A new approach to the synthesis of racemic analogs of 1,5-dimethyl-branched insect pheromones from 4-methyltetrahydropyran*

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A new procedure was developed for the synthesis of racemic analogs of 1,5-dimethyl-branched insect pheromones based on monoalkylation of ethyl acetoacetate with 1-acetoxy-5-bromo-3-methylpentane produced upon decyclization of 4-methyltetrahydropyran.

Key words: 1-acetoxy-5-bromo-3-methylpentane, 8-acetoxy-6-methyloctan-2-one, ethyl acetoacetate, racemic analogs of pheromones, 4-methyltetrahydropyran, Wittig reaction, cross-coupling.

4-Methyltetrahydropyran (**1**) acid-catalyzed ring-opening products, among them 1-acetoxy-5-bromo-3-methylpentane (**2**), find rather wide use in the synthesis of methyl-branched low-molecular-weight insect bioregulators.[1,2]

In the present study, we examined new approaches to the synthesis of biologically active[3] racemic analogs of 1,5-dimethyl-branched insect pheromones (**3—5**) based on chemoselective transformations of the monoalkylation product of ethyl acetoacetate with bromoacetate **2** (Scheme 1).

It should be noted that the low yield (25%) of a mixture of diastereomeric ethyl 7-acetoxy-2-acetyl-5-methylheptanoates (**6**) obtained in the reaction performed under standard conditions (EtONa/EtOH, 10 h) is attributed to the fact that this transformation was accompanied by cyclization of **2** as a side reaction giving rise to the starting pyran **1**.

The chemical shifts and multiplicities of the signals in the ^{13}C NMR spectrum of a mixture of diastereomers **6** are consistent with the assumed structure. The signals for the C(4), C(5), C(6), and $CH_3C(5)$ atoms are observed as pairs of closely spaced lines, which is attributable to the difference in shielding of the above-mentioned nuclei of diastereomers **6**. Equal integral intensities of the signals for the corresponding atoms in the ^{13}C NMR spectra, which were acquired using a longer pulse delay (20 s), suggest that compound **6** represents a racemic mixture of diastereomers.

The NMR spectra of sample **6** have no signals for the protons and carbon atoms of the starting compounds and other structural impurities.

The reaction involving lower-basic EtOLi [4] instead of EtONa proceeded much more slowly (~50 h). However, this process was not accompanied by the above-mentioned cyclization and a mixture of diastereomeric acetoxy oxo esters **6** was obtained in 92% yield. Even a higher yield (96%) was attained in the reaction performed in a 1 : 1 mixture of aprotic solvents DMF and benzene with sodium hydride as a base.

Decarbethoxylation of **6** under the standard conditions[5] afforded the key product, *viz.*, 8-acetoxy-6-methyloctan-2-one (**7**). The Wittig olefination of the latter compound with ethylidene- and *n*-hexylidenetriphenylphosphoranes (0→20 °C) afforded mixtures ($E : Z \sim 1 : 1$) of unsaturated acetates **8** and **9**, respectively. The ratios of stereoisomers in these mixtures were determined based on the GLC data and the integral intensity ratios for the signals of the methyl groups at the double bond ($7\text{-}CH_3$) in the ^1H NMR spectra, which show resonances at δ 1.65 (for the *Z* isomer) and 1.56 (for the *E* isomer).[6]

Alcohols **10** prepared by hydrolysis of acetates **8** were further subjected to hydrogenation. Saturated alcohols **11** were transformed into a mixture of diastereomeric 4,8-dimethyldecanals **3** according to a procedure developed by us earlier.[7] The latter mixture is a biologically active analog of the aggregation pheromone of *Tribolium* flour beetles, *viz.*, of 4*R*,8*R*-dimethyldecanal.[3]

Besides, *p*-toluenesulfonates **13** and **14** prepared from alcohols **10** as well from alkenols **12** corresponding to

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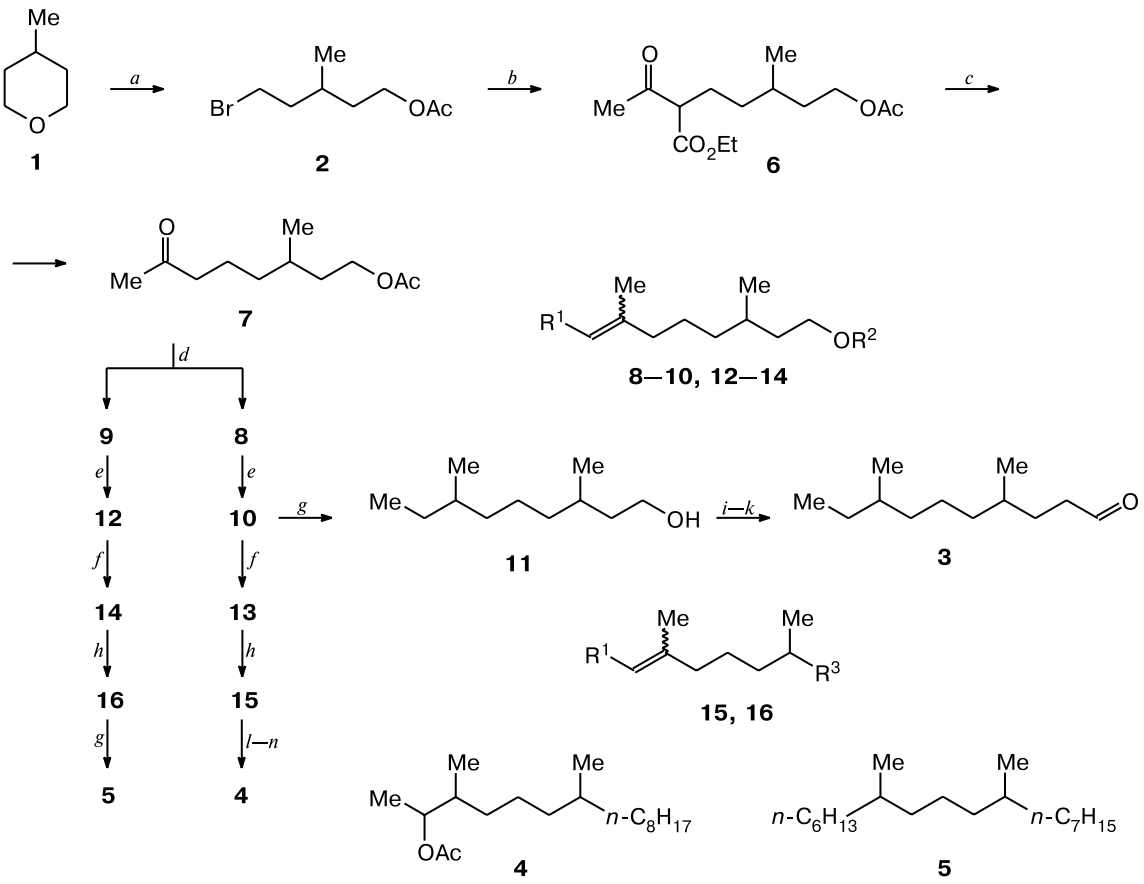
Scheme 1



R^1 = Me (**8**, **10**, **13**, **15**), n-C_5H_{11} (**9**, **12**, **14**, **16**); R^2 = H (**10**, **12**), Ac (**8**, **9**), Ts (**13**, **14**); R^3 = n-C_8H_{17} (**15**), n-C_7H_{15} (**16**)

Reagents and conditions: *a*) $AcBr/ZnCl_2$ (see Ref. 2); *b*) $AcCH_2CO_2Et/EtOLi$ or $AcCH_2CO_2Et/NaH/PhH—DMF$; *c*) LiI/DMF; *d*) $R^1CH{=}PPh_3$ (R^1 = Me, n-C_5H_{11}); *e*) KOH—MeOH; *f*) TsCl/Py; *g*) H_2/Pd—C; *h*) n-$C_6H_{13}MgBr$ or n-$C_5H_{11}MgBr/Li_2CuCl_4$; *i*) HBr/H_2SO_4; *j*) Mg; *k*) DMF (see Ref. 7); *l*) B_2H_6; *m*) H_2O_2; *n*) Ac_2O/Py (see Ref. 6).

acetates **9** can be involved into catalyzed cross-coupling with *n*-hexyl- and *n*-pentylmagnesium bromides, respectively.

The first of the above-mentioned mixtures of monoenes **15** and **16** thus synthesized was transformed into a mixture of diastereomeric acetates **4** according to a procedure described earlier.[6] The resulting mixture is a biologically active analog of diprionyl acetate, *viz.*, of 2*S*-acetoxy-3*S*,7*S*-dimethylpentadecane,[3] which is the sex pheromone of *Diprion* and *Neodiprion* pine sawflies.

Catalytic hydrogenation of a mixture of olefins **16** afforded diastereomeric 7,11-dimethyloctadecanes **5**, which are analogs of the oviposition attractant of yellow fever mosquito *Aedes aegypti*.[8] The stereochemistry of the latter compound remains to be established.

To summarize, we developed a new approach to the synthesis of racemic analogs of acyclic 1,5-dimethyl-branched insect pheromones based on monoalkylation of ethyl acetoacetate with 1-acetoxy-5-bromo-3-methylpentane, which is a decyclization product of 4-methyltetrahydropyran.

Experimental

The IR spectra were recorded on a UR-20 instrument in thin layers. The NMR spectra were measured on a Bruker AM-300 spectrometer (300.13 MHz for ^1H and 75.47 MHz for ^{13}C) in $CDCl_3$ with Me_4Si as the internal standard. The GLC analysis was carried out on a Chrom-5 instrument (the column length was 1.2 m; silicon SE-30 (5%) on Chromaton N-AW-DMCS (0.16—0.20 mm) as the stationary phase; the column temperature was 50—300 °C) using helium as the carrier gas. Column chromatography and TLC were carried out with the use of light petroleum (LP), b.p. 40—70 °C. 4-Methyltetrahydropyran was prepared according to a known procedure.[9]

Ethyl 7-acetoxy-2-acetyl-5-methylheptanoates (6). ***A.*** Ethyl acetoacetate (9.42 g, 72.5 mmol) was added dropwise to a stirred (Ar, 20 °C) solution of EtONa prepared from Na (1.55 g, 67.3 mg-at.) in anhydrous EtOH (34 mL). Then bromide **2** (10.00 g, 44.8 mmol), which was prepared from 4-methyltetrahydropyran (**1**) according to a known procedure,[2] was added with refluxing. The reaction mixture was refluxed for 10 h (TLC control on SiO_2, LP—Et_2O, 1 : 1), cooled, and filtered. The precipitate was washed on a filter with EtOH and the filtrate was concentrated. The residue was chromatographed on a column with SiO_2 (LP—Et_2O, 5 : 1). A mixture of diastereomers **6** was obtained in a yield of 2.45 g (25%), R_f 0.18 (LP—Et_2O, 1 : 1). Found (%): C, 61.61; H, 8.83. $C_{14}H_{24}O_5$. Calculated (%): C, 61.74; H, 8.88. IR, ν/cm^{-1}: 1755, 1745 (O—C=O); 1718 (C=O); 1245, 1140, 1055 (C—O—C). ^{1}H NMR ($CDCl_3$), δ: 0.91 (d, 2 H, $H_3C(5)$, J = 6.5 Hz); 1.27 (t, 3 H, $C\underline{H}_3CH_2O$, J = 7.0 Hz); 1.39—1.99 (m, 7 H, H(3), H(4), H(5), H(6)); 2.03 (s, 3 H, CH_3CO); 2.22 (s, 3 H, CH_3CO_2); 3.36 (t, 1 H, H(2), J = 7.0 Hz); 4.03—4.12 (m, 2 H, H(7)); 4.19 (q, 2 H, $CH_3C\underline{H}_2O$, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 13.81 (q, $\underline{C}H_3CH_2O_2C$); 18.95 (18.89) (q, $CH_3C(5)$); 20.68 (q, $\underline{C}H_3CO_2$); 25.23 (t, C(3)); 28.54 (q, $\underline{C}H_3CO$); 29.48 (29.43) (d, C(5)); 34.08 (34.00) (t, C(4)); 34.91 (34.86) (t, C(6)); 59.62 (d, C(2)); 61.01 (t, $CH_3\underline{C}H_2O_2C$); 62.33 (t, C(7)); 169.47 (s, C(1)); 170.78 (s, $CH_3\underline{C}O_2$); 202.75 (s, $CH_3\underline{C}O$).

B. Ethyl acetoacetate (9.09 g, 70.0 mmol) was added dropwise to a stirred (Ar, 20 °C) solution of EtOLi prepared from Li (0.38 g, 53.8 mg-at.) in anhydrous EtOH (27 mL). Then bromoacetate **2** (10.00 g, (44.8 mmol) was added with refluxing. The reaction mixture was refluxed for 50 h and then treated as described in the method ***A***. A mixture **6** was obtained in a yield of 11.17 g (92%). According to the spectroscopic data, this mixture is identical with that prepared according to the method ***A***.

C. Ethyl acetoacetate (4.77 g, 36.7 mmol) was added dropwise to a stirred (Ar, 0 °C) suspension of NaH (0.88 g, 36.7 mmol) in anhydrous benzene (37 mL) and anhydrous DMF (37 mL). The reaction mixture was kept at ~20 °C until the reaction mixture became homogeneous (~3 h). Then compound **2** (7.96 g, 36.7 mmol) was added dropwise to the resulting solution at 0 °C. The reaction mixture was kept at ~20 °C for 11 h and then refluxed for 12 h, after which water (40 mL) was added. Then the reaction mixture was extracted with benzene (4×40 mL). The combined extracts were washed with water (20 mL), dried with $MgSO_4$, filtered, and concentrated. The residue was chromatographed on SiO_2 (LP—Et_2O, 5 : 1). A mixture **6** was obtained in a yield of 9.58 g (96%). According to the spectroscopic data, this mixture is identical with that prepared according to the method ***A***.

8-Acetoxy-6-methyloctan-2-one (7). Lithium iodide (12.87 g, 95.5 mmol) was added in one portion to a stirred (20 °C) solution of ester **6** (10.00 g, 36.8 mmol) in anhydrous DMF (104 mL). The reaction mixture was refluxed until liberation of CO_2 ceased (~12 h). Then the resulting mixture was cooled and extracted with Et_2O (4×50 mL). The combined extracts were washed successively with saturated solutions of $Na_2S_2O_3$ and NaCl, dried with Na_2SO_4, and filtered. The solvent was evaporated. Acetoxy ketone **7** was obtained in a yield of 5.96 g (81%), R_f 0.23 (LP—Et_2O, 1 : 1). Found (%): C, 65.70; H, 10.11. $C_{11}H_{20}O_3$. Calculated (%): C, 65.97; H, 10.07. IR, ν/cm^{-1}: 1740 (O—C=O); 1720 (C=O); 1250, 1055 (C—O—C). ^{1}H NMR ($CDCl_3$), δ: 0.88 (d, 3 H, 6-CH_3, J = 6.5 Hz); 1.05—1.70 (m, 7 H, H(4), H(5), H(6), H(7)); 2.01 (s, 3 H, CH_3CO); 2.13 (s, 3 H, CH_3CO_2); 2.44 (t, 2 H, H(3), J = 7.0 Hz); 3.99—4.10 (m, 2 H, H(8)). ^{13}C NMR ($CDCl_3$), δ: 18.93 (q, $\underline{C}H_3C(6)$); 20.55 (q, $\underline{C}H_3CO_2$); 20.67, 34.93, and 35.85 (all t, C(4), C(5), C(7)); 29.30 (q, C(1)); 29.44 (d, C(6)); 43.33 (t, C(3)); 62.34 (t, C(8)); 170.58 (s, $CH_3\underline{C}O_2$); 208.32 (s, C(2)).

3,7-Dimethylnon-7*Z*/*E*-en-1-yl acetates (8). A 1 *M* Bu^{n}Li solution in hexane (33.0 mL, 33.0 mmol) was added dropwise with stirring to a suspension of ethyltriphenylphosphonium bromide (12.24 g, 33.0 mmol) in anhydrous THF (100 mL) (Ar, 0 °C). The reaction mixture was stirred at ~20 °C for 1 h and cooled to 0 °C. Then a solution of acetoxy ketone **7** (4.00 g, 20.0 mmol) in anhydrous THF (14 mL) was added dropwise. The reaction mixture was stirred at 0 °C for 15 min, kept at ~20 °C for 12 h, diluted with light petroleum (200 mL), and filtered through a layer of SiO_2. The solvent was evaporated and the residue was chromatographed on SiO_2 (LP—Et_2O, 10 : 1). A mixture of acetates **8** (*Z*/*E* ~ 1 : 1) was obtained in a yield of 3.60 g (85%), R_f 0.78 (LP—Et_2O, 1 : 1). Found (%): C, 73.46; H, 11.35. $C_{13}H_{24}O_2$. Calculated (%): C, 73.53; H, 11.39. IR, ν/cm^{-1}: 1745 (C=O); 1658 (C=C); 1240, 1055 (C—O—C). ^{1}H NMR ($CDCl_3$), δ: 0.90 (d, 3 H, $H_3C(3)$, J = 6.5 Hz); 1.25 (br.s, 7 H, H(2), H(3), H(4), H(5)); 1.55 and 1.66 (both s, 1.5 H each, $H_3C(7)$); 1.50—1.65 (m, 3 H, H(9)); 1.88—2.00 (m, 2 H, H(6)); 2.02 (s, 3 H, CO_2CH_3); 4.03—4.15 (m, 2 H, H(1)); 5.12—5.25 (m, 1 H, H(8)). ^{13}C NMR ($CDCl_3$), δ: 13.24 (13.32) (q, C(9)); 15.51 (*E*) (23.35 (*Z*)) (q, $CH_3C(7)$); 19.47 (19.50) (q, $CH_3C(3)$); 21.03 (q, $\underline{C}H_3CO_2$); 25.17, 35.49, and 36.68 (all t, C(2), C(4), C(5)); 29.73 (29.76) (d, C(3)); 35.49 (39.84) (t, C(6)); 63.07 (t, C(1)); 118.24 (118.93) (d, C(8)); 135.85 (136.06) (s, C(7)); 171.27 (s, $CH_3\underline{C}O_2$).

3,7-Dimethylnon-7*Z*/*E*-en-1-ols (10). A mixture of acetates **8** (3.56 g, 16.8 mmol) was dissolved in MeOH (17 mL), KOH (0.98 g, 17.5 mmol) was added, and the reaction mixture was refluxed for 4 h. Then MeOH was evaporated and the residue was extracted with Et_2O (3×30 mL). The combined extracts were washed with a saturated NaCl solution, dried with Na_2SO_4, filtered, and concentrated. A mixture of alcohols **10** was obtained in a yield of 2.51 g (88%), R_f 0.52 (LP—Et_2O, 1 : 1). Found (%): C, 77.47; H, 12.99. $C_{11}H_{22}O$. Calculated (%): C, 77.58; H, 13.02. IR, ν/cm^{-1}: 3450—3300 (OH); 1650 (C=C). ^{1}H NMR ($CDCl_3$), δ: 0.91 (d, 3 H, $H_3C(3)$, J = 6.5 Hz); 1.29 (br.s, 6 H, H(2), H(4), H(5)); 1.56 and 1.65 (both s, 1.5 H each, $H_3C(7)$); 1.54 (s, 3 H, H(9)); 1.61—1.67 (m, 1 H, H(3)); 1.87 (t, 2 H, H(6), J = 7 Hz); 3.53 (br.s, 1 H, OH); 3.79 (t, 2 H, H(1), J = 6.5 Hz); 5.15—5.25 (m, 1 H, H(8)). ^{13}C NMR ($CDCl_3$), δ: 13.00 (13.20) (q, C(9)); 15.40 (*E*) (23.30 (*Z*)) (q, $CH_3C(7)$); 19.55 (19.57) (q, $CH_3C(3)$); 25.40, 35.56, and 36.80 (all t, C(2), C(4), C(5)); 27.40 (27.41) (d, C(3)); 33.68 (*Z*) (39.20 (*E*)) (t, C(6)); 59.57 (t, C(1)); 118.40 (119.20) (d, C(8)); 136.21 (136.70) (d, C(7)).

3,7-Dimethyl-1-tosyloxy-7*Z*/*E*-nonenes (13). A mixture of alcohols **10** (2.00 g, 11.6 mmol) was dissolved in dry Py (3.5 mL). Then TsCl (2.43 g, 12.8 mmol) was added portionwise at 0—5 °C. The reaction mixture was kept at 0 °C for 12 h, diluted with Et_2O (50 mL), washed successively with saturated solutions of $CuSO_4$, Na_2CO_3, and NaCl, dried with $MgSO_4$, filtered, and concentrated. A mixture of *p*-toluenesulfonates **13** was obtained in a yield of 3.16 g (84%). IR, ν/cm^{-1}: 1660 (C=C); 1600 (Ar); 1350, 1180 (S=O).

3,7-Dimethyltridec-7*Z*/*E*-en-1-yl acetates (9). *n*-Hexyltriphenylphosphonium bromide (6.80 g, 15.9 mmol) was converted into phosphorane and the reaction of the latter with ketone **7** (1.93 g, 9.7 mmol) was performed analogously to the synthesis of **8**. A mixture of acetates *Z*-**9**/*E*-**9** (~ 1 : 1) was obtained in a yield of 1.69 g (65%), R_f 0.79 (LP—Et_2O, 1 : 1). Found (%): C, 75.96; H, 11.98. $C_{17}H_{32}O_2$. Calculated (%): C, 76.06; H, 12.02. IR, ν/cm^{-1}: 1750 (C=O); 1660 (C=C); 1245, 1050 (C—O—C). ^{1}H NMR ($CDCl_3$), δ: 0.90 (d, 3 H, $H_3C(3)$, J = 6.0 Hz); 0.93 (t, 3 H, $H_3C(13)$, J = 7.0 Hz); 1.26 (br.s, 13 H, H(2), H(3), H(4), H(5), H(10), H(11), H(12)); 1.48 and 1.63 (both s, 1.5 H each, $H_3C(7)$); 1.88—2.01 (m, 4 H, H(6), H(9)); 2.03 (s, 3 H, CH_3CO_2); 4.03—4.15 (m, 2 H, H(1)); 5.12—5.25 (m, 1 H, H(8)). ^{13}C NMR ($CDCl_3$), δ: 14.05 (q, C(13)); 15.42 (*E*) (23.30 (*Z*)) (q, $CH_3C(7)$); 19.70 (19.73) (q, $CH_3C(3)$); 21.04 (q, $\underline{C}H_3CO_2$); 22.80, 25.42, 29.56, 29.70, and 30.89 (all t, C(2), C(4), C(5), C(10)—C(12)); 27.40 (27.48) (d, C(3)); 33.68 (39.20) (t, C(6)); 35.56 (36.80) (t, C(9)); 63.02 (t, C(1)); 126.72 (127.00) (d, C(8)); 134.47 (134.77) (s, C(7)); 170.96 (s, $CH_3\underline{C}O_2$).

3,7-Dimethyltridec-7*Z*/*E*-en-1-ols (12). A mixture of acetates **9** (1.60 g, 6.0 mmol) was treated with KOH in MeOH as described in the synthesis of **10**. A mixture of alcohols **12** was obtained in a yield of 1.22 g (90%), R_f 0.54 (LP—Et_2O, 1 : 1). Found (%): C, 79.51; H, 13.39. $C_{15}H_{30}O$. Calculated (%): C, 79.57; H, 13.36. IR, ν/cm^{-1}: 3450—3300 (OH); 1645 (C=C). ^{1}H NMR ($CDCl_3$), δ: 0.90 (d, 3 H, $H_3C(3)$, J = 6.0 Hz); 0.94 (t, 3 H, $H_3C(13)$, J = 7.0 Hz); 1.31 (br.s, 13 H, H(2), H(3), H(4), H(5), H(10), H(11), H(12)); 1.50 and 1.61 (both s, 1.5 H each, $H_3C(7)$); 1.88—2.00 (m, 4 H, H(6), H(9)); 3.80 (t, 2 H, H(1), J = 6.5 Hz); 5.10—5.20 (m, 1 H, H(8)). ^{13}C NMR ($CDCl_3$), δ: 14.00 (q, C(13)); 15.38 (*E*) (23.00 (*Z*)) (q, $CH_3C(7)$); 19.54 (19.60) (q, $CH_3C(3)$); 22.85, 25.40, 29.50, 29.85, 30.85, 35.56 (all t, C(2), C(4), C(5), C(10)—C(12)); 28.50 (28.55) (d, C(3)); 33.70 (39.12) (t, C(6)); 35.50 (36.80) (t, C(9)); 59.57 (t, C(1)); 118.30 (119.10) (d, C(8)); 134.45 (135.00) (s, C(7)).

3,7-Dimethyl-1-tosyloxytridec-7*Z*/*E*-ene (14). A mixture of alcohols **12** (1.20 g, 5.3 mmol) was transformed into a mixture of *p*-toluenesulfonates **14** according to the procedure used for the preparation of sulfonates **13**. The yield was 1.73 g (86%). IR, ν/cm^{-1}: 1665 (C=C); 1600 (Ar); 1360, 1185 (S=O).

3,7-Dimethylnonan-1-ols (11). A mixture of unsaturated alcohols **10** (0.50 g, 2.9 mmol) and 5% Pd—C (0.15 g) in anhydrous MeOH (15 mL) was stirred under H_2 until absorption of the latter ceased (~20 h). The precipitate was filtered off and the filtrate was concentrated. A mixture of diastereomers **11** was obtained in a yield of 0.48 g (97%), R_f 0.28 (hexane—Et_2O, 7 : 3). Found (%): C, 76.58; H, 13.94. $C_{11}H_{24}O$. Calculated (%): C, 76.67; H, 14.04. The parameters of the IR and ^{1}H NMR spectra are virtually identical with those described earlier.[7]

3,7-Dimethylpentadec-2*Z*/*E*-enes (15). A 0.1 *M* Li_2CuCl_4 solution in THF (2.4 mL) was added to a stirred solution of a mixture of *p*-toluenesulfonates **13** (3.12 g, 9.6 mmol) in anhydrous Et_2O (38 mL) (−78 °C, Ar). Then a solution of hexylmagnesium bromide, which was prepared from Mg (0.58 g, 24 mg-at.) and *n*-$C_6H_{13}Br$ (2.85 g, 17.3 mmol), was added dropwise. The reaction mixture was stirred at −70 °C for 2 h and then at ~20 °C for 12 h. Then Et_2O (20 mL) was added. The reaction mixture was stirred for 0.5 h and poured into a cooled saturated NH_4Cl solution (15 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (3×20 mL). The combined extracts were washed successively with saturated solutions of Na_2CO_3 and NaCl, dried with $MgSO_4$, and concentrated. The residue was chromatographed on neutral Al_2O_3 (pentane—Et_2O, 9 : 1). A mixture of alkenes **15** was obtained in a yield of 1.90 g (83%), R_f 0.78 (pentane—Et_2O, 9 : 1). Found (%): C, 85.61; H, 14.30. $C_{17}H_{34}$. Calculated (%): C, 85.63; H, 14.37. The parameters of the IR and ^{1}H NMR spectra are virtually identical with those described earlier.[6]

7,11-Dimethyl-6-octadecenes (16). Analogously to the above-described synthesis, the reaction of *p*-toluenesulfonates **14** (1.70 g, 4.5 mmol) in anhydrous Et_2O (18 mL) with a 0.1 *M* Li_2CuCl_4 solution in THF (1.2 mL), Mg (0.27 g, 11.2 mg-at.), and *n*-$C_5H_{11}Br$ (1.34 g, 8.1 mmol) afforded a mixture of alkenes **16** in a yield of 1.02 g (81%), R_f 0.77 (pentane—Et_2O, 9 : 1). Found (%): C, 85.61; H, 14.30. $C_{20}H_{40}$. Calculated (%): C, 85.63; H, 14.37. ^{1}H NMR ($CDCl_3$), δ: 0.88 (t, 9 H, H(1), $H_3C(11)$, H(18), J = 7.0 Hz); 1.26 (br.s, 22 H, H(2), H(3), H(4), H(9), H(10), H(12), H(13), H(14), H(15), H(16), H(17)); 1.50 and 1.61 (both s, 1.5 H each, $H_3C(7)$); 1.87—2.10 (m, 4 H, H(5), H(8)); 5.15—5.20 (m, 1 H, H(6)). ^{13}C NMR ($CDCl_3$), δ: 14.05 and 14.12 (both q, C(1), C(18)); 19.28 (q, $H_3CC(11)$); 22.71, 24.73, 25.42, 27.53, 30.56, 31.91, 33.00, 36.48, 36.80, 37.07, and 37.63 (all t, C(2), C(3), C(4), C(9), C(10), C(12), C(13), C(14), C(15), C(16), C(17)); 28.26 (d, C(11)); 33.00 (39.20) (t, C(8)); 35.49 (39.72) (t, C(5)); 118.30 (119.10) (d, C(6)); 134.47 (134.92) (s, C(7)).

4,8-Dimethyldecanals (3) were prepared in 70% yield from a mixture of diastereomeric alcohols **11** according to a procedure developed earlier.[7] The parameters of the IR and ^{1}H NMR spectra are virtually identical with those described earlier.[7]

2-Acetoxy-3,7-dimethylpentadecanes (4) were prepared in 76% yield from a mixture of alkenes **15** according to a procedure developed earlier.[6] The parameters of the IR and ^{1}H NMR spectra are virtually identical with those described earlier.[6]

7,11-Dimethyloctadecanes (5). A mixture of alkenes **16** (0.50 g, 1.8 mmol) and 5% Pd—C (0.18 g) in anhydrous EtOH (36 mL) was stirred under an atmosphere of hydrogen until adsorption of the latter ceased (~3 h). The precipitate was filtered off, the filtrate was concentrated, and a mixture of alkanes **5** was obtained in a yield of 0.49 g (97%), R_f 0.80 (hexane—Et_2O, 7 : 3). Found (%): C, 84.98; H, 14.95. $C_{20}H_{42}$. Calculated (%): C, 85.02; H, 14.98. The parameters of the ^{1}H and ^{13}C NMR and IR spectra are virtually identical with those described earlier.[10,11]

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