

# A Practical Synthesis of (Z)- and (E)-8-Dodecene-1-yl Acetate, Components of Lepidoptera Insect Sex Pheromones

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*New and practical synthesis of (Z)-8-dodecene-1-yl acetate and (E)-8-dodecene-1-yl acetate were developed. The synthesis were based on a  $C_3+C_6=C_9$  and  $C_9+C_3=C_{12}$  coupling scheme, the starting material being 2-propyn-1-ol and 1,6-hexandiol. The routes involve, as the key step, the use of the same mercury derivative of the terminal-alkyne  $\omega$ -functionalised as intermediate. The first coupling reaction took place between methoxyallene and Grignard reagent of 1-tert-butoxy-6-bromo-hexan obtaining 1-tert-butoxy-non-8-yne, which is transformed in di[1-tert-butoxy-non-8-yne]mercury, the common intermediate in the synthesis of the two pheromones. In order to obtain (Z)-8-dodecene-1-yl acetate and (E)-8-dodecene-1-yl acetate, the mercury derivative was directly lithiated and then alkylated with 1-bromo-propan obtaining 1-tert-butoxy-dodec-8-yne. After acetylation of 1-tert-butoxy-dodec-8-yne and stereoselective reduction in the presence of NiP-2 catalyst gave (Z)-8-dodecene-1-yl acetate with 85 % isomeric purity. After reduction with lithium aluminium hydride of 1-tert-butoxy-dodec-8-yne and acetylation was obtained (E)-8-dodecene-1-yl acetate with 90% isomeric purity.*

**Keywords:** (Z)-8-dodecene-1-yl acetate, (E)-8-dodecene-1-yl acetate, Lepidoptera, sex pheromone

(Z)-8-dodecene-1-yl acetate and (E)-8-dodecene-1-yl acetate are components for a lot of *Lepidoptera* insect sex pheromones [1]. In our country some important economic pest insects are: *Grapholita molesta* (oriental fruit moth), *Grapholita funebrana* (plum fruit moth), *Hedya nubiferana* (green budworm moth).

The synthesis of (Z)-8-dodecene-1-yl acetate and (E)-8-dodecene-1-yl acetate are well known in the literature [2-5]. The paper [6] describes synthesis of the (11Z, 13Z)-hexadecadiene-1-yl acetate and (13Z)-hexadecen-11-ynyl acetate, using cross-coupling reactions for the stereospecific introduction of double bonds.

The paper describes new and practical synthesis of (Z)-8-dodecene-1-yl acetate and (E)-8-dodecene-1-yl acetate based on the C-alkylation reaction, using the same mercury derivative of the terminal alkyne  $\omega$ -functionalized.

## Experimental part

GS-MS analysis were performed on a GS-MS spectrometer Agilent 7890A GC&5975 GS/MS.  $^1\text{H-NMR}$  (300 MHz) and  $^{13}\text{C-NMR}$  (75 MHz) spectra were recorded at *rt* in  $\text{CDCl}_3$  on a Bruker 300 MHz spectrometer, using TMS line as reference. A Perkin Elmer Spectrometer Model 700 was used for IR spectra.

### Methyl propargyl ether (4)

To a mixture of 86.36 g (1.540 moles) of distilled 2-propyn-1-ol (3) and 22 mL of water was added with cooling a solution of 89g (2.225 moles) of NaOH in 141 mL  $\text{H}_2\text{O}$  with such a rate that the temperature did not exceed 30°C. After the addition is complete was added dropwise 84 mL of methyl sulfate. Dripping is made within 2 h so that the temperature does not exceed 50-60°C. The mixture was refluxed for 2.5 h and then was distilled at 95-97°C. The flask was cooled externally with ice and salt. The organic layer was separated and washed with a saturated solution of  $\text{NH}_4\text{Cl}$ , finally dried over anhydrous  $\text{MgSO}_4$ .

After removal of the solvent, 77g (1.1 moles) g of methyl propargyl ether (4) were obtained. Yield: 71 %.

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### Methoxyallene (5)

Potassium *tert*-butoxide was prepared by refluxing 40g (1.850 moles) of dry *tert*-butanol with 4.3g (110 mmoles) of metal potassium up to the total consumption of the metal. Excess of alcohol was removed by distillation from rotavapor and finally to vacuum at 2-3 mm Hg. Bath water temperature was maximum 50° C. It was obtained 14.4g (128 mmoles) of potassium *tert*-butoxide. Yield: 80%.

Over 14.4g (128 mmoles) of previously prepared potassium *tert*-butoxide was added 77g (1.1 moles) of methyl propargyl ether (4). It was heated to 50-60° C with magnetic stirrers in the stream of inert gas on a thermostated water bath. The reaction mixture was refluxed 4 h and after that was distilled in vacuum of 2-3 mm Hg. The collection flask was cooled externally up to -70° C. It was obtained 67g (957 mmoles) of methoxyallene (5). Yield: 87%.

### 6-Bromo-hexane-1-ol (7)

To a solution 118 g (1 mole) of 1,6-hexan-diol (6) solved in 500 mL benzene was added 81g (1 mole) of hydrobromic acid 47%. The reaction mixture was refluxed for 3h. The organic layer was separated and washed with brine, saturated  $\text{NaHCO}_3$  solutions and dried over anhydrous  $\text{MgSO}_4$ . After removal of the solvent the product was purified by liquid-liquid distribution (petroleum ether: aqueous methanol) obtaining 83.48 g (0.458 moles) of 6-bromo-hexane-1-ol (7). Yield: 65 %, GC purity: 95 %.

Mass spectrum (m/z, %): 164(<1); 162(1.47); 149(<1); 135(12.74); 133(13.72); 121(<1); 108(3.92); 1096(4.41); 96(1.96); 94(1.96); 84(3.92); 83(57.84); 82(16.17); 81(4.9); 80(<1); 79(1.96); 69(15.68); 68(2.45); 67(13.72); 57(6.86); 56(8.82); 55(100); 54(11.76); 53(8.82); 51(1.96); 50(<1); 45(2.94); 44(4.41); 43(19.6); 42(28.43); 41(80.39); 40(7.35); 39(41.17); 38(2.94); 31(50.98); 29(27.45); 28(9.8);

### 1-tert-Butoxy-6-bromo-hexane (8)

To a solution 75.45 g (410 mmoles) of 6-bromo-hexan-1-ol (7) and 452 mL *tert*-butyl-methyl-ether (MTBE) [7] was

added dropwise 27.33 mL concentrated sulfuric acid under cooling. The reaction mixture was maintained at 40°C. The reaction was checked by TLC on silica gel G (benzene:ether 2:1, detection with H<sub>2</sub>SO<sub>4</sub> d=1.25). The reaction mixture was diluted with water. After removal of the *tert*-butyl-methyl-ether under reduced pressure, the mixture was extracted with ethyl ether (3x50 mL). The combined ethereal extracts were washed with saturated NaHCO<sub>3</sub> solution up to basic and dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, 62.54 (263 mmoles) g of 1-*tert*-butoxy-6-bromo-hexane (**8**) were obtained. Yield: 64 %, GC purity: 95 %.

Mass spectrum (m/z, %): 236(<1); 221(24.16); 207(<1); 192 (<1); 181(<1); 163 (<1); 163(19.58); 149 (<1); 135(<1); 121(3.33); 107(2.07); 95(<1); 71(<1); 57 (100); 41(27.91);

#### 1-*tert*-Butoxy-non-8-yne (**10**)

All operations were performed in an inert gas atmosphere and under vigorous stirring.

A solution of Grignard compounds in 250 mL of dry ethyl ether was prepared in the usual manner from 60 g (252 mmoles) 1-*tert*-butoxy-6-bromo-hexane (**8**) and 6.66 g (277.5 mmoles) of Mg. The solution was cooled to the room temperature and 3 g (30 mmoles) of CuCl dissolved in 11 mL hexamethylphosphortriamide (HMPT) were added. Thereafter a solution of 16.09 g (229 mmoles) of methoxyallene (**5**) in 250 mL dry ethyl ether was added dropwise under external ice cooling within 20-30 min [8]. The reaction was brought to completion by stirring for 30 min at room temperature. A solution of 100 mL NH<sub>4</sub>Cl was added in dropwise under good external ice cooling. The reaction mixture was extracted with ethyl ether (4 x 50 mL). The combined ethereal solutions were washed successively with brine, aqueous NaHCO<sub>3</sub> and dried over MgSO<sub>4</sub>. After removal of the solvent the residue was distilled at 70-71°C/ 2-3 mmHg obtaining 29.7 g (151 mmoles) of 1-*tert*-butoxy-non-8-yne (**10**). Yield: 60 %, GC purity: 95 %.

Mass spectrum (m/z, %) 207(<1); 181(30.4); 140(<1); 123(2.91); 107(2.5); 95(6.25); 181(64.58); 57(100); 41(30.83)

#### Di[1-*tert*-butoxy-non-8-yne]mercury (**11**)

To 43.19 g (260 mmoles) of potassium iodide dissolved in 43.19 mL water were added 17.49 (64 mmoles) g mercury (II) chloride and the mixture was stirred till the mercury salt was dissolved. To the mixture were added 33.12 mL of 10% sodium hydroxide solution [9]. After external cooling of reaction mixture with ice, were added dropwise 10.4 g (53 mmoles) of 1-*tert*-butoxy-non-8-yne (**10**) dissolved in 220 mL cooled ethyl alcohol. The obtained precipitate was filtrated and washed on the filter with cooled aqueous ethylic alcohol 50%. After drying were obtained 21.94 g (37 mmoles) of di(1-*tert*-butoxy-non-8-yne) mercury (**11**). Yield: 70%, m.p.=100°C.

#### 1-*tert*-Butoxy-dodec-8-yne (**12**)

All operations were performed in an inert gas atmosphere and under stirring.

7 g (12 mmoles) of compound **11** in 33 mL diglyme was treated with 0.168 g lithium (24 mmoles) at 110°C for 3 h.

3.69 g (30 mmoles) of 1-bromo-propan dissolved in 10 mL diglyme was added dropwise at 90°C afterwards the temperature was raised to 120-125°C under stirring for 4.5 h. The mixture was poured out over 100 g of crushed ice. The reaction mixture was extracted with petroleum ether. The ethereal solution was washed successively with 10% HCl, water and brine till neutral pH of the washings. After

drying over MgSO<sub>4</sub>, the solvent was removed and 2.3 g (9.6 mmoles) of 1-*tert*-butoxy-dodec-8-yne (**12**) was obtained. Yield: 81 %, GC purity: 80%.

Mass spectrum (m/z, %) 223(5.83); 207(2.91); 164(1.25); 138(2.91); 123(7.91); 109(25.83); 95(26.66); 81(35); 67(28.75); 57(100); 41(30.83); 32(26.25);

(<sup>1</sup>H-NMR, 300MHz, CDCl<sub>3</sub>, δ, ppm): 0.93(H<sub>12</sub>, t, J=7.2 Hz, -CH<sub>3</sub>, 3H); 1.42-1.49(H<sub>11</sub>, H<sub>6</sub>, H<sub>2</sub>, m, J=6.7Hz, -(CH<sub>2</sub>)<sub>3</sub>, 6H), 1.23-1.37 (H<sub>9</sub>, H<sub>1</sub>, H<sub>3</sub>, m, J=6.7Hz, -(CH<sub>2</sub>)<sub>3</sub>, 6H) 2.06-2.16 (H<sub>10</sub>, H<sub>7</sub>, m, -(CH<sub>2</sub>)<sub>2</sub>, 4H), 3.28 (H<sub>1</sub>, t, J=6.3 Hz, -CH<sub>2</sub>-OtBu), 1.14 (H<sub>1</sub>, s, -OC(CH<sub>3</sub>)<sub>3</sub>, -(CH<sub>3</sub>)<sub>3</sub>, 9H)

(<sup>13</sup>C-NMR, 75MHz, CDCl<sub>3</sub>, δ, ppm): 13.4(C<sub>12</sub>), 22.1 (C<sub>11</sub>), 20.7 (C<sub>10</sub>), 79.9 (C<sub>9</sub>, -C≡C-), 80.2(C<sub>8</sub>, -C≡C-), 18.7(C<sub>7</sub>), 29.1(C<sub>6</sub>), 28.7(C<sub>5</sub>), 28.8(C<sub>4</sub>), 26.1(C<sub>3</sub>), 30.6(C<sub>2</sub>), 61.5(C<sub>1</sub>, -CH<sub>2</sub>O-), 72.3(C<sub>2</sub>, -OC(CH<sub>3</sub>)<sub>3</sub>), 29.6(C<sub>1</sub>, -OC(CH<sub>3</sub>)<sub>3</sub>)

#### 8-Dodecyne-1-yl acetate (**13**)

2.3 g (9.66 mmoles) of 1-*tert*-butoxy-dodec-8-yne (**12**) was dissolved in 9.66 mL of 1:10 mixture of acetyl chloride : acetic acid and was refluxed for 4-5 h. The reaction development was checked up by TLC on silica gel G (hexane : ether, 15:1, detection with H<sub>2</sub>SO<sub>4</sub> d=1.25). The solution was poured on crushed ice, extracted with petroleum ether, washed with brine and with aqueous NaHCO<sub>3</sub> till neutral pH of the washings. After drying over MgSO<sub>4</sub> and removal of the solvent was obtained 2 g (8.9 mmoles) of 8-dodecyne-1-yl acetate (**13**). Yield: 80%, GC purity: 85%.

Mass spectrum (m/z, %): 207(<1); 195(<1); 181(<1); 164(<1); 149(<1); 135(7.5); 121(15); 107(17.08); 93(40.41); 82(100); 67(67.5); 55(31.66); 43(60); 32(<1)

#### (Z)-8-Dodecen-1-yl acetate (**1**)

8-Dodecyne-1-yl acetate (**13**) was hydrogenated at (Z)-8-dodecene-1-yl acetate (**1**) in the presence of the NiP-2/EDA catalyst, prepared in situ according to the standard procedure [10]. (Z)-8-Dodecene-1-yl acetate (**1**) was obtained in yield of 74 %, GC purity: 85 %.

Mass spectrum (m/z, %): 207(<1); 183(<1); 166(23.64); 151(<1); 137(6.4); 123(8.37); 109(29.06); 96(61.57); 82(100); 67(96.55); 55(79.31); 43(76.84); 32(15.76)

(<sup>1</sup>H-NMR, 300MHz, CDCl<sub>3</sub>, δ, ppm): 0.89(H<sub>12</sub>, t, J=7.2 Hz, -CH<sub>3</sub>, 3H); 1.31-1.42(H<sub>11</sub>, H<sub>3</sub>, H<sub>6</sub>, m, J=7.5Hz, 11-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>4</sub>, 10H), 1.96-2.01(H<sub>10</sub>, H<sub>7</sub>, t, -(CH<sub>2</sub>)<sub>2</sub>, 4H), 5.35 (H<sub>9</sub>, H<sub>8</sub>, m, J=10.8Hz -CH=CH-, 2H), 4.04 (H<sub>1</sub>, t, -CH<sub>2</sub>-O-, 2H), 2.03 (H<sub>1</sub>, s, -OCOCH<sub>3</sub>, 3H)

(<sup>13</sup>C-NMR, 75MHz, CDCl<sub>3</sub>, δ, ppm): 13.8(C<sub>12</sub>), 22.8(C<sub>11</sub>), 29.4 (C<sub>10</sub>), 129.5(C<sub>9</sub>, -CH=CH-), 129.8(C<sub>8</sub>, -CH=CH-), 27.3(C<sub>7</sub>), 29.7(C<sub>6</sub>), 29.1(C<sub>5</sub>), 28.8(C<sub>4</sub>), 25.5(C<sub>3</sub>), 28.2(C<sub>2</sub>), 64.6(C<sub>1</sub>, -CH<sub>2</sub>O-), 171.1(C<sub>2</sub>, -OCOCH<sub>3</sub>), 20.4(C<sub>1</sub>, -OCOCH<sub>3</sub>)

#### 1-*tert*-Butoxy-E-8-dodecene (**14**)

All operations were performed in an inert gas atmosphere and under stirring.

2.15 g (56.7 mmoles) of LiAlH<sub>4</sub> was placed in a solution of 3 mL of anhydrous THF and 50 mL of diglyme. The mixture was heated at 140°C. The solvent was partially removed. After cooling at 0°C, the suspension was treated with 3 g (12.6 mmoles) of compounds **12** in 7 mL diglyme maintaining the temperature below 10°C. The mixture was heated at 145-150°C where was maintained for 20 h. The reaction was checked by TLC on silicagel G (benzene:ether,5:1, detection with H<sub>2</sub>SO<sub>4</sub> d=1.25). After cooling, the solution was treated with 20 mL of H<sub>2</sub>SO<sub>4</sub> dil. (d=1.25). The reaction mixture was extracted with diethyl ether, washed with brine and dried over MgSO<sub>4</sub>. After removal of the solvent and distillation (80°-82°C/1 mmHg)

was obtained 2.5 g (10.5 mmoles) of 1-*tert*-butoxy-E-8-dodecene (**14**). GC purity: 93 %. Yield: 83 %.

Mass spectrum (m/z, %): 240(1.12), 225(2.24), 184(<1); 166(4.49); 138(<1); 111(10.11); 97(19.10); 83(15.73); 71(24.71); 41(32.58); 29(13.48)

#### (E)-8-Dodecene-1-yl acetate (**2**)

2.5 g (10.5 mmoles) of 1-*tert*-butoxy-dodec-8-ene (**14**) was dissolved in 10.5 mL of 1:10 mixture of acetyl chloride: acetic acid and was refluxed for 4-5 h. The reaction development was checked up by TLC on silica gel G (hexane:ether, 15:1, detection with H<sub>2</sub>SO<sub>4</sub> d=1.25). The solution was poured on crushed ice, extracted with petroleum ether, washed with brine and with aqueous NaHCO<sub>3</sub> till neutral pH of the washings. After drying over MgSO<sub>4</sub> and removal of the solvent the product was purified by distillation (70-80°C/2-3 mmHg) obtaining 2 g (8.84 mmoles) of E-8-dodecene-1-yl acetate (**2**). Yield: 80 %, GC purity: 90%.

Mass spectrum (m/z, %): 240(1.12); 225(2.24); 184(<1); 166(8.03); 123(5.3); 109 (10.61); 95(26.54); 81(46); 67(58.4); 55(55.75); 41(57.52); 29(15.04)

<sup>1</sup>H-NMR, 300MHz, CDCl<sub>3</sub>, δ, ppm): 0.81(H<sub>12</sub>, t, J=7.2 Hz, -CH<sub>3</sub>, 3H); 1.25-1.35(H<sub>11</sub>, H<sub>3</sub>-H<sub>6</sub>, m, 11-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>4</sub>-10H), 1.85-1.91(H<sub>10</sub>, H<sub>7</sub>, m, -(CH<sub>2</sub>)<sub>2</sub>-4H), 5.30(H<sub>9</sub>, H<sub>8</sub>, m, J=15.3Hz, -CH=CH-, 2H), 1.54 (H<sub>1</sub>, m, -CH<sub>2</sub>-, 2H) 3.98(H<sub>1</sub>, t, -CH<sub>2</sub>-O, 2H), 1.96 (H<sub>1</sub>, s, -OCOCH<sub>3</sub>, 3H)

(<sup>13</sup>C-NMR, 75MHz, CDCl<sub>3</sub>, δ, ppm): 13.1(C<sub>12</sub>), 22.7 (C<sub>11</sub>), 34.7(C<sub>10</sub>), 129.7(C<sub>9</sub>, -CH=CH-), 130.1(C<sub>8</sub>, -CH=CH-), 32.3(C<sub>7</sub>, -CH<sub>2</sub>-), 29.3(C<sub>6</sub>), 29.1 (C<sub>5</sub>), 28.4(C<sub>4</sub>), 25.8(C<sub>3</sub>), 28.7(C<sub>2</sub>), 64.2(C<sub>1</sub>, -CH<sub>2</sub>O-), 170.7(C<sub>2</sub>, -OCOCH<sub>3</sub>), 20.3(C<sub>1</sub>, -OCOCH<sub>3</sub>)

#### Results and discussions

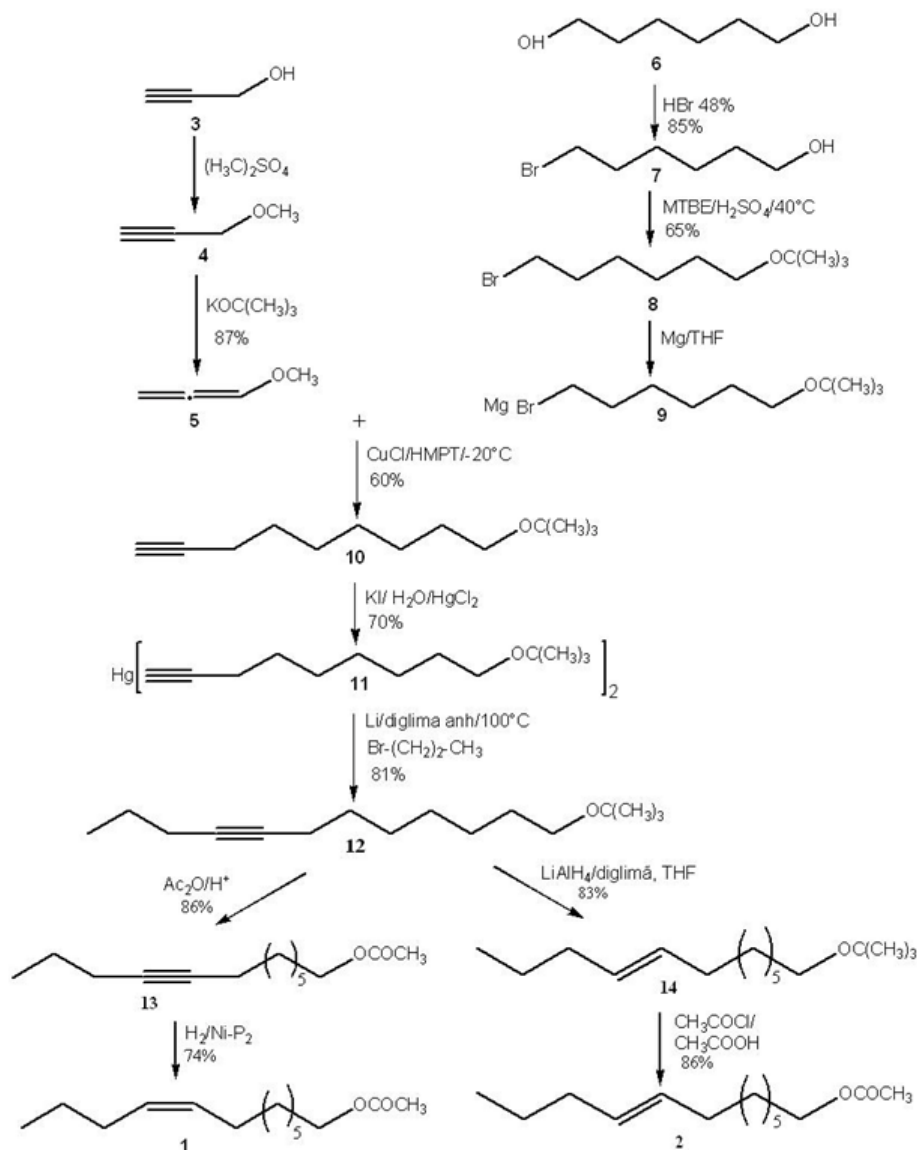
For the synthesis of (Z)-8-dodecene-1yl acetate (**1**) and (E)-8-dodecene-1-yl acetate (**2**) we explored the pathway outlined in scheme 1. The synthesis were based on C<sub>6</sub>+C<sub>3</sub>=C<sub>9</sub> and C<sub>9</sub>+C<sub>3</sub>=C<sub>12</sub> coupling schemes, the routes involving the use of the same mercury derivative of the terminal alkyne ω-functionalised as intermediate.

The first coupling reaction took place between methoxyallene (**5**) and Grignard reagent of 1-*tert*-butoxy-6-bromo-hexan (**9**) obtaining 1-*tert*-butoxy-non-8-yne (**10**), which is transformed in di[1-*tert*-butoxy-non-8-yne]mercury (**11**), the common intermediate in the synthesis of the two pheromones.

2-Propyn-1-ol (**3**) with dimethyl sulfate was transformed in methyl propargyl ether (**4**) which under action of potassium *tert*-butoxyd gave methoxyallene (**5**).

Use has been made of methyl-*t*-butyl-ether [6] in acid catalysis in order to protect the -OH function of the 6-bromo-hexane-1-ol (**7**).

1-*tert*-Butoxy-non-8-yne (**10**) was checked by means of IR spectrum (film, cm<sup>-1</sup>: 895 m, 1110 vs, 1220 vs, 2160 w -C≡C-, 3280 s a"CH), which presents the vibration of



Scheme 1

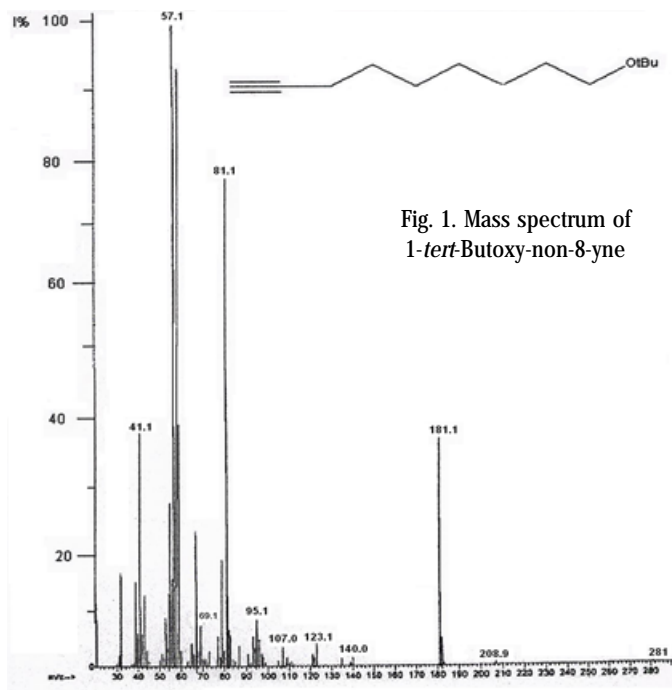


Fig. 1. Mass spectrum of 1-*tert*-Butoxy-non-8-yne

terminal triple bond and the mass spectrum characteristic to a *tert*-butyl ether (fig. 1).

The molecular peak of 1-*tert*-butoxy-non-8-yne (**10**) was not identified, the mass spectrum presenting only characteristic fragmentations ( $m/z$  57,  $m/z$ =59). It is necessary to mention the base peak in the spectrum ( $m/z$ =59), the peak  $m/z$  57 which is generated by the very stable tertiary carbocation  $+C(CH_3)_3$ , the peak corresponding to the cleavage of a methyl group from the branch part ( $m/z$ =181) and of a neutral molecule of isobutylene ( $m/z$ =140).

1-*tert*-Butoxy-non-8-yne (**10**) with mercuric chloride in an aqueous solution containing potassium iodide and sodium hydroxide (Nessler's reagent) [9] was precipitated as di[1-*tert*-butoxy-non-8-yne]mercury (**11**), the common intermediate in the synthesis of the two sex pheromones.

The key step in our acetylenic route consisted in transmetallation of compound **11**, which was directly lithiated by treating with metal lithium in diglyme and then alkylated with 1-bromo-propan obtaining 1-*tert*-butoxy-dodec-8-yne (**12**).

In order to obtain (*Z*)-8-dodecene-1-yl acetate (**1**), the *tert*-butyl ether **12** was converted into the acetate **13** with acetic anhydride. 8-Dodecyn-1-yl acetate (**13**) was hydrogenated using Ni-P2/EDA catalyst [9], obtaining (*Z*)-8-dodecen-1-yl acetate (**1**) with 85 % isomeric purity.

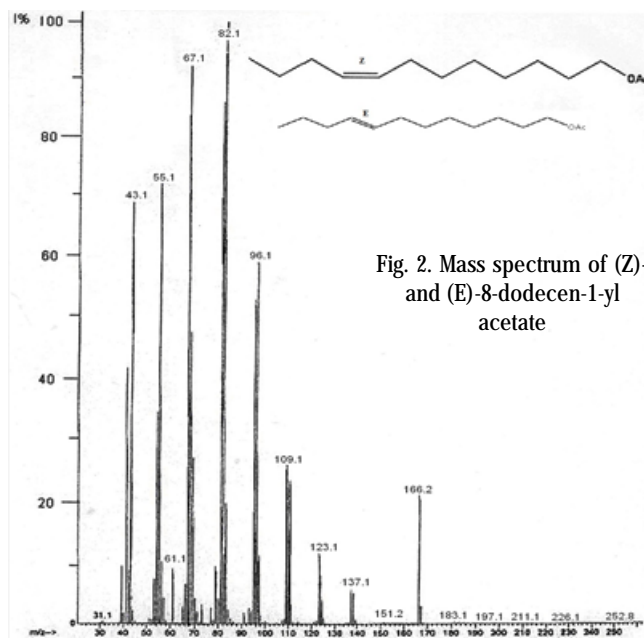


Fig. 2. Mass spectrum of (*Z*)- and (*E*)-8-dodecen-1-yl acetate

In order to obtain (*E*)-8-dodecene-1-yl acetate (**2**), 1-*tert*-butoxy-dodec-8-yne (**12**) was reduced with lithium aluminium hydride and then acetylated.

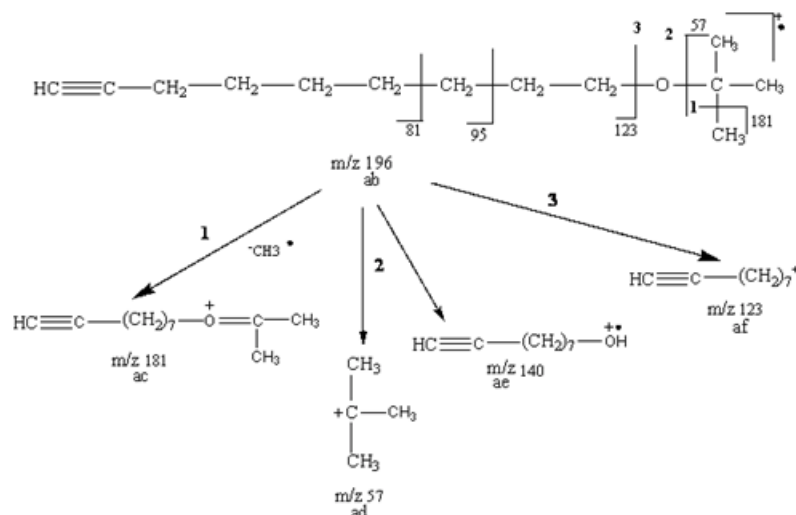
The mass spectrum of (*Z*)-8-dodecene-1-yl acetate (**1**) and (*E*)-8-dodecene-1-yl acetate (**2**) are identical, characteristic to alkenol acetates, by mass spectrometry the geometry of double bond can not be established (fig. 2).

Are present:  $m/z$  166 resulted from the cleavage of acetic acid from the molecular ion,  $m/z$  61 as ion of double transposition ( $CH_2COOH_2^+$ ) and  $m/z$  43 ( $CH_3CO^+$ ).

The chemical structure of the compounds **1** and **2** was confirmed by  $^1H$ -NMR and  $^{13}C$ -NMR spectrum.

$^1H$ -NMR spectrum (fig. 3) of (*Z*)-8-dodecene-1-yl acetate (**1**) includes the following signals: triplet at  $\delta=0.96$  ppm corresponding to the protons of the methyl group from position 12 (3H,  $J=7.5$ Hz), multiplet ( $\delta=1.31$ -1.42 ppm) for methylene protons from positions 3,4,5,6 and 11 (10H), multiplet at  $\delta=1.60$  ppm (2H), for methylene protons from position 2, triplet ( $\delta=1.96$ -2.01ppm) for methylene protons from position 7 and 10 (4H), triplet at  $\delta=4.04$  ppm corresponding to the protons of the methylene group from position 1 (2H), singlet at  $\delta=2.03$  ppm for methyl group protons from position 1' (3H) and multiplet  $\delta=5.35$  ppm for the olefinic group protons (2H,  $J=10.8$ Hz)

$^{13}C$ -NMR spectrum, confirms the existence of *Z*-configuration, the chemical shifts of allylic carbons ( $C_{\alpha}$  and  $C_{\beta}$ ) according with data obtained from a series of related



Scheme 2

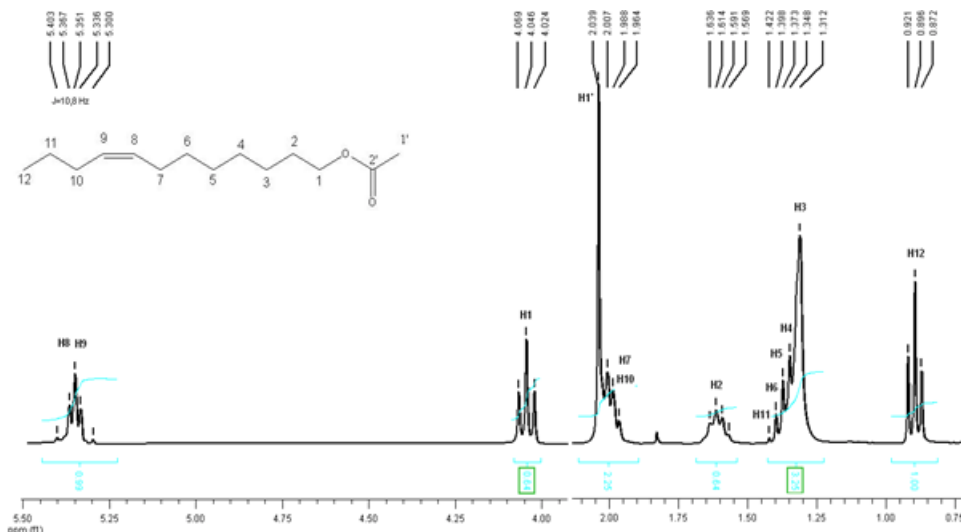


Fig. 3.  $^1\text{H}$ -NMR spectrum (300 MHz,  $\text{CDCl}_3$ ) of (Z)-8-dodecen-1-yl acetate

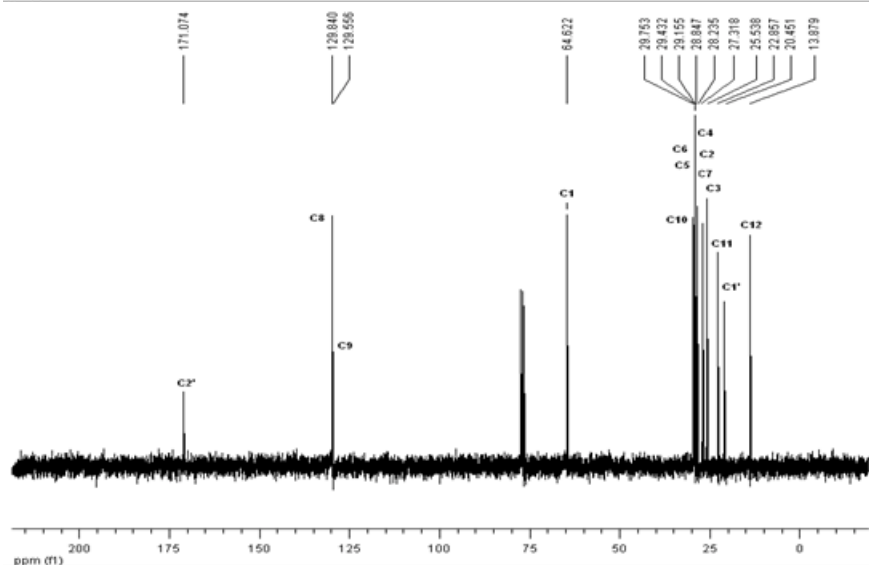


Fig. 4.  $^{13}\text{C}$ -NMR spectrum (75 MHz,  $\text{CDCl}_3$ ) of (Z)-8-dodecen-1-yl acetate

compounds with 12 C-atoms in the molecule [11, 12], values of the chemical shifts being  $\delta = 27.3$  ppm for  $\text{C}_7$  and 29.4 ppm for  $\text{C}_{10}$ . The acetoxy group from compound **1** was confirmed by  $\delta = 171.1$  ppm for  $\text{C}2'$  and  $\delta = 20.4$  ppm for  $\text{C}1'$  (fig. 4).

The  $^1\text{H}$ -NMR spectrum of *E*-(8)-dodecene-1-yl acetate (**2**) shows a triplet at  $\delta = 3.98$  ppm, assigned of the methylene group protons bearing of acetoxy group, a multiplets at  $\delta = 5.30$  ppm showing presence of olefinic bond with trans geometry. The singlet at  $\delta = 2.01$  ppm

corresponding of the methyl group protons from acetoxy group and the multiplets ( $\delta = 1.25 - 1.35$  ppm) for methylene protons from the center of the molecule (fig. 5).

$^{13}\text{C}$ -NMR spectrum, confirms the existence of *E*-configuration, the chemical shifts of allylic carbons ( $\text{C}_7$  and  $\text{C}_{10}$ ) according with data obtained from a series of related compounds with 12 C-atoms in the molecule [11, 12], values of the chemical shifts being  $\delta = 32.3$  ppm for  $\text{C}_7$  and 34.7 ppm for  $\text{C}_{10}$  (fig. 6).

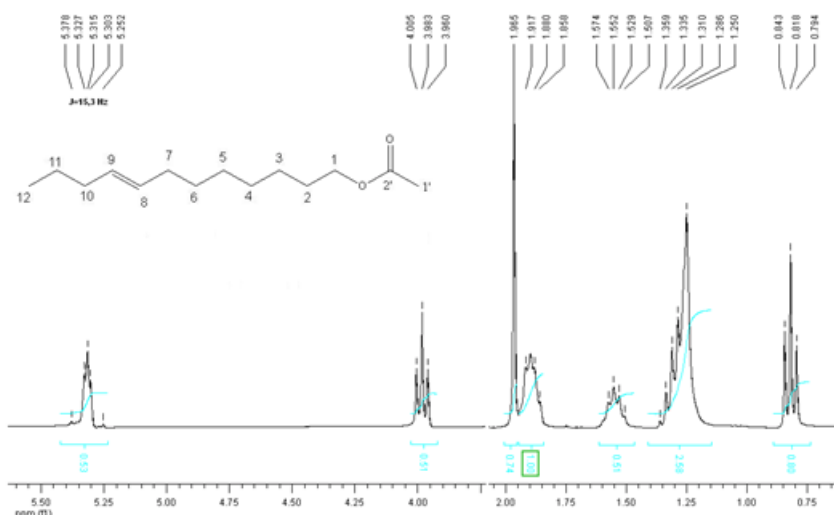


Fig. 5.  $^1\text{H}$ -NMR spectrum (300 MHz,  $\text{CDCl}_3$ ) of (E)-8-dodecen-1-yl acetate

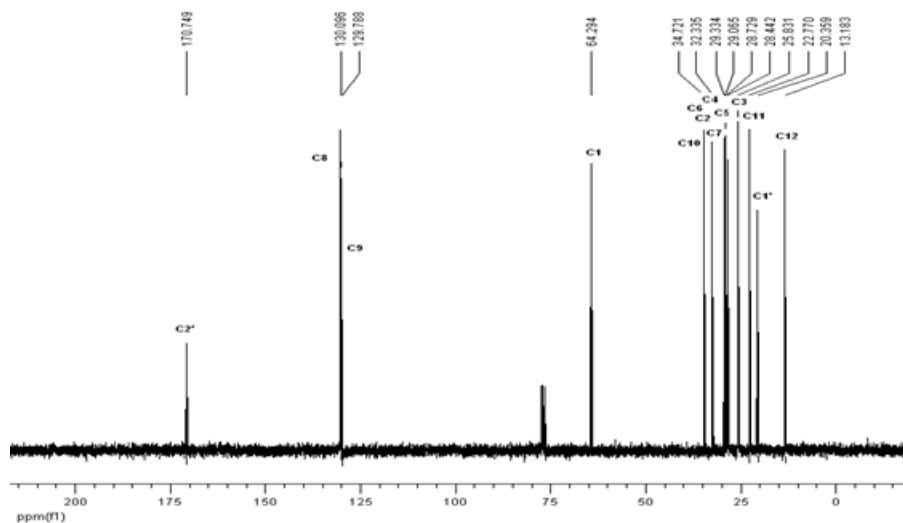


Fig. 6.  $^{13}\text{C}$ -NMR spectrum (75 MHz,  $\text{CDH}_3$ ) of (E)-8-dodecen-1-yl ac

### Conclusions

It was presented new synthesis of (Z)-8-dodecene-1-yl acetate and (E)-8-dodecene-1-yl acetate, components of Lepidoptera insects sex pheromones, using the same intermediate, di[*tert*-butoxy-non-8-yne] mercury, which is directly lithiated and then alkylated with 1-bromo-propan.

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