Synthesis of a biologically active analog of the sex pheromone of cigarette beetle (*Lasioderma serricorne*)*

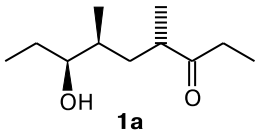
A. V. Lozanova, A. V. Stepanov, and V. V. Veselovsky

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: + 7 (095) 135 5328. E-mail: ves@ioc.ac.ru

A simple synthesis of a diastereomeric mixture of 7-hydroxy-4,6-dimethylnonan-3-ones was carried out. In the biological action, it is an analog of serricornin, the sex pheromone of the cigarette beetle (*Lasioderma serricorne*).

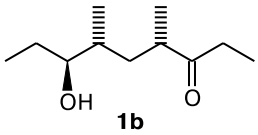
Key words: 7-hydroxy-4,6-dimethylnonan-3-ones, serricornin analog, pheromones, cigarette beetle (*Lasioderma serricorne*).

The sex pheromone of the female cigarette beetle *Lasioderma serricorne*, a plant foodstuff pest, is (4*S*,6*S*,7*S*)-7-hydroxy-4,6-dimethylnonan-3-one, whose structure was confirmed by a number of multistep syntheses.[1] A mixture of all possible enantio- and diastereomers of 7-hydroxy-4,6-dimethylnonan-3-one **1a—d** is known[2] to exhibit a rather high attractant activity.



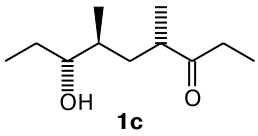
1a

4*S**,6*S**,7*S**



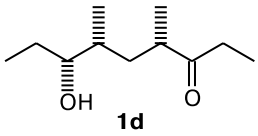
1b

4*S**,6*R**,7*S**



1c

4*S**,6*S**,7*R**



1d

4*S**,6*R**,7*R**

The key step of the simplest known synthesis of a mixture of isomers **1** is the condensation of pentan-3-one (**2**) with methacrylonitrile (**3**) in the presence of a catalytic amount of Bu^{t}OK (Scheme 1);[2] however, the general efficiency of this synthetic route is low due to the poor yield of the condensation product, a mixture of diastereomeric ketonitriles **4**. Our attempts to optimize this process have shown that during the reaction performed under the indicated conditions[2] and the following distillation brings about much tar material containing mainly a high-boiling component, which was identified as (4*R**,6*S**)-3-amino-2,4,6-trimethylcyclohex-2-en-1-one (**5**). The stereoselective formation of this compound is due to the intramolecular condensation of ketonitriles **4** in the presence of a base under thermodynamic control (Thorpe—Ziegler type reaction, for similar examples, see Ref. 3). The formation of enaminoketone **5** is facilitated by a longer reaction time and a greater amount of the base used. Indeed, with an equimolar amount of nitrile **3** and Bu^{t}OK, only traces of ketonitrile **4** were detected in the mixture after the reaction, while compound **5** was the major reaction product isolated in ~40 % yield. This was accompanied by substantial resinification.

In view of the simplicity of the preparation of compound **5**, it appeared promising to attempt to use it as the starting compound in the synthesis of target ketoalcohols **1**. It was first planned to carry out hydrolysis of enaminoketone **5** into diketone **6** followed by its transformation into ketoacid **7** (taking into account the known susceptibility of cyclic diketones to "acid cleavage" under the action of bases[4]). Hydrolysis of enaminoketone **5** was found to require fairly drastic conditions, namely, refluxing of **5** in a EtOH—50% H_2SO_4 mixture. Unexpectedly, it was found that the process does not stop after the formation of diketone **6**. After complete conversion of the starting compound **5** (TLC data), a mixture of diastereomeric ketoesters **8** was isolated from the reaction mixture in a high yield. It is noteworthy that this type of cleavage of cyclic diketones in an acid medium has been described only for a few examples.** This transformation is accompanied by epimerization of a methyl-branched asymmetric centers of the molecule (the mixture of ketoesters **8** contains approximately equal amounts of two diastereomers, ^{1}H NMR data).

The possibility of subsequent transformation of ketoesters **8** into ketoalkohols of series **1** seemed rather obvious. The mixture of ketoesters **8** was reduced by $NaBH_4$

* Dedicated to Academician N. K. Kochetkov on the occasion of his 90th birthday.

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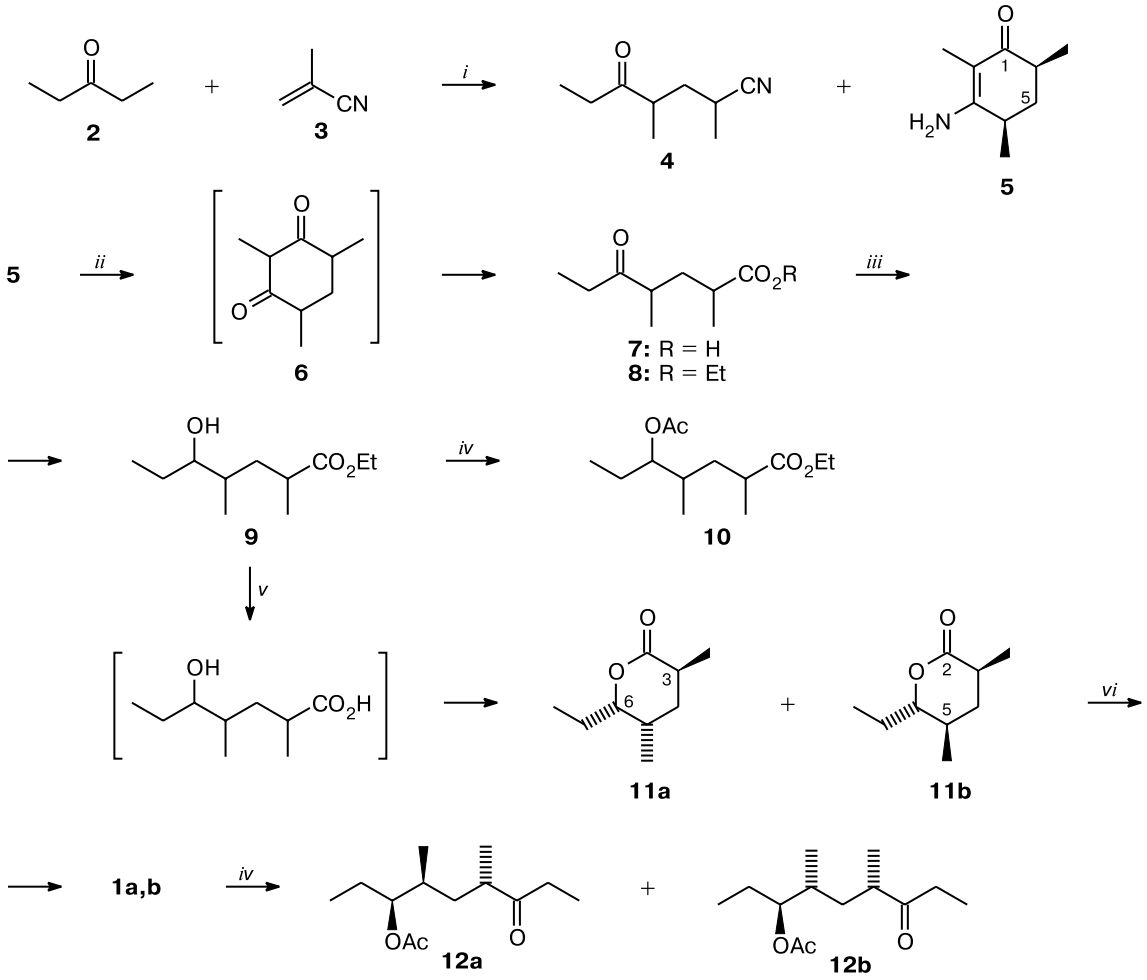
Scheme 1



Reagents and conditions: *i.* Bu^{t}OK/THF, 0 °C; *ii.* aq. EtOH—50% H_2SO_4, refluxing; *iii.* $NaBH_4$/MeOH, 0 °C; *iv.* Ac_2O/Py/DMAP, 20 °C; *v.* 3 *M* aq. KOH/MeOH, Δ; *vi.* EtMgBr/THF—Et_2O, −40 °C.

to give hydroxyesters **9** (characterized also as acetates **10**), which were saponified to give a ~1 : 1 mixture of diastereomeric lactones **11** (two pairs of enantiomers) in a reasonable yield. Since one can hardly expect a high degree of stereocontrol in the above transformations of ketoesters **8**, this stereochemical outcome is apparently due to thermodynamic factors, finally giving rise to an equilibrium mixture of isomers **11** (see related examples[6]). Then the mixture of previously described lactones **11a** [6a] and **11b** [7] was condensed with EtMgBr using a known procedure.[8] Ketoalcohols **1** obtained in this way, which are known to exist as equilibrium mixtures of open and semiketal forms,[9] were converted into acetates **12** (**12a** : **12b** ≈ 1 : 1, NMR data), which are used traditionally to identify stereoisomers **1**.

The structures of newly obtained compounds **5**, **8**, and **9** were established based on spectroscopic and elemental analyses. The previously described components of mixtures of acetoxyesters **10**,[6a] lactones **11**,[6a,7] hydroxyketones **1**,[2] and their acetates **12a** [1b,9] and **12b** [7] were identified by comparing their spectroscopic characteristics with published ones. ^{13}C NMR spectra are most informative for proving the stereochemistry of acetoxy ketones **12**.

Experimental

IR spectra were recorded on a Specord M-80 instrument. ^1H and ^{13}C NMR spectra of solutions in $CDCl_3$ were measured on a Bruker AC-200 spectrometer relative to the residual protons of the deuterated solvent (δ 7.27 and 77.0). Mass spectra (EI, 70 eV) were obtained on a Finigan MAT ITD-700 instrument.

The R_f values were measured on Silufol plates with fixed SiO_2 layer. Column chromatography was carried out on Silica gel 60 (0.04—0.06 mm, Fluka).

The solvents were purified and dried by standard procedures. Commercial pentan-3-one, methacrylonitrile, $KOBu^t$, $NaBH_4$, Ac_2O, and DMAP (Aldrich) were used.

(4*R,6*S**)-3-Amino-2,4,6-trimethylcyclohex-2-en-1-one (5).** Nitrile **3** (2.01 g, 30.0 mmol) was added dropwise over a period of 20 min to a solution of ketone **2** (5.16 g, 60.0 mmol) and $KOBu^t$ (3.36 g, 30.0 mmol) in 40 mL of THF stirred at 0 °C (Ar). The reaction mixture was stirred for 2 h at 0 °C and for 1 h at 20 °C and treated with $MeOBu^t$ (50 mL) and water (20 mL). The organic layer was separated, washed with water (2×10 mL) and brine (3×10 mL), dried (Na_2SO_4), and concentrated *in vacuo*. The residue (3.9 g) was distilled and the fraction (2.32 g) with b.p. 140—160 °C (2 Torr) was chromatographed on 100 g of SiO_2. Elution with EtOAc gave 1.75 g (38%) of enaminoketone **5** as colorless crystals with m.p. 99—100 °C (petroleum ether (here and below, b.p. 40—70 °C)—$MeOBu^t$). Found (%): C, 70.69; H, 10.05; N, 9.11. $C_9H_{15}NO$. Calculated (%): C, 70.55; H, 9.87; N, 9.14. MS, *m*/*z* (I_{rel} (%)): 153 $[M]^+$ (45), 138 (5), 124 (7), 112 (7), 111 (98), 110 (34), 105 (4), 101 (6), 96 (9), 95 (8), 94 (8), 91 (9), 84 (4), 83 (54), 82 (100), 81 (11), 80 (10), 69 (9), 68 (30), 67 (16), 66 (12). IR ($CHCl_3$), ν/cm^{-1}: 664, 720, 792, 1016, 1116, 1180, 1296, 1352, 1396, 1460, 1580, 1608, 2860, 2932, 2968, 3004. 3432, 3536. ^1H NMR, δ: 1.09 and 1.20 (both d, 6 H, MeC(4) and MeC(6), J = 7.1 Hz); 1.39 (ddd, 1 H, HC(5), ^2J = 12.8 Hz, 2 ^3J = 12.9 Hz); 1.63 (s, 3 H, MeC(2)); 1.95 (ddd, 1.H, HC(5), ^2J = 12.8 Hz, 2 ^3J = 6.7 Hz); 2.20 and 2.60 (both m, 2 H, HC(4) and HC(6)); 4.63 (br.s, 2 H, H_2N).

Ethyl 2,4-dimethyl-5-oxoheptanoates (8). A solution of enaminoketone **5** (1.69 g, 11.0 mmol) in a mixture of 30 mL of EtOH and 6 mL of 50% H_2SO_4 was refluxed for 30 h and concentrated *in vacuo* and the residue was treated with 30 mL of $MeOBu^t$ and water (10 mL). The organic layer was separated, washed with water (2×5 mL) and brine (2×10 mL), dried (Na_2SO_4), and concentrated *in vacuo*. The residue (1.85 g) was chromatographed on 50 g of SiO_2. Elution with a petroleum ether—$MeOBu^t$ mixture (4 : 1) gave 1.50 g (68%) of a mixture of diastereomers **8** as a colorless oil with b.p. 50—54 °C (2 Torr), R_f 0.59 (hexane—$MeOBu^t$, 7 : 3). Found (%): C, 65.87; H, 10.39. $C_{11}H_{20}O_3$. Calculated (%): C, 65.97; H, 10.06. MS, *m*/*z* (I_{rel} (%)): 200 $[M]^+$ (3), 183 (2), 171 (24), 158 (5), 156 (6), 155 (37), 154 (31), 153 (15), 143 (39), 127 (36), 126 (20), 115 (60), 113 (10), 112 (20), 111 (53), 110 (18), 103 (8), 102 (54), 101 (12), 99 (18), 98 (11), 97 (26), 91 (8), 87 (16), 86 (28), 83 (25), 82 (37), 81 (8), 77 (6), 74 (35), 73 (16), 71 (14). 70 (24), 69 (70), 68 (12), 67 (20), 59 (57), 57 (100), 56 (63). IR (film), ν/cm^{-1}: 856, 976, 1028, 1048, 1104, 1184, 1228, 1256, 1348, 1380, 1416, 1464, 1720, 1736, 2880, 2940, 2976. ^1H NMR, δ: 0.97—1.08 (m, 6 H, MeC(2), MeC(4)); 1.11 (br.t, 3 H, MeC(6), J = 6.7 Hz); 1.23 (br.t, 3 H, $\underline{Me}CH_2O$, J = 7.0 Hz); 1.30 (ddd, 0.5 H, HC(3), J = 13.8 Hz, J = 7.6 Hz, J = 5.9 Hz);★ 1.57 (ddd, 0.5 H, HC(3), J = 14.1 Hz, J = 9.0 Hz, J = 4.8 Hz);★ 1.77 (ddd, 0.5 H, HC(3), J = 14.1 Hz, J = 8.9 Hz, J = 5.3 Hz);★ 2.03 (ddd, 0.5 H, HC(3), J = 13.9 Hz, J = 8.9 Hz, J = 6.0 Hz);★ 2.25 (m, 4 H, HC(2), HC(4), $H_2C(6)$); 4.09 (br.q, 2 H, H_2CO, J = 7.0 Hz). ^{13}C NMR, δ: 7.6 (C(7)); 14.8 ($\underline{Me}CH_2O$); 16.7, 17.3 and 17.5 (MeC(2), MeC(4)); 34.4 and 35.2 (C(3)); 36.8 and 37.1 (C(6)); 38.0 and 38.5 (C(2)); 44.9 (C(4)); 60.5 (CH_2O); 175.8 and 176.0 (C(1)); 214.6 and 215.0 (C(5)).

★ Non-overlapping signals of protons of the stereoisomers.

Ethyl 5-hydroxy-2,4-dimethylheptanoates (9). To a stirred solution of a mixture of ketoesters **8** (2.60 g, 13.0 mmol) in MeOH (30 mL) $NaBH_4$ (0.34 g, 9.0 mmol) was added in portions at 0 °C (Ar) for 30 min. The reaction mixture was stirred for 1 h at 0 °C, quenched with water (2 mL), neutralized with 5% HCl, and concentrated *in vacuo*. Water (10 mL) was added to the residue and the product was extracted with 100 mL of $MeOBu^t$. The organic layer was washed with water (3×10 mL) and brine (2×15 mL), dried (Na_2SO_4), and concentrated *in vacuo* and the residue was distilled to give 2.50 g (95%) of a mixture of diastereomeric hydroxyesters **9** as a colorless oil, b.p. 53—56 °C (2 Torr), R_f 0.26 (hexane—$MeOBu^t$, 7 : 3). MS, *m*/*z* (I_{rel} (%)): 185 $[M - 17]^+$ (3), 173 (12), 160 (4), 157 (20), 144 (11), 143 (24), 139 (33), 128 (10), 127 (56), 115 (39), 111 (39), 103 (32), 102 (100), 99 (43), 98 (30), 97 (15), 95 (7), 88 (6), 87 (18), 86 (12), 83 (13), 82 (35), 80 (14), 75 (29), 74 (62), 73 (34), 71 (25). 70 (42), 69 (59), 66 (8), 60 (6), 59 (51), 57 (56), 56 (60), 55 (49). IR (film), ν/cm^{-1}: 688, 768, 856, 976, 1028, 1096, 1184, 1260, 1336, 1380, 1464, 1732, 2876, 2936, 2972, 3430. ^1H (δ: 0.78—0.99 (m, 6 H, MeC(2) and MeC(4)); 1.14 (br.t, 3 H, MeC(7), J = 6.7 Hz); 1.23 (br.t, 3 H, $\underline{Me}CH_2O$, J = 7.0 Hz); 1.30—1.90 (m, 5 H, HC(3), HC(4), HC(6)); 2.50 (m, 1 H, HC(2)); 3.22—3.40 (m, 1 H, HC(5)); 4.09 (br.q, 2 H, H_2CO, J = 7.0 Hz).

Ethyl 5-acetoxy-2,4-dimethylheptanoates (10). A solution of a mixture of hydroxy esters **9** (202 mg, 1.0 mmol) and DMAP (5 mg, 0.04 mmol) in 1 mL of Ac_2O and 1 mL of pyridine was kept for 20 h at 20 °C (Ar), diluted with 20 mL of $MeOBu^t$ and washed successively with 5% HCl (5 mL), a saturated solution of $NaHCO_3$ (2×5 mL), and brine (2×10 mL), dried (Na_2SO_4), and concentrated *in vacuo*. The residue was chromatographed on 5 g of SiO_2 with a petroleum ether—$MeOBu^t$ mixture (4 : 1) as the eluent to give 0.20 g (82%) of a mixture of diastereomers **10** as a colorless oil, R_f 0.58 (hexane—$MeOBu^t$, 7 : 3). MS, *m*/*z* (I_{rel} (%)): 244 $[M]^+$ (0.5), 215 (13), 202 (3), 201 (8), 187 (5), 186 (14), 185 (14), 184 (37), 174 (6), 173 (52), 171 (6), 158 (14), 157 (66), 156 (12), 155 (43), 144 (45), 143 (42), 141 (14), 140 (54), 139 (32), 138 (8), 137 (7), 128 (11), 127 (55), 121 (5), 116 (6), 115 (37), 113 (7), 112 (17), 111 (32), 110 (7), 103 (20), 102 (100), 101 (25), 99 (20), 97 (10), 95 (12), 87 (16), 84 (11), 83 (6), 82 (52), 81 (7), 80 (11), 75 (8), 74 (50), 73 (17), 72 (22), 71 (9), 70 (26), 69 (65), 67 (16), 59 (15), 58 (10), 57 (48), 56 (31), 55 (56). ^1H NMR, δ: 0.76—0.91 (m, 6 H, MeC(2) and MeC(4)); 1.02—1.17 (m, 3 H, $H_3C(7)$); 1.23 (br.t, 3 H, $\underline{Me}CH_2O$, J = 7.3 Hz); 1.30—1.85 (m, 5 H, HC(3), HC(4), HC(6)); 1.99 (s, 3 H, MeCO); 2.46 (m, 1 H, HC(2)); 4.08 (br.q, 2 H, H_2CO, J = 7.3 Hz); 4.60—3.80 (m, 1 H, HC(5)).

(3*S,5*S**,6*S**)-3,5-Dimethyl-6-ethyltetrahydro-2*H*-pyran-2-one (11a) and (3*S**,5*R**,6*S**)-3,5-dimethyl-6-ethyltetrahydro-2*H*-pyran-2-one (11b).** A solution of a mixture of hydroxyesters **9** (2.30 g, 11.5 mmol) in 30 mL of a 3 *M* solution of KOH in MeOH was stirred with gentle boiling for 2 h, cooled to 0 °C, acidified with 15% HCl to pH ~5, and concentrated *in vacuo*. Petroleum ether (100 mL) and water (10 mL) were added to the residue. The organic layer was separated, washed with water (2×15 mL) and brine (2×10 mL), dried (Na_2SO_4), and concentrated *in vacuo*. The residue (1.7 g) was chromatographed on 60 g of SiO_2 using a petroleum ether—$MeOBu^t$ mixture (7 : 3) as the eluent to give 1.35 g (76%) of a mixture of diastereomeric lactones **11** as a colorless oil, b.p. 55—58 °C (2 Torr), R_f 0.30 (hexane—$MeOBu^t$, 7 : 3). MS, *m*/*z* (I_{rel} (%)): 156 $[M]^+$ (2), 149 (3), 144 (3), 140 (4), 128 (5), 127 (46), 114 (10), 102 (14), 99

(30), 98 (50), 95 (3), 88 (3), 83 (7), 82 (19), 80 (7), 78 (6), 71 (17), 70 (74), 69 (58), 67 (10), 59 (9), 58 (17), 57 (67), 56 (100), 55 (72). IR (film), ν/cm^{-1}: 744, 812, 936, 988, 1040, 1108, 1172, 1212, 1324, 1380, 1464, 1732, 2880, 2936, 2968. ^{1}H (δ: 0.92—1.04 (m, 6 H, MeC(5) and $MeCH_2$); 1.22, 1.26 (both d, 1.5 H each, MeC(3), J = 6.9 Hz)★; 1.39—2.08 (m, 4 H, HC(4), H_2CMe); 2.49 (m, 1 H, HC(3)); 3.84 (ddd, 0.5 H, HC(6), **11b**, J = 9.9 Hz, J = 7.0 Hz, J = 2.8 Hz);★ 4.17 (ddd, 0.5 H, HC(6), **11a**, J = 8.6 Hz, J = 6.1 Hz, J = 3.0 Hz).★ ^{13}C NMR, δ, **11a**: 9.88, 11.28, 17.90, 26.21, 29.39, 31.34, 35.97, 85.37, 174.51 (*cf.* Ref. **1b**); **11b**: 8.63, 17,26, 25.56, 32.72, 36.25, 37.66, 87.94, 174.57.

7-Hydroxy-4,6-dimethylnonan-3-ones (1). A 1.36 *M* solution of EtMgBr (7 mL, 9.52 mmol) in Et_2O was added over a period of 5 min to a solution of a mixture of lactones **11** (1.25 g, 8.0 mmol) in 20 mL of THF stirred at –40 °C (Ar). The reaction mixture was stirred for 2 h at –40 °C and for 2 h at 20 °C and quenched with a saturated solution of NH_4Cl (5 mL). The aqueous layer was separated and extracted with 50 mL of MeOBu^t. The combined organic layer was washed with water (2×10 mL) and brine (2×10 mL), dried (Na_2SO_4), and concentrated *in vacuo*. The residue (1.55 g) was chromatographed on 60 g of SiO_2, using a petroleum ether—MeOBu^t mixture (2 : 1) as the eluent to give 1.28 g (86%) of a mixture of diastereomers **1** as a colorless oil, R_f 0.56—0.21 (hexane—MeOBu^t, 2 : 1) (*cf.* Ref. 9). MS, m/z (I_{rel} (%)): 168 [M – H_2O]$^+$ (100), 139 (12), 125 (14), 111 (9), 99 (72), 95 (15), 83 (30), 71 (42), 69 (39), 67 (25), 57 (54), 55 (67), 53 (12) (*cf.* Ref. 2).

(4*S,6*S**,7*S**)-7-Acetoxy-4,6-dimethylnonan-3-one (12a) and (4*S**,6*R**,7*S**)-7-acetoxy-4,6-dimethylnonan-3-one (12b).** A solution of a mixture of hydroxyketones **1** (0.45 g, 2.42 mmol) and DMAP (5 mg, 0.04 mmol) in 2 mL of Ac_2O and 2 mL of pyridine was kept for 20 h at 20 °C (Ar), diluted with 20 mL of MeOBu^t, washed successively with 5% HCl (10 mL), a saturared solution of $NaHCO_3$ (2×10 mL), and brine (2×10 mL), dried (Na_2SO_4), and concentrated *in vacuo*. The residue was chromatographed on 10 g of SiO_2 using a 5 : 1 petroleum ether—MeOBu^t mixture as the eluent to give 0.43 g (78%) of a mixture of diastereomers **12** as a colorless oil, b.p. 66—68 °C (2 Torr). MS, m/z (I_{rel} (%)): 168 [M – AcOH]$^+$ (24), 157 (12), 140 (2), 139 (10), 128 (4), 127 (4), 125 (3), 117 (3), 112 (5), 111 (18), 101 (2), 99 (9), 97 (3), 91 (2), 87(6), 86 (23), 84 (5), 83 (13), 82 (6), 70 (21), 69 (23), 57 (100), 56 (9), 55 (26). ^{1}H NMR, δ: 0.69—0.91 (m, 6 H, H_3C(7) and MeC(6)); 0.96—1.08 (m, 6 H, H_3C(1), MeC(4)); 1.16—1.81 (m, 5 H, H_2C(5), HC(6), H_2C(8)); 2.01 (s, 3 H, MeCO); 2.28—2.66 (m, 3 H, H_2C(2), HC(4)); 4.57—4.74 (m, 1 H, HC(7)). The ^{13}C NMR spectrum of isomer **12a** (*cf.* Ref. **1b**), δ: 7.75 (C(1)); 10.08 (C(9)); 14.32 (CH_3—C(6)); 16.53 (CH_3—C(4)); 21.03 (CH_3CO); 24.05 (C(5)); 33.52 (C(6)); 34.22 (C(2)); 35.76 (C(8)); 43.37 (C(4)); 78.76 (C(7)); 170.96 (MeCO); 215.05 (C(3)). The ^{13}C NMR spectrum of isomer **12b** (*cf.* Ref. **7**), δ: 7.69 (C(1)); 9.92 (C(9)); 15.72 (CH_3—C(6)); 18.08 (CH_3—C(4)); 21.03 (CH_3CO); 24.05 (C(5)); 33.91 (C(6)); 34.22 (C(2)); 35.31 (C(8)); 43.73 (C(4)); 77.97 (C(7)); 170.96 (MeCO); 214.97 (C(3)).

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★ Non-overlapping signals of protons of the stereoisomers.

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