SOME STEREOSELECTIVE PALLADIUM-CATALYZED TRANSFER SEMI-HYDROGENATION OF INTERNAL ALKYNE TO *(Z)*-ALKENE FOR INSECT PHEROMONES SYNTHESIS

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Le Van Dung[1,2], Dao Van Nam[2], Le Thi Yen Nghi[2], Nguyen Vinh Hien[2], Vo Duy Can[2], Dang Thi Kim Phuong[2], Nguyen Le Kim Thuy[2], Tran Minh Trong[2], Huynh Thi Thuy Trang Thanh[3], Nguyen Thanh Danh[1,2], Dang Chi Hien[1,2*]

[1]*Graduated University of Science and Technology, VAST*

[2]*Institute of Chemical Technology, VAST*

[3]*Binh Duong Economics and Technology University*

[*]Email: dangchihien@gmail.com

TÓM TẮT

MỘT SỐ XÚC TÁC PALLADIUM CHỌN LỌC LẬP THỂ BÁN HYDRO HÓA ALKYNE THÀNH (Z)-ALKENE TRONG TỔNG HỢP PHEROMONE CÔN TRÙNG

*Các dạng xúc tác palladium khác nhau như $Pd(OAc)_2$ (palladium(II) acetate), $Pd(PPh_3)_2Cl_2$ (bis(triphenylphosphine)palladium(II) dichloride), nano PdNPs/PEG (palladium(0)/polyethylene glycol) và $Pd_2(dba)_3$ (tris(dibenzylidene acetone)dipalladium(0)) đã được sử dụng cho quá trình bán hydrogen hóa alkyn thành (Z)-alkene với hiệu suất và tính chọn lọc lập thể cao mà không cần sử dụng hydro phân tử. Khi đó, KOH/DMF hoặc NaOH/DMF được dùng như là nguồn cấp hydro hiệu quả để khử hoá các alkyne. Các hệ xúc tác khử kiểu này đã được dùng thành công trong tổng hợp (Z)-3-hexen-1-yl tetrahydropyran-2-yl ether (**II**) từ 3-hexyn-1-yl tetrahydropyran-2-yl ether (**I**), cho hiệu suất tốt (> 90%). Đặc biệt, ứng dụng hệ xúc tác $Pd_2(dba)_3$/KOH/DMF vào thực tiễn tổng hợp pheromone giới tính của sâu tơ Plutella xylostella ((Z)-11-hexadecen-1-yl acetate) qua 5 bước, từ nguyên liệu đầu 1,10-decandiol và 1-hexyne, đã cho được hiệu suất toàn phần đạt 60%.*

Từ khoá: *Alkyne, (Z)-alkene, pheromone, palladium, bán hydrogen hóa, Plutella xylostella, (Z)-11-hexadecen-1-yl acetate.*

1. INTRODUCTION

It can be challenging to synthesize (*Z*)-alkene compounds from alkynes through a reduction reaction with high stereoselectivity and good reaction efficiency, especially when synthesizing insect pheromones. For example, the configuration (*Z*)-alkenol is the sex pheromone of the diamondback moth (*Plutella xylostella* Linnaeus), which consists of three components: (*Z*)-11-hexadecen-1-ol, (*Z*)-11-hexadecenal, and (*Z*)-11-hexadecen-1-yl acetate [1]. Similarly, the sex pheromone of the sweet potato weevil (*Cylas formicarius* Fabricius) is (*Z*)-3-dodecen-1-yl (*E*)-2-butenoate [2], and the main component in the sex pheromone complex of the fall armyworm (*Spodoptera frugiperda* (J.E. Smith)) is (*Z*)-9-tetradecenyl acetate [3]. Molecular hydrogen with Pd/C or Pd-$BaSO_4$/quinoline catalyst has been commonly used for the reduction of alkyne to (*Z*)-alkene. However, the selectivity and conversion efficiency are good but limited in consistency. Recently, in organic synthesis, catalytic systems of palladium complexes have been used to reduce triple bonds to double bonds by using semi-hydrogen instead of molecular hydrogen [4-8]. This method has shown positive results, especially when the stereoselectivity of the reaction and the synthesis efficiency are high. Previously, in synthesizing the sex pheromone precursor of the tea mosquito bug (*Helopeltis theivora* Waterhouse), we used the $Pd(OAc)_{2/}$KOH/DMF catalytic system on magnetic stirring at 145 ºC [9] to perform the reduction reaction of (*Z*)-3-hexen-1-yl tetrahydropyran-2-yl ether (**II**) from 3-hexyn-1-yl tetrahydropyran-2-yl ether (**I**). An efficiency of about 90%, in which (*Z*)-(**II**) isomers predominate in the mixture was obtained after the reaction.

In this article, new results on the ability to reduce alkyne derivatives to (*Z*) selectively-alkene derivatives using other palladium catalytic systems, such as $Pd(PPh_3)_2Cl_2$ with a +2 oxidation number, and PdNPs/PEG (palladium nanoparticles/ polyethylene glycol) system, which has an oxidation number of 0, are introduced. All reactions use KOH/DMF or NaOH/DMF as a source of reducing agent in semi-hydrogen, magnetic stirring, and heating maintained at 145 ºC for 6 hours, giving an isolation efficiency of over 90%. The $Pd_2(dba)_3$ system reduces (**4**) to (5), which is the precursor to synthesize (*Z*)-11-hexadecen-1-yl acetate (**1**), the main sex pheromone of the diamondback moth (*Plutella xylostella* Linnaeus).

2. MATERIALS AND METHODS

2.1 Equipment and chemicals

RE200/VC rotary evaporator, RCT Basic IKAMAG® heating magnetic stirrer, Pyrex® pressure-resistant screw cap culture tube for reduction reaction, thin layer chromatography (TLC) on aluminum plate, layer Adsorbed with Merck silica gel 60F-254, visualized with potassium permanganate solution. Nuclear magnetic resonance spectra (^{1}H NMR, ^{13}C NMR), measured on BRUKER AC 500MHz and 125MHz (Institute of Chemistry - Vietnam Academy of Science and Technology), GC measured on GC-2030 Shimadzu with FID detector at the Institute of Technology Chemical Technology - Vietnam Academy of Science and Technology.

All reagents were purchased from Acros Organics Co., and purified when necessary according to conventional experimental procedures described in the literature.

2.2 Experiments

2.2.1. General method of alkyne reduction to (Z)-alkene

Add 0.50 mmol (**I**), 0.75 mmol of either NaOH or KOH and 0.01 mmol of 2% Pd catalyst dissolved in 1 mL DMF to a 50 mL pressure-resistant Pyrex® screw cap culture tube for the reduction reaction. Fill the tube with N_2 gas and stir the mixture at 145 ºC for 6 hrs. Monitor the reaction by performing TLC with the eluant solvent *n*-hexane/EtOAc: 9/1. Once the reaction is complete, let it cool down to room temperature. Next, dilute the reaction with 20 mL of CH_2Cl_2 and 2 mL of *n*-hexane. Extract and dry the organic layer with $MgSO_4$, and evaporate the solvent under low pressure to get the crude product. The GC analysis results of the crude product showed that the GC conversion efficiency was over 90%. Filter the pure product through a silica gel column with the eluant solvent *n*-hexane/EtOAc: 9/1 to obtain (**II**) with a *(Z)*-alkene isomer ratio of over 91%. B.p: 255 ^{o}C/760 mmHg. MS (*m/z*): 41, 55, 69, 85 (100), 101, 115, 139, 155, 169, 184. ^{1}H

NMR *(500 MHz, $CDCl_3$, δppm):* 0.97 (*t*, *J* = 7.5 Hz, 3H), 1.49-1.85 (*m*, 6H), 2.06 (*m*, 2H, CH_3-CH_2-); 2.35 (*m*, 2H, -CH_2-CH=CH-), 3.39-3.52 (*m*, 2H, CH_2O tetrahydropyranyl), 3.71-3.9 (*m*, 2H, -CH_2-CH_2-O-), 4.61 (*m*, 1H, OC*H*O), 5.34-5.39 (*dt*, *J* = 11 Hz, *J* = 7.0 Hz, 1H, CH_3CH_2-C*H*=), 5.44-5.49 (*dt*, *J* = 10.5 Hz, *J* = 7.25 Hz, 1H, CH_3CH_2CH=C*H*-). ^{13}C NMR (*125 MHz, $CDCl_3$, δppm*): 14.3 (C_6), 19.6 (C_3'), 20.6 (C_5), 25.5 (C_4'), 27.9 (C_2), 30.7 (C_3'), 62.3 (C_5'), 67.1 (C_1), 98.7 (C_1'), 125 (C_3), 133.6 (C_4).

2.2.2. Processes for synthesizing pheromone components of the diamondback moth Plutella xylostella

Synthesis of 10-bromodecan-1-ol (**2**)

Follow the procedure outlined in documents [10] for synthesizing *n*-bromoalkan-1-ol, but use decane-1,10-diol (155 mmol, 27 g), HBr (185 mmol, 26 mL) in 200 mL heptane. After the reaction, purify the crude product via fractional distillation at 126 ^{o}C/3 mmHg. This should yield 32.2 g of (**2**) with a yield of 88%. ^{1}H NMR *(500 MHz, $CDCl_3$, δppm)*: 1.30-1.36 (*m*, 10H), 1.39-1.44 (*m*, 2H), 1.54-1.59 (*m*, 2H), 1.82-1.88 (*m*, 2H), (*t*, *J* = 7.0 Hz, 2H), 3.63-3.65 (*t*, *J* = 6.5 Hz, 2H). ^{13}C NMR (*125 MHz, $CDCl_3$, δppm*): 25.7, 28.2, 28.7, 29.4, 29.4, 29.5, 32.4, 32.8, 34.0, 63.1.

Synthesis of 2-((10-bromodecyl)oxy)tetrahydro-2H-pyran (**3**)

Using the documents [10], follow the same procedure with 10-bromodecan-1-ol (41.25 mmol, 9.78 g), 3,4-dihydro-2*H*-pyran (DHP, 45.38 mmol, 3.96 g), and *p*-toluenesulfonic acid monohydrate (*p*TSA, 41.25 mmol, 0.075 g) in 50 mL CH_2Cl_2. After the reaction, purify the crude product using silica gel column chromatography (with eluant solvent *n*-hexane/diethyl ether: 9/1) to yield 12.67 g of (**3**) as a colorless liquid, with a yield of 96%. ^{1}H NMR *(500 MHz, $CDCl_3$, δppm):* 1.30-1.39 (*m*, 10H); 1.41-1.50 (*m*, 2H), 1.51-1.74 (*m*, 8H), 1.82-1.89 (*m*, 2H), 3.36-3.52 (*m*, 4H), 3,70-3.89 (*m*, 2H), 4.57-4.58 (*m*, 1H). ^{13}C NMR (*125 MHz, $CDCl_3$, δppm*): 19.7, 25.5, 26.2, 28.2, 28.7, 29.4, 29.4, 29.4, 29.7, 30.8, 32.8, 33.9, 62.4, 67.7, 98.9.

Synthesis of 2-(hexadec-11-yn-1-yloxy)tetrahydro-2H-pyran (**4**)

Follow the steps outlined in references [4,5] to perform the following procedure: Add 25 mL of 2.5 M *n*-BuLi (29.25 mol) in *n*-hexane to a solution of 1-hexyne (30 mmol; 2.34 g) in 15 mL of anhydrous THF, along with KI (2.25 mmol, 0.375 g) and 2-((10-bromodecyl)oxy)-tetrahydro-2*H*-pyran (22.5 mmol, 7.23 g) in 60 mL of anhydrous THF. The resulting crude product can be purified using silica gel column chromatography (eluting with *n*-hexane/diethyl ether: 9/1) to yield 6.23 g of (**4**) as a colorless liquid, with a yield of 86%. ^{1}H NMR *(500 MHz, $CDCl_3$, δppm)*: 0.90 (*t*, *J* = 7.5 Hz, 3H), 1.28-1.48 (*m*, 18H), 1.52-1.84 (*m*, 8H), 2.12-2.16 (*m*, 4H), 3.36-3.52 (*m*, 2H), 3.70-3.89 (*m*, 2H), 4.57-4.58 (*m*, 1H). ^{13}C NMR (*125 MHz, $CDCl_3$, δppm*): 13.6, 18.5, 18.8, 19.7, 21.9, 25.5, 26.3, 28.9, 29.1, 29.2, 29.5, 29.6, 29.8, 29.8, 31.3, 62.3, 67.7, 80.2, 80.2, 98.9.

Synthesis of (Z)-2-(hexadec-11-en-1-yloxy)tetra hydro-2H-pyran (**5**)

Perform the same procedure as described in documents [10] using (**4**) (2.55 mmol, 0.83 g), KOH (3.83 mmol, 0.21 g), $Pd_2(dba)_3$ (0.05 mmol, 0.046 g) in 5 mL of DMF. The resulting crude product is a brown liquid that can be purified through column chromatography (using the eluant solvent of *n*-hexane/diethyl ether: 9/1). The yield is 0.75 g of (**5**), which is a colorless liquid, with a yield of 91%. ^{1}H NMR *(500 MHz, $CDCl_3$, δppm)*: 0.88 (*t, J* = 7.0 Hz, 3H), 1.28-1.49 (*m*, 18H), 1.52-

1.85 (*m*, 8H), 1.95-2.02 (*m*, 4H), 3.36-3.52 (*m*, 2H), 3.70-3.89 (*m*, 2H), 4.57-4.58 (*m*, 1H), 5.34-5.39 (*m*, 2H). ^{13}C NMR (*125 MHz, $CDCl_3$, δppm*): 13.9, 19.5, 22.3, 25.5, 26.9, 27.2, 29.1, 29.3, 29.4, 29.4, 29.5, 29.5, 29.8, 31.8, 31.9, 32.6, 62.3, 67.7, 129.8, 129.9.

Synthesis of (Z)-11-hexadecenyl acetate (**1**)

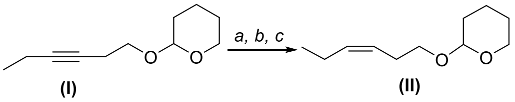
In a 15 mL anhydrous MeOH solution, a mixture of 0.60 g (2.01 mmol) of compound (**5**) and 0.017 g (0.101 mmol) of *p*TSA.H_2O was stirred with a magnetic stirrer at room temperature for 12 hrs. After verifying the completion of the reaction *via* TLC, the MeOH was removed. Then, 50 mL of $NaHCO_3$ solution was added to the mixture, and the resultant product was extracted with diethyl ether. The organic layer was washed with water, saturated NaCl solution, and dried with $MgSO_4$. The solvent was filtered and evaporated under low pressure to obtain a brown liquid crude product (**5**). The crude product was then purified by column chromatography (using the eluant solvent of *n*-hexane/diethyl ether: 4/1), which yielded 0.45 g of (**5**), resulting in a 94% yield.

In the next experiment, 0.4 g (1.66 mmol) of (**5**), 0.16 g (2.08 mmol) of pyridine, and 0.21 g (2.08 mmol) of acetic anhydride were mixed and stirred at 0 °C for 2 hrs and then at room temperature for 24 hrs. After the reaction was completed, the mixture was cooled with ice, and 30 mL of 10% HCl was added to it. The reaction mixture was extracted with diethyl ether (3 × 50 mL). The organic layer was washed with a saturated solution of $CuSO_4$, $NaHCO_3$, H_2O, and saturated NaCl, dried with $MgSO_4$, filtered, and evaporated under low pressure to obtain the crude product. Silica gel column chromatography was used to purify the crude product (using the eluant solvent of *n*-hexane/diethyl ether: 9/1), which yielded 0.41 g of (*Z*)-11-hexadecenyl acetate (**1**), resulting in an 88% yield. ^1H NMR *(500 MHz, $CDCl_3$, δppm)*: 0.89 (*t*, *J* = 7.5 Hz, 3H), 1.26-1.34 (*m*, 18H), 1.60-1.63 (*m*, 2H), 2.04 (*s*, 3H), 2.01-2.03 (*m*, 4H), 4.05 (*t*, *J* = 7.5 Hz, 2H), 5.34-5.39 (*m*, 2H). ^{13}C NMR (*125 MHz, $CDCl_3$, δppm*): 13.9, 21.0, 22.4, 25.9, 26.9, 27.2, 28.6, 29.3, 29.3, 29.5, 29.5, 29.7, 29.8, 31.9, 64.7, 129.9, 129.9, 171.2.

3. RESULTS AND DISCUSSION

3.1 Synthesis of (*Z*)-alkene from alkyne with certain palladium catalytic systems

In 2003, A.V. Martynov *et al.* used $Pd(OAc)_2$ (2.0 mol%)/KOH (1.5 *equiv.*)/DMF at 145°C for 6 hours to convert 5-decyne to *(Z)*-5-decene. The reaction achieved an 87% conversion efficiency with 99% selectivity for *(Z)*-alkene configuration [11]. We investigated the reduction reaction of 3-hexyn-1-yl tetrahydropyran-2-yl ether (**I**) to *(Z)*-alkene (**II**) by selecting the catalytic conditions as shown in *Table 1*. The results, as shown in *Table 1*, indicate that the palladium catalytic systems have an efficiency of over 75% in reducing (**I**) to (**II**).



Scheme 1. Synthesis of *(Z)*-3-hexen-1-yl tetrahydropyran-2-yl ether **(II)** from 3-hexyn-1-yl tetrahydropyran-2-yl ether **(I)** *Reagents.* a) Catalysis: $Pd(OAc)_2$, $Pd(PPh_3)_2Cl_2$, PdNPs/PEG; b) Base: KOH or NaOH; c) DMF, stirred at 145 °C.

The mechanism of semi-hydrogenation of alkynes to *(Z)*-alkenes was proposed by A.V. Martynov *et al.* in 2003 (*Figure 1*). The first step involves hydrolyzing DMF in KOH to produce HCOOH at a suitable concentration. This HCOOH acts as a source of hydrogen, which is then oxidized to Pd(0) to create the intermediate (C) by selectively combining alkyne and Pd-H. After that, the intermediate group is decarboxylated and the C-C bond is cleaved to form *(Z)*-alkene and regenerate Pd(0). Zargarian and Brunel proposed that HCOOH oxidized towards Pd(0) and the formation of vinyl-Pd by alkyne insertion into the Pd-H bond.[12,13] Among them, HCOOH/NEt_3 can be used as a hydrogen source for the hydrogenation reaction in the presence of Pd(II). The decomposition of HCOOH into H_2 and CO_2 in the reaction is the limiting point of semi-hydrogenation. Therefore, the formation of HCOOH with an appropriate concentration in the reaction is the decisive factor in the dehydrogenation process with alkynes.

Table 1. The reduction reaction of 3-hexyn-1-yl tetrahydropyran-2-yl ether (**I**) with some Pd catalyst systems.

No	Catalysis	Base	Sol.	Time (hrs.)	Temp.^{a}	% H^b *(Z)*-alkene
1	$Pd(OAc)_2$	KOH	DMF	6	145 °C	90
2	$Pd(OAc)_2$	NaOH	DMF	6	145 °C	88
3	PdNPs/PEG	KOH	DMF	6	145 °C	78
4	PdNPs/PEG	NaOH	DMF	6	145 °C	75
5	$Pd(PPh_3)_2Cl_2$	KOH	DMF	6	145 °C	78
6	$Pd(PPh_3)_2Cl_2$	NaOH	DMF	6	145 °C	76

^{a}Magnetic stirring; ^{b}Isolation yields

In addition, using KOH or NaOH as a base affects the reaction efficiency and selectivity of the product. Experiments have shown that the reduction reaction's efficiency using NaOH as a base is lower than using KOH. In 2010, Li *et al.* [4], replaced KOH with Cs_2CO_3 to reduce diphenylacetylene to *cis*-stilbene, but this reaction almost did not occur. In another attempt to improve the reaction, $NaBH_4$ was used to replace the bases, but the conversion efficiency was only about 30%.

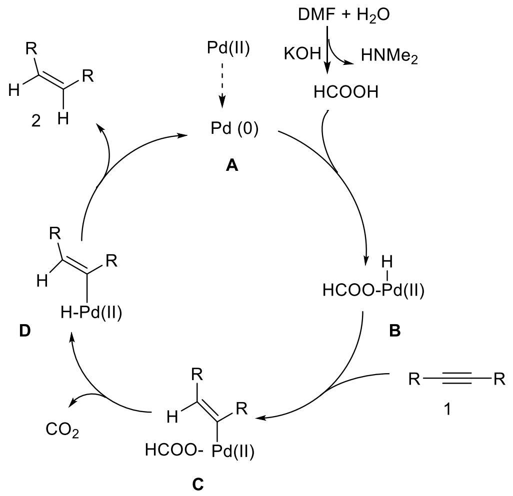


Figure 1. Mechanism of reducing alkyne to *(Z)*-alkene using palladium catalyst

The reduction reaction with the $Pd(PPh_3)_2Cl_2$ catalyst system in DMF/KOH stirring at 145°C gives the same efficiency as using the $Pd(OAc)_2$ catalyst and gives better performance than the results of Li *et al.* (2010) published (36% yield with *(Z)*-alkene only 88%) [4]. As seen in the palladium catalyst reaction mechanism (*Figure 1*), Pd(II) needs to be converted to Pd(0) to participate in the reduction cycle. Therefore, in addition to the $Pd(OAc)_2$ and $Pd(PPh_3)_2Cl_2$ catalysts with an oxidation number of +2, we also researched the use of PdNPs/PEG and $Pd_2(dba)_3$ nanocatalyst systems with an oxidation number of 0 to reduce the alkyne to *(Z)*-alkene.

The dominant ratio of *(Z)*-alkene isomers also occurs similarly when using $Pd(OAc)_2$ and $Pd(PPh_3)_2Cl_2$ (*Table 1*), while the PdNPs/PEG nanocatalyst system has a reduction efficiency of over 78% with 99% *(Z)*-alkene [14]. Through experiments, it is shown that the isomer ratio is affected by reaction conditions. $Pd(OAc)_2$ catalyst uses base (KOH or NaOH) in DMF to create a hydrogen source for the reaction. Combined with stirring and heating at 145°C for about 6 hrs, the *(Z)*-alkene ratio is >99% [4]. The same thing happens with other palladium systems such as $Pd(PPh_3)_2Cl_2$ with oxidation number +2, PdNPs/PEG, and $Pd_2(dba)_3$ systems with oxidation number 0, with the effectiveness of insect trap tests above school being proof.[10]

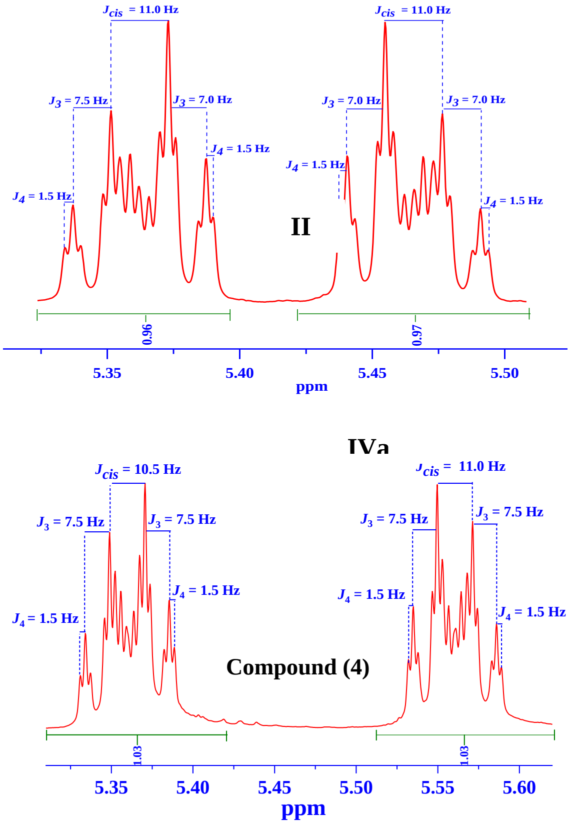


Figure 2. a) Signal of 2 protons on *(Z)*-alkene of compound (**II**) at positions C3 and C4 *at* δ_H 5.34-5.39 ppm and δ_H 5.44 - 5.49 ppm (see section 2.2.1); b) Signal of 2 protons on the *(Z)*-alkene of compound (**IVa**) at positions C3 and C4 at δ_H 5.33-5.39 ppm and δ_H 5.53 - 5.58 ppm (see [10])

The analysis of the ^1H NMR spectrum of (**II**) reveals that the double bond (-C*H*= and =C*H*-) in this molecule produces two distinct groups of proton signals. These signals appear at the chemical shift δ_H = 5.34-5.39 (*dtt*, J = 11.0 Hz, 7.5 Hz, 1.5 Hz, 1H) and δ_H = 5.44 - 5.49 (*dtt*, *J* = 11.0 Hz, 7.5 Hz, 1.5 Hz, 1H) respectively, as shown in *Figure 2a*. As both of these groups of proton signals have coupling constants $J \leq 11$Hz, the *(Z)*-alkene isomer is significantly dominant in the product (**II**). This finding is similar to the results obtained from the ^1H NMR spectrum of (**IVa**), which also exhibits a dominant *(Z)*-alkene isomer, as shown in *Figure 2b*. Compound (**IVa**) was used to synthesize the sex pheromone of sweet potato weevil. The results of the pheromone's attraction to insects in the field were reported in [10].

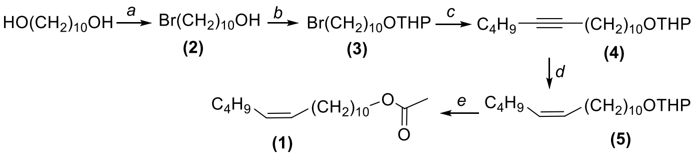
The $Pd_2(dba)_3$/DMF/KOH catalyst system is a highly effective method for synthesizing (*Z*)-3-dodecen-1-ol, which serves as the precursor to the sex pheromone of the sweet potato weevil (*Cylas formicarius*). The system yields a remarkable 92%, with an impressive *(Z)-alkene* selectivity of 99%. Based on these findings, we have decided to use the $Pd_2(dba)_3$ catalytic system in combination with DMF/KOH as the hydrogen source for synthesizing (*Z*) pheromones, without molecular hydrogen. We have also successfully applied this system to the synthesis of (*Z*)-11-hexadecen-1-yl acetate (**1**), which is the primary sex pheromone component of the diamondback moth (*Plutella xylostella*).

3.2 Synthesis of sex pheromone components for diamondback moth (*Plutella xylostella*)

Many different research findings have emerged in the synthesis of (**1**), including studies involving the use of 1-undecenic acid as the starting material. The pivotal reaction involved is the Wittig reaction. By employing a dibenzo-18-crown-6 phase transfer catalyst, the aim is to yield products with a dominant (*Z*) configuration. In a separate study utilizing 10-bromodecan-1-ol as the starting material and also relying on the Wittig reaction, an overall yield of 42% was achieved [15]. Nonetheless, products resulting from this reaction often exhibit low configuration selectivity, with (*E*)-alkene isomers present in a significant proportion (>10%). This challenge represents the most formidable obstacle to overcome in the context of the Wittig reaction.

In 2006, G. Luciane *et al.* carried out the synthesis of pheromone (**1**) by utilizing 1,10-decandiol and 1-hexyne as initial substances, employing a Lindlar catalyst to selectively convert the alkyne into a *(Z)*-alkene. The resulting yield from the reaction ranged between 75-85% [3]. Subsequently, in 2020, B. Liu *et al.* synthesized (*Z*)-11-hexadecen-1-ol, a precursor of (**1**), by extending the carbon chain through the use of *n*-BuLi, starting with 1,10-decandiol and 1-hexyne. They achieved an efficient reduction of the alkyne to *(Z)*-alkene at a remarkable rate of 92% by employing a $Pd(OAc)_2$/KOH/DMF catalytic system [16]. More recently, we have employed a $Pd_2(dba)_3$/DMF/KOH catalytic system to convert the alkyne into *(Z)*-alkene (as shown in Table 2) with an impressive reduction efficiency exceeding 90% [10].

Within this study, *Scheme 2* is employed to synthesize (**1**) from the same initial materials, 1,10-decandiol and 1-hexyne, through a five-step process. We have consistently used the $Pd_2(dba)_3$/DMF/ KOH catalytic system to achieve a 91% reduction efficiency. This system has demonstrated selectivity for the *(Z)*-alkene configuration, resulting in an overall efficiency of around 60%. The successful synthesis of compound (**5**), as listed in *Table 2,* provides further evidence of the stability and isolation efficiency of *(Z)*-alkenes when using this catalytic system. Therefore, when aiming to synthesize insect pheromones with the (*Z*) configuration, $Pd_2(dba)_3$/DMF/KOH is the preferred choice catalytic system due to its ability to reduce alkynes.



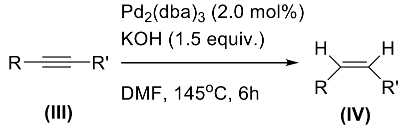
Scheme 2. Synthesis of (*Z*)-11-hexadecen-1-yl acetate, the primary sex pheromone component of the diamondback moth (*Plutella xylostella*), from 1,10-decandiol and 1-hexyne. *Reagents.* a) HBr/heptane, reflux 6 hrs.; b) DHP/*p*-TSA/CH_2Cl_2; c) 1. 1-hexyne/*n*-BuLi/THF, -78 ^oC; 2. KI, **(3)**/THF, reflux 16 hrs.; d) $Pd_2(dba)_3$/DMF/KOH, 145 ^oC, 6 hrs; e) 1. *p*-TSA/MeOH, 12 hrs.; 2. $(CH_3CO)_2O$/Py, 24 hrs.

Upon analyzing the pheromone structure (**1**) with the ^1H NMR spectrum, it was observed that the CH_3CH_2- group had three protons, which appeared as a triplet signal at the chemical shift δ_H 0.89 (*t*, J = 7.5 Hz). Additionally, the three protons of the CH_3CO- group appeared as a singlet signal at δ_H 2.04 (*s*). Furthermore, the -CH_2O- group had two protons, which appeared as a triplet signal at δ_H 4.05 (*t, J* = 7.5 Hz). Based on these observations, it was confirmed that the pheromone structure is (*Z*)-11-hexadecene-1-yl acetate.

The chemical shifts of the two protons of the double bond (-C*H*= and =C*H*-) are at δ_H 5.34-5.39 (*m*, 2H), while the ^{13}C NMR spectrum shows signals at δ_C 13.9, 21.4, 64.7, 129.9 (2C), and 171.2 *ppm*. These signals correspond to the C of groups CH_3-, CH_3CO-, -CH_2O-, *C*=*C*, and -*C*O-. The results are similar to previous publications about pheromone (**1**) by G. Luciane *et al.*,[3] and V.V. Le *et al.*,[15] where the chemical shifts of the two protons of the double bond were δ_H 5.31-

5.44 (*m*, 2H) and 5.25-5.50 (*m*, 2H), respectively. The ^{13}C NMR signals for these publications were reported as δ_C 13.9, 20.9, 64.6, 129.8 (2C), 171.1 *ppm*,[3] and δ_C 13.9, 21.0, 64.7, 130.3 (2C), 172.3 *ppm*,[15]. Field tests of the sex pheromone (**1**) have demonstrated its effective attraction to insects. The results will be included in the upcoming publication.

Table 2. Synthesis efficiency of some (*Z*)-alken-1-yl tetrahydropyran-2-yl ether using $Pd_2(dba)_3$/DMF/KOH catalytic system, at 145°C for 6 hours



No.	R	R'	*(Z)*-alkene	% H[a]	Ref.
1	C_8H_{17}	$(CH_2)_2$OTHP (**IIIa**)	(**IVa**)	92	[13]
2	C_4H_9	$(CH_2)_6$OTHP (**IIIb**)	(**IVb**)	94	[12]
3	C_4H_9	$(CH_2)_8$OTHP (**IIIc**)	(**IVc**)	90	[12]
4	C_4H_9	$(CH_2)_{10}$OTHP (**IIId**)	(**IVd**)	91	[12]
5	C_4H_9	$(CH_2)_{10}$OTHP (**4**)	(**5**)	91	Scheme 2

4. CONCLUSION

The following compound 3-hexyn-1-yl tetrahydropyran-2-yl ether (**I**), can be converted into *(Z)*-alkene isomers with a conversion efficiency of 75-90% using palladium catalyst systems in KOH/DMF. This reduction reaction is carried out at 145 °C for 6 hrs, where KOH/DMF acts as an efficient hydrogen source system for alkynes elimination. In the synthesis scheme of the sex pheromone of the diamondback moth (*Plutella xylostella*) (**1**), the $Pd_2(dba)_3$/KOH/DMF catalytic system is the best choice, as it provides high conversion efficiency (>90%) and good stereoselectivity.

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