



EXO- AND ENDOHORMONES. XXIV.<sup>1</sup>  
A CONVENIENT SYNTHESIS OF (Z)-11-TETRADECEN-1-YL ACETATE,  
COMPONENT OF *LEPIDOPTERA* INSECT SEX PHEROMONE

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Received May 19, 2010

A new and practical synthesis of (Z)-11-tetradecene-1-yl acetate was developed using commercially raw material. The synthesis was based on a  $C_{10}+C_2=C_{12}$  and  $C_{12}+C_2=C_{14}$  coupling scheme, starting from 1,10-decane-diol. The route involves, as the key step, the use of the mercury derivative of the terminal alkyne  $\omega$ -functionalised as intermediate, which is lithiated and then alkylated. The first coupling reaction took place between monosodium acetylene obtained in situ and 1-*tert*-butoxy-10-bromo-decane. The second coupling reaction consisted in directly lithiated of di (*t*-butoxy-dodec-11-yne) mercury and then alkylated with ethyl bromide obtaining 1-*tert*-butoxy-tetradec-11-yne. After acetylation and stereoselective reduction in the presence of NiP-2 catalyst of 1-*tert*-butoxy-tetradec-11-yne gave (Z)-11-tetradecene-1-yl acetate with 99% isomeric purity.

## INTRODUCTION

(Z)-11-Tetradecene-1-yl acetate is component for a lot of *Lepidoptera* insect sex pheromones.<sup>2</sup> Some important economic pest insects are: *Tortrix viridana* (European oak leafroller), *Adoxophyes reticulana* (summerfruit tortrix), *Archips podana* (large fruit-tree tortrix) and *Ostrinia nubilalis* (European corn borer).

The synthesis of (Z)-11-tetradecene-1-yl acetate is well known in the literature.<sup>3-13</sup>

coupling reaction<sup>15</sup> was effected by adding 1-*tert*-butoxy-10-bromo-decane (**4**) to monosodate acetylene, obtained in situ from DMSO and sodium hydride. The second coupling reaction consisted in directly lithiated of the mercury compound **7** and then alkylated with ethyl bromide obtaining 1-*tert*-butoxy-tetradec-11-yne (**9**). After acetylation and stereoselective reduction of 1-*tert*-butoxy-tetradec-11-yne (**9**), in the presence of NiP-2 catalyst, gave (Z)-11-tetradecene-1-yl acetate (**1**) with 99% isomeric purity.

## RESULTS

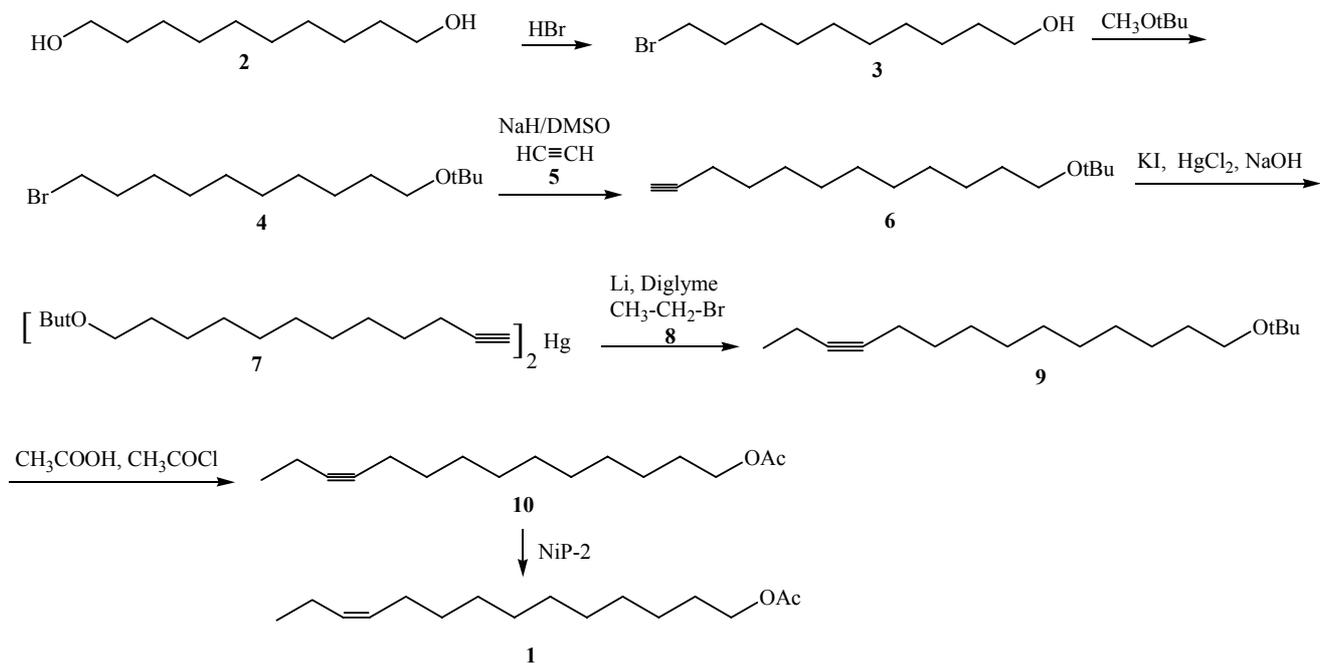
The synthesis of (Z)-11-tetradecene-1-yl acetate was based on a  $C_{10}+C_2=C_{12}$  and  $C_{12}+C_2=C_{14}$  coupling schemes, starting from 1,10-decandiol (Scheme 1).

Use has been made of methyl-*t*-butyl-ether<sup>14</sup> in acid catalysis in order to protect the -OH function of the 10-bromo-decane-1-ol (**3**). The first

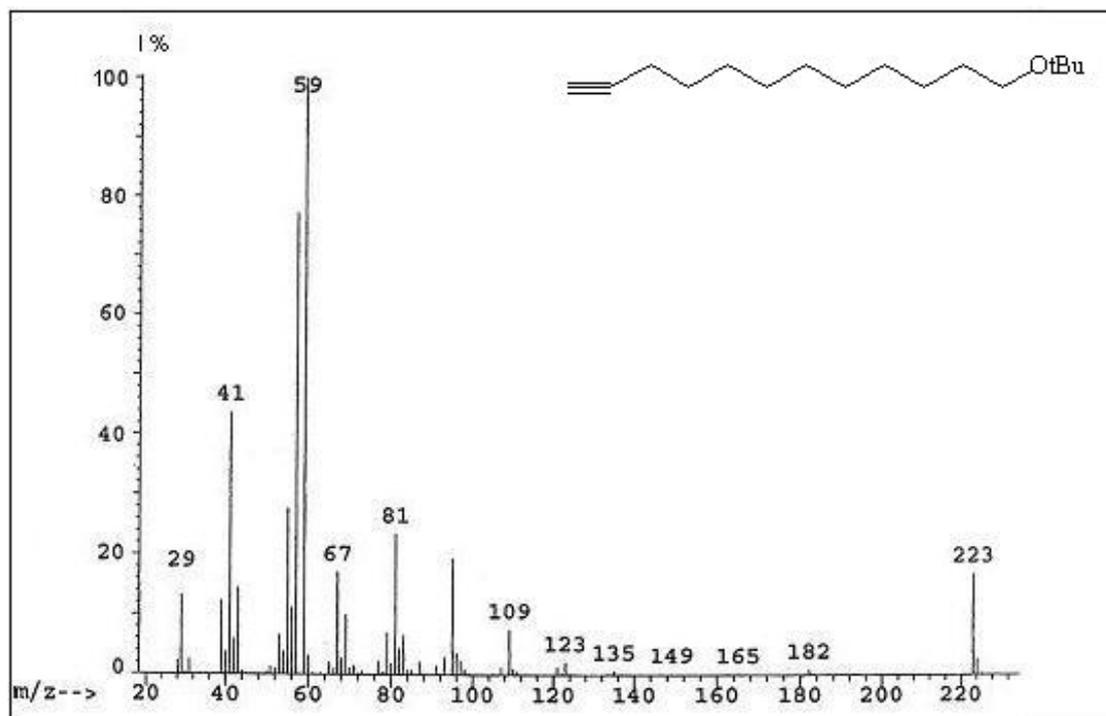
## DISCUSSION

1-*tert*-Butoxy-dodec-1-yne (**6**) was checked by means of IR spectrum (film,  $cm^{-1}$ : 895 m, 1110 vs, 1220 vs, 2160 w  $-C \equiv C-$ , 3280 s  $\equiv CH$ ), which presents the vibration of terminal triple bond and the mass spectrum characteristic to a *tert*-butyl ether, Fig. 1.

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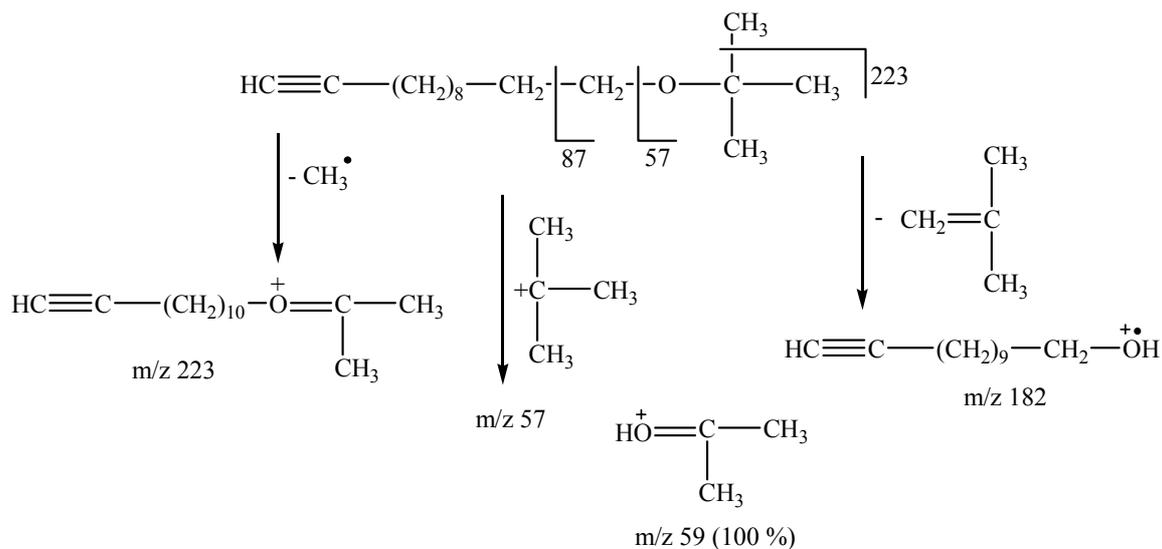


Scheme 1

Fig. 1 – Mass spectrum of 1-*tert*-butoxy-dodec-11-yne.

The molecular peak of **6** was not identified, the mass spectrum presenting only characteristic fragmentations. It is necessary to mention the base peak in the spectrum ( $m/z=59$ ), the peak  $m/z$  57 which is generated by very stable tertiary

carbocation  $+C(\text{CH}_3)_3$ , the peak corresponding to the cleavage of a methyl group from the branch part ( $m/z=223$ ) and of a neutral molecule of isobutylene ( $m/z=182$ ), Scheme 2.



1-*tert*-Butoxy-tetradec-11-yne (**6**) with mercuric chloride in an aqueous solution containing potassium iodide and sodium hydroxide (Nessler's reagent)<sup>16</sup> was precipitated as di(1-*tert*-butoxy-tetradec-11-yne) mercury (**7**).

The key step in our acetylenic route consisted in transmetallation of compound **7**, which was directly lithiated by heating with lithium metal in diglyme and then alkylated with ethyl bromide

obtaining 1-*tert*-butoxy-tetradec-11-yne (**9**). The conversion of the *tert*-butyl ether **9** into the acetate **10** was effected with acetyl chloride. 11-Tetradecyne-1-yl acetate (**10**) was hydrogenated using Ni-P2/EDA catalyst<sup>17</sup>, obtaining (Z)-11-tetradecene-1-yl acetate (**1**) with 99% isomeric purity. The mass spectrum is characteristic to an alkenol acetate, Fig. 2.

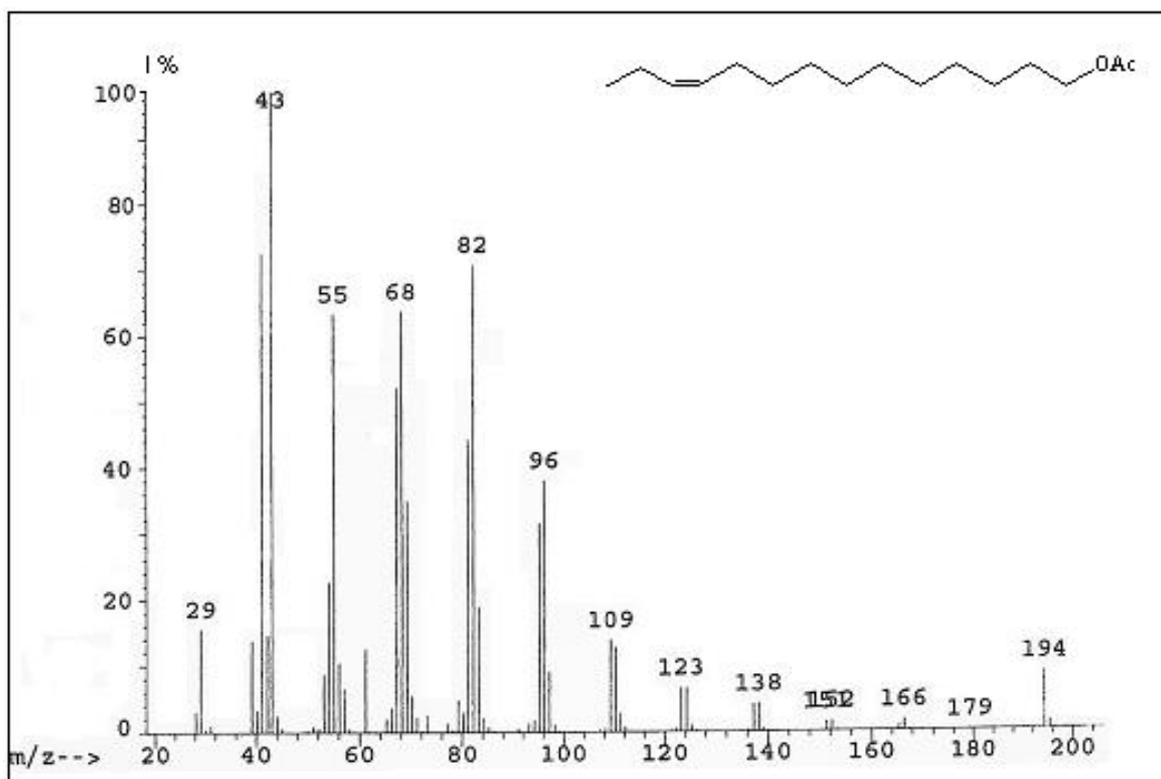


Fig. 2 – Mass spectrum of (Z)-11-tetradecene-1-yl acetate.

The peak at  $m/z$  194 results from the cleavage of acetic acid from the molecular ion and  $m/z$  61 is the ion of double transposition ( $\text{CH}_3\text{COOH}_2^+$ ). Other very important fragment appears at  $m/z$  43 ( $\text{CH}_3\text{CO}^+$ ).

## EXPERIMENTAL

GC-MS analysis were performed on a Hewlett Packard GL-MSD 5890-5972 instrument using a HP-5MS 30 m x 0.25 mm capillary column cross linked 5% phenyl methyl silicon 0,25  $\mu\text{m}$ . A Perkin Elmer Spectrometer Model 700 was used for IR spectra.

### 10-Bromo-decane-1-ol (3)

To a solution 87 g (0.5 mole) of 1,10-decane-diol solved in 250 mL benzene was added 86 mL hydrobromic acid 47%. The reaction mixture was refluxed for 2.5 hours. The organic layer was separated and washed with brine, saturated  $\text{NaHCO}_3$  solution and dried over anhydrous  $\text{MgSO}_4$ . After distillation of the solvent, 73.47 g of 10-bromo-decane-1-ol (**3**) were obtained. Yield: 62%, GC purity: 94%.

Mass spectrum ( $m/z$ , %): 190 ( $\leq 1$ ), 178 ( $\leq 1$ ), 164 ( $\leq 1$ ), 151 ( $\leq 1$ ), 111 ( $\leq 1$ ), 109 ( $\leq 1$ ), 148 (34.80), 97 (26.47), 83 (43.13), 69 (87.25), 55 (100), 41 (74.01), 31 (29.41).

### 1-tert-Butoxy-10-bromo-decane (4)

To a solution 68 g (232 mmoles) of 10-bromo-decane-1-ol (**3**) and 317 mL *tert*-butyl-methyl-ether was added dropwise 19.12 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  $\text{H}_2\text{SO}_4$   $d=1,25$ ). 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  $\text{NaHCO}_3$  solution up to basic and dried over  $\text{Na}_2\text{SO}_4$ . After the removal of the solvent, 64.39 g of 1-*tert*-butoxy-10-bromo-decane (**4**) were obtained. Yield: 76,61%, GC purity: 97%.

Mass spectrum ( $m/z$ , %): 277 ( $\leq 1$ ), 236 ( $\leq 1$ ), 219 ( $\leq 1$ ), 177 ( $\leq 1$ ), 163 ( $\leq 1$ ), 137 ( $\leq 1$ ), 121 ( $\leq 1$ ), 97 ( $\leq 1$ ), 83.29 ( $\leq 1$ ), 59 (100), 41 (21.56).

### 1-tert-Butoxy-dodec-11-yne (6)

Apparatus: 1L reactor provided with a thermometer dipping into the liquid, a dropping funnel, a stirrer and a 20-30 cm long tube for preventing any splashing out of the reaction mixture.

All operations took place in inert atmosphere and vigorous stirring.

16.30 g sodium hydride (60%) were added to 100 mL of dry DMSO and the temperature was risen up to 65°-68°. The conversion was finished when no more hydrogen was evolved.

Acetylene (freed from acetone) was introduced for 15 min. at a rate of about 2L/min. with external cooling in order to moderate the reaction.

During this process the temperature is maintained between 20° and 30° C.

49 mL of DMSO were added and afterwards, between 20°-30°, 20 g (68 mmoles) of 1-*tert*-butoxy-10-bromo-decane (**4**) with external cooling.

The reaction was led to completion by stirring for 3 hours at room temperature and was interrupted with 50 g crushed ice. The reaction mixture was extracted with four portions of 100 mL petroleum ether. The combined ethereal extracts were

washed with brine up to the neutral pH of the washings and dried over  $\text{Na}_2\text{SO}_4$ .

After removal of the solvent 19.4 g of 1-*tert*-butoxy-dodec-11-yne (**6**) were obtained in yield of 89 %, GC purity: 90%.

Mass spectrum ( $m/z$ , %): 223 (17.56), 182 ( $\leq 1$ ), 165 ( $\leq 1$ ), 149 ( $\leq 1$ ), 135 ( $\leq 1$ ), 123 ( $\leq 1$ ), 109 ( $\leq 1$ ), 81 (23.41), 67 (16.58), 59 (100), 41 (40.97), 29 (14.63).

### Di(*t*-Butoxy-dodec-11-yne)mercury (7)

To the 66.42 g of potassium iodide dissolved in 66.42 mL water were added 26.89 g mercury (II) chloride and the mixture was stirred till the mercury salt was dissolved. To the mixture were added 51 mL of 10% sodium hydroxide solution. After external cooling of reaction mixture with ice, were added dropwise 19.4 g (81.5 mmoles) of 1-*tert*-butoxy-dodec-11-yne (**6**) dissolved in 285 mL cooling ethyl alcohol. The obtained precipitate was filtrated and washed on the filter with cooling aqueous ethylic alcohol 50%. The compound **7** was obtained in yield of 31,98 %. m.p.=105°

### 1-tert-Butoxy-tetradec-11-yne (9)

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

5.32 g (7.8 mmoles) of compound **7** in 20 mL diglyme was treated with 0.1 g lithium (15.6 mmoles) at 120°-125° for 2 hours.

21.63 g (15 mmoles) of ethyl bromide (**8**) was added dropwise at 90°-95°C then the temperature was raised to 120°-125° under stirring for 4 hours.

The mixture was poured out over the 100 g of break 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  $\text{MgSO}_4$ , the solvent was removed and 1.77 g (60%) of 1-*tert*-butoxy-tetradec-11-yne (**9**) was obtained. Yield: 60%, GC purity: 78%.

Mass spectrum ( $m/z$ , %): 251 (23.90), 237 ( $\leq 1$ ), 211 ( $\leq 1$ ), 210 ( $\leq 1$ ), 181 ( $\leq 1$ ), 163 ( $\leq 1$ ), 151 ( $\leq 1$ ), 123 (13.65), 109 (41.95), 95 (40.97), 81 (47.80), 57 (100), 41 (80), 29 (21.95)

### 11-tetradecyne-1-yl acetate (10)

5.55 g (16.99 mmoles) of 1-*tert*-butoxy-tetradec-11-yne (**9**) was dissolved in 17 mL of 1:10 mixture of acetyl chloride: acetic acid and was refluxed for 4-5 hours. The reaction development was checked up by TLC on silica gel G (hexane : ether, 15:1, detection with  $\text{H}_2\text{SO}_4$   $d=1,25$ ).

The solution was poured on crushed ice, extracted with petroleum ether, washed with brine and with aqueous  $\text{NaHCO}_3$  till neutral pH of the washings. After drying over  $\text{MgSO}_4$ , the solvent was removed and 3.41 g of 11-tetradecyne-1-yl acetate (**10**) was obtained. Yield: 65%, GC purity: 85%.

Mass spectrum ( $m/z$ , %): 163 ( $\leq 1$ ), 149 ( $\leq 1$ ), 135 ( $\leq 1$ ), 121 ( $\leq 1$ ), 96 ( $\leq 1$ ), 29 ( $\leq 1$ ), 93 (22.54), 82 (57.8), 68 (100), 55 (41.11), 43 (89.21), 39 (12.25).

### (Z)-11-tetradecene-1-yl acetate (1)

11-Tetradecyne-1-yl acetate (**10**) was hydrogenated at (Z)-11-tetradecene-1-yl acetate (**1**) in the presence of the NiP-2/EDA catalyst, prepared in situ according to the standard procedure.<sup>17</sup> (Z)-11-Tetradecene-1-yl acetate (**1**) was obtained in yield of 90%, GC purity: 92%.

Mass spectrum ( $m/z$ , %): 194 ( $\leq 1$ ), 165 ( $\leq 1$ ), 166 ( $\leq 1$ ), 152 ( $\leq 1$ ), 138 ( $\leq 1$ ), 123 ( $\leq 1$ ); 109 (12.25), 96 (32.35), 82 (57.84), 68 (50), 55 (60.29), 43 (100), 29 (14.70).

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