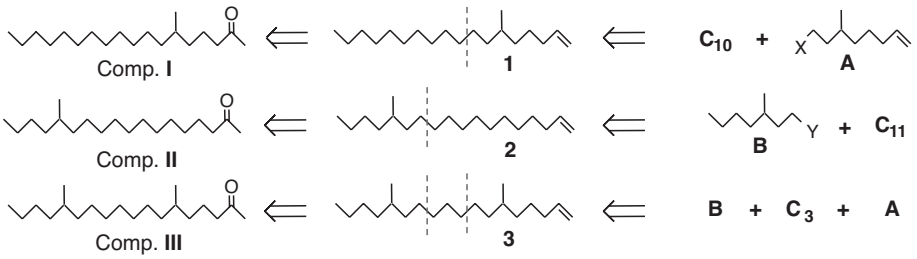


Fig. 1. Synthetic Strategy for Three Methyl-Branched Pheromone Components (**I–III**) Using 3-Methyl-Branched C_8 and C_7 Units (**A** and **B**) as Key Synthetic Blocks.
X = OTs ($\mathbf{A_1}$) and X = I ($\mathbf{A_2}$) in **A**; Y = OTs ($\mathbf{B_1}$), Y = I ($\mathbf{B_2}$), and Y = MgBr ($\mathbf{B_3}$) in **B**

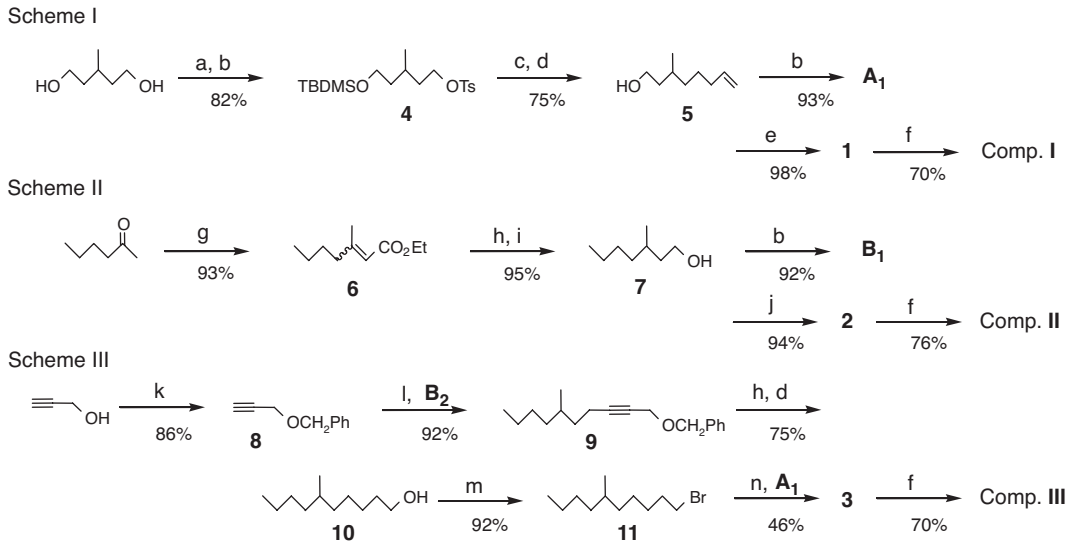


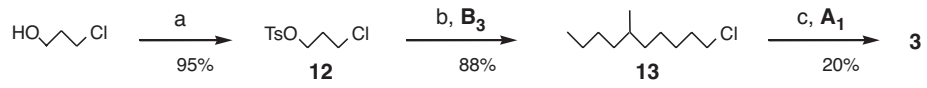
Fig. 2. Synthetic Routes to 6-Methyl-2-octadecanone (Component **I**, Scheme I), 14-Methyl-2-octadecanone (Component **II**, Scheme II), and 6,14-Dimethyl-2-octadecanone (Component **III**, Scheme III).
a, 1) BuLi, THF, 2) TBDMSCl; b, TsCl, DMAP, pyridine; c, $CH_2{=}CHCH_2MgBr$, Li_2CuCl_4, Et_2O; d, TBAF, THF; e, $CH_3(CH_2)_9MgBr$, Li_2CuCl_4, THF; f, O_2, $PdCl_2$, CuCl, DMF-H_2O; g, $(EtO)_2POCH_2CO_2Et$, NaH, THF; h, H_2, Pd-C, MeOH; i, $LiAlH_4$, Et_2O; j, $CH_2{=}CH(CH_2)_9MgBr$, Li_2CuCl_4, THF; k, $PhCH_2Br$, NaH, NaI, DMF; l, BuLi, THF-HMPA; m, HBr, H_2SO_4; n, 1) Mg, Et_2O, 2) Li_2CuCl_4, THF

was removed to yield 3-methyl-7-octen-1-ol (**5**) which was converted into tosylate $\mathbf{A_1}$ by TsCl. This unit ($\mathbf{A_1}$) was coupled with *n*-decylmagnesium bromide to yield 1-alkene **1**, and 6-methyl-2-ketone **I** was obtained by Wacker oxidation of **1**. Scheme II in Fig. 2 is a summary of the synthesis of another key block ($\mathbf{B_1}$; **B**, Y = OTs) and its conversion to **II**. 2-Hexanone was coupled with the anion prepared from triethyl phosphonoacetate[8] to yield a mixture of (*Z*)- and (*E*)-ethyl 3-methyl-2-heptenoate (**6**), which was converted into 3-methyl-1-heptanol (**7**) by catalytic hydrogenation and $LiAlH_4$ reduction. Alcohol **7** was treated with TsCl to build up tosylate $\mathbf{B_1}$, which was coupled with 10-undecenylmagnesium bromide to construct another 1-alkene **2**. 14-Methyl-2-ketone **II** was obtained by Wacker oxidation of **2**.

Scheme III in Fig. 2 shows the synthesis of **III** *via* dimethyl-1-alkene **3** which utilized propargyl alcohol as a linchpin. The alcohol was converted into benzyl ether (**8**) and coupled with an iodide[9] ($\mathbf{B_2}$; **B**, Y = I), which had been prepared from **7**, to yield a compound with a methyl-branched C_{10}-chain (**9**). Hydrogenation of the triple bond and deprotection of the benzyl ether of **9** gave 6-methyl-1-octanol (**10**). Alcohol **10** was converted to a Grignard reagent *via* bromide (**11**) and coupled with $\mathbf{A_1}$ to yield **3** under the same copper-catalyzed condition as that for the syntheses of **1** and **2**.[7] 6,14-Dimethyl-2-ketone **III** was obtained by Wacker oxidation of **3**.

Dimethyl-1-alkene **3** was also synthesized with the other C_3 linchpins as shown in Fig. 3. The tosylate of 3-chloro-1-propanol (**12**) was coupled with a Grignard reagent ($\mathbf{B_3}$; **B**, Y = MgBr) to yield 1-chloro-6-methyldecane (**13**). Chloride **13** was converted to a Grignard reagent and coupled with $\mathbf{A_1}$ to yield **3** (Scheme IV). We also attempted to use *tert*-butyl acetoacetate as the C_3 linchpin (Scheme V). The dianion of *tert*-butyl acetoacetate, which had been generated by treating with NaH and butyllithium (BuLi),[10] was coupled with $\mathbf{B_2}$ to yield a ketoester (**14**). This step was more smoothly accomplished by the iodide than by the tosylate $\mathbf{B_1}$. As a second alkylation, the activated enolate of **14**, which had been generated by treating with potassium *tert*-butoxide, was coupled with another iodide ($\mathbf{A_2}$; **A**, X = I). Since it was not easy to separate the required ketoester with a long chain (**15**), the reaction mixture was used in further steps involving dealkoxycarbonylation under an acidic condition and Wollf-Kishner reduction after partial purification. While no intermediates other than **14** in Scheme V were isolated and characterized, the GC-MS analysis confirmed the formation of **3**, and a pure sample was obtained after the usual silica gel column chromatography. The insufficient yield might be improved by

Scheme IV



Scheme V

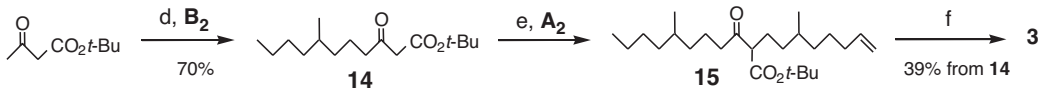


Fig. 3. Synthetic Routes to 6,14-Dimethyl-1-octadecene (**3**) Starting from 3-Chloropropan-1-ol (Scheme IV) and *tert*-Butyl Acetoacetate (Scheme V).

a, TsCl, DMAP, C_5H_5N; b, Li_2CuCl_4, THF; c, Mg, MeMgBr, THF, Li_2CuCl_4; d, NaH, THF-HMPA, BuLi; e, *t*-BuOK, *t*-BuOH, Δ; f, 1) TsOH, Δ, 2) NH_2NH_2, KOH, DEG, Δ

examining the conditions for each step in detail and by applying other starting esters such as ethyl acetoacetate. The corresponding alkylated ethyl acetoacetate might be easily dealkoxycarbonylated under a neutral condition.[11)]

The improved synthetic routes shown in Fig. 2 enable three 2-ketones **I–III** to be synthesized in 18–58% total yields, while our previous syntheses achieved less than 10% total yields.[4,5)] The GC-MS data for new synthetic **I–III** coincided well with those of the corresponding natural pheromone components, and the NMR data were the same as those of the compounds previously synthesized.[4,5,12)] 14-Methyl-1-octadecene **2**, our synthetic intermediate for **II**, is a pheromone component of the peach leafminer moth, *Lyonetia clerkella* L. (Lyonetiidae).[13)] While several reports have described its synthesis and ^{1}H-NMR data,[13–17)] assignment of the ^{13}C-NMR signals has not been reported. We assigned the ^{13}C signals of 1-alkenes **1–3** by comparing them with those of 2-ketones **I–III** previously analyzed[5)] and confirmed the results with the use of two-dimensional experiments (Table 1). Signal separation in the ^{13}C-NMR spectra was markedly better than that in the ^{1}H-NMR spectra, indicating the ^{13}C-NMR analysis as one of the most reliable tools to confirm the structure of a synthetic pheromone with a methyl-branched skeleton.

Studies on pheromones with the structure of a 1-alkene or 2-ketone are still very limited.[1–3)] Further investigation of the communication systems of many lepidopteran species, particularly in the families of Arctiidae and Lyonetiidae, make it necessary to systematically synthesize many authentic standards with a methyl-branched structure. Synthetic blocks **A** and **B** can be respectively utilized for 6-methyl and ω5-methyl compounds for this purpose. In the case of the *L. d. dharma* pheromone, optically active isomers of each component have been synthesized by olefin cross-metathesis, utilizing blocks with a C_{10}-chain.[12)] We are going to prepare optically active **A** and **B** to establish a different route.

Experimental

Instruments. ^{1}H- and ^{13}C-NMR spectra were recorded by a Delta 2 Fourier transform spectrometer (Jeol, Tokyo, Japan) at 399.8 and 100.5 MHz, respectively, for $CDCl_3$ solutions containing TMS as an internal standard. ^{1}H-^{1}H COSY, HMQC, and HMBC spectra were also measured with the same spectrometer, using the usual pulse sequences and parameters. GC-MS was conducted in the EI mode (70 eV) with an HP5973 mass spectrometer (Hewlett-Packard) equipped with a split/splitless injector and a DB-23 column (0.25 mm ID × 30 m, 0.25 μm film; J & W Scientific, Folsom, CA, USA). The column temperature program was 50 °C for 2 min, 10 °C/min to 160 °C, and 4 °C/min to 220 °C. The carrier gas was He. IR spectra were recorded as a thin film (neat liquid) with an FT/IR-350 instrument (Jasco, Tokyo, Japan).

Table 1. ^{13}C-NMR Assignments for the Synthetic 1-Alkenes **1–3** and 2-Alkanone **III**[a]

Position	Chemical shift (δ ppm)			
	1	**2**	**3**	**III**
1	114.1	114.1	114.1	29.9
2	139.3	139.3	139.3	209.4
3	34.2	33.9	34.2	44.2
4	26.4	~30	26.4	21.4
5	36.6	~30	36.6	36.5
6	32.67	~30	32.68	32.65
7	37.05	~30	37.06	36.90
8	27.09	~30	27.10[c]	27.05[e]
9–11	~30	~30	~30[g]	~30[h]
12	~30	27.12	27.12[c]	27.11[e]
13	~30	36.82[b]	36.81[d]	36.79[f]
14	~30	32.76	32.75	32.74
15	~30	37.13[b]	37.13[d]	37.11[f]
16	32.0	~30	~30[g]	~30[h]
17	22.7	23.1	23.1	23.1
18	14.1	14.2	14.2	14.2
6Me	19.69	—	19.70	19.55
14Me	—	19.74	19.74	19.73

[a]6-Methyl-1-octadecene (**1**), 14-methyl-1-octadecene (**2**), 6,14-dimethyl-1-octadecene (**3**), and 6,14-dimethyl-2-octadecanone (**III**). NMR data for **III** have been reported in a previous paper.[5)]
[b–f]Chemical shift values may be reversed.
[g]29.4, 29.8, 30.05, and 30.07.
[h]29.4, 29.8, 30.02, and 30.05.

*5-(*tert*-Butyldimethylsilyl)oxy-3-methylpentyl tosylate (**4**).* BuLi (a 1.65 M hexane solution, 30 ml) was added dropwise to a solution of 3-methyl-1,5-pentanediol (5.9 g, 50 mmol) in dry THF (60 ml) in a three-necked flask while stirring under an Ar atmosphere. After stirring at room temperature (rt) for 10 min, TBDMSCl (7.5 g, 50 mmol) dissolved in dry THF (10 ml) was added *via* a syringe. The mixture was stirred for 45 min at rt, poured into a saturated aqueous solution of NH_4Cl, and extracted with Et_2O (3 × 100 ml). The resulting organic layer was successively washed with H_2O, a $NaHCO_3$ solution and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The crude product was chromatographed over SiO_2 (200 g), and elution with hexane/EtOAc (from 10:1 to 5:1) gave 5-(*tert*-butyldimethylsilyl)oxy-3-methyl-1-pentanol (9.7 g, 42 mmol, 84%). This alcohol was added to a mixture of dry pyridine (30 ml), TsCl (8.8 g, 46 mmol), and 4-(dimethylamino)-pyridine (DMAP, 100 mg) which were stirred in a three-necked flask cooled in an ice bath under Ar. The crude product was stirred for 2 h in the bath, poured into an HCl solution (1.0 M, 250 ml), and extracted

with EtOAc (3 × 100 ml). The resulting organic layer was successively washed with H_2O, a $NaHCO_3$ solution and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residual materials were chromatographed over SiO_2 (200 g), elution with hexane/EtOAc (10:1) gave tosylate **4** (16 g, 41 mmol, 98%). ^{1}H-NMR δ: 0.02 (6H, s, Si(C*H*$_3$)$_2$), 0.83 (3H, d, J = 6.5 Hz, C*H*$_3$CH), 0.87 (9H, s, SiC(C*H*$_3$)$_3$), 1.32 (1H, m), 1.47 (2H, m), 1.69 (2H, m), 2.45 (3H, s, C*H*$_3$Ph), 3.59 (2H, m, TBDMSOC*H*$_2$), 4.07 (2H, m, TsOC*H*$_2$), 7.34 (2H, d, J = 8.5 Hz), 7.79 (2H, d, J = 8.5 Hz). ^{13}C-NMR δ: −5.4 (×2), 18.3, 19.2, 21.6, 25.9 (×3), 26.2, 35.7, 39.4, 60.9, 68.9, 127.9 (×2), 129.8 (×2), 133.2, 144.6. IR ν_{max} cm^{-1}: 2929, 1604, 1475, 1363, 1178, 1097, 943, 837, 775, 663, 555.

*3-Methyl-7-octen-1-ol (**5**).* Tosylate **4** (15.5 g, 40 mmol) dissolved in dry Et_2O (60 ml) was treated with Li_2CuCl_4 (a 0.1 M THF solution, 1.0 ml) and allylmagnesium bromide (a 1.0 M Et_2O solution, 44 ml) while stirring at 0 °C under Ar. The mixture was stirred at 0 °C for 8 h and poured into an H_2SO_4 solution (2.0 M, 200 ml), and the product was extracted with Et_2O (3 × 100 ml). After the usual work-up, the crude product was chromatographed over SiO_2 (200 g) with an eluent of hexane/EtOAc (10:1) to give the TBDMS ether of **5** (8.5 g, 33 mmol, 83%). Next, to remove the protective group, the ether dissolved in dry THF (10 ml) was treated with tetrabutylammonium fluoride (TBAF, a 1.0 M THF solution, 40 ml) under Ar. The mixture was stirred at rt for 3 h, poured into a saturated aqueous solution of NH_4Cl (100 ml), and extracted with Et_2O (3 × 100 ml). After the usual work-up, the crude product was chromatographed over SiO_2 (200 g) with an eluent of hexane/EtOAc (from 10:1 to 5:1) to give **5** (4.3 g, 30 mmol, 91%). ^{1}H-NMR δ: 0.90 (3H, d, J = 6.5 Hz, C*H*$_3$CH), ∼1.3 (4H, m), ∼1.6 (2H, m), 1.87 (1H, m), 2.04 (2H, dt, J = 7, 7 Hz, C*H*$_2$CH=C), 3.68 (2H, m, C*H*$_2$OH), 4.94 (1H, d, J = 10.5 Hz, CH=C*H*H), 5.00 (1H, d, J = 17 Hz, CH=CH*H*), 5.81 (1H, ddt, J = 17, 10.5, 6.5 Hz, C*H*=CH$_2$). ^{13}C-NMR δ: 19.6, 26.3, 29.4, 34.0, 36.5, 39.9, 61.2, 114.3, 139.1. IR ν_{max} cm^{-1}: 3365, 3078, 2929, 1641, 1460, 1057, 999, 910. GC-MS (relative intensity): t_R 9.97 min; m/z 124 ([M − 18]$^+$, 1%), 109 (11%), 81 (55%), 55 (100%).

*3-Methyl-7-octenyl tosylate (**A$_1$**).* In a similar manner to that for the preparation of **4**, alcohol **5** (4.3 g, 30 mmol) was tosylated with TsCl (6.9 g, 36 mmol) and DMAP (200 mg). The crude product was chromatographed over SiO_2 (150 g) with an eluent of hexane/EtOAc (10:1) to give **A$_1$** (8.4 g, 28 mmol, 93%). ^{1}H-NMR δ: 0.81 (3H, d, J = 6.5 Hz, C*H*$_3$CH), 1.0–1.6 (6H, m), 1.66 (1H, m), 1.97 (2H, dt, J = 7, 7 Hz, C*H*$_2$CH=C), 2.45 (3H, s, C*H*$_3$Ph), 4.05 (2H, m, TsOC*H*$_2$), 4.92 (1H, d, J = 10.5 Hz, CH=C*H*H), 4.95 (1H, d, J = 17 Hz, CH=CH*H*), 5.76 (1H, ddt, J = 17, 10.5, 6.5 Hz, C*H*=CH$_2$), 7.34 (2H, d, J = 8.5 Hz), 7.78 (2H, d, J = 8.5 Hz). ^{13}C-NMR δ: 19.1, 21.6, 26.0, 29.0, 33.8, 35.6, 36.0, 69.0, 114.4, 127.8 (×2), 129.8 (×2), 133.1, 138.7, 144.6. IR ν_{max} cm^{-1}: 3074, 2927, 1639, 1599, 1460, 1361, 1176, 1097, 945, 891, 816, 665, 555.

*8-Iodo-6-methyl-1-octene (**A$_2$**).* NaI (4.5 g, 30 mmol) was added to a solution of tosylate **A$_1$** (5.7 g, 20 mmol) in dimethylformamide (DMF, 25 ml) at rt, and the mixture was stirred at 100 °C for 2 h. After cooling to rt, the mixture was poured into water (400 ml) and extracted with hexane (3 × 100 ml). The crude product was chromatographed over SiO_2 (100 g) after the usual work-up. Elution with hexane gave **A$_2$** (4.5 g, 18 mmol, 90%). ^{1}H-NMR δ: 0.88 (3H, d, J = 6.5 Hz, C*H*$_3$CH), ∼1.3 (4H, m), ∼1.55 (1H, m), 1.65 (1H, m), 1.87 (1H, m), 2.04 (2H, dt, J = 7, 7 Hz, C*H*$_2$CH=C), 3.17 (1H, ddd, J = 9.5, 8, 8 Hz, C*H*HI), 3.25 (1H, ddd, J = 9.5, 9.5, 5.5 Hz, CH*H*I), 4.95 (1H, d, J = 10.5 Hz, CH=C*H*H), 5.00 (1H, d, J = 17 Hz, CH=CH*H*), 5.81 (1H, ddt, J = 17, 10.5, 6.5 Hz, C*H*=CH$_2$). ^{13}C-NMR δ: 5.2, 18.7, 26.1, 33.7, 33.9, 35.7, 40.9, 114.4, 138.9. IR ν_{max} cm^{-1}: 3076, 2927, 1639, 1460, 1178, 995, 910, 606. GC-MS: t_R 9.80 min; m/z 252 (M$^+$, 1%), 155 (6%), 97 (13%), 55 (100%).

*6-Methyl-1-octadecene (**1**).* In a similar manner to that for the alkylation of **4**, tosylate **A$_1$** (3.0 g, 10 mmol) was coupled with decylmagnesium bromide (a 1.0 M Et_2O solution, 14 ml) by using Li_2CuCl_4 (a 0.1 M THF solution, 1.0 ml) as a catalyst. The crude product was chromatographed over SiO_2 (150 g) with an eluent of hexane to give **1** (2.6 g, 9.8 mmol, 98%). ^{1}H-NMR δ: 0.85 (3H, d, J = 6.5 Hz, C*H*$_3$CH), 0.88 (3H, t, J = 6.5 Hz, C*H*$_3$CH$_2$), ∼1.1 (2H, m), ∼1.25 (22H, m), ∼1.35 (3H, m), 2.02 (2H, dt, J = 7, 7 Hz, C*H*$_2$CH=C), 4.93 (1H, d, J = 10.5 Hz, CH=C*H*H), 4.99 (1H, d, J = 17 Hz, CH=CH*H*), 5.82 (1H, ddt, J = 17, 10.5, 6.5 Hz, C*H*=CH$_2$). IR ν_{max} cm^{-1}: 3078, 2924, 2846, 1641, 1464, 993, 908. GC-MS: t_R 12.74 min; m/z 266 (M$^+$, 1%), 97 (100%), 57 (90%).

*Ethyl 3-methyl-2-heptenoate (**6**).* Triethyl phosphonoacetate (18.9 g, 72 mmol) dissolved in dry THF (40 ml) was treated with NaH (60%, 2.9 g, 72 mmol) while stirring at rt under Ar. The reaction mixture was stirred for 20 min at rt, and EtOH (4.0 ml) was then added to quench the remaining NaH. Next, 2-hexanone (6.0 g, 60 mmol) was added dropwise and the mixture stirred for 1 h at rt and for an additional 30 min under reflux. The mixture was then cooled to rt, poured into a saturated aqueous solution of NH_4Cl (100 ml), and extracted with Et_2O (3 × 100 ml). After the usual work-up, the crude product was chromatographed over SiO_2 (300 g) with eluention by hexane and hexane/EtOAc (10:1) to give a 1:1 mixture of (*Z*)-2-heptenoate and its (*E*)-isomer (**6**; 9.5 g, 56 mmol, 93%). ^{1}H-NMR (*Z*)-isomer δ: 0.92 (3H, t, J = 7 Hz, C*H*$_3$CH$_2$CH$_2$), 1.27 (3H, t, J = 7 Hz, C*H*$_3$CH$_2$O), ∼1.4 (4H, m), 1.88 (3H, d, J = 1.5 Hz, C*H*$_3$C=C), 2.62 (2H, t, J = 7.5 Hz, C*H*$_2$C=C), 4.13 (2H, q, J = 7 Hz, CH$_3$C*H*$_2$O), 5.65 (1H, m, C*H*=C); (*E*)-isomer δ: 0.91 (3H, t, J = 7 Hz, C*H*$_3$CH$_2$CH$_2$), 1.28 (3H, t, J = 7 Hz, C*H*$_3$CH$_2$O), ∼1.4 (4H, m), 2.13 (2H, m, C*H*$_2$C=C), 2.15 (3H, d, J = 1.5 Hz, C*H*$_3$C=C), 4.14 (2H, q, J = 7 Hz, CH$_3$C*H*$_2$O), 5.66 (1H, m, C*H*=C). ^{13}C-NMR δ: 13.9, 14.0, 14.3, 14.4, 18.7, 22.3, 22.9, 25.2, 29.6, 30.4, 33.2, 40.7, 59.40, 59.44, 115.4, 116.0, 160.4, 160.8, 166.4, 166.9. IR ν_{max} cm^{-1}: 2908, 1739, 1649, 1461, 1367, 1149, 1039, 731. GC-MS: t_R 8.20 min; m/z 170 (M$^+$, 40%), 141 (46%), 125 (59%), 55 (100%).

*3-Methyl-1-heptanol (**7**).* A mixture of the heptenoate **6** (9.4 g, 55 mmol), Pd-C (10%, 250 mg), and MeOH (100 ml) was stirred under H_2 at rt for 1.5 h. After filtering off the catalyst, the solvent was evaporated. The produced heptanoate dissolved in dry THF (20 ml) was added dropwise to $LiAlH_4$ (2.1 g, 55 mmol) suspended in dry THF (30 ml) cooled in an ice bath. After stirring at rt for 1 h, an HCl solution (1.0 M, 150 ml) was added dropwise to the reaction mixture, and the crude product was extracted with Et_2O (3 × 100 ml). After the usual work-up, the product was chromatographed over SiO_2 (200 g) with an elution by hexane and hexane/EtOAc (from 10:1 to 2:1) to give **7** (6.8 g, 52 mmol, 95%). ^{1}H-NMR δ: 0.89 (3H, d, J = 6.5 Hz, C*H*$_3$CH), 0.89 (3H, t, J = 6.5 Hz, C*H*$_3$CH$_2$), ∼1.3 (7H, m), ∼1.6 (2H, m), 3.69 (2H, m, C*H*$_2$OH). ^{13}C-NMR δ: 14.1, 19.7, 23.0, 29.2, 29.5, 36.8, 40.0, 61.2. IR ν_{max} cm^{-1}: 3334, 2924, 1460, 1379, 1057. GC-MS: t_R 8.23 min; m/z 112 ([M − 18]$^+$, 2%), 97 (4%), 84 (67%), 55 (100%).

*3-Methylheptyl tosylate (**B$_1$**).* In a similar manner to that for the preparation of **4**, alcohol **7** (6.5 g, 50 mmol) was tosylated with TsCl (11.4 g, 60 mmol) and DMAP (300 mg). The product was chromatographed over SiO_2 (200 g) with elution by hexane/EtOAc (10:1) to give **B$_1$** (8.4 g, 46 mmol, 92%). ^{1}H-NMR δ: 0.80 (3H, d, J = 6.5 Hz, C*H*$_3$CH), 0.86 (3H, t, J = 6.5 Hz, C*H*$_3$CH$_2$), 1.0–1.3 (6H, m), ∼1.4 (1H, m), ∼1.5 (1H, m), 1.65 (1H, m), 2.45 (3H, s, C*H*$_3$Ph), 4.06 (2H, m, TsOC*H*$_2$), 7.35 (2H, d, J = 8.5 Hz), 7.79 (2H, d, J = 8.5 Hz). ^{13}C-NMR δ: 14.1, 19.2, 21.6, 22.8, 29.0, 29.1, 35.7, 36.3, 69.1, 127.9 (×2), 129.8 (×2), 133.2, 144.6. IR ν_{max} cm^{-1}: 2927, 1599, 1466, 1362, 1176, 945, 887, 816, 665, 555.

*1-Iodo-3-methylheptane (**B$_2$**).* In a similar manner to that for the iodination of **A$_1$**, tosylate **B$_1$** (5.7 g, 20 mmol) was converted to **B$_2$** (4.3 g, 18 mmol, 90%). ^{1}H-NMR δ: 0.87 (3H, d, J = 6.5 Hz, C*H*$_3$CH), 0.89 (3H, t, J = 6.5 Hz, C*H*$_3$CH$_2$), 1.1–1.35 (6H, m), ∼1.55 (1H, m), 1.64 (1H, m, C*H*HCH$_2$I), 1.87 (1H, m, CH*H*CH$_2$I), 3.17 (1H, ddd, J = 9.5, 8, 8 Hz, C*H*HI), 3.25 (1H, ddd, J = 9.5, 9.5, 5.5 Hz, CH*H*I). ^{13}C-NMR δ: 5.3, 14.1, 18.8, 22.9, 29.0, 33.9, 35.9, 41.0. IR ν_{max} cm^{-1}: 2925, 1464, 1379, 1214, 1178, 606. GC-MS: t_R 7.96 min; m/z 240 (M$^+$, 2%), 155 (7%), 127 (3%), 113 (20%), 57 (100%).

*14-Methyl-1-octadecene (**2**).* To dry THF (30 ml) containing Mg turnings (0.97 g, 40 mmol), 11-bromo-1-undecene (4.7 g, 20 mmol) in dry THF (4 ml) was added while stirring at 0 °C under Ar. After stirring at 0 °C for 1 h, the mixture was warmed to rt. The produced Grignard

reagent was taken up in a syringe and added to a solution of **B_1** (4.3 g, 18 mmol) and Li_2CuCl_4 (a 0.1 M THF solution, 1.0 ml) in dry THF (20 ml) at −78 °C under Ar. The mixture was gradually warmed to rt. Stirring was continued for 14 h, the mixture was poured into a cool H_2SO_4 solution (1.0 M, 150 ml), and the product was extracted with hexane (3 × 100 ml). After the usual work-up, the extract was chromatographed over SiO_2 (90 g) impregnated with $AgNO_3$ (10 g) with elution by hexane and benzene to give **2** (4.5 g, 17 mmol, 94%). ^{1}H-NMR δ: 0.84 (3H, d, J = 6.5 Hz, C*H*$_3$CH), 0.89 (3H, t, J = 6.5 Hz, C*H*$_3$CH$_2$), ∼1.1 (2H, m), ∼1.25 (22H, m), ∼1.35 (3H, m), 2.04 (2H, dt, J = 7, 7 Hz, C*H*$_2$CH=C), 4.92 (1H, d, J = 10.5 Hz, CH=C*H*H), 4.99 (1H, d, J = 17 Hz, CH=CH*H*), 5.81 (1H, ddt, J = 17, 10.5, 6.5 Hz, C*H*=CH$_2$). IR ν_{max} cm^{-1}: 3078, 2924, 2854, 1641, 1466, 991, 908. GC-MS: t_R 12.78 min; m/z 266 (M$^+$, 1%), 97 (66%), 57 (100%).

*Benzyl ether of propargyl alcohol (**8**).* To a mixture of NaH (60%, 2.0 g, 50 mmol) and NaI (0.75 g, 5 mmol), propargyl alcohol (2.8 g, 50 mmol) in dry DMF (30 ml) was added dropwise while stirring at 0 °C under Ar. After stirring for 30 min, benzyl bromide (8.6 g, 50 mmol) was added dropwise to the mixture while stirring. The reaction mixture was stirred at 0 °C for 30 min and at rt for 2 h, and then poured into water (300 ml). The product was extracted with hexane/EtOAc (1:1, 3 × 100 ml). After the usual work-up, the extract was chromatographed over SiO_2 (150 g) with elution by hexane/EtOAc (10:1) to give **8**, which was further purified by distillation (6.3 g, 43 mmol, 86%; boiling point, 190 °C at 80 mm Hg). ^{1}H-NMR δ: 2.45 (1H, t, J = 2.5 Hz, *H*C≡C), 4.15 (2H, d, J = 2.5 Hz, C*H*$_2$C≡C), 4.59 (2H, s, OC*H*$_2$Ph), ∼7.3 (5H, m). ^{13}C-NMR δ: 57.0, 71.5, 74.7, 79.6, 127.9, 128.1 (×2), 128.4 (×2), 137.2. IR ν_{max} cm^{-1}: 3292, 3032, 2856, 2117, 1454, 1356, 1074, 742, 698. GC-MS: t_R 11.32 min; m/z 145 ([M − 1]$^+$, 11%), 91 (100%).

*Benzyl ether of 6-methyl-2-decyn-1-ol (**9**).* To a solution of 1-alkyne **8** (3.8 g, 26 mmol) in dry THF (25 ml), BuLi (a 1.6 M hexane solution, 16 ml) was added dropwise while stirring at −35 °C under Ar. After additional stirring for 30 min, **B_2** (6.2 g, 26 mmol) dissolved in hexamethylphosphoramide (HMPA, 6 ml) was added to the mixture. The reaction mixture was stirred at −35 °C for 30 min and at rt for 1 h, and then poured into water (300 ml). The product was extracted with EtOAc (3 × 100 ml). After the usual work-up, the extract was chromatographed over SiO_2 (200 g) with elution by hexane/EtOAc (10:1) to give **9** (6.2 g, 24 mmol, 92%). ^{1}H-NMR δ: 0.87 (3H, d, J = 6.5 Hz, C*H*$_3$CH), 0.88 (3H, t, J = 6.5 Hz, C*H*$_3$CH$_2$), ∼1.1 (1H, m), ∼1.3 (6H, m), 1.55 (2H, m), 2.24 (2H, m, C≡CC*H*$_2$CH$_2$), 4.15 (2H, t, J = 2 Hz, C≡CC*H*$_2$O), 4.58 (2H, s, OC*H*$_2$Ph), ∼7.3 (5H, m). ^{13}C-NMR δ: 14.2, 16.5, 19.2, 23.0, 29.1, 31.9, 35.7, 36.3, 57.7, 71.3, 75.6, 87.4, 127.7, 128.1 (×2), 128.3 (×2), 137.6. IR ν_{max} cm^{-1}: 3030, 2927, 1454, 1354, 1072, 737, 698. GC-MS: t_R 20.19 min; m/z 257 ([M − 1]$^+$, 2%), 145 (79%), 91 (100%).

*6-Methyl-1-decanol (**10**).* A mixture of alkyne **9** (6.2 g, 24 mmol), Pd-C (10%, 700 mg), and MeOH (100 ml) was stirred for two days under H_2 at rt. After filtering off the catalyst, the solvent was evaporated. The product was chromatographed over SiO_2 (150 g) with elution by hexane/EtOAc (from 10:1 to 2:1) to give **10** (3.1 g, 18 mmol, 75%). ^{1}H-NMR δ: 0.84 (3H, d, J = 6.5 Hz, C*H*$_3$CH), 0.89 (3H, t, J = 6.5 Hz, C*H*$_3$CH$_2$), ∼1.1 (2H, m), ∼1.3 (11H, m), 1.56 (2H, m, C*H*$_2$CH$_2$OH), 3.63 (2H, t, J = 6.5 Hz, C*H*$_2$OH). ^{13}C-NMR δ: 14.2, 19.7, 23.1, 26.1, 26.9, 29.3, 32.7, 32.9, 36.8, 37.0, 63.0. IR ν_{max} cm^{-1}: 3330, 2931, 1464, 1377, 1055, 729. GC-MS: t_R 11.67 min; m/z 154 ([M − 18]$^+$, 1%), 97 (66%), 55 (100%).

*1-Bromo-6-methyldecane (**11**).* A mixture of the alcohol **10** (2.1 g, 12 mmol), HBr (48%, 5.1 g, 30 mmol), and H_2SO_4 (590 mg, 6 mmol) was stirred under a refluxing condition at 120 °C for 6 h. The reaction mixture was added dropwise to a saturated aqueous solution of $NaHCO_3$ (100 ml) and extracted with hexane (3 × 100 ml). After the usual work-up, the product was chromatographed over SiO_2 (100 g) with elution by hexane to give **11** (2.6 g, 11 mmol, 92%). ^{1}H-NMR δ: 0.84 (3H, d, J = 6.5 Hz, C*H*$_3$CH), 0.89 (3H, t, J = 6.5 Hz, C*H*$_3$CH$_2$), ∼1.1 (2H, m), ∼1.3 (11H, m), 1.86 (2H, tt, J = 7, 7 Hz, C*H*$_2$CH$_2$Br), 3.41 (2H, t, J = 7 Hz, C*H*$_2$Br). ^{13}C-NMR δ: 14.2, 19.7, 23.1, 26.2, 28.5, 29.3, 32.7, 32.9, 34.1, 36.7, 36.8. IR ν_{max} cm^{-1}: 2925, 1464, 1377, 1252, 729, 648, 565. GC-MS: t_R 10.40 min; m/z 221 and 219 ([M − 15]$^+$, 1%), 151 and 149 (63%), 85 (100%).

*6,14-Dimethyl-1-octadecene (**3**) from bromide **11**.* In a similar manner to that for the preparation of **2**, a Grignard reagent prepared from **11** (2.4 g, 10 mmol) and Mg turnings (490 mg, 20 mmol) was coupled with **A_1** (1.5 g, 5.0 mmol). The crude product was chromatographed over SiO_2 (90 g) impregnated with $AgNO_3$ (10 g) with elution by hexane/benzene to give **3** (1.3 g, 4.6 mmol, 46% from **11**, 92% from **A_1**). ^{1}H-NMR δ: 0.84 (3H, d, J = 6.5 Hz, C*H*$_3$CH), 0.85 (3H, d, J = 6.5 Hz, C*H*$_3$CH), 0.88 (3H, t, J = 6.5 Hz, C*H*$_3$CH$_2$), ∼1.1 (4H, m), ∼1.25 (17H, m), ∼1.35 (5H, m), 2.02 (2H, dt, J = 7, 7 Hz, C*H*$_2$CH=C), 4.93 (1H, d, J = 10.5 Hz, CH=C*H*H), 4.99 (1H, d, J = 17 Hz, CH=CH*H*), 5.82 (1H, ddt, J = 17, 10.5, 6.5 Hz, C*H*=CH$_2$). IR ν_{max} cm^{-1}: 3078, 2925, 2856, 1639, 1460, 993, 908. GC-MS: t_R 13.11 min; m/z 280 (M$^+$, 1%), 97 (100%), 57 (94%).

*Wacker oxidation of 1-alkenes **1**–**3**.* $PdCl_2$ (89 mg, 0.50 mmol) and CuCl (0.50 g, 5.0 mmol) were added to a solution of **1** (1.3 g, 5.0 mmol) in DMF (17.5 ml) and water (2.5 ml). The mixture was stirred at rt, and then O_2 was bubbled into it for 22 h. After the reaction, the mixture was poured into an HCl solution (1.0 M, 50 ml) and extracted with Et_2O (3 × 100 ml). After the usual work-up, the crude product was chromatographed over SiO_2 (180 g) with elution by hexane/EtOAc (from 10:1 to 5:1) to give **I** (0.98 g, 3.5 mmol, 70%). IR λ_{max} cm^{-1}: 2924, 2854, 1720, 1464, 1383, 1165. GC-MS: t_R 19.13 min; m/z 282 (M$^+$, 2%), 264 ([M − 18]$^+$, 37%), 58 (100%). In the same manner, **2** (1.0 g, 3.8 mmol) and **3** (0.56 g, 2.0 mmol) were oxidized to **II** (0.81 g, 2.9 mmol, 76%) and **III** (0.41 g, 1.4 mmol, 70%), respectively. IR λ_{max} cm^{-1} **II**: 2924, 2854, 1720, 1466, 1383, 1161; **III**: 2926, 2854, 1720, 1464, 1377, 1165. GC-MS **II**: t_R 19.32 min; m/z 282 (M$^+$, 11%), 264 ([M − 18]$^+$, 8%), 58 (100%); **III**: t_R 19.68 min; m/z 296 (M$^+$, 2%), 278 ([M − 18]$^+$, 32%), 58 (100%).

*3-Chloro-1-propyl tosylate (**12**).* 3-Chloro-1-propanol (3.8 g, 40 mmol) was tosylated with TsCl (9.2 g, 48 mmol) and DMAP (200 mg) in a similar manner to that for the preparation of **4**. The crude product was chromatographed over SiO_2 (150 g) with elution by hexane/EtOAc (10:1) to give **12** (9.4 g, 38 mmol, 95%). ^{1}H-NMR δ: 2.09 (2H, tt, J = 6, 6 Hz, C*H*$_2$CH$_2$Cl), 2.46 (3H, s, C*H*$_3$Ph), 3.57 (2H, t, J = 6 Hz, C*H*$_2$Cl), 4.19 (2H, t, J = 6 Hz, TsOC*H*$_2$), 7.36 (2H, d, J = 8.5 Hz), 7.80 (2H, d, J = 8.5 Hz). ^{13}C-NMR δ: 21.7, 31.7, 40.3, 66.8, 127.9 (×2), 129.9 (×2), 132.7, 145.0. IR ν_{max} cm^{-1}: 2968, 1599, 1448, 1360, 1176, 1097, 1001, 935, 816, 667, 575, 555.

*1-Chloro-6-methyldecane (**13**).* In a similar manner to that for the preparation of bromide **11**, alcohol **7** was converted to 1-bromo-3-methylheptane in an 88% yield. To Mg turnings (0.97 g, 40 mmol) in dry Et_2O (30 ml), this bromide (3.5 g, 18 mmol) in dry Et_2O (4 ml) was added while stirring at 0 °C under Ar. After stirring at 0 °C for 1 h, the mixture was warmed to rt. The produced Grignard reagent **B_3** was taken up in a syringe and added dropwise to a solution of tosylate **12** (4.0 g, 16 mmol) and Li_2CuCl_4 (a 0.1 M THF solution, 1.0 ml) in dry THF (40 ml) at −78 °C under Ar. The mixture was gradually warmed to rt. Stirring was continued for 14 h, the mixture was poured into a cool H_2SO_4 solution (1 M, 150 ml), and the product was extracted with hexane (3 × 100 ml). After the usual work-up, the extract was chromatographed over SiO_2 (150 g) with elution by hexane to give **13** (2.7 g, 14 mmol, 88%). ^{1}H-NMR δ: 0.84 (3H, d, J = 6.5 Hz, C*H*$_3$CH), 0.89 (3H, t, J = 6.5 Hz, C*H*$_3$CH$_2$), ∼1.1 (2H, m), ∼1.3 (11H, m), 1.62 (2H, tt, J = 7, 7 Hz, C*H*$_2$CH$_2$Cl), 3.43 (2H, t, J = 7 Hz, C*H*$_2$Cl). ^{13}C-NMR δ: 14.2, 19.7, 23.2, 26.5, 27.2, 29.4, 33.1, 32.7, 32.8, 36.7, 45.0. IR ν_{max} cm^{-1}: 2923, 1466, 1309, 723, 654. GC-MS: t_R 8.55 min; m/z 107 (6%), 105 (20%), 93 (31%), 91 (100%).

*6,14-Dimethyl-1-octadecene (**3**) from chloride **13**.* To Mg turnings (0.49 g, 20 mmol) in dry THF (20 ml), a catalytic amount of MeMgBr (a 2.0 M Et_2O solution, two drops) was added under Ar *via* a syringe. Next, chloride **13** (1.9 g, 10 mmol) in dry THF (4.0 ml) was added while stirring at 0 °C under Ar. After stirring at 0 °C for 2 h, the reaction mixture was warmed to rt, and stirring continued for 2 h. This Grignard reagent was taken up in a syringe and added to a solution of **A_1** (1.5 g, 5.0 mmol) and Li_2CuCl_4 (a 0.1 M THF solution, 1.0 ml) in

dry THF (40 ml) in another flask at −78 °C under Ar. The mixture was gradually warmed to rt. Stirring was continued for 14 h, the mixture was poured into an H_2SO_4 solution (1.0 M, 150 ml), and the product was extracted with hexane (3 × 100 ml). After the usual work-up, the extract was chromatographed over SiO_2 (90 g) impregnated with $AgNO_3$ (10 g) with elution by hexane and hexane/benzene (3:1) to give **3** (0.57 g, 2.0 mmol, 20% from **13**, 40% from $\mathbf{A_1}$).

tert-*Butyl 7-methyl-3-oxoundecanoate (**14**).* Into a suspension of NaH (60% in oil, 0.80 g, 20 mmol) with dry THF (15 ml) and HMPA (3.5 ml), *tert*-butyl acetoacetate (3.2 g, 20 mmol) was added dropwise under Ar. The mixture was refluxed at 85 °C for 1 h. After cooling, BuLi (1.65 M, 13 ml, 21 mmol) was added, and the mixture was stirred at rt for 30 min. Next, iodide $\mathbf{B_2}$ (4.8 g, 20 mmol) in dry THF (5 ml) was added at 0 °C. After stirring at rt for 1 h, the mixture was poured into a saturated NH_4Cl solution. The crude product was extracted with EtOAc (3 × 50 ml) and chromatographed over SiO_2 (200 g) after the usual work-up. Elution with hexane/EtOAc (30:1) yielded **14** (3.8 g, 14 mmol, 70%). ^{1}H-NMR δ: 0.85 (3H, d, J = 6.5 Hz, CH_3CH), 0.88 (3H, t, J = 6.5 Hz, CH_3CH$_2$), ~1.25 (11H, m), 1.47 (9H, s, C(CH_3)$_3$), 2.45 (2H, t, J = 7.5 Hz, CH$_2$CH_2C=O), 3.34 (2H, s, O=CCH_2C=O). ^{13}C-NMR δ: 14.2, 19.5, 21.0, 23.0, 28.0 (×3), 29.2, 32.6, 36.4, 36.5, 43.3, 50.7, 81.9, 166.6, 203.6. IR ν_{max} cm^{-1}: 2929, 1738, 1716, 1643, 1458, 1369, 1252, 1149.

*6,14-Dimethyl-1-octadecene (**3**) from ketoester **14**.* A mixture of potassium *tert*-butoxide (1.6 g, 14 mmol) and *tert*-butanol (20 ml) was stirred and heated at 100 °C. After complete dissolution of the base, ketoester **14** (3.2 g, 12 mmol) was added to the solution, which was stirred at 100 °C for 15 min. Iodide $\mathbf{A_2}$ (3.0 g, 12 mmol) was then added to the mixture, which was stirred under the same condition for 6 h. After evaporation of most of the solvent, the residue was poured into a saturated NH_4Cl solution. The crude product was extracted with EtOAc (3 × 50 ml) and chromatographed over SiO_2 (100 g) after the usual work-up. While characterization of the elongated ketoester **15** could not be accomplished because of the contamination of some unknown compounds, a fraction expected to include **15** was treated with *p*-toluenesulfonic acid monohydrate (700 mg) and stirred at 100 °C for 30 min on neat condition. The dealkoxycarbonylation of **15** was indicated by the appearance of many small bubbles. After cooling, the crude product was dissolved in diethylene glycol (DEG, 40 ml), and KOH (2.81 g, 50 mmol) and $NH_2NH_2 \cdot H_2O$ (1.6 g, 50 mmol) were added to the solution. The mixture was stirred at 200 °C for 4 h, and the mixture was poured into water (300 ml) after cooling. The crude product was extracted with hexane (3 × 100 ml) and chromatographed over SiO_2 (100 g) after the usual work-up. Elution with hexane yielded **3** (1.31 g, 4.7 mmol, 39%).

References

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