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A new synthesis of (*Z,E*)-tetradec-11-enyl acetate, the sex attractant of the omnivorous leafroller (*Archips podana*)

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A four-step synthesis of the title pheromone was elaborated starting from accessible (*Z*)-cyclooctene and but-1-ene.

Key words: cometathesis, pheromones, omnivorous leafroller.

It is known that the main components of the sex pheromone of the omnivorous leafroller are (*Z*)- and (*E*)-tetradec-11-enyl acetates with the ratio of *Z/E*-isomers from 50/50 [1] to 63/37, and that the latter composition is the most efficient.[2]

Two approaches to the synthesis of monoenic components of insect pheromones are most popular in the laboratory and technological practice. The first approach is based on the use of acetylenic compounds followed by the stereoselective hydrogenation.[3] The second approach is based on the Wittig reaction.[3] Considerable attention has been given recently to the use of the catalytic cometathesis for the synthesis of components of insect pheromones, because this makes it possible to decrease substantially the number of synthetic stages and to use accessible petroleum raw material.[4–6] We have previously reported[6] on the successful application of this approach for the synthesis of monoenic components of pheromones with double bonds in positions 6—11. For example, a mixture of (*Z,E*)-isomers of tetradec-11-enyl acetate was obtained by the cometathesis of (*Z*)-cyclodecene and but-1-ene followed by the selective hydroboration—oxidation of (*Z,E*)-tetradeca-1,11-diene to (*Z,E*)-tetradec-11-en-1-ol, whose acetylation gave

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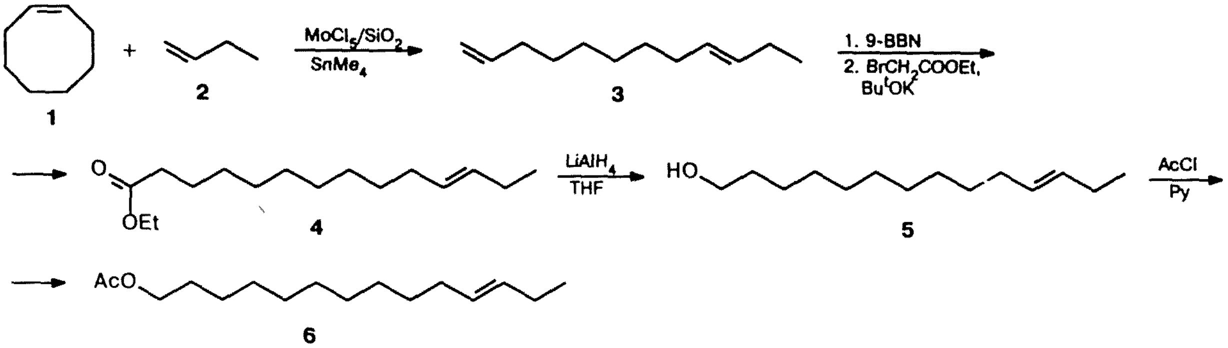
Scheme 1



(*Z*,*E*)-tetradec-11-enyl acetate. However, a content of (*Z*)-tetradeca-1,11-diene above 18 % could not be achieved in this case. Even at low conversions of (*Z*)-cyclodecene, this value is close to the thermodynamically equilibrium value typical of the metathesis and cometathesis of linear olefins.[5] Unlike smaller cycles (cyclopentene, cycloheptene, and cyclooctene),[6] the initial (*Z*)-cyclodecene does not manifest any tendency to form the *cis*-isomer. In the present work, we synthesized a mixture with the necessary stereocomposition (Scheme 1) using the cometathesis of (*Z*)-cyclooctene (**1**) and but-1-ene (**2**) in the presence of an $MoCl_5/SiO_2$—$SnMe_4$ catalytic system[7] as the key stage.

We managed to find the conditions of cometathesis under which the conversion of compound **1** was 75 % in 65 min and the yield of a mixture of (*Z*,*E*)-dodeca-1,9-diene isomers (**3**) with the *Z*/*E* composition 63/37 reached 11 %. Hydroboration of compound **3** with a highly regioselective reagent 9-borabicyclo[3.3.1]nonane (9-BBN) followed by the hydrocarbon chain elongation by two carbon atoms in the reaction with $BrCH_2COOEt$ in the presence of BuᵗOK [8] resulted in the formation of ethyl (*Z*,*E*)-tetradec-11-enoate (**4**) in a 63 % yield. Product **4** contained an insignificant amount of admixtures (GLC), which could affect negatively the biological activity of the pheromone and, hence, the results of field assay. For the preparation of pure samples of the pheromone, we used the following procedure: ester **4** was saponified with a 0.5 *M* solution of KOH in alcohol, and then an aqueous solution of the salt was washed with Et_2O and acidified with HCl; a sample of **4** with 99 % purity was obtained after the esterification of (*Z*,*E*)-tetradec-11-enoic acid (**7**) with ethanol. We have also shown that the reduction of compound **7** according to a procedure similar to that used for the reduction of compound **4** is convenient for the efficient synthesis of pure samples of **6**.

The assay of compound **6** as a sex pheromone of the omnivorous leafroller in gardens in the Moscow Region (A. F. Safonkin, A. N. Severtsev Institute of Evolution Morphology and Ecology of Animals, RAS, Moscow) has shown its high attractant activity.[9]

Experimental

Reactions were monitored by GLC on an LKhM-8MD chromatograph with a flame-ionization detector and an ITs-26 integrator (column 50 m×0.2 mm, stationary phase SKTFT, gas-carrier H_2). ^1H NMR spectra were recorded on Bruker WP-200 or Bruker MSL-300 spectrometers in CCl_4 relative to Me_4Si or D_2O. IR spectra were recorded in thin layers on a Specord IR-75 instrument. Mass spectra were obtained on a Kratos MS-80 instrument (70 eV). The stereoisomeric composition was determined by GLC, ^1H NMR, and IR spectroscopic data. All reactions and the preparation of the initial compounds and solvents were carried out in an atmosphere of argon of special purity.

(*Z*,*E*)-Dodeca-1,9-diene (3). A mixture of $MoCl_5/SiO_2$ (10 g, $1.64 \cdot 10^{-3}$ g-at. Mo), but-1-ene **2** (84 g, 1.5 mol), (*Z*)-cyclooctene **1** (55 g, 0.5 mol), and Me_4Sn (1.6 g, $1.3 \cdot 10^{-2}$ mol) was placed in a steel autoclave equipped with a stirrer, manometer, and a device for withdrawal of aliquots. After 65 min at 6 °C, the reaction mass was separated from the catalyst and diene **3** (15.3 g, 99 % purity) was obtained after rectification. B.p. 206 °C (760 Torr). Mass spectrum, *m*/*z* (I_{rel} (%)): 166 $[M]^+$ (3), 138 $[M-28]^+$ (7), 41 $[M-125]^+$ (100). ^1H NMR (CCl_4), δ: 0.89 (t, 3 H, Me); 1.29—1.38 (m, 8 H, 4 CH_2); 2.00 (m, 6 H, $\underline{H}_2$—CH=); 4.91 (t, 2 H, $C\underline{H}_2$=CH—); 5.31 (m, 2 H, —C$\underline{H}$=C$\underline{H}$—); 5.74 (m, 1 H, —C$\underline{H}$=CH_2). IR, ν/cm⁻¹: 730 (*Z*-H—C=C—H); 970 (*E*-H—C=C—H); 1640 (C=C).

Ethyl (*Z*,*E*)-tetradec-11-enoate (4). 9-BBN (6 g, 0.025 mol) and dry THF (40 mL) were placed in a flask equipped with a magnetic stirrer, dropping funnel, and thermometer. Then a mixture was cooled to 12 °C, and diene **3** (7.74 g, 0.045 mol) was added. The mixture was stirred for 1 h at 12 °C and for 1 h at 25 °C. THF was removed *in vacuo*, the residue was cooled to 12 °C, and $BrCH_2COOEt$ (12 g, 0.07 mol) was added. Then a solution of BuᵗOK (8 g, 0.07 mol) in BuᵗOH (60 mL) was added in such a way that the temperature did not exceed 20 °C. The mixture was stirred for 2 h, and a 3 *M* solution of AcONa was added. Then 30 % H_2O_2 (20 mL) was added dropwise. BuᵗOH and water were removed *in vacuo*, and the residue was extracted with hexane. The extract was washed with water and dried with $MgSO_4$, and hexane was removed. Compound **4** was obtained (7.1 g, 63 %). Mass spectrum, *m*/*z* (I_{rel} (%)): 254 $[M]^+$ (3), 209 $[M-OEt]^+$ (8), 208 $[M-HOEt]^+$ (8), 166 $[M-CH_2=COHOEt]^+$ (12), 101 $[M-153]^+$ (20), 88 $[M-166]^+$ (30), 83 $[M-171]^+$ (21), 69 $[M-185]^+$ (42), 55 $[M-199]^+$ (100), 41 $[M-213]^+$ (76), 29 $[M-255]^+$ (51). ^1H NMR (CCl_4), δ: 0.86 (m, 3 H, Me); 1.27

(m, 15 H, —O—CH$_2$—C$\underline{H}_3$, 6 CH$_2$); 1.59 (m, 2 H, C$\underline{H}_2$—CH$_2$—COO—); 1.96 (s, 4 H, 2 C$\underline{H}_2$—CH=); 2.17 (t, 2 H, CH$_2$—C$\underline{H}_2$—COO—, J = 7.0 Hz); 4.02 (q, 2 H, —O—C$\underline{H}_2$—CH$_3$, J = 7.1 Hz); 5.30 (m, 2 H, CH); 5.27 (s, 2 H, *Z*-H—C=C—H); 5.31 (s, 2 H, *E*-H—C=C—H). IR, ν/cm^{-1}: 710 (*Z*-H—C=C—H); 950 (*E*-H—C=C—H).

(*Z,E*)-Tetradec-11-en-1-ol (5). LiAlH$_4$ (1.9 g, 0.05 mol) and anhydrous THF (25 mL) were placed in a flask with a stirrer, reflux condenser, and dropping funnel. Then a solution of ester **4** (4.2 g, 0.0165 mol) in THF (10 mL) was added dropwise with stirring to the suspension. The mixture was heated to 50 °C and stirred for 1 h. Then excess LiAlH$_4$ was decomposed with HCl (7 mL) in H$_2$O (14 mL). THF was removed *in vacuo*, and the residue was extracted with hexane. The extract was washed with water, and dried with MgSO$_4$. Alkenol **5** (3.3 g, 94 %) was obtained after removal of hexane.

(*Z,E*)-Tetradec-11-enyl acetate (6). A mixture of alcohol **5** (3.3 g, 0.0156 mol) and pyridine (2.3 g, 0.03 mol) in anhydrous hexane (7 mL) were placed in a flask with a stirrer, reflux condenser, thermometer, and dropping funnel. Then a solution of AcCl (2.1 g, 0.027 mol) in hexane (5 mL) was added at 12 °C with stirring so that the temperature did not exceed 20 °C. The mixture was stirred for 2 h, then the reaction mass was treated with water, and the product was extracted with hexane. The extract was washed (H$_2$O) and dried (MgSO$_4$). Compound **6** (3.9 g, 98 %) was obtained after the removal of hexane.

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The weak interaction between C_{60} and molecular iodine in solution

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Fullerene C_{60} forms a weak molecular complex with iodine. Its stability constant is much less (<0.1 L^{-1} mol^{-1}) than that determined in another study.

Key words: fullerene C_{60}, iodine, molecular complex, stability constant.

We found a few years ago that C_{60} forms a molecular complex with iodine in different organic solvents.[1] However, this complex is so unstable that the stability constant could not be determined. We estimated that the stability constant at room temperature is smaller than 0.1 L mol^{-1} and planned to make measurements at a much lower temperature, down to −50 °C, where a measurable stability constant could be expected.

It was most surprising to learn from the paper by Turanov and Kremenskaya[2] that they found the formation of a very stable complex of C_{60} with I_2 in the same organic solvents at 20 °C. They used three different methods: i) spectrophotometry, ii) effect of iodine on the solubility of C_{60}, and iii) effect of C_{60} on the extraction of iodine from a toluene solution by aqueous potassium iodine solution. The composition of the complex was determined spectrophotometrically using the Job method[3] and the ratio of C_{60} : I_2 was found to be strictly 1 : 3; no indication of the formation of other complexes was determined from the data obtained by the third method and was found to be as great as $10^{8.9}$ L^3 mol^{-3}.

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