Experimental

Reaction of compound 1 with $MgSO_4 \cdot 7H_2O$. Enamine **1** (35.9 g, 0.17 mol), $MgSO_4 \cdot 7H_2O$ (18.33 g, 0.51 mol), and 50 mL of CH_2Cl_2 were placed in a loosely covered glass vessel. The conversion of compound **1** was controlled by ^{19}F NMR spectroscopy (the external standard was CF_3COOH). After 28 days the organic part was poured into a distillation flask and rectified. A fraction with b.p. 35—42 °C was removed at atmospheric pressure, which was a CH_2Cl_2 admixured with aldehyde **5**. ^1H NMR spectrum without considering CH_2Cl_2 ($CDCl_3$), δ: 2.61 (qd, 2 H, CH_2, $^3J_{H,H}$ = 2.1 Hz, $^3J_{H,F}$ = 10.8 Hz); 9.11 (m, 1 H, CHO). ^{19}F NMR ($CDCl_3$), δ: 15.30 (t, 3 F, CF_3, $^3J_{F,H}$ = 10.8 Hz). Dioxine **3** (10.6 g, 36%) was obtained on further rectification *in vacuo* (water-jet pump) as a colorless liquid, b.p. 57—59 °C (14 Torr). Found (%): C, 28.58; H, 1.01; F, 61.13. $C_8H_3F_{11}O_2$. Calculated (%): C, 28.25; H, 0.89; F, 61.45. ^1H NMR ($CDCl_3$), δ: 3.55 (sept of d, 1 H, $CH(CF_3)_2$, $^3J_{H,H}$ = 2.3 Hz, $^3J_{H,F}$ = 7.4 Hz); 5.79 (br.s, 1 H, OCHO); 7.38 (m, 1 H, HC=C). ^{19}F NMR ($CDCl_3$), δ: −9.37 (dq, 1 F, F_A, $^2J_{F,F}$ = 164.6 Hz, $^4J_{F,F}$ = 6.2 Hz); 13.58 (d, 6 F, $CH(CF_3)_2$, $^3J_{F,H}$ = 7.4 Hz); 14.48 (m, 3 F, $C{=}CCF_3$); 21.70 (d of quint, 1 F, F_B, $^2J_{F,F}$ = 164.6 Hz, $^4J_{F,F}$ = 3.7 Hz, $^4J_{F,H}$ = 3.7 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 51.19 (sept, $\underline{C}H(CF_3)_2$, $^2J_{C,F}$ = 29.8 Hz); 92.44 (m, OCHO); 105.39 (d of quint, $CF_2\underline{C}CF_3$, $^2J_{C,F}$ = 28.5 Hz, $^2J_{C,F}$ = 35.3 Hz); 117.04 (dd, CF_2, $^1J_{C,F}$ = 248.2 Hz, $^1J_{C,F}$ = 265.8 Hz); 121.36 (q, $C{=}C\underline{C}F_3$, $^1J_{C,F}$ = 270.0 Hz); 121.50 (q, $CH(\underline{C}F_3)_2$, $^1J_{C,F}$ = 282.1 Hz); 152.55 (m, $H\underline{C}{=}C$).

Then, using a forevacuum pump, fluoride **4** (9.9 g, 31%) was obtained, b.p. 93—97 °C (1.5 Torr). The spectral characteristic of compound **4** are consistent with published data.[2]

This work was financially supported by the Russian Foundation for Basic Research (Project No. 95-03-09332).

References

1. A. N. Chekhlov, A. V. Popov, and A. N. Pushin, *Dokl. Akad. Nauk*, 1993, **331**, 62 [*Dokl. Chem.*, 1993 (Engl. Transl.)].
2. D. C. England, L. Solomon, and C. G. Krespan, *J. Fluor. Chem.*, 1973, **3**, 63.
3. Yu. A. Cheburkov and I. L. Knunyants, *Fluorine Chem. Rev.*, 1967, **1**, 107.
4. Yu. A. Cheburkov, N. Mukhamadaliev, Yu. E. Aronov, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1965, **14**, 1476 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1965, **14**, 1440 (Engl. Transl.)].

Received January 8, 1997

Enantiospecific synthesis of (*S*)-(+)-3-methylheneicosan-2-one, an analog of the sex pheromone of the German cockroach (*Blatella germanica* L.) from (−)-(1*R*,4*S*)-menthone

G. Yu. Ishmuratov,* M. P. Yakovleva, R. Ya. Kharisov, I. M. Muslimova, R. R. Muslukhov, R. L. Safiullin, and G. A. Tolstikov

Institute of Organic Chemistry, Ufa Research Center of the Russian Academy of Sciences, 71 prosp. Oktyabrya, 450054 Ufa, Russian Federation. Fax: 007 (347 2) 35 6066

An enantiospecific synthesis of (*S*)-(+)-3-methylheneicosan-2-one, an analog of the sex pheromone of the German cockroach (*Blatella germanica* L.), was carried out through selective transformations of (3*R*,6*S*)-3,7-dimethyloctane-6-olide obtained from (−)-menthone *via* the Baeyer—Villiger reaction.

Key words: (*S*)-(+)-3-methylheneicosan-2-one, pheromone analog; (−)-(1*R*,4*S*)-menthone; (3*R*,6*S*)-3,7-dimethyloctane-6-olide; Baeyer—Villiger, Wittig, and Wacker—Tsuji reactions.

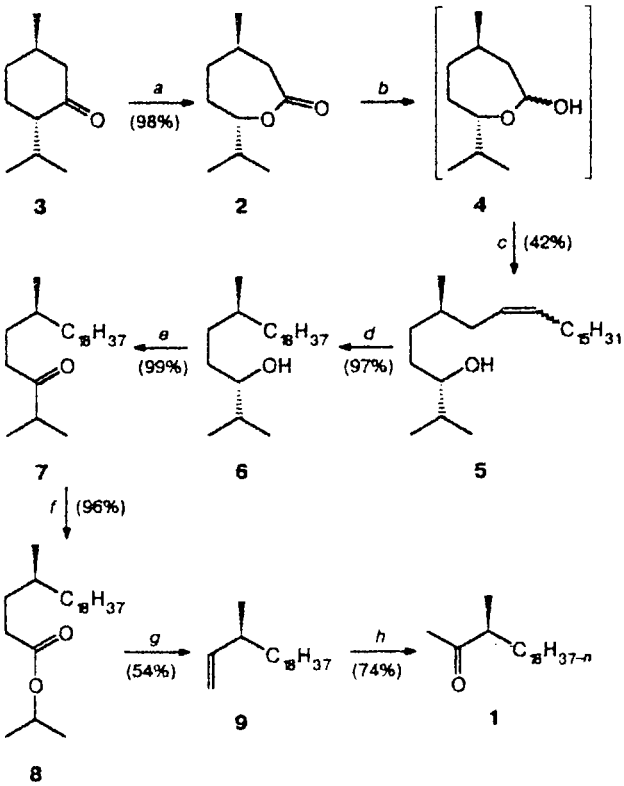
The starting compounds for the known syntheses of (*S*)-(+)-3-methylheneicosan-2-one (**1**), a biologically active analog of the sex pheromone of the German cockroach (*Blatella germanica* L.), are (*S*)-2-methyl-4-pentenoic acid[1] and enantiomerically enriched monoterpenoid (*S*)-(+)-dihydromyrcene.[2]

We carried out an alternative synthesis of optically pure attractant **1** from (3*R*,6*S*)-3,7-dimethyloctane-6-olide (**2**), the product of regio- and stereospecific oxidation of (−)-menthone (**3**) by decaneperoxysulfonic acid by the Baeyer—Villiger reaction[3] (Scheme 1).

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 1071—1073, May, 1997.

1066-5285/97/4605-1033 $18.00

Scheme 1



Reagents and conditions: *a*. See Ref. 3; *b*. Bu^i_2AlH, −70 °C; *c*. $[n\text{-}C_{15}H_{31}CH_2PPh_3]Br/Bu^nLi$; *d*. H_2, Ni; *e*. PCC; *f*. MCPBA; *g*. KOH/MeOH, $Pb(OAc)_4/Cu(OAc)_2 \cdot H_2O$; *h*. $O_2/PdCl_2—Cu_2Cl_2$.

To construct the lipophilic part of molecule **1**, lactone **2** was converted into the corresponding lactol **4*** by hydride reduction, and the latter was olefinated by the Wittig reaction to give *Z*-unsaturated alcohol **5** (the content of the main stereoisomer was 78%, according to the capillary GLC data). Alcohol **5** was catalytically hydrogenated to form its saturated analog **6**. A chain of consecutive transformations, which occur without involving the C(6) asymmetric center, was used for the formation of the structure of the target α-methylketone **1** with an *S*-configuration: consecutive oxidation of alcohol **6** with pyridinium chlorochromate into ketone **7** followed by regiospecific Baeyer—Villiger reaction to afford isopropyl (*S*)-4-methyldocosanate (**8**), oxidative decarboxylation of the corresponding acid, and Wacker—Tsuji transformation[4] of the resulting terminal alkene **9** by molecular oxygen in the presence of a palladium catalyst.

The total yield of the target attractant **1** from ketone **3** was 15.2% over the nine steps of the synthesis.

* The structure of the formed lactol will be discussed in one of the following communications.

Experimental

IR spectra were recorded on a UR-20 instrument in thin layers. ^1H NMR spectra were obtained on a Tesla BS-567 spectrometer (working frequency 100 MHz) and a Bruker AM-300 instrument (300 MHz) in $CDCl_3$ with $SiMe_4$ as the internal standard. ^{13}C NMR spectra were recorded on a Bruker AM-300 instrument (75.47 MHz) in $CDCl_3$ with $SiMe_4$ as the internal standard. Optical rotation was measured on a Perkin-Elmer-241-MC polarimeter. GLC analyses were carried out on a Chrom-5 instrument (column length 1.2 m, stationary phase 5% SE-30 silicone on Chromaton N-AW-DMCS (0.16—0.20 mm), operating temperature 50—300 °C) and Shimadzu GC-9A instrument (25 m × 0.2 mm quartz capillary column, stationary phase PEG-20M, operating temperature 30—220 °C) with helium as the carrier gas.

(3*S*,6*R*)-2,6-Dimethyltetracos-8-en-3-ol (5). An 1.17 *M* solution of Bu^nLi in hexane (18.2 mL, 21.3 mmol) was added dropwise at 0 °C under argon to a suspension of $[Me(CH_2)_{15}PPh_3]Br$ (11.58 g, 20.4 mmol) in dry THF (106 mL). The mixture was kept at −20 °C for 1 h and cooled to −70 °C, and a solution of lactone **2** (1.18 g, 6.8 mmol) in dry THF (4 mL) and a 60.5% solution of DIBAH in toluene (4.2 mL, 13.6 mmol) were added dropwise in sequence. The reaction mixture was kept at −70 °C for 1 h, at −55 °C for 1 h, and at 20 °C for 16 h, decomposed with cold water (3 mL), stirred for 15 min, and concentrated. The residue was diluted with pentane, filtered through a SiO_2 layer (5 cm), and chromatographed on SiO_2 (pentane) to afford 1.08 g (42%) of alcohol **5**, $[\alpha]_D^{24}$ −12.0° (*c* 1.2, hexane). IR, ν/cm^{-1}: 1650, 3020 (=CH); 3625 (O—H). ^1H NMR, δ: 0.80—1.00 (m, 12 H, CH_3); 1.22—1.60 (br.s, 30 H, CH_2); 1.61—1.72 (m, 1 H, H(6)); 1.82—1.95 (m, 1 H, H(2)); 1.95—2.10 (m, 4 H, CH_2—C=C); 3.30—3.42 (m, 1 H, CH—O). ^{13}C NMR, δ: 16.40, 19.05, 19.77 (q, C(1), $\underline{C}H_3C(2)$, $\underline{C}H_3C(6)$); 33.69 (d, C(2)); 77.16 (d, C(3)); 34.41 (t, C(4)); 33.02 (t, C(5)); 33.67 (d, C(6)); 32.78 (t, C(7)); 128.23 (d, C(8)); 130.95 (d, C(9)); 27.45 (t, C(10)); 29.70 (t, C(11)); 29.92 (t, C(12)—C(20)); 29.48 (t, C(21)); 31.69 (t, C(22)); 22.80 (t, C(23)); 14.23 (q, C(24)).

(3*S*,6*S*)-2,6-Dimethyltetracosan-3-ol (6). The hydrogenation of alcohol **5** (1.00 g, 2.63 mmol) was carried out in dry THF (20 mL) in the presence of Raney nickel (0.06 g) at 90 °C and at hydrogen pressure of 75 atm for 24 h. The reaction mixture was then filtered off, and the solvent was evaporated to give 0.97 g (97%) of alcohol **6**, $[\alpha]_D^{25}$ −19.0° (*c* 4.43, hexane). IR, ν/cm^{-1}: 3625 (O—H). ^1H NMR, δ: 0.80—1.00 (m, 12 H, H(1), $CH_3C(2)$, $CH_3C(6)$, H(24)); 1.18—1.36 (m, 38 H, H(4), H(5), H(7)—H(23)); 1.41—1.55, 1.64—1.69 (both m, 2 H, H(6), H(2)); 3.23—3.35 (br.s, 1 H, OH); 3.44—3.51 (m, 1 H, H(3)).

(*S*)-2,6-Dimethyltetracosan-3-one (7). A solution of alcohol **6** (0.72 g, 1.88 mmol) in dry CH_2Cl_2 (2 mL) was added in one portion to a suspension of PCC (0.95 g, 4.41 mmol) in dry CH_2Cl_2 (9 mL). The reaction mixture was kept for 2 h, diluted with Et_2O, and filtered through a SiO_2 layer (5 cm). The solvent was evaporated to give 0.71 g (99%) of ketone **7**. $[\alpha]_D^{21}$ +7.90° (*c* 0.5, hexane). IR, ν/cm^{-1}: 1720 (C=O). ^1H NMR, δ: 0.80—0.90 (m, 6 H, $CH_3C(6)$, H(24)); 1.05—1.13 (m, 6 H, H(1), $CH_3C(2)$); 1.13—1.35 (m, 36 H, H(5), H(7)—H(23)); 1.50—1.61 (m, 1 H, H(6)); 2.40—2.49 (m, 2 H, CH_2CO); 2.54—2.58 (m, 1 H, CHCO).

Isopropyl-(*S*)-4-methyldocosanate (8). A solution of ketone **7** (0.26 g, 0.68 mmol) in heptane (1 mL) was added at −20 °C to a suspension of MCPBA (0.18 g, 1.01 mmol) in dry $CHCl_3$ (2 mL). The mixture was stirred for 48 h at −20 °C,

diluted with $CHCl_3$ (20 mL), washed gradually with saturated $NaHCO_3$ and NaCl solutions, dried with $MgSO_4$, and concentrated. Chromatography on SiO_2 (heptane) yielded 0.26 g (96%) of ester **8**, $[\alpha]_D^{21}$ −1.53° (*c* 4.5, $CHCl_3$). IR, ν/cm^{-1}: 1745 (C=O). ^{13}C NMR, δ: 22.01 (q, $\underline{C}H_3CO$); 67.40 (d, $\underline{C}$—O); 173.74 (s, C(1)); 30.18 (t, C(2)); 36.94 (t, C(3)); 32.64 (t, C(4)); 19.48 (q, $\underline{C}H_3C(4)$); 32.65 (d, C(5)); 27.22 (t, C(6)); 29.61 (t, C(7)); 29.95 (t, C(8)—C(19)); 32.19 (t, C(20)); 22.19 (t, C(21)); 14.27 (q, C(22)).

(*S*)-3-Methylheneicosene-1 (9). KOH (0.03 g) was added to a solution of ester **8** (0.19 g, 0.48 mmol) in MeOH (0.5 mL). The mixture was refluxed for 3 h, then cooled to ~20 °C, acidified with 10% HCl, extracted with Et_2O (20 mL), dried with $MgSO_4$, and concentrated. The residue (0.12 g) [IR, ν/cm^{-1}: 1715 (C=O)] was dissolved in dry benzene (1.5 mL), and then $Cu(OAc)_2 \cdot H_2O$ (0.01 g, 0.05 mmol), dry pyridine (0.02 mL), and $Pb(OAc)_4$ in portions (0.23 g, 0.52 mmol each) were added at 75 °C to the solution. The mixture was boiled until liberation of gas stopped (~1.5 h), diluted with Et_2O (50 mL), and filtered through a SiO_2 layer (10 cm). The filtrate was concentrated to give 0.08 g (54%) of olefin **9**, $[\alpha]_D^{19}$ +0.50° (*c* 1.6, $CDCl_3$). ^1H NMR, δ: 0.86 (t, 3 H, H(21), J = 6.6 Hz); 0.91—0.98 (d, 3 H, $CH_3C(3)$, J = 6.7 Hz); 1.25—1.38 (br.s, 34 H, H(4)—H(20)); 2.00—2.15 (m, 1 H, H(3)); 4.9 (dd, 2 H, H(1), J = 17.2 Hz, J = 10.2 Hz); 5.70 (ddd, 1 H, H(2), J = 17.2 Hz, J = 10.2 Hz, J = 7.3 Hz). ^{13}C NMR, δ: 112.28 (t, C(1)); 145.15 (d, C(2)); 37.88 (d, C(3)); 20.29 (q, $\underline{C}H_3C(3)$); 38.80 (t, C(4)); 27.39 (t, C(5)); 29.50 (t, C(6)); 29.83 (t, C(7)—C(18)); 32.07 (t, C(19)); 22.83 (t, C(20)); 13.63 (q, C(21)).

(*S*)-3-Methylheneicosan-2-one (1). To prepare the catalytic system, CuCl (0.03 g, 0.30 mmol) was added at 60 °C to a suspension of $PdCl_2$ (0.01 g, 0.06 mmol) in THF (2.3 mL) and H_2O (0.3 mL), and the mixture was stirred for 5 min with bubbling of oxygen at a rate of 5 L h^{-1}. Olefin **9** (0.08 g, 0.26 mmol) was added dropwise to the catalytic system. The reaction mixture was stirred under the conditions used for the preparation of the catalytic system (60 °C, O_2) for 6 h and filtered. The filtrate was diluted with $CHCl_3$ (30 mL), washed with 5% HCl (3×5 mL) and saturated NaCl, dried with $MgSO_4$, and concentrated. Gradient chromatography of the residue on SiO_2 with the hexane—Et_2O system (from 0 to 10% of the latter) afforded 0.06 g (74%) of attractant **1**, m.p. 34.0—35 °C, $[\alpha]_D^{20}$ +6.6° (*c* 2.4, $CHCl_3$) (*cf.* Ref. 2). Its ^1H NMR and IR spectra were identical to those described previously.[2]

References

1. R. Rossi, A. Carpita, and M. Marasco, *Chim. Ind. (Milano)*, 1981, **63**, 503.
2. Nguen Kong Khao, M. V. Mavrov, and E. P. Serebryakov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 693 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 592 (Engl. Transl.)].
3. V. N. Odinokov, G. Yu. Ishmuratov, M. P. Yakovleva, R. R. Muslukhov, R. L. Safiullin, A. N. Volgarev, V. D. Komissarov, and G. A. Tolstikov, *Dokl. Akad. Nauk*, 1992, **326**, 842 [*Dokl. Chem.*, 1992 (Engl. Transl.)].
4. J. Tsuji, *Synthesis*, 1984, 369.

Received January 17, 1997

Stereospecific synthesis of 11*E*-tetradecenal, 11*E*-tetradecen-1-ol, and its acetate, pheromone components of insects of *Lepidoptera* order, from 10-undecenoic acid

G. Yu. Ishmuratov, M. P. Yakovleva, R. Ya. Kharisov, R. R. Muslukhov, and G. A. Tolstikov*

Institute of Organic Chemistry, Ufa Research Center of the Russian Academy of Sciences, 71 prosp. Oktyabrya, 450054 Ufa, Russian Federation. Fax: 007 (347 2) 35 6066

A regio- and stereospecific synthesis of 11*E*-tetradecen-1-ol and its derivatives, which are pheromone components of many insect species of *Lepidoptera* order, by means of a reaction of methylmagnesium cuprate reagent with 1,12-tridecadien-3-yl acetate by the S_N2' mechanism, was carried out.

Key words: 10-undecenoic acid; 1,12-tridecadien-3-yl acetate; 11*E*-tetradecen-1-ol, pheromone.

A series of syntheses[1—7] of 11*E*-tetradecenal and the corresponding alcohol and acetate, which are pheromone components of many insect species of the *Lepidoptera* order, *e.g.*, meadow moth (*Loxostege sticticalis*), a very dangerous agricultural pest, have been reported.[1] A method for synthesizing 11*E*-tetradecenal from

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 1074—1075, May, 1997.

1066-5285/97/4605-1035 $18.00