New synthesis of (*Z*)-5- and (*Z*)-7-monoene components of insect sex pheromones of the Lepidoptera order

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A new procedure was developed for the synthesis of (*Z*)-5- and (*Z*)-7-monoene components of sex pheromones of Lepidoptera insects based on cometathesis of readily accessible cycloocta-1,5-diene and ethylene.

Key words: cometathesis; cycloocta-1,5-diene, ethylene; pheromones, Lepidoptera, cutworms.

(*Z*)-Dec-5-en-1-ol, (*Z*)-dodec-5-en-1-ol, and the corresponding acetates are components of sex pheromones (SP) of more than 60 species of lepidopterous insects (Lepidoptera).[1] These compounds are characteristic of sex pheromones of plurivorous insects of the noctuid family (Noctuidae) and, in particular, of the cutworm subfamily (Agrotinae). The typical representative of the latter is the turnip moth (*Agrotis segetum*), which is a pest of sprouts of winter crop, maize, cotton, and many other plants.[2] The sex pheromone of this insect involves (*Z*)-dec-5-en-1-ol and its acetate.[2] Generally, syntheses of sex pheromones, like other *Z*-ene compounds, are based on *Z*-stereoselective versions of the Wittig reaction[1,3–7] or on the transformation of the triple bond into the *Z*-double bond.[1,4–6] The use of sodium hexamethyldisilazide (−78 °C) in the Wittig reaction made it possible to prepare *Z* isomers with a purity of 98%.[7] In the case of partial hydrogenation of acetylenic compounds with the use of the "P-2 Ni-en" catalyst[8] or Lindlar catalysts at low temperature,[5] the stereoselectivity increased to 99%. Similar stereopurities were achieved in the hydroboration of alkynes with 9-BBN followed by protonolysis[9] or carbocupration of acetylenic compounds.[10] Catalytic cometathesis of olefins makes it possible to decrease the number of stages of the synthesis of pheromone components,[4,11–20] to use readily available starting materials,[4,11–20] and to employ technologically effective heterogeneous catalysts.[15,16,18–20] The drawback of this approach is the fact that it always affords mixtures of *E* and *Z* isomers. Metathesis or cometathesis of linear olefins and their functional derivatives produced predominantly thermodynamically favorable *E* isomers regardless of the nature of the catalytic system used.[4,11–13,16,17,21] Previously,[18–20] we have demonstrated that cometathesis of cycloolefins (C_5, C_7, or C_8) with α-olefins can afford predominantly (*Z*)-di-1,*k*-enes (*k* = 6—11). Based on these compounds, efficient procedures were developed[18–20] for the two-to-four-stage syntheses of monoene components of pheromones containing a double bond at positions 6—11 with respect to the functional group. However, the synthesis of 5-monoene components of pheromones according to this procedure is hampered because the starting cyclobutene is a difficultly accessible compound. At the same time, cyclohexene virtually does not enter into cometathesis. Therefore, we proposed a scheme for the synthesis of 7-monoene components of pheromones based on cometathesis of cyclopentene and the appropriate α-olefin followed by hydroboration—carbonylation of intermediate 1,6-dienes.[18] In particular, the cyclopentene-hex-1-ene pair was used for the synthesis of dodec-7-en-1-ol. The resulting mixture of isomeric undeca-1,6-dienes contained only 59% of the *Z* isomer even at low temperatures and conversions.[20]

In this work we used stereoselective cometathesis of cycloocta-1,5-diene (**1**) with ethylene (**2**) for the synthesis of (*Z*)-5- and (*Z*)-7-monoene components of insect pheromones (Scheme 1).

We found that 80% of diene **1** was converted upon cometathesis of **1** with **2** in the presence of $MoCl_5/SiO_2$—$SnMe_4$[22] under mild conditions (20 °C, the pressure of ethylene was 25 atm, the molar ratio **1** : Mo = 500) for 24 h. In this case, (*Z*)-deca-1,5,9-triene (**3**) (68.4%) containing an admixture of the *E* isomer (1.2%) was obtained as the major ethenolysis product. The stereoselectivity and selectivity of the cometathesis can be enhanced by terminating the process at lower degrees of conversion of **1**. Thus when the degrees of conversion of **1** were 50% and 20%, the selectivity was 87% and 92% and the stereoselectivity was 99.3% and 99.7%, respectively. Such high stereoselectivity was observed for the first time in metathesis and cometathesis. This stereoselectivity is comparable with or is even superior to that achieved in the above-mentioned classical procedures. With the aim of unambiguously establishing the structure and purity of triene **3**, we synthe-

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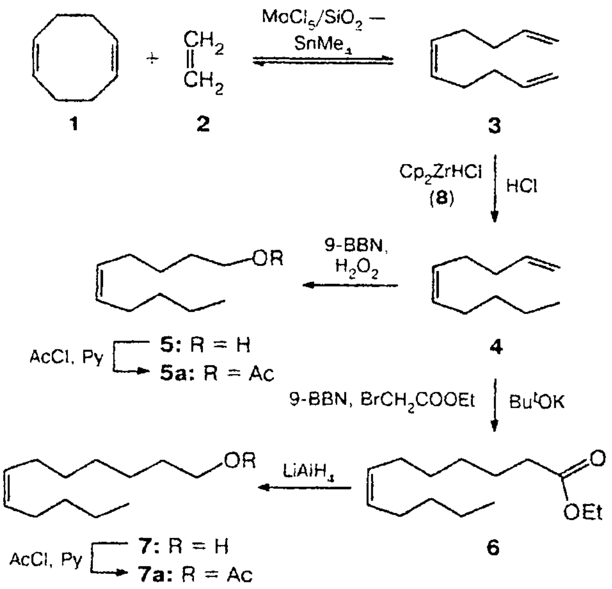
Scheme 1



sized a sample of the triene containing 80% and 20% of the *E* and *Z* isomers, respectively, using metathesis of hexa-1,5-diene. The IR and NMR spectra of this sample have bands characteristic of the *E* isomer of **3** along with bands typical of the *Z* isomer.[16,19] IR, ν/cm^{-1}: 950 ((*E*)-H—C=C—H). ^{1}H NMR, (CDCl$_3$), δ: 5.42 (m, 2 H, $C\underline{H}=C\underline{H}$). ^{13}C NMR (CDCl$_3$), δ: 130.2 ($\underline{C}H=\underline{C}H$). Then triene **3** was subjected to hydrozirconation—protonolysis[23] resulting in (*Z*)-deca-1,5-diene (**4**) in high yield. This diene is the intermediate in the synthesis of alcohols **5** and **7** and acetates **5a** and **7a**.

We used a simple procedure for hydrozirconation of triene **3**. This procedure was based on the facts that the synthesis of Cp_2ZrHCl (**8**) is performed in the presence of triene **3** and hydrozirconation proceeds at the moment of formation of reagent **8**. To increase the selectivity of hydrozirconation, we used a twofold excess of triene **3**. After completion of the reaction, unconsumed triene **3** was distilled off *in vacuo* and the remaining nonvolatile zirconocene derivative was subjected to protonolysis. The target diene **4** contained (*Z*)-dec-5-ene (**9**) as an admixture. According to the published data,[24] internal double bonds are less reactive in hydroboration than terminal bonds. Hence, compound **9** does not undergo hydroboration under the action of 9-BBN and can be readily separated. This allows one to prepare the target products with high purity (>99%). From the practical viewpoint, it is important that Cp_2ZrCl_2 is recovered upon protonolysis of zirconocene derivatives with HCl. Then Cp_2ZrCl_2 can be isolated and reused.[23] It should be noted that we failed to find conditions for the selective preparation of diene **4** using the hydroboration—protonolysis sequence. In all experiments, we obtained mixtures of triene **3**, diene **4**, and dec-5-ene. Hydroboration of diene **4** with 9-BBN afforded intermediate borane, which was oxidized to form alcohol **5** or introduced into the reaction with $BrCH_2COOEt$ in the presence of Bu^{t}OK to increase the hydrocarbon chain by two carbon atoms[25] and to prepare ester **6**. Previously, we have already used combinations of these reactions for the synthesis of insect pheromones[18—20] and, in particular, the pheromone of the omnivorous leafroller (*Archips podana*).[19] We have developed a procedure for the purification of enoates **6**, which was used in this work. This procedure involves saponification of enoate, dissolution of the salt in water, and extraction of the solution with ether, as a result of which admixtures pass into ethereal extracts. Then the aqueous solution of the salt is acidified, the acid is isolated, and ester **6** or purified acid obtained from **6** is reduced with $LiAlH_4$ to produce alkenol **7**. Acetylation of the latter afforded acetate **7a**.

To summarize, *Z*-stereoselective cometathesis of cyclooctadiene **1** with ethylene **2** is a convenient procedure for the preparation of (*Z*)-deca-1,5,9-triene (**3**), which is a versatile intermediate in the synthesis of various compounds containing a *Z*-double bond.

Experimental

The purities of the solvents, starting compounds, and resulting products and the course of the reactions were monitored by GLC on an LKhM-8MD chromatograph equipped with a flame ionization detector and an ITs-26 integrator (a 50 m × 0.2-mm quartz column, SKTFP or SE-30 as the stationary phase, H_2 as the carrier gas) in the linear temperature-programming mode (12 °C min^{-1}) from 35 °C to a temperature 100 °C lower than the boiling point of the corresponding compound. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker MSL-300 spectrometer in CDCl$_3$ relative to Me$_4$Si. The IR spectra were measured on a Specord IR-75 instrument in a thin layer. The mass spectra (EI) were obtained on a Kratos MS-80 instrument (70 eV). Elemental analysis was carried out on a Carlo Erba CHNSO elemental analyzer. The stereoisomeric compositions were determined based on the data of GLC and ^{1}H and ^{13}C NMR spectroscopy. All reactions and the preparation of the starting compounds and solvents were carried out under an atmosphere of argon of special purity grade using $LiAlH_4$ as the drying agent.

(Z)-Deca-1,5,9-triene (3). The $MoCl_5/SiO_2$ catalyst[22] (10 g, 1.5 mmol of Mo) and cycloocta-1,5-diene (**1**) (Fluka) (81 g, 0.75 mol) were placed into a steel autoclave equipped with a stirrer, manometer, and an apparatus for sampling. The pressure of ethylene **2** was increased to 25 atm. Then a solution of Me_4Sn (Fluka) (1.07 g, 6.0 mmol) in toluene (93 mL) saturated with ethylene at 27 atm was added. After 24 h (20 °C), the reaction mixture was separated from the catalysts. After rectification, triene **3** was obtained in a yield of 55 g, b.p. 169 °C (760 Torr), n_D^{20} 1.4502. The content of the major compound was 99.0%. Found (%): C, 88.11; H, 11.85 $C_{10}H_{16}$. Calculated (%): C, 88.16; H, 11.84. MS, *m/z* (I_{rel} (%)): 136 [M]$^+$ (3), 41 [M − 95]$^+$ (100). ^{1}H NMR (CDCl$_3$), δ: 2.15 (m, 8 H, $C\underline{H}_2-CH=$); 4.90 (m, 4 H, $C\underline{H}_2=CH$); 5.39 (t, 2 H, $C\underline{H}=C\underline{H}$, *J* = 6.0 Hz); 5.80 (m, 2 H, $C\underline{H}=CH_2$). ^{13}C NMR (CDCl$_3$), δ: 27.0 ($\underline{C}H_2-CH=CH$); 34.0 ($CH_2=CH-\underline{C}H_2$);

114.8 ($\underline{C}H_2{=}CH$); 129.6 ($\underline{C}H{=}\underline{C}H$); 138.5 ($CH_2{=}\underline{C}H$). IR, ν/cm^{-1}: 730 ((*Z*)-H—C=C—H); 1640 (C=C).

(*Z*)-Deca-1,5-diene (4). A 0.455 *M* $LiAlH_4$ solution (1.1 g, 32 mmol) in THF (70.3 mL) was added dropwise to a solution of Cp_2ZrCl_2 (Fluka) (18 g, 62.3 mmol) and triene **3** (16.9 g, 124 mmol) in anhydrous THF (180 mL). The mixture was stirred at 20 °C for 1 h. Then THF and unconsumed **3** were distilled off *in vacuo*. Hexane (90 mL) was added to the residue. Then a 5% aqueous HCl solution (70 mL) was added dropwise. The aqueous layer was separated. The solution of diene **4** in hexane was neutralized with K_2CO_3, washed with water, and dried with $MgSO_4$. The hexane was distilled off and the residue was distilled. Diene **4** was obtained in a yield of 7.74 g (90%), b.p. 173 °C (760 Torr), n_D^{20} 1.4391. The content of the major component was 94.0%. MS, *m/z* (I_{rel} (%)): 138 $[M]^+$ (5), 41 $[M - 97]^+$ (100). ^1H NMR ($CDCl_3$), δ: 0.85 (m, 3 H, $C\underline{H}_3{-}CH_2$); 1.29 (m, 4 H, $C\underline{H}_2{-}C\underline{H}_2$); 2.15 (m, 6 H, $C\underline{H}_2{-}CH{=}$); 4.9 (m, 2 H, $C\underline{H}_2{=}CH$); 5.39 (t, 2 H, $C\underline{H}{=}C\underline{H}$, J = 6.0 Hz); 5.8 (m, 1 H, $CH{=}CH_2$) (*cf.* lit. data[26]).

(*Z*)-Dec-5-en-1-ol (5). Diene **4** (4.2 g, 30.4 mmol) was added to a stirred suspension of 9-BBN (Fluka) (3.7 g, 15.2 mmol) in anhydrous THF (30 mL) at 12 °C. The reaction mixture was stirred at 12 °C for 1 h and then at 25 °C for 1 h. Then the mixture was cooled to 6 °C and methanol (30 mL), 3 *M* NaOH (5 mL), and 30% H_2O_2 (20 mL) were added in such a way as to keep the temperature below 20 °C. Methyl alcohol, water, and THF were distilled off *in vacuo* and the residue was extracted with hexane. The extract was washed with water and dried with $MgSO_4$. After removal of the hexane and distillation, alcohol **5** was obtained in a yield of 4.4 g (92%), b.p. 90 °C (10 Torr), n_D^{20} 1.4535. The content of the major component was 99.2%. ^1H NMR ($CDCl_3$), δ: 0.90 (br.s, 3 H, $C\underline{H}_3{-}CH_2$); 1.31 (br.s, 6 H, $C\underline{H}_2{-}C\underline{H}_2$); 1.51 (m, 2 H, $C\underline{H}_2{-}CH_2O$); 1.99 (br.s, 4 H, $C\underline{H}_2{-}CH{=}CH$); 2.24 (br.s, 1 H, OH); 3.52 (m, 2 H, $C\underline{H}_2{-}O$); 5.29 (br.s, 2 H, $C\underline{H}{=}C\underline{H}$). ^{13}C NMR ($CDCl_3$), δ: 13.9 ($\underline{C}H_3{-}CH_2$); 22.8, 26.7, 29.4, 29.9, 31.6, 32.3 (6 CH_2); 62.4 ($\underline{C}H_2{-}O$); 129.9, 130.1 ($\underline{C}H{=}\underline{C}H$) (*cf.* lit. data[26]).

(*Z*)-Dec-5-en-1-yl 1-acetate (5a). A solution of AcCl (3.0 g, 38 mmol) in hexane (10 mL) was added with stirring to a solution of alcohol **5** (4.4 g, 28.2 mmol) and Py (3.2 g, 40 mmol) in anhydrous hexane (10 mL) at 12 °C in such a way as to keep the temperature below 20 °C. The reaction mixture was stirred for 2 h, decomposed with water, and extracted with hexane. The extract was washed with water and dried with $MgSO_4$. After removal of the hexane and distillation, acetate **5a** was obtained in a yield of 5.2 g (93%), b.p. 105 °C (8 Torr), n_D^{20} 1.4406. The content of the major compound was 99.2%. ^1H NMR ($CDCl_3$), δ: 0.90 (m, 3 H, $C\underline{H}_3{-}CH_2$); 1.30 (br.s, 6 H, $C\underline{H}_2{-}C\underline{H}_2$); 1.51 (m, 2 H, $C\underline{H}_2{-}CH_2O$); 2.0 (m, 7 H: 3 H, $C\underline{H}_3{-}CO$ and 4 H, 2 $C\underline{H}_2{-}CH{=}CH$); 3.99 (t, 2 H, $C\underline{H}_2O$, J = 7.0 Hz); 5.29 (t, 2 H, $C\underline{H}{=}C\underline{H}$, J = 6.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 14.0 ($\underline{C}H_3{-}CH_2$); 20.8 ($\underline{C}H_3{-}CO$); 22.8, 26.3, 28.9, 29.4, 31.1, and 32.9 (6 $\underline{C}H_2$); 64.6 ($\underline{C}H_2O$); 129.3, 130.2 ($\underline{C}H{=}\underline{C}H$); 170.7 ($\underline{C}OO$) (*cf.* lit. data[26]).

Ethyl (*Z*)-dodec-7-enoate (6). Diene **4** (7.74 g, 45 mmol) was added to a stirred suspension of 9-BBN (6 g, 25 mmol) in anhydrous THF (40 mL) at 12 °C. The mixture was stirred at 12 °C for 1 h and then at 25 °C for 1 h and THF was distilled off *in vacuo*. $BrCH_2COOEt$ (12 g, 70 mmol) was added to the residue cooled to 12 °C and then a solution of Bu^tOK (8 g, 70 mmol) in Bu^tOH (60 mL) was added dropwise in such a way as to keep the temperature below 20 °C. The reaction mixture was stirred for 2 h. Then the mixture was successively treated with a 3 *M* AcONa solution (40 mL) and a 30% H_2O_2 solution (20 mL). Water and Bu^tOH were distilled off *in vacuo* and the residue was extracted with hexane. The extract was washed with water and dried with $MgSO_4$. After removal of the hexane and distillation, ester **6** was obtained in a yield of 6.2 g (55%), b.p. 98 °C (0.3 Torr), n_D^{20} 1.4430. The content of the major component was 90.0%. MS, *m/z* (I_{rel} (%)): 226 $[M]^+$ (5); 181 $[M - OEt]^+$ (11); 180 $[M - HOEt]^+$ (12); 138 $[M - CH_2{=}COHOEt]^+$ (16); 55 $[M - 171]^+$ (100). ^1H NMR ($CDCl_3$), δ: 0.86 (m, 3 H, Me); 1.30 (m, 11 H, $OCH_2{-}C\underline{H}_3$, 4 CH_2); 1.59 (m, 2 H, $C\underline{H}_2{-}CH_2{-}COO$); 1.96 (br.s, 4 H, 2 $C\underline{H}_2{-}CH{=}$); 2.18 (t, 2 H, $CH_2{-}C\underline{H}_2{-}COO$, J = 7.0 Hz); 4.02 (q, 2 H, $OC\underline{H}_2{-}CH_3$, J = 7.1 Hz); 5.28 (m, 2 H, (*Z*)-HC=CH). IR, ν/cm^{-1}: 710 ((*Z*)-HC=CH) (*cf.* lit. data[24]).

(*Z*)-Dodec-7-en-1-ol (7). A solution of ester **6** (3.8 g, 16.8 mmol) in THF (10 mL) was added to a stirred suspension of $LiAlH_4$ (1.9 g, 50 mmol) in anhydrous THF (25 mL) at 20 °C. The mixture was heated to 50 °C and stirred for 1 h. An excess of $LiAlH_4$ was decomposed with 10% HCl (21 mL), THF was removed *in vacuo*, and the residue was extracted with hexane, washed with water, and dried with $MgSO_4$. After removal of the hexane and distillation, alkenol **7** was obtained in a yield of 3.0 g (95%), b.p. 105 °C (0.3 Torr), n_D^{20} 1.4552. The content of the major compound was 99.2%. ^1H NMR ($CDCl_3$), δ: 0.90 (br.s, 3 H, $C\underline{H}_3{-}CH_2$); 1.31 (br.s, 10 H, $C\underline{H}_2{-}C\underline{H}_2$); 1.51 (br.s, 2 H, $C\underline{H}_2{-}CH_2O$); 1.99 (br.s, 4 H, $C\underline{H}_2{-}CH{=}CH$); 2.24 (br.s, 1 H, OH); 3.52 (m, 2 H, $C\underline{H}_2O$); 5.29 (br.s, 2 H, $\underline{C}H{=}\underline{C}H$). ^{13}C NMR ($CDCl_3$), δ: 14.1 ($\underline{C}H_3{-}CH_2$); 22.2, 25.9, 27.0, 27.3, 29.2, 29.9, 31.2, and 32.9 (8 $\underline{C}H_2$); 62.0 ($\underline{C}H_2{-}O$); 129.8 and 130.2 ($\underline{C}H{=}\underline{C}H$) (*cf.* lit. data[27]).

(*Z*)-Dodec-7-en-1-yl acetate (7a). A solution of AcCl (2.1 g, 27 mmol) in hexane (5 mL) was added with stirring to a solution of alcohol **7** (3.0 g, 16 mmol) and Py (2.3 g, 30 mmol) in anhydrous hexane (7 mL) at 12 °C in such a way as to keep the temperature below 20 °C. The reaction mixture was stirred for 2 h, decomposed with H_2O, and extracted with hexane. The hexane extracts were washed with H_2O and dried with $MgSO_4$. After removal of the hexane and distillation, acetate **7a** was obtained in a yield of 3.5 g (95%), b.p. 90 °C (0.3 Torr), n_D^{20} 1.4432. The content of the major component was 99.1%. ^1H NMR ($CDCl_3$), δ: 0.90 (m, 3 H, $C\underline{H}_3{-}CH_2$); 1.30 (br.s, 10 H, $C\underline{H}_2{-}C\underline{H}_2$); 1.51 (m, 2 H, $C\underline{H}_2{-}CH_2O$); 2.0 (m, 7 H: 3 H, $C\underline{H}_3{-}CO$ and 4 H, $C\underline{H}_2{-}CH{=}CH$); 3.99 (t, 2 H, $C\underline{H}_2O$, J = 7.0 Hz); 5.29 (t, 2 H, $C\underline{H}{=}C\underline{H}$, J = 6.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 14.0 ($C\underline{H}_3{-}CH_2$); 20.8 ($C\underline{H}_3{-}CO$); 22.5, 26.1, 27.0, 27.3, 28.8, 29.1, 29.9, and 32.0 (8 $\underline{C}H_2$); 64.6 ($\underline{C}H_2{-}O$); 129.3, 130.2 ($\underline{C}H{=}\underline{C}H$); 170.6 ($\underline{C}OO$) (*cf.* lit. data[27]).

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