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## Palladium on carbon in PEG-400/cyclohexane: Recoverable and recyclable catalytic system for efficient decarbonylation of aldehydes

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**Abstract:** A simple methodology for the decarbonylation of aldehydes catalysed by commercially available palladium on carbon in a green two-solvent system is reported. Various aromatic, aliphatic and heteroaromatic aldehydes were transformed to the corresponding decarbonylated products in good yields. Product isolation from the reaction mixture is simple in practice, and the catalyst can be reused three times.

**Keywords:** green chemistry; defunctionalization; heterogeneous catalysis.

### INTRODUCTION

The transformation of aldehydes into hydrocarbons (deformylation/decarbonylation) promoted by enzymes,<sup>1</sup> transition-metals<sup>2</sup> or metal-free reagents<sup>3</sup> is an important reaction in academic research<sup>4</sup> and industry.<sup>5</sup> The aldehyde group is an useful promoter of certain transformations, such as the Diels–Alder reaction, C–H activation, and domino oxa-Michael-aldol reaction, and its simple removal *via* decarbonylation after it has served its purpose has been extensively applied in numerous methodologies<sup>6</sup> and in the synthesis of complex molecules and natural products.<sup>7</sup> Some metals of the first, second and third transition series, including Ni,<sup>8</sup> Ru,<sup>9</sup> Rh,<sup>10</sup> Pd<sup>11</sup> and Ir<sup>12</sup> as well as complexes thereof, efficiently perform the mentioned transformation (Fig. 1). However, the toxicity and high cost of these metals is a major drawback from an economic and environmental point of view. Therefore, the use of recyclable heterogeneous catalysts for decarbonylation is both a greener and more economical alternative to homogeneous catalysis.<sup>13</sup>

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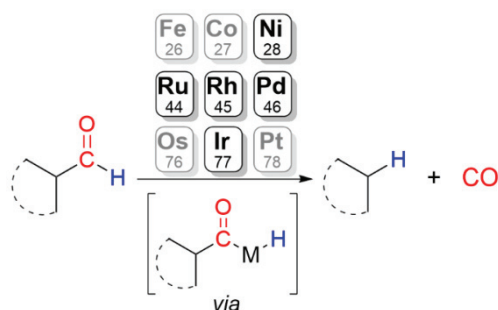


Fig. 1. Decarbonylation of aldehydes promoted by transition-metals.

## EXPERIMENTAL

### The general information

Pd/C (10 wt.% loading) was purchased from Sigma Aldrich. Aldehydes were mostly obtained from commercial sources and used without further purification, except for the 1-adamantanecarboxaldehyde,<sup>14</sup> 1-adamantaneacetaldehyde,<sup>14</sup> 1-prop-2-yn-1-yl-1*H*-indole-3-carbaldehyde<sup>15</sup> and 1-benzyl-1*H*-indole-3-carbaldehyde,<sup>15</sup> which were synthesized according to known procedures. Unless stated otherwise, solvents and other reagents were obtained from commercial sources and used without further purification. Dry-flash chromatography was performed on SiO<sub>2</sub> (0.018–0.032 mm). <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded on a Bruker Ultrashield Avance III spectrometer (at 500 and 125 MHz, respectively) and Varian 400/54 Premium Shielded spectrometer (at 400 and 101 MHz, respectively) using CDCl<sub>3</sub> (unless stated otherwise) as the solvent and tetramethylsilane (TMS) as an internal standard. The chemical shifts are expressed in ppm on the  $\delta$  scale and they were calibrated relative to those of the solvent. GC–MS spectra of the synthesized compounds were acquired on an Agilent Technologies 7890A apparatus equipped with a DB-5 MS column (30 m×0.25 mm×0.25  $\mu$ m), a 5975C MSD and FID detector. The selected values are as follows: carrier gas was He (1.0 mL/min), temperature linearly increased from 40–315 °C (10 °C/min), injection volume: 1  $\mu$ L, temperature: 250 °C, temperature (FID detector): 300 °C, and EI mass spectra range: *m/z* 40–550. For determination of GC–MS yield, the internal standard (naphthalene) was added to the reaction mixture after the workup.

### General procedure for decarbonylation of aldehydes **2a–n**

*Decarbonylation of biphenyl-4-carbaldehyde to biphenyl (2a)* (CAS Reg. No. 92-52-4). Dry glass reaction tube purged with argon and equipped with a magnetic stir bar was charged with aldehyde (90 mg, 0.5 mmol), Pd/C (26 mg, 5 mol.% Pd), cyclohexane (750  $\mu$ L) and PEG-400 (750  $\mu$ L). The sealed tube was heated at 140 °C for 24 h. The reaction medium was then cooled to room temperature. The mixture of water and cyclohexane was then added to the reaction mixture. The layers were afterwards separated and the aqueous layer was washed with cyclohexane (5×5 mL). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was evaporated under reduced pressure. Compound **2a** was obtained after dry-flash column chromatography (SiO<sub>2</sub>:cyclohexane) as a white solid (69.0 mg, 90 %).

*Decarbonylation of 2-naphthaldehyde to naphthalene (2b)* (CAS Reg. No. 91-20-3). Following the general procedure for decarbonylation, compound **2b** was prepared from aldehyde (78.0 mg, 0.5 mmol) using Pd/C (26.0 mg, 5 mol.% Pd) in a mixture of cyclohexane (750  $\mu$ L) and PEG-400 (750  $\mu$ L) and was obtained after dry-flash column chromatography (SiO<sub>2</sub>:cyclohexane) as a white solid (45.1 mg, 70 %).

*Decarbonylation of anthracene-9-carbaldehyde to anthracene (2c)* (CAS Reg. No. 120-12-7). Following the general procedure for decarbonylation, compound **2c** was prepared from aldehyde (103.2 mg, 0.5 mmol) using Pd/C (26.0 mg, 5 mol % Pd) in a mixture of cyclohexane (750  $\mu$ L) and PEG-400 (750  $\mu$ L) and was obtained after dry-flash column chromatography (SiO<sub>2</sub>:cyclohexane) as a white crystalline solid (73.2 mg, 82 %).

*Decarbonylation of 4-nitrobenzaldehyde to nitrobenzene (2d)* (CAS Reg. No. 98-95-3). Following the general procedure for decarbonylation, compound **2d** was prepared from aldehyde (75.6 mg, 0.5 mmol) using Pd/C (26.0 mg, 5 mol % Pd) in a mixture of cyclohexane (750  $\mu$ L) and PEG-400 (750  $\mu$ L) and was obtained as a yellow oil (GC-MS yield 90 % based on naphthalene).

*Decarbonylation of 5-fluoro-2-methoxybenzaldehyde to 4-fluoroanisole (2e)* (CAS Reg. No. 459-60-9). Following the general procedure for decarbonylation, compound **2e** was prepared from aldehyde (77 mg, 0.5 mmol) using Pd/C (26 mg, 5 mol % Pd) in a mixture of cyclohexane (750  $\mu$ L) and PEG-400 (750  $\mu$ L) (GC-MS yield 60 % based on methyl benzoate as standard).

*Decarbonylation of diphenylacetaldehyde to diphenylmethyl (2h)* (CAS Reg. No. 101-81-5). Following the general procedure for decarbonylation, compound **2h** was prepared from aldehyde (89  $\mu$ L, 0.5 mmol) using Pd/C (26.0 mg, 5 mol % Pd) in a mixture of cyclohexane (750  $\mu$ L) and PEG-400 (750  $\mu$ L) and was obtained after dry-flash column chromatography (SiO<sub>2</sub>:cyclohexane) as a colorless oil (78.1 mg, 93 %).

*Decarbonylation of 3-(1,3-benzodioxol-5-yl)-2-methylpropanal to dihydrosafrole (2i)* (CAS Reg. No. 94-58-6). Following the general procedure for decarbonylation, compound **2i** was prepared from aldehyde (83  $\mu$ L, 0.5 mmol) using Pd/C (26 mg, 5 mol % Pd) in a mixture of cyclohexane (750  $\mu$ L) and PEG-400 (750  $\mu$ L) and was obtained after dry-flash column chromatography (SiO<sub>2</sub>:cyclohexane) as a colorless oil (59.3 mg, 72 %).

*Decarbonylation of 1-adamantanecarboxaldehyde to adamantane (2j)* (CAS Reg. No. 281-23-2). Following the general procedure for decarbonylation, compound **2j** was prepared from aldehyde (82.3 mg, 0.5 mmol) using Pd/C (26.0 mg, 5 mol % Pd) in a mixture of cyclohexane (750  $\mu$ L) and PEG-400 (750  $\mu$ L) and was obtained after dry-flash column chromatography (SiO<sub>2</sub>:cyclohexane) as a colorless solid (67.3 mg, 84 %).

*Decarbonylation of 1-adamantaneacetaldehyde to 1-methyl adamantane (2k)* (CAS Reg. No. 768-91-2). Following the general procedure for decarbonylation, compound **2k** was prepared from aldehyde (89.1 mg, 0.5 mmol) using Pd/C (26.0 mg, 5 mol % Pd) in a mixture of cyclohexane (750  $\mu$ L) and PEG-400 (750  $\mu$ L) and was obtained after dry-flash column chromatography (SiO<sub>2</sub>:cyclohexane) as a colorless solid (74.0 mg, 73 %).

*Decarbonylation of benzo[b]thiophene-3-carboxaldehyde to benzo[b]thiophene (2l)* (CAS Reg. No. 95-15-8). Following the general procedure for decarbonylation, compound **2l** was prepared from aldehyde (81.1 mg, 0.5 mmol) using Pd/C (26.0 mg, 5 mol % Pd) in a mixture of cyclohexane (750  $\mu$ L) and PEG-400 (750  $\mu$ L) and was obtained after dry-flash column chromatography (SiO<sub>2</sub>:cyclohexane) as a colorless solid (47.1 mg, 70 %).

*Decarbonylation of 1-prop-2-yn-1-yl-1H-indole-3-carbaldehyde to 1-prop-2-yn-1-yl-1H-indole (2m)* (CAS Reg. No. 19017-00-6). Following the general procedure for decarbonylation, compound **2m** was prepared from aldehyde (92.3 mg, 0.5 mmol) using Pd/C (26.1 mg, 5 mol % Pd) in a mixture of cyclohexane (750  $\mu$ L) and PEG-400 (750  $\mu$ L) and was obtained after dry-flash column chromatography (SiO<sub>2</sub>:cyclohexane) as a colorless solid (53.3 mg, 68 %).

*Decarbonylation of 1-benzyl-1H-indole-3-carbaldehyde to 1-benzyl-1H-indole (2n)* (CAS Reg. No. 3377-71-7). Following the general procedure for decarbonylation, compound

**2n** was prepared from aldehyde (89.2 mg, 0.5 mmol) using Pd/C (118.0 mg, 5 mol % Pd) in a mixture of cyclohexane (750  $\mu$ L) and PEG-400 (750  $\mu$ L) and was obtained after dry-flash column chromatography (SiO<sub>2</sub>:cyclohexane) as a colorless solid (68.0 mg, 66 %).

Spectral data of the compounds are given in Supplementary material to this paper

*Recycling of Pd/C and PEG-400 catalytic system for decarbonylation of aldehyde (1a)*

Dry glass reaction tube purged with argon and equipped with a magnetic stir bar was charged with aldehyde (**1a**, 90 mg, 0.5 mmol), Pd/C (26 mg, 5 mol % Pd), cyclohexane (750  $\mu$ L) and PEG-400 (750  $\mu$ L). The sealed tube was heated at 140 °C for 24 h. After the completion of the reaction, the cyclohexane layer was decanted with a pipette and PEG-400 layer was washed with cyclohexane (5 $\times$ 2 mL). The formed residue (Pd/C in PEG-400) was used for next reaction cycles following the general reaction procedure.

## RESULTS AND DISCUSSION

Herein we report the efficient decarbonylation of aromatic, heteroaromatic and aliphatic aldehydes mediated by palladium on carbon in ecologically acceptable solvents, cyclohexane and PEG-400. To determine the optimal reaction conditions, biphenyl-4-carboxaldehyde (**1a**) was used as the model substrate (TABLE I).

TABLE I. Optimization of reaction conditions

The reaction scheme shows biphenyl-4-carboxaldehyde (**1a**) reacting with Pd/C (5 mol %) in Argon to produce biphenyl (**2a**).

Entry	Solvent	<i>t</i> / °C	Time, h	Yield <sup>a</sup> , %
1	H <sub>2</sub> O	160	24	trace
2	PEG-400	140	24	42
3	PEG-400	140	44	26
4	PEG-400/ cyclohexane (1:1, v,v)	140	24	90

<sup>a</sup>Isolated yield

The initial conditions of 5 mol % palladium on carbon in H<sub>2</sub>O at 160 °C provided only trace amounts of the corresponding decarbonylated product (entry 1). When PEG-400 was used instead of H<sub>2</sub>O, the yield increased to 42 % (entry 2). Increasing the reaction time from 24 to 44 h led to a significant reduction in the yield (26 %, entry 3). After a detailed analysis of the reaction mixture, it was found that the reduced yield resulted from product evaporation. Finally, the addition of cyclohexane as a co-solvent increased the yield to 90 %.

To our surprise, after the reaction mixture had cooled, the catalyst particles were located exclusively in the PEG-400 layer (Fig. 2).

The product was isolated by careful decantation of cyclohexane and additional extraction of the PEG-400 layer with cyclohexane. The residual catalyst in PEG-400 was used successively three more times under the same reaction conditions, without a significant loss of activity (Fig. 3).



Fig. 2. Reaction mixture after completion of the reaction.

Employing the optimized decarbonylation conditions, the aldehyde substrate scope was investigated (Scheme 1). The non-functional polycyclic aromatic aldehydes (**1a–c**) were efficiently decarbonylated and the corresponding products (**2a–c**) were obtained in good yields. Benzaldehyde bearing an electron-withdrawing substituent ( $\text{NO}_2$ ) **1d** generated the desired product **2d** in high yield. 2-Fluoro-4-methoxybenzaldehyde afforded the decarbonylated product **2e** in moderate yield. In the case of 4-bromobenzaldehyde (**1f**) and 4-formylbenzoic acid (**1g**) there was no reaction.

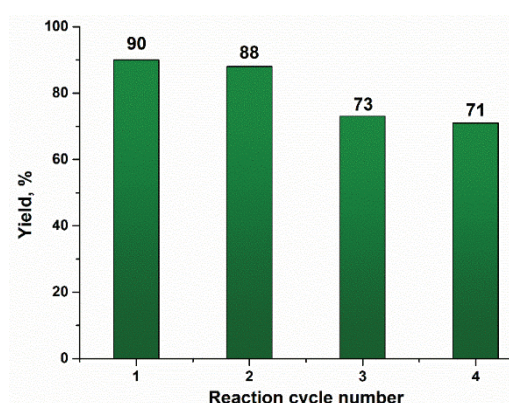
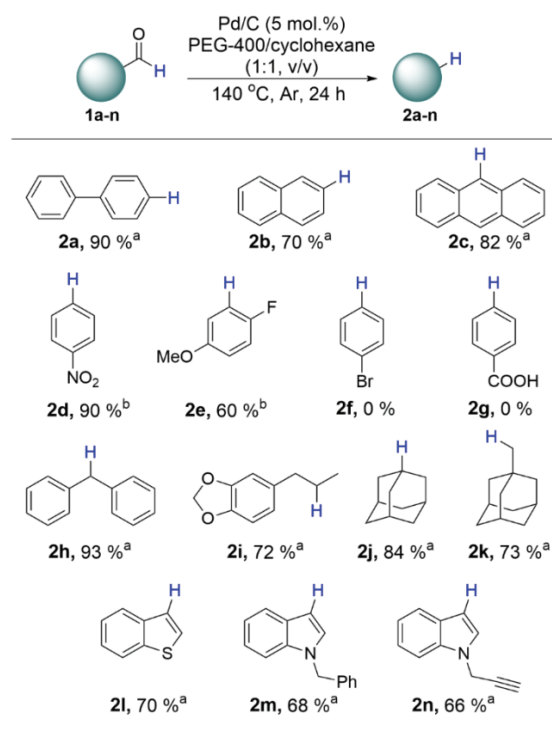


Fig. 3. Reusability of the Pd/C/PEG-400 catalytic system.

The substrate scope was then extended to aliphatic aldehydes. The aliphatic aldehydes with an aromatic core successfully produced the desired products (**2h**, and **i**) in good to excellent yields. Furthermore, the methodology was applied to the sterically demanding aldehydes, adamantane-1-carbaldehyde (**1j**) and 1-adamantylacetaldehyde (**1k**). The decarbonylated products, adamantane (**2j**) and methyladamantane (**2k**) were isolated in good yields. The decarbonylation of several heterocyclic aldehydes was also explored under the optimal reaction conditions. The decarbonylation of benzo[*b*]thiophene-3-carboxaldehyde (**1l**) afforded the desired product benzo[*b*]thiophene (**2l**) in good yield. In addition, the *N*-substituted indole derivatives (**1m** and **n**) gave the corresponding decarbonylated products (**2m** and **n**) in good yields.

<sup>a</sup> Isolated yield<sup>b</sup> Yields by GC/MS with naphthalene as an internal standard

Scheme 1. Substrate scope.

## CONCLUSION

To conclude, the ligand-free palladium-on-carbon-catalysed decarbonylation of aldehydes in ecologically acceptable solvents as an alternative to homogeneous catalysis was reported in this study. Various aldehydes were successfully decarbonylated in moderate to excellent yields. The formation of byproducts during the reaction and chromatography was not observed. Also, Pd/C and PEG-400 system could be recycled and reused in at least four consecutive reaction cycles, without significant loss of catalytic activity.

## SUPPLEMENTARY MATERIAL

Additional data and information are available electronically at the pages of journal website: <https://www.shd-pub.org.rs/index.php/JSCS/article/view/11599>, or from the corresponding author on request.

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## ИЗВОД

ПАЛАДИЈУМ НА УГЉЕНИКУ У РЕГ-400/ЦИКЛОХЕКСАНУ: КАТАЛИТИЧКИ СИСТЕМ  
КОЈИ СЕ МОЖЕ РЕЦИКЛИРАТИ И ПОНОВО УПОТРЕБИТИ ЗА ЕФИКАСНО  
ДЕКАРБЕНИЛОВАЊЕ АЛДЕХИДАНАТАША ТЕРЗИЋ-ЈОВАНОВИЋ<sup>1</sup> и ВЛАДИМИР АЈДАЧИЋ<sup>2</sup><sup>1</sup>Универзитет Београда, Институт за хемију, технологију и металургију (ИХТМ), Њеишова 12,  
11000 Београд и <sup>2</sup>Иновациони центар Хемијског факултета, Сивуленски бр 12–16, 11000 Београд

Развијена је једноставна метода за декарбониловање алдехида користећи комерцијално доступни паладијум на угљенику уз употребу зелених растварача. Различити ароматични, алифатични и хетероароматични алдехиди могу се трансформисати у декарбониловане производе у добром приносу и без настајања споредних производа. Производи се једноставно изолоју из реакционе смеше, а исти катализатор се може употребити још три пута без значајног смањења приноса.

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