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Novel and Rapid Palladium-Assisted 6π Electrocyclic Reaction Affording 9,10-Dihydrophenanthrene and Its Analogues†

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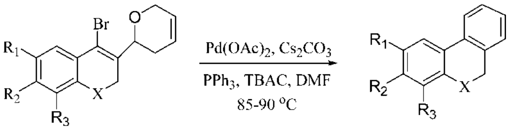
ABSTRACT



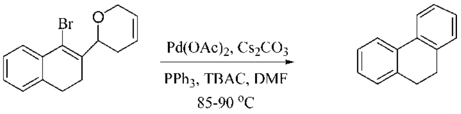
A novel methodology for the synthesis of 9,10-dihydrophenanthrene and its analogues has been developed via a palladium-assisted 6π electrocyclic reaction followed by formaldehyde elimination.

The extraordinary C−C bond-forming ability of palladium places it among the most versatile and useful metals in organic synthesis.[1] Among these, polycyclic aromatic and heteroaromatic hydrocarbons have been widely studied for their unique properties in material science.[2] Heck first reported the synthesis of 9,10-diphenylphenanthrene from 2-iodobiphenyl and diphenyl acetylene by a palladium-catalyzed annulation process; however, the yield was 14%.[3] Later, Larock improved the product yield by changing the reaction condition[4] and also synthesized fused polycycles by 1,4-palladium migration followed by C−H activation.[5]

Fagnou synthesized 9,10-dihydophenanthrene by a direct arylation process,[6] but the reaction condition was more vigorous. Trost synthesized polycyclic molecules via a pallladium-catalyzed electrocyclic process.[7] Recently, a palladium-catalyzed electrocyclization strategy for the synthesis of fused bicyclic and tricyclic rings has been reported.[8]

In this letter, we report a novel and rapid convenient approach to the synthesis of substituted 9,10-dihydrophenanthrene along with its analogues by a palladium-catalyzed 6π electrocyclic reaction. Recently, we described the palladium-catalyzed intramolecular Heck reaction by β-H elimination or C−H activation to afford a polycyclic pyran moiety.[9] We were planning to apply this reaction for the synthesis of a bicyclicpyran ring, but surprisingly we obtained 9,10-dihydrophenanthrene in good yield (Scheme 1).

Scheme 1



The convergent approach involved preparation of the cyclic precursors **4(a−j)** which were efficiently synthesized starting from vinylbromoaldehydes, as per Scheme 2.

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† Dedicated to Professor Miguel Yus, University of Alicante, Spain, on his 60th birthday.

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(2) For reviews, see:(a) Watson, M. D.; Fethtenkotter, A.; Mullen, K. *Chem. Rev.* **2001**, *101*, 1267. (b) Chandrasekhar, S. *Liq. Cryst.* **1993**, *14*, 3. (c) Chandrasekhar, S.; Kumar, S. *Sci. Spectra* **1997**, *8*, 66. (d) Pérez, D.; Guitián, E. *Chem. Soc. Rev.* **2004**, *33*, 274. (e) Buess, C. M.; Lawson, D. D. *Chem. Rev.* **1960**, *60*, 313. (f) Watson, M.; Fechtenkö tter, A.; Mü llen, K. *Chem. Rev.* **2001**, *101*, 1267.

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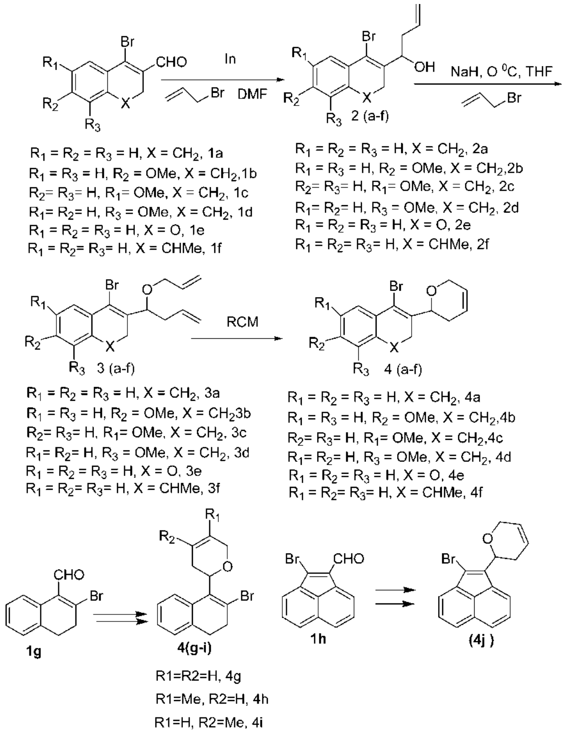
10.1021/ol801882t CCC: $40.75

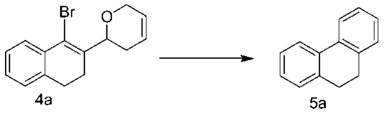
Scheme 2



When we treated substrate **4a** with $Pd(OAc)_2$ (10 mol %), Cs_2CO_3 (2 equiv), PPh_3(0.5 equiv), and TBAC(1 equiv), in DMF solvent, followed by heating at 85−90 °C for 1.5−2 h, the unexpected product **5a** was obtained in 70% yield. A fused aromatic ring resulted from cleavage of the pyran ring present in the substrate followed by ring closure and aromatization. The reaction was then attempted by changing the base and solvent to optimize the reaction conditions. The results are summarized in Table 1.

In acetonitrile (Table 1; entries 4, 5, 6, and 8), yield was poor; however, in DMF, yields were improved with both Cs_2CO_3 and NaOAc (Table 1; entries 1 and 7).

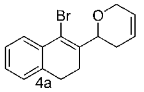
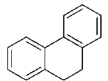
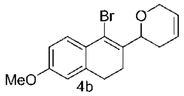
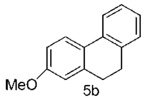
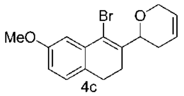
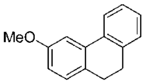
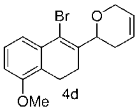
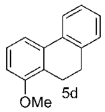
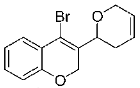
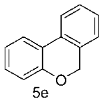
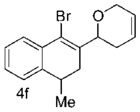
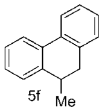
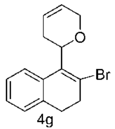
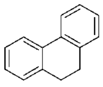
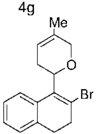
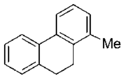
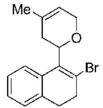
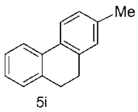
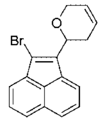
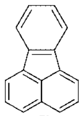
Table 1. Optimization Studies[a]



entry	base[b]	solvent	temp (°C)	yield (%)
1	Cs_2CO_3	DMF	90	70
2	Na_2CO_3	DMF	90	62
3	K_2CO_3	DMF	90	61
4	Cs_2CO_3	CH_3CN	85	35
5	Na_2CO_3	CH_3CN	85	30
6	K_2CO_3	CH_3CN	80	33
7	NaOAc	DMF	90	68
8	NaOAc	CH_3CN	85	33

[a] All the reactions were carried out in the presence of $Pd(OAc)_2$ (10 mol %), PPh_3 (0.5 equiv), and *n*-Bu_4NCl (1 equiv). [b] All the reactions were carried out in the presence of 2 equiv of base.

Table 2. Palladium-Catalyzed Electrocyclic Reaction[a]

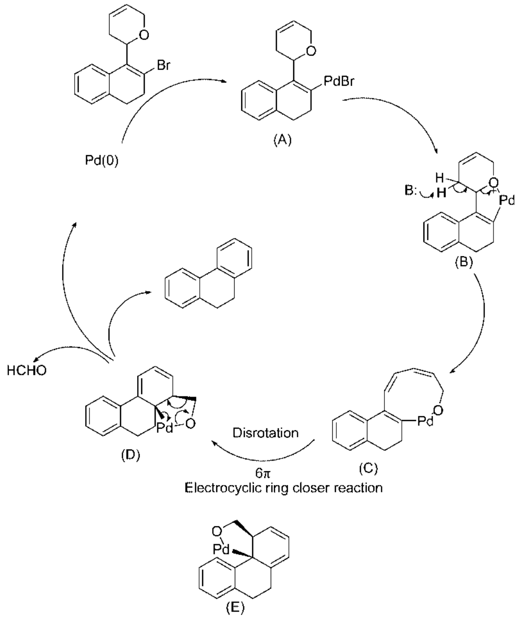
Entry	Substrate	*T(m)*	Product	Yield[b] (%)
1	 4a	120	 5a	70
2	 4b	110	 5b	72
3	 4c	120	 5c	69
4	 4d	115	 5d	66
5	 4e	120	 5e	58
6	 4f	120	 5f	64
7	 4g	110	 5g	82
8	 4h	100	 5h	81
9	 4i	110	 5i	80
10.	 4i	90	 5j	80

[a] Reagent and conditions: **4(a−j)** (1equiv), $Pd(OAc)_2$ (10 mol %), PPh_3 (0.5 equiv), Cs_2CO_3 (2 equiv), *n*-Bu_4NCl (1 equiv), DMF (6−7 mL), heated at 85−90 °C. [b] Isolated yield obtained after column chromatography.

Finally, we concluded that our optimization conditions were 10 mol % of $Pd(OAc)_2$, 0.5 equiv of PPh_3, and 2 equiv of Cs_2CO_3 in DMF solvent heated at 85−90 °C for 1.5−2 h.

We next examined the scope of this reaction with different substituted 2-(1-bromo-3,4-dihydro-napthenen-2-yl)-3,6-dihydro-2*H*-pyran, 2-(2-bromo-3,4-dihydro-napthenen-1-yl)-3,6 dihydro-2*H*-pyran, 4-bromo-3-(3,6-dihydro-2*H*-pyran-2-yl)-2*H*-chromene, and 2-(2-bromo-acenaphthylen-yl)-3,6-

Scheme 3. Proposed Mechanism for the Formation of 9,10-Dihydrophenanthrene[a]

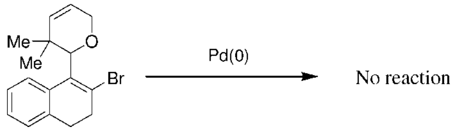


[a]Steric interaction of complex (E) in substrate **4a**.

dihydro-2*H*-pyran (Table 2) to obtain overall good yield in each case. This process represents a very powerful new tool for the preparation of 9,10-dihydrophenanethrene and its analogues from vinyl bromoaldehydes **1(a−h)**. In the case of substrates **4(g−i)**, a slightly better result than substrates **4(a−f)** was observed. This is presumably due to the fact that in later cases the complex formed (E) interacted with the adjacent benzene ring (peri-interaction), but such an interaction was absent in the former cases (Scheme 3).

The reaction mechanism presumely involves a 6π electrocyclic reaction followed by formaldehyde elimination. The catalytic cycle involves initial oxidation of the Pd(0) to generate alkenyl palladium(II) intermediate (A) via oxidative addition of the Pd(0) to the substrate, which then coordinates with oxygen to generate the intermediate (B). This undergoes proton abstraction followed by rearrangement to afford a nine-membered cyclic Pd−O complex (C). This complex involves a 6π electrocyclic reaction forming complex (D), followed by formaldehyde extrusion to afford 9,10-dihydrophenanthrene. The plausible mechanism of the reaction is outlined below (Scheme 3).

Scheme 4



From the above cycle, it can be assumed that the oxo-palladium complex (B) decomposes to the nine-membered cyclic Pd−O complex (C) by H elimination. Next, we thought that the introduction of two methyl groups instead of 2H could lead to a situation where further H-elimination is impossible and hence the reaction will stop. This hypothesis was found to be valid with the experimental results. The substrate 2-(2-bromo-3,4-dihydro-naphthalen-1-yl)-3,3-dimethyl-3,6-dihydro-2*H*-pyran did not react under similar conditions (Scheme 4).

In summary, we have developed a novel and efficient methodology for the synthesis of 9,10-dihydrophenanthrene and its analogue by the palladium-catalyzed 6π electrocyclic reaction. This methodology will also be helpful to synthesize highly substituted phenanthrene derivatives providing an efficient route to a wide variety of substituted polycyclic aromatics from readily available starting materials.

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Supporting Information Available: Detailed experimental procedures and spectral data for all the compounds **1(a−h)**, **2(a−i)**, **3(a−j)**, **4(a−j)**, **5(a−j)**, and **6(b−d)**. This material is available free of charge via the Internet at http://pubs.acs.org.

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