Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 81 (12) 1335–1343 (2016)
JSCS–4931
UDC 547.361'811+542.913+544.4:
66.095.25:547.1–41
Original scientific paper

Synthesis of vinyldihydropyran by cooperative catalysis

BOJAN VULOVIĆ[1]**, IVANA MARIĆ[1#], RADOMIR MATOVIĆ[2] and RADOMIR N. SAIČIĆ[1]*

[1]*Faculty of Chemistry, University of Belgrade, Studentski trg 16, P. O. Box 51, 11158 Belgrade 118, Serbia and* [2]*ICTM, Center for Chemistry, University of Belgrade, Njegoševa 12, Belgrade, Serbia*

(Received 2 November, revised 10 November, accepted 16 November 2016)

Abstract: Δ^5-Unsaturated aldehydes with a suitably positioned allylic halide, or phosphate, leaving group undergo doubly-catalyzed cyclization to give dihydropyran derivatives. The cyclization proceeds under the synergetic action of diazabicycloundecene and $Pd(PPh_3)_4$. This type of transformation was also accomplished with an aryl ketone.

Keywords: dihydropyran; cooperative catalysis; cyclization; organopalladium reagents.

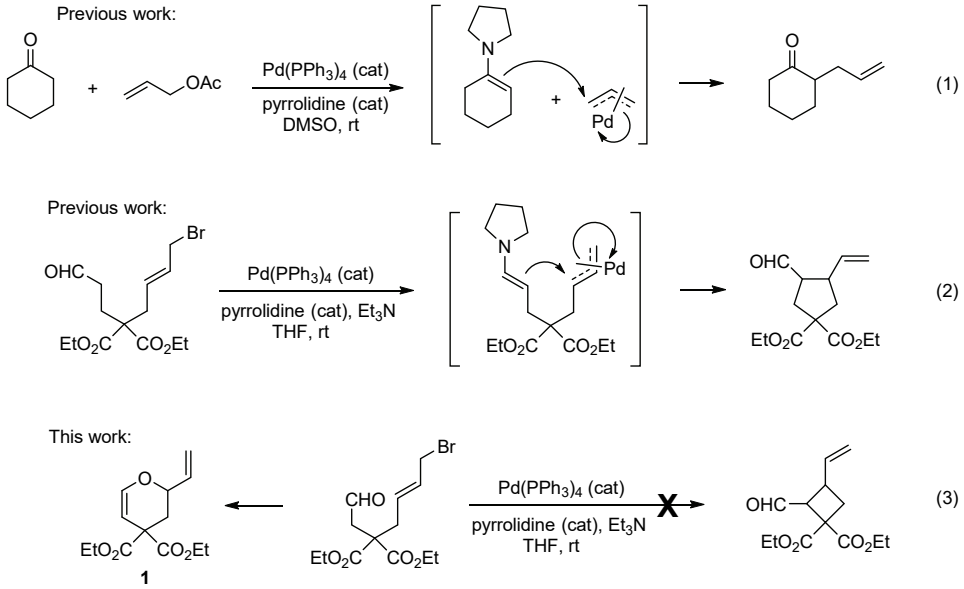
INTRODUCTION

Catalytic methods are the most important tools in the armamentarium of organic synthesis. Traditionally, organotransition metal catalysis[1] and organocatalysis[2] were considered as two distinct, separate and mutually exclusive approaches. However, within the last decade, the scientific community has witnessed a merger of these two approaches into a sophisticated catalytic procedure named cooperative catalysis[3] (also known as dual catalysis, or tandem catalysis; terminological classification has recently been proposed).[4] With a proper design of the reaction sequence and the appropriate choice of catalysts, a rapid increase in complexity is possible within a single synthetic step, which contributes greatly to the efficiency of the synthetic procedure. Alternatively, under conditions of cooperative catalysis, the double activation of the reaction partners allows reactions that are otherwise difficult, or impossible, to proceed under "conventional" reaction set-ups.

A prominent example of cooperative catalysis is a combination of enamine catalysis with palladium catalysis. The first example of intermolecular carbon–

*,** Corresponding authors. E-mail: (*)rsaicic@chem.bg.ac.rs; (**)bvulovic@chem.bg.ac.rs
Serbian Chemical Society member.
doi: 10.2298/JSC161102103V

–carbon bond formation, described by Cordova and coworkers, involved the enamine-catalyzed allylation of cyclohexanone with *in situ* created π-allylpalladium complex (Scheme 1, example 1).[5] This was followed by the intramolecular variant, which gave rise to five- and six-membered rings (Scheme 1, example 2).[6] In this variant, a secondary amine and a Pd-complex simultaneously reacted with the aldehyde and allylic parts of the substrate, respectively, thus creating two reactive species within the same molecule (the enamine and π-allylpalladium complex), which gave rise to a ring closure. Further improvements allowed the cyclization to proceed in a catalytic asymmetric fashion, with excellent levels of asymmetric induction.[7] However, attempts to apply this protocol to the synthesis of vinylcyclobutane analogues resulted in heterocyclization and the vinyldihydropyrane derivative **1** was formed (Scheme 1, example 3). This compound could be a useful intermediate in the syntheses of sugars. To the best of our knowledge, such a reaction (double-activated aldehydes can cyclize) had not hitherto been reported in literature,[8] but no examples of simple aldehydes giving enol-ethers are known, and hence, it was decided to examine the reaction in detail.

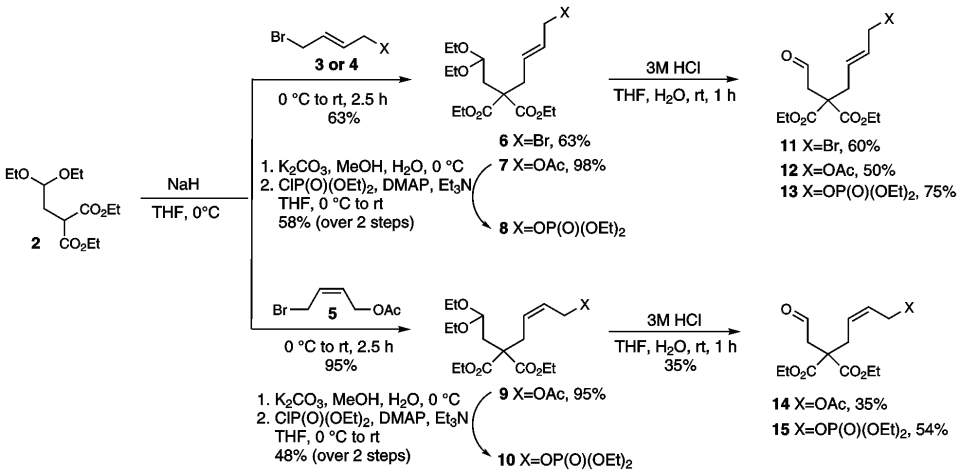


Scheme 1. The aim of this study: previous works and the present work.

RESULTS AND DISCUSSION

The most often used and the most easily accessible precursors of π-allylpalladium complexes are halides, acetates and phosphates.[9] Therefore, it was decided to prepare all three types of precursors. Their syntheses were accomplished as presented in Scheme 2. Malonic ester **2**, the preparation of which was

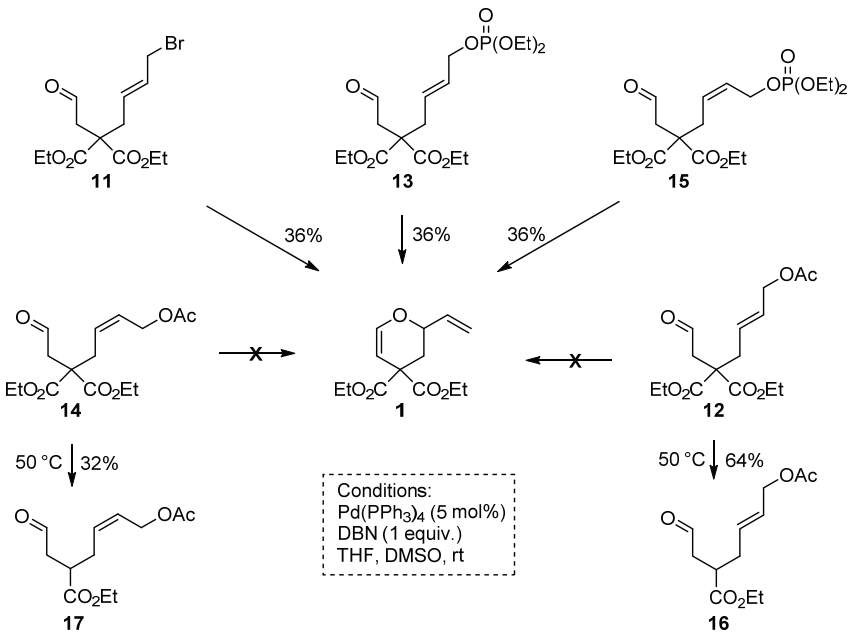
described earlier,[10] was alkylated with difunctional halides **3**–**5**, to give esters **6**–**9**, respectively. Acetates **7** and **9** were converted into the corresponding phosphates **8** and **10** upon treatment with diethylphosphoryl chloride; both *E*- and *Z*-isomer were prepared. Upon treatment with 3 M hydrochloric acid, acetals **6**–**10** were then hydrolyzed into the corresponding aldehydes **11**–**15**.



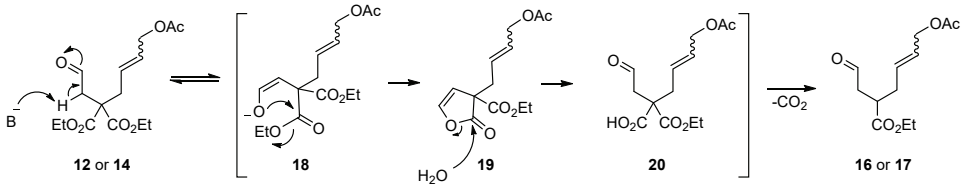
Scheme 2. Synthesis of the cyclization precursors.

Initial experiments were performed with bromide **11**. Tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$) was used as a metal catalyst, whereas optimization of the reaction conditions involved screening of the base (triethylamine (Et_3N), *N*,*N*-diisopropylethylamine (DIPEA), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), the phosphazene base 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP)) and solvent (tetrahydrofuran (THF), dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and acetonitrile (CH_3CN)). The best result was obtained using 5 mol % of $Pd(PPh_3)_4$ in the presence of 1 equivalent of DBN as the base, in a solvent mixture THF/DMSO, at room temperature; under these conditions the reaction was complete within 1 h and afforded the targeted dihydropyrane derivative **1** in 36 % yield (in one experiment, product **1** was obtained in 56 % yield, but subsequently, this result could not be repeated; Scheme 3). Substrates with phosphate leaving groups (**13** and **15**) behaved similarly, affording the product in identical yield, albeit the reaction was somewhat faster (with respect to bromide **11**). The geometry of the alkene bond was without importance for the reaction outcome, as the *E*- and the *Z*-isomers (**13** and **15**) gave identical results. No side reactions were observed; in addition to the starting compounds, dihydropyran **1** was the only spot that could be noticed on TLC. Therefore, it remains unclear what happened with a part of the material and why the yield of **1** was modest.

Acetate precursors (**12** and **14**) did not react at room temperature. When left over night at 50 °C, both **12** and **14** gave the corresponding decarbethoxylated products **16** (64 %) and **17** (32 %), with retention of geometry of the alkene bond. It is well known that decarbethoxylations in DMSO require relatively harsh reaction conditions (*i.e.*, temperatures higher than 140 °C)[11] and therefore, it was surprising to find that this reaction occurred at 50 °C. The possible mechanistic explanation, presented in Scheme 4, involves anchimeric assistance: if the formation of the π-allylpalladium complex is slow (which is apparently the case with the acetate precursors), enolate **18** attacks the ester group intramolecularly and creates the enol-lactone **19**. This species then hydrolyses to give the mono-acid **20** that could undergo decarboxylation at relatively low temperatures.



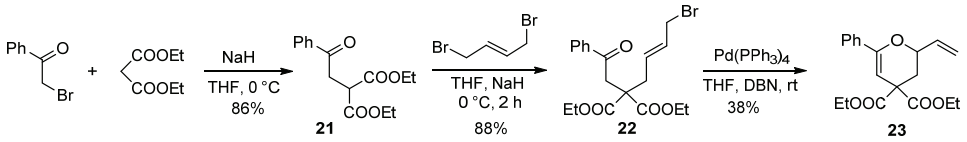
Scheme 3. Cyclization reactions of various substrates.



Scheme 4. Mechanism of the side reaction with acetates.

To find out whether ketones could be used as substrates for the reaction, substrate **22** was prepared, as shown in Scheme 5. The phenyl substituent was

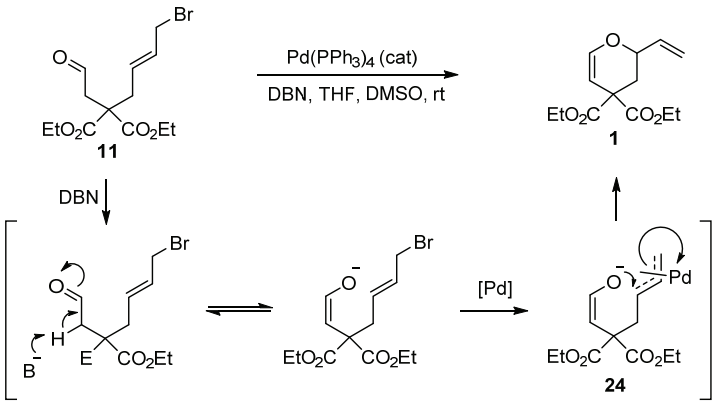
expected to both direct (only one side of the ketone is available for deprotonation) and facilitate enolization (through conjugation in the styrene-like enolate). When submitted to the reaction conditions, **22** afforded the corresponding dihydropyran derivative **23** in 38 % yield. Here again, no other products could be detected by TLC, or isolated during the purification of the reaction mixture.



Scheme 5. Synthesis of the ketone precursor and its cyclization.

An attractive possibility would be to perform the reaction with chiral ligands on palladium and obtain a chiral product in a catalytic asymmetric reaction. Unfortunately, substituting axially chiral ligands (BINAP, BIPHEP) for PPh_3 resulted in no reaction at all.

A plausible reaction mechanism is represented in Scheme 6. Whereas DBN effects enolization of the starting aldehyde, $Pd(PPh_3)_4$ creates π-allylpalladium complex within the same molecule. The doubly activated species **24** undergoes cyclization to **1** and expels the Pd complex that starts a new catalytic cycle.



Scheme 6. The proposed reaction mechanism.

To conclude, aldehydes and ketones with a suitably positioned allylic leaving group undergo Pd-catalyzed 6-*exo*-heterocyclization to give vinyldihydropyran derivatives. Further studies are needed in order to establish the scope and limitations of the reaction, and to accomplish it with asymmetric induction.

EXPERIMENTAL

All chromatographic separations were performed on silica, 10–18, 60 Å, ICN Biomedicals.[12] Petroleum ether refers to a fraction with a boiling point range 68–72 °C. Standard

techniques were used for the purification of reagents and solvents.[13] The NMR spectra were recorded on a Varian Gemini 200 (^{1}H-NMR at 200 MHz and ^{13}C-NMR at 50 MHz), and on Bruker Avance III 500 (^{1}H-NMR at 500 MHz and ^{13}C-NMR at 125 MHz) instruments. Chemical shifts are expressed in ppm (δ) using tetramethylsilane as an internal standard, coupling constants (J) are in Hz. The IR spectra were recorded on a Nicolet 6700 FT instrument, and are expressed in cm^{-1}. Mass spectra were obtained on an Agilent Technologies 6210 TOF LC/MS instrument (LC: series 1200).

Analytical and spectral data of the synthesized compounds are given in Supplementary material to this paper.

*(*E*)-Diethyl 2-(4-bromobut-2-en-1-yl)-2-(2,2-diethoxyethyl)malonate (**6**)*. This compound was prepared according to the procedure described earlier.[10]

*(*E*)-Diethyl 2-(4-acetoxybut-2-en-1-yl)-2-(2,2-diethoxyethyl)malonate (**7**)*. Sodium hydride (195 mg, 8.0 mmol) was added to a cold (0 °C) solution of compound **2** (840 mg; 3.04 mmol) in THF (10 mL) and the mixture was stirred for 15 min under an argon atmosphere. Compound **4** (1.40 g; 7.25 mmol) was added and the reaction mixture was stirred for 2.5 h, during which time the mixture was allowed to reach room temperature. The reaction mixture was partitioned between water and dichloromethane, the organic layer was washed with water and saturated *aq*. $NaHCO_3$, dried over anh. $MgSO_4$ and concentrated under reduced pressure. Purification of the residue by dry-flash chromatography (SiO_2; eluent: petroleum ether/EtOAc = = 9/1) afforded 1.19 g (98 %) of the title compound **7**, as a pale yellow liquid.

*(*E*)-Diethyl 2-(2,2-diethoxyethyl)-2-{4-[(diethoxyphosphoryl)oxy]but-2-en-1-yl}malonate (**8**)*. Part 1: Hydrolysis of **7** and preparation of (*E*)-diethyl 2-(2,2-diethoxyethyl)-2-(4-hydroxybut-2-en-1-yl)malonate. A solution of compound **7** (802 mg; 2.06 mmol) and K_2CO_3 (285 mg; 2.06 mmol) in a solvent mixture MeOH/H_2O (1:1; 16 mL) was stirred for 5 h at 0 °C, then diluted with dichloromethane (120 mL). The organic extract was washed with water (2×30 mL), dried over anh. $MgSO_4$ and concentrated under reduced pressure. Purification by dry flash chromatography (SiO_2, eluent: petroleum ether/EtOAc = 4/1 to 1/1) afforded 28 mg of the starting compound **7**, followed by 661 mg (96 %) of (*E*)-diethyl 2-(2,2-diethoxyethyl)--2-(4-hydroxybut-2-en-1-yl)malonate, as a pale-yellow oil.

Part 2: Phosphorylation of (*E*)-diethyl 2-(2,2-diethoxyethyl)-2-(4-hydroxybut-2-en-1-yl)-malonate. Diethyl chlorophosphate (250 μL; 1.73 mmol) was added to a cold (0 °C) solution of (*E*)-diethyl 2-(2,2-diethoxyethyl)-2-(4-hydroxybut-2-en-1-yl)malonate (600 mg; 1.73 mmol), Et_3N (362 μL; 2.60 mmol) and 4-(dimethylamino)pyridine (DMAP, 10.6 mg; 0.09 mmol) in THF (5.6 mL) and the reaction mixture was stirred for 8 h. The reaction mixture was diluted with dichloromethane (100 mL), washed with water (2×70 mL), dried over anh. $MgSO_4$ and concentrated under reduced pressure. Purification of the residue by dry-flash chromatography (SiO_2, eluent: petroleum ether/EtOAc = 9/1) afforded 505 mg (60 %) of the title compound **8**, as a pale-yellow liquid.

*(Z)-Diethyl 2-(4-acetoxybut-2-en-1-yl)-2-(2,2-diethoxyethyl)malonate (**9**)*. According to the procedure for compound **7**, starting from compounds **2** (1.1 g; 4.01 mmol) and **5** (1.9 g; 9.37 mmol), the title compound **9** was obtained (1.48 g; 95 %) as a colorless liquid.

*(Z)-Diethyl 2-(2,2-diethoxyethyl)-2-{4-[(diethoxyphosphoryl)oxy]but-2-en-1-yl}malonate (**10**)*. Part 1: Hydrolysis of **9** and preparation of (*Z*)-diethyl 2-(2,2-diethoxyethyl)-2-(4-hydroxybut-2-en-1-yl)malonate. According to the procedure for the hydrolysis of compound **7**, starting from compound **9** (579 mg; 1.5 mmol), 348 mg (67 %) of (*Z*)-diethyl 2-(2,2-diethoxyethyl)-2-(4-hydroxybut-2-en-1-yl)malonate was obtained, as a colorless viscous liquid.

Part 2: Phosphorylation of (*Z*)-diethyl 2-(2,2-diethoxyethyl)-2-(4-hydroxybut-2-en-1-yl)-malonate. According to the procedure for the phosphorylation of (*E*)-diethyl 2-(2,2-diethoxyethyl)-2-(4-hydroxybut-2-en-1-yl)malonate, starting from (*Z*)-diethyl 2-(2,2-diethoxyethyl)-2-(4-hydroxybut-2-en-1-yl)malonate (250 mg; 0.72 mmol), the title compound **10** was obtained (250 mg; 72 %) as a colorless, viscous liquid.

*(*E*)-Diethyl 2-(4-bromobut-2-en-1-yl)-2-(2-oxoethyl)malonate (**11**)*. 3 M HCl (1.8 mL) was added dropwise to a solution of compound **6** (250 mg; 0.61 mmol) in THF (1.5 mL), and the reaction mixture was stirred at r.t. for 1 h. The reaction mixture was neutralized by the addition of saturated aq. $NaHCO_3$ (10 mL), extracted with EtOAc (3×20 mL), dried over anh. $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography (SiO_2, eluent: petroleum ether/EtOAc = 9/1) afforded 110 mg (60 %) of the title aldehyde **11**, as a colorless oil. The compound is unstable, and was immediately used for the cyclization step.

*(*E*)-Diethyl 2-(4-acetoxybut-2-en-1-yl)-2-(2-oxoethyl)malonate (**12**).* According to the procedure for the preparation of **11**, starting from compound **7** (89 mg; 0.23 mmol), 36 mg (50 %) of the title compound **12** was obtained, as a colorless oil (purification by column chromatography, SiO_2, eluent: petroleum ether/EtOAc = 9/1). The compound is unstable, and was immediately used for the cyclization step.

*(*E*)-Diethyl 2-{4-[(diethoxyphosphoryl)oxy]but-2-en-1-yl}-2-(2-oxoethyl)malonate (**13**).* According to the procedure for the preparation of **11**, starting from compound **8** (50 mg; 0.10 mmol), 41 mg (75 %) of the title compound **13** was obtained, as a colorless oil (purification by column chromatography, SiO_2, eluent: petroleum ether/EtOAc = 9/1). The compound is unstable, and was immediately used for the cyclization step.

*(*Z*)-Diethyl 2-(4-acetoxybut-2-en-1-yl)-2-(2-oxoethyl)malonate (**14**)*. According to the procedure for the preparation of **11**, starting from compound **9** (156 mg; 0.40 mmol), 30 mg (35 %) of the title compound **14** was obtained, as a colorless oil (purification by column chromatography, SiO_2, eluent: petroleum ether/EtOAc = 9/1). The compound is unstable, and was immediately used for the cyclization step.

*(*Z*)-Diethyl 2-{4-[(diethoxyphosphoryl}oxy]but-2-en-1-yl}-2-(2-oxoethyl)malonate (**15**).* According to the procedure for the preparation of **11**, starting from compound **10** (45 mg; 0.09 mmol), 21 mg (54 %) of the title compound **15** was obtained, as a colorless oil (purification by column chromatography, SiO_2, eluent: toluene/EtOH = 98/2). The compound is unstable, and was immediately used for the cyclization step.

*Diethyl 2-vinyl-2,3-dihydro-4*H*-pyran-4,4-dicarboxylate (**1**). The cyclization procedure.* $Pd(PPh_3)_4$ (2.6 mg; 5 mol %) was added to a solution of compound **11** (15 mg; 0.04 mmol) in THF (0.5 mL), followed by the addition of DBN (5.3 μL) and the reaction mixture was stirred at r.t. for 10 min under an argon atmosphere. DMSO (0.5 mL) was added and the reaction mixture was stirred at r.t. for 1 h, when TLC indicated the complete consumption of the starting material. The reaction mixture was concentrated under reduced pressure and the residue was purified by dry flash chromatography (SiO_2, eluent: petroleum ether/EtOAc = = 9/1) to give 4.1 mg (36 %) of the title dihydropyrane derivative **1**, as a colorless oil.

*(*E*)-Ethyl 6-acetoxy-2-(2-oxoethyl)hex-4-enoate (**16**). De-ethoxycarbonylation of compound **12***. According to the procedure for the synthesis of compound **1**, save that the reaction was performed at 50 °C for 7 h, starting from compound **12** (16.5 mg; 0.05 mmol), after purification by dry flash chromatography (SiO_2, eluent: petroleum ether/EtOAc = 9/1), the title compound **16** (10 mg, 64 %) was obtained as a colorless, viscous liquid.

*(*Z*)-Ethyl 6-acetoxy-2-(2-oxoethyl)hex-4-enoate (**17**). De-ethoxycarbonylation of compound **14**.* According to the procedure for the synthesis of compound **1**, save that the reaction was performed at 50 °C, for 17 h. Starting from compound **14** (12.0 mg; 0.04 mmol), after

purification by dry flash chromatography (SiO_2, eluent: benzene/EtOAc = 9/1), the title compound **17** (3 mg, 32 %) was obtained as a colorless, viscous liquid.

*Diethyl 2-(2-oxo-2-phenylethyl)malonate (**21**).* To a suspension of NaH (0.18 g, 0.75 mmol) in THF (10 mL) was added diethyl malonate (1.2 g, 0.75 mmol) in THF (15 mL) at 0 °C, followed by the addition of 2-bromo-1-phenylethan-1-one (1.25 g, 0.75 mmol). The mixture was stirred at room temperature overnight and then saturated aqueous solution of NH_4Cl was added. The aqueous layer was extracted with Et_2O, the combined organic extract was washed with water and brine, dried over anh. Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2; eluent: petroleum ether/ethyl acetate = = 8/2) to afford 1.79 (86 %) of the title compound **21**, as a colorless oil.

*Diethyl (*E*)-2-(4-bromobut-2-en-1-yl)-2-(2-oxo-2-phenylethyl)malonate (**22**).* A solution of compound **21** (0.278 g, 1 mmol) in THF (7 mL) was added to a stirred suspension of sodium hydride (0.028 g, 1.2 mmol) in THF (5 mL), at 0 °C. After 15 min, (*E*)-1,4-dibromo--2-butene (0.535 g, 2.5 mmol, 2.5 equiv.) was added in one portion, and the reaction mixture was stirred for 2 h at 0 °C. The reaction mixture was diluted with dichloromethane (30 mL), washed with water (4×15 mL), saturated aq. $NaHCO_3$ (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by dry flash chromatography (SiO_2; eluent: petroleum ether/ethyl acetate = 9/1) afforded 0.360 g (88 %) of the title compound **22** as a colorless, viscous oil.

*Diethyl 6-phenyl-2-vinyl-2,3-dihydro-4*H*-pyran-4,4-dicarboxylate (**23**).* A solution of compound **22** (0.043 g, 0.104 mmol), $Pd(PPh_3)_4$ (6 mg, 5.2 μmol, 5mol %), DBN (7.7 mg, 0.062 mmol, 60 mol %) in a solvent mixture THF/DMSO (1/1, 1 mL) was stirred at r. t. under an argon atmosphere. The reaction was monitored by TLC (eluent: petroleum ether/ethyl acetate = 9/1). After 2 h, the reaction mixture was diluted with dichloromethane (40 mL), washed with water (4×15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residue by dry flash chromatography (SiO_2; eluent: petroleum-ether/ethyl acetate = 9/1) afforded 10.2 mg (38 %) of the title compound **23**, as a colorless oil.

SUPPLEMENTARY MATERIAL

Analytical and spectral data of the synthesized compounds are available electronically at the pages of the journal website: http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

Acknowledgment. This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. ON172027).

ИЗВОД

СИНТЕЗА ВИНИЛДИХИДРОПИРАНА КООПЕРАТИВНОМ КАТАЛИЗОМ

БОЈАН ВУЛОВИЋ[1], ИВАНА МАРИЋ[1], РАДОМИР МАТОВИЋ[2] и РАДОМИР Н. САИЧИЋ[1]

[1]Хемијски факултет, Универзитет у Београду, Студентски трг 16, п. пр. 51, 11158 Београд и [2]ИХТМ Центар за хемију, Универзитет у Београду, Његошева 12, Београд

Δ[5]-Незасићени алдехиди, који у погодном положају поседују одлазећу групу као што је алилни бромид или фосфат, подлежу двоструко катализованој циклизацији и дају дериват дихидропирана. Циклизација се одвија под синергичким дејством диазабициклоундецена и тетракис(трифенилфосфин)паладијума. Ова трансформација остварена је и на арил-кетону.

Примљено 2. новембра, ревидирано 10. новембра, прихваћено 16. новембра 2016)

REFERENCES

1. a) J. F. Hartwig, *Organotransition Metal Chemistry From Bonding to Catalysis*, University Science Books, Mill Valley, CA, USA, 2010; b) M. Beller, C. Bolm, *Transition Metals for Organic Synthesis: Building Blocks and Fine Chemicals*, 2nd ed., Vols. 1 and 2, Wiley–VCH, Weinheim, Germany, 2004
2. a) P. I. Dalko, *Enantioselective Organocatalysis: Reactions and Experimental Procedures*, Wiley–VCH, Weinheim, Germany, 2007; b) A. Berkessel, H. Groger, *Asymmetric Organocatalysis - From Biomimetic Concepts to Applications in Asymmetric Synthesis*, Wiley–VCH, Weinheim, Germany, 2005; c) H. Pellissier, *Tetrahedron* **63** (2007) 9267
3. Review articles on cooperative catalysis: a) Z. Shao, H. Zhang, *Chem. Soc. Rev*. **38** (2009) 2745; b) C. Zhong, X. Shi, *Eur. J. Org. Chem*. **2010**, 2999; c) Z. Du, Z. Shao, *Chem. Soc. Rev*. **42** (2013) 1337; d) S. M. Inamdar, V. S. Shinde, N. T. Patil, *Org. Biomol. Chem*. **13** (2015) 8116; e) S. Afewerki, A. Cordova, C*hem. Rev*. **116** (2016) 13512
4. N. T. Patil, V. S. Shinde, B. Gajula, *Org. Biomol. Chem.* **10** (2012) 211
5. I. Ibrahem, A. Cordova, *Angew. Chem. Int. Ed.* **45** (2006) 1952
6. F. Bihelovic, R. Matovic, B. Vulovic, R. N. Saicic, *Org. Lett*. **9** (2007) 5063; Additions and Corrections: *Org. Lett*. **9** (2007) 5649
7. B. Vulovic, F. Bihelovic, R. Matovic, R. N. Saicic, *Tetrahedron* **65** (2009) 65, 10485; Corrigendum: **66** (2010) 3275
8. a) J. Tsuji, Y. Kobayashi, H. Kataoka, T. Takahashi, *Tetrahedron Lett*. **21** (1980) 1475; b) B. M. Trost, L. N. Jungheim, *J. Am. Chem. Soc*. **102** (1980) 7910; c) Y. Huang, X. Lu, *Tetrahedron Lett*. **28** (1987) 6219
9. V. Maslak, Z. Tokic-Vujosevic, R. N. Saicic, *Tetrahedron Lett*. **50** (2009) 1858
10. A. Ivković, R. Matović, R. N. Saičić, *J. Serb. Chem. Soc*. **67** (2002) 141
11. A. P. Krapcho, *Synthesis* **1982** (1982) 805
12. For descriptions of the technique of dry flash chromatography, see: a) L. M. Harwood, *Aldrichim. Acta* **18** (1985) 25; b) *Vogel's Textbook of Practical Organic Chemistry*, Longman Scientific & Technical, 5th ed., London, 1989, p. 220; c) for an account which includes some improvements of the separation technique, see: D. S. Pedersen, C. Rosenbohm, *Synthesis* **2001**, 2431
13. W. L. F. Armarego, C. L. L. Chai, *Purification of Laboratory Chemicals*, 6th ed., Elsevier, Oxford, 2009.