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, $CDCl_3$). ^{1}H 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 ^{1}H NMR and IR spectra were identical to those described previously.[2]

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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

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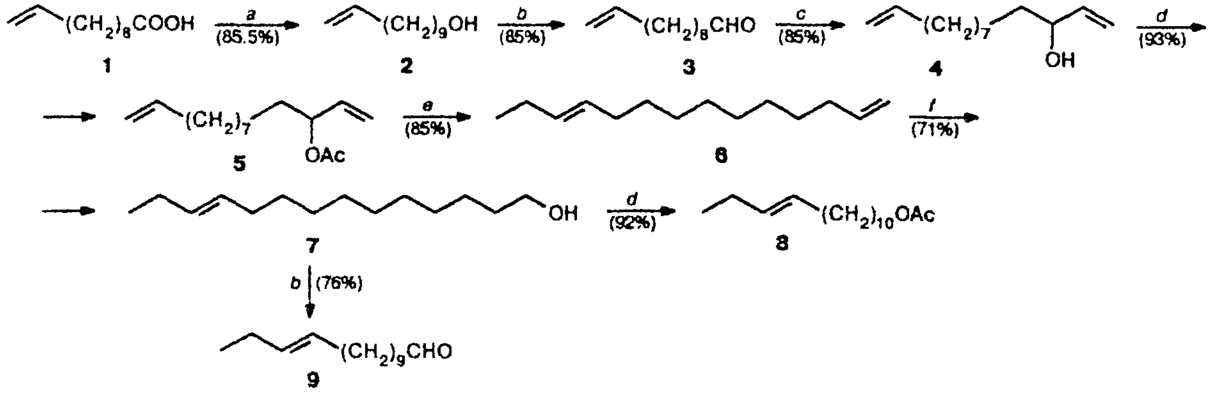
A regio- and stereospecific synthesis of 11*E*-tetradecen-1-ol and its derivatives, which are pheromone components of many insect species of *Lepidoptera* order, by means of a reaction of methylmagnesium cuprate reagent with 1,12-tridecadien-3-yl acetate by the S_N2' mechanism, was carried out.

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.

Scheme 1



Reagents and conditions: *a.* See Ref. 8; *b.* PCC; *c.* MgBr ; *d.* Ac_2O/Py; *e.* MeMgI/CuI; *f.* BBN, H_2O_2/AcONa.

10-undecenoic acid (**1**) using a modified Knoevenagel reaction at the step of the formation of the (*E*)-double bond is also known.[8]

We have developed an alternative approach (Scheme 1) to the synthesis of the compounds indicated above (**7**—**9**) using the reaction of a methylmagnesium cuprate reagent with secondary allyl acetate **5** by a S_N2' mechanism at the key step of the formation of the carbon skeleton. Compound **5** was obtained from unsaturated acid **1** (steps **2** → **4**) by condensation of 10-undecenal (**3**) with vinylmagnesium bromide. Selective anti-Markovnikov hydration of the coupling product, 1,11*E*-tetradecadiene (**6**) was carried out through an organoboron intermediate to afford alcohol **7** (in a >70% yield) that was further transformed into acetate **8**. Oxidation of alcohol **7** gave the third target compound, aldehyde **9**. The yield of the pheromone component **7** obtained by our scheme was 35% with respect to the starting acid **1**. The yields of the other two target compounds, acetate **8** and aldehyde **9**, were 32 and 26.5%, respectively.

Stereochemical purity of pheromones **7**—**9** was controlled by capillary GLC that confirmed a high (*E*)-stereoselectivity of the synthesis: the content of the main compound was no less than 99% in all samples.

Experimental

IR spectra were recorded on a UR-20 instrument in thin layers. ^1H NMR spectra were obtained on Tesla BS-567 (100 MHz) and Bruker AM-300 (300 MHz) instruments in $CDCl_3$. Chromatographic analysis was carried out on a Chrom-5 instrument (stationary phase SE-30 silicone, column length 1.2 m, operating temperature 50—300 °C) and a Shimadzu GC-9A instrument (stationary phase PEG-20M, 25 000×0.2 mm quartz capillary column, operating temperature 50—220 °C) with helium as the carrier gas.

10-Undecenal (3). A solution of alcohol **2** (synthesized from undecylenic acid **1** by the previously described procedure[8] in 85.5% total yield) (3.8 g, 22.4 mmol) in CH_2Cl_2 (24 mL) was added in one portion to a suspension of PCC (6.57 g, 30.5 mmol) in dry CH_2Cl_2 (70 mL) at ~20 °C. The reaction mixture was stirred for 2 h, diluted with Et_2O (100 mL), and filtered through a SiO_2 layer (15 cm). The precipitate was washed with Et_2O and the combined filtrates were concentrated to afford 3.18 g (85%) of aldehyde **3**, n_D^{20} 1.4727. IR, ν/cm^{-1}: 930, 1010, 1645, 3090 ($CH=CH_2$); 1725, 2730 (C=O).

1,12-Tridecadien-3-ol (4). A solution of aldehyde **3** (3.18 g, 19.0 mmol) in dry THF (8 mL) was added dropwise (−15 °C, Ar) to a solution of a Grignard reagent prepared from vinyl bromide (5.56 g, 52.0 mmol) and Mg (0.84 g, 31.0 mg-at) in dry THF (55 mL). The reaction mixture was stirred at −15 °C for 1 h and at 20 °C for 12 h, decomposed at 0 °C with a saturated solution of NH_4Cl (30 mL), and extracted with Et_2O (3×100 mL). The extract was washed with a saturated solution of NaCl, dried with Na_2SO_4, and concentrated. The residue was chromatographed (SiO_2, heptane—ethyl acetate, 10 : 1) to yield 3.15 g (85%) of alcohol **4**. IR, ν/cm^{-1}: 920, 1000, 1640 ($CH=CH_2$); 3600 (OH). ^1H NMR ($CDCl_3$), δ: 1.19—1.47 (m, 12 H, H(5)—H(10)); 1.47—1.55 (m, 2 H, H(4)); 1.71 (br.s, 1 H, OH); 1.97—2.09 (m, 2 H, H(11)); 4.89—5.25 (m, 5 H, H(1), H (3), H(13)); 5.70—5.93 (m, 2 H, H(2), H(12)).

1,12-Tridecadien-3-yl acetate (5). An Ac_2O—Py mixture (2 : 3, 4.1 mL) was added to alcohol **4** (1.32 g, 6.7 mmol) and a DMAP crystal was added to the mixture. The mixture was stirred for 48 h, diluted with Et_2O (100 mL), washed consecutively with saturated $CuSO_4$, $NaHCO_3$, and NaCl solutions, dried with $MgSO_4$, and concentrated to yield 1.49 g (93%) of acetate **5**. IR, ν/cm^{-1}: 930, 1010, 1640, 3090 ($CH=CH_2$); 1745 (C=O). ^1H NMR ($CDCl_3$), δ: 1.20—1.42 (m, 12 H, H(5)—H(10)); 1.55—1.67 (m, 2 H, H(4)); 2.00—2.05 (m, 5 H, H(11), CH_3CO); 4.88—5.28 (m, 5 H, H(1), H(3), H(13)); 5.71—5.88 (m, 2 H, H(2), H(12)).

1,11*E*-Tetradecadiene (6). CuI (1.63 g, 8.5 mmol) was added (−10 °C, Ar) to a a solution of a Grignard reagent prepared from Mg (0.28 g, 11.7 mg-at) and MeI (1.32 g, 9.3 mmol) in dry THF (11 mL). Then a solution of acetate **5** (1.49 g, 6.3 mmol) in dry THF (7 mL) was added dropwise. The mixture was kept at −10 °C for 2 h, decomposed with a saturated NH_4Cl solution (9 mL) at 0 °C, and extracted with pentane (2×50 mL). The extract was washed successively with saturated $NaHCO_3$ and NaCl solutions, dried with $MgSO_4$, and concentrated. The residue was chromatographed (SiO_2, pentane) to afford 1.04 g (85%) of diene **6**, n_D^{21} 1.4422. ^1H NMR and IR spectra of **6** were similar to those reported previously.[8]

11*E*-Tetradecen-1-ol (7). A solution of diene **6** (1.0 g, 5.1 mmol) in dry THF (3 mL) was added at 10 °C over a period of 0.5 h to a suspension of BBN (0.89 g, 7.3 mmol) in dry THF (9 mL). After 2 h, a solution of AcONa (1.48 g, 18.0 mmol) in H_2O (3.6 mL) was added at 0 °C to the mixture, and then 30% H_2O_2 (5.3 mL) was added dropwise over 0.5 h. The reaction mixture was stirred at 25 °C for 2 h, diluted with Et_2O (100 mL), washed successively with saturated NaCl, 0.1 *N* $Na_2S_2O_3$, and again with the NaCl solution, dried with Na_2SO_4, and concentrated. The residue was chromatographed (SiO_2, hexane—Et_2O, 7 : 3) to afford 0.79 g (73%) of alcohol **7** containing, according to the GLC data, no less than 99% of the main compound; n_D^{20} 1.4560. The ^1H NMR and IR spectra of **7** were identical to those described previously.[1]

11*E*-Tetradecen-1-yl acetate (8). A 2 : 3 mixture of Ac_2O and Py (3 mL) was added to alcohol **7** (0.51 g), and the reaction mixture was further treated as described earlier in Ref. 8 to afford 0.56 g (92%) of acetate **8** containing, according to the capillary GLC data, no less than 99% of the main compounds, n_D^{20} 1.4478. The ^1H NMR and IR spectra of **8** were identical to those described previously.[1]

11*E*-Tetradecenal (9). A solution of alcohol **7** (0.39 g) in dry CH_2Cl_2 (1 mL) was added (Ar, 20 °C) with stirring to a suspension of PCC (0.6 g) in CH_2Cl_2 (7 mL), and the reaction mixture was treated as described earlier in Ref. 8 to afford 0.29 g (76%) of aldehyde **9** containing, according to the capillary GLC data, no less than 99% of the main compounds, n_D^{20} 1.4485. The ^1H NMR and IR spectra of **9** were identical to those described previously.[8]

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Received January 17, 1997