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Platinum-Catalyzed Intramolecular Hydroarylation of Allenyl Arenes: Efficient Synthesis of 1,4-Dihydronaphthalenes

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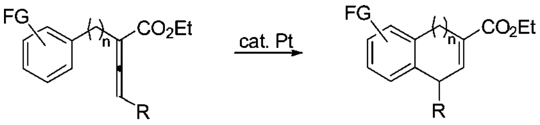
ABSTRACT



n = 1, 2 R = H, Me, Et, $PhCH_2CH_2$
FG = 2-Me, 4-Me, 3,5-Me_2, 3-MeO, 2-I, 4-Br, 2-Br-5-MeO

An efficient synthetic method of 1,4-dihydronaphthalenes having various alkyl groups on the 4-position and/or ethoxycarbonyl group on the 2-position through selective intramolecular Pt-catalyzed 6-*endo* cyclohydroarylation of ethyl 2-benzyl-2,3-alkadienoates was developed. The present method could be further extended to two-fold Pt-catalyzed 6-*endo* and 7-*endo* cyclizations.

Since 1,4-dihydronaphthalene is an important structural motif frequently found in natural products and has been used as an essential skeleton in pharmaceutics, development of efficient and versatile synthetic methods for 1,4-dihydronaphthalene derivatives has been continuously required,[1] and many synthetic strategies for 1,4-dihydronaphthalenes have been reported in the literature.[2] Among them, Birch reduction has been widely used for obtaining 1,4-dihydronaphthalene due to the availability and stability of naphthalene derivatives.[3] However, the Birch reduction has some limitations. Only unfunctionalized alkyl groups can be introduced during the dearomatization, and many functional groups are not tolerable under the reaction conditions. Regioselectivity is often poor, and over-reduction is another common problem. Although recent modifications of the Birch reduction, such as the use of silylated naphthalenes, expand its utility,[4] regio- and stereocontrol are still difficult. Lautens has reported that the aryne Diels−Alder reaction with acyclic dienes is a useful method for the synthesis of functionalized 1,4-dihydronaphthalenes.[5] Recently, intramolecular transition-metal-catalyzed hydroarylation of alkynes[6] and allenes[7] has been intensively investigated, providing a wide range of carbocyclic as well as heterocyclic compounds. In addition, Widenhoefer reported intramolecular

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(1) (a) Gozler, T.; Gozler, B.; Patra, A.; Leet, J. E.; Freyer, A. J.; Shamma, M. *Tetrahedron* **1984**, *40*, 1145. (b) Castro, M. A.; Gordaliza, M.; Del Corral, J. M. M.; Feliciano, A. S. *Phytochemistry* **1996**, *41*, 995. (c) Ward, R. S. *Nat. Prod. Rep.* **1997**, *14*, 43. (d) Winemiller, M. D.; Harman, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 7835.

(2) (a) Stephan, D.; Gorgues, A.; Coq, A. L. *Tetrahedron Lett.* **1984**, *25*, 5649. (b) Mander, L. N.; Morris, J. C. *J. Org. Chem.* **1997**, *62*, 7497. (c) Kawahata, N. H.; Goodman, M. *Tetrahedron Lett.* **1999**, *40*, 2271.

(3) (a) Hook, J. M.; Mander, L. N. *Nat. Prod. Rep.* **1986**, *3*, 35. (b) Rabideau, P. W.; Marcinow, Z. *Org. React.* **1992**, *42*, 1. (c) Rabideau, P. W. *Tetrahedron* **1989**, *45*, 1579. (d) Rabideau, P. W.; Fronczek, F. R. *Chem. Commun.* **1992**, 79. (e) Birch, A. J. *Pure Appl. Chem.* **1996**, *68*, 553. (f) Subba Rao, G. S. R. *Pure Appl. Chem.* **2003**, *75*, 1443.

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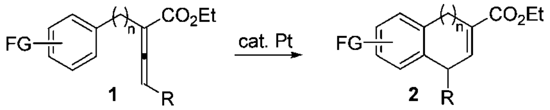
(5) Dockendorff, C.; Sahli, S.; Olksen, M.; Milhau, L.; Lautens, M. *J. Am. Chem. Soc.* **2005**, *127*, 15028, and references therein.

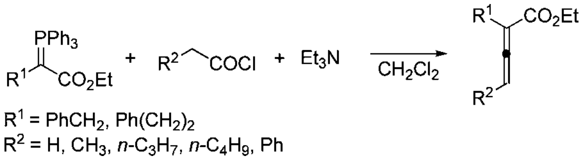
10.1021/ol1007857

Pt- or Au-catalyzed hydroarylation of alkenes and allenes with indole derivatives.[8] In this respect, we envisioned that 1,4-dihydronaphthalene derivatives might be formed by intramolecular transition-metal-catalyzed hydroarylation reaction of allenyl arenes. In this paper, we report the direct formation of 1,4-dihydronaphthalenes having a variety of alkyl groups on the 4-position and/or ethoxycarbonyl group on the 2-position through selective intramolecular Pt-catalyzed hydroarylation of ethyl 2-benzyl-2,3-alkadienoates in a 6-*endo* mode (Scheme 1). Also, two-fold-selective intramolecular Pt-catalyzed hydroarylation in a 6-*endo* mode is described, producing tetrahydroanthracene and tetrahydrophenanthrene derivatives. Furthermore, intramolecular Pt-catalyzed hydroarylation in a selective 7-*endo* mode is reported.

Scheme 1. Intramolecular Hydroarylation Catalyzed by Platinum



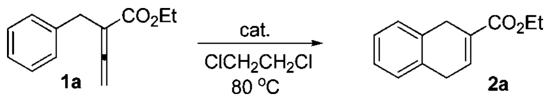
Scheme 2. Preparation of Ethyl 2-Benzyl- and 2-Phenethyl-2,3-alkadienoates



First, a variety of ethyl 2-benzyl- and 2-phenethyl-1,2-alkadienoates were prepared by treatment of (carbethoxybenzylidene)triphenylphosphorane or (carbethoxyphenethylidene)triphenylphosphorane with alkanoyl chloride having an α-hydrogen in the presence of triethylamine in dichloromethane (Scheme 2).[2a,c,9]

To examine the feasibility of intramolecular hydroarylation of ethyl 2-benzyl-2,3-butadienoate (**1a**), when the reaction was carried out with several gold catalysts such as 5 mol % of $AuCl_3$, 5 mol % of $AuCl_3$/15 mol % of AgOTf, and 5 mol % of Ph_3PAuCl/5 mol % of AgOTf in DCE, the reaction did not proceed. Although hydroarylation catalyzed by 5 mol % of $PtCl_4$ and 5 mol % of $PtCl_2$ did not occur, we found that 2.5 mol % of $PtCl_4$/10 mol % of $AgSbF_6$ was effective for hydroarylation, yielding 2-ethoxycarbonyl-1,4-dihydronaphthalene (**2a**) in 72% yield in $ClCH_2CH_2Cl$ at 80 °C for 2 h. Encouraged by this preliminary result, we further examined several catalysts and silver cocatalysts. As shown in Table 1, a better result was obtained with 2.5 mol % of $PtCl_2$/5 mol % of $AgSbF_6$ (89%, 2 h, entry 7). The individual use of 5 mol % of $AgSbF_6$ without $PtCl_2$ did not afford the cyclized compound (entry 8). Among various silver cocatalysts examined, AgOTf turned out to be the most effective, thus providing **2a** selectively in a 6-*endo* mode in 93% yield in $ClCH_2CH_2Cl$ at 80 °C for 2 h (entry 9). $AgNTf_2$ was slightly less effective (88%, entry 10). It is noteworthy that use of 5 mol % of $AgPF_6$, $AgAsF_6$, and $AgBF_4$ as a cocatalyst in the presence of 2.5 mol % of $PtCl_2$ was totally ineffective for intramolecular hydroarylation (entries 11−13). Interestingly, the isomerized α,*β*-unsaturated ester **3** and five-membered cyclic compound **4** in 5-*exo* mode were not detected.

Table 1. Reaction Optimization



entry	catalyst	time (h)	yield[a] (%)
1	5 mol % of $AuCl_3$	12	0
2	5 mol % of $AuCl_3$/15 mol % of AgOTf	12	0
3	5 mol % of Ph_3PAuCl/5 mol % of AgOTf	12	0
4	5 mol % of $PtCl_4$	18	0
5	5 mol % of $PtCl_2$	6	0
6	2.5 mol % of $PtCl_4$/10 mol % of $AgSbF_6$	2	72 (14)[b]
7	2.5 mol % of $PtCl_2$/5 mol % of $AgSbF_6$	2	89
8	5 mol % of $AgSbF_6$	6	0
9	2.5 mol % of $PtCl_2$/5 mol % of AgOTf	2	93
10	2.5 mol % of $PtCl_2$/5 mol % of $AgNTf_2$	2	88
11	2.5 mol % of $PtCl_2$/5 mol % of $AgPF_6$	6	0
12	2.5 mol % of $PtCl_2$/5 mol % of $AgAsF_6$	6	0
13	2.5 mol % of $PtCl_2$/5 mol % of $AgBF_4$	6	0

[a] Isolated yield.; 0% yield means no reaction and then **1a** was recovered. [b] Ethyl 2-naphthoate.

Quenching of the reaction mixture with D_2O after intramolecular hydroarylation of **1a** gave rise to the corresponding deuterated adduct **2a** in 96% yield with 10%

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(6) (a) Chatani, N.; Inoue, H.; Ikeda, T.; Murai, S. *J. Org. Chem.* **2000**, *65*, 4913. (b) Fürstner, A.; Mamane, V. *J. Org. Chem.* **2002**, *67*, 6264. (c) Nishizawa, M.; Takao, H.; Yadav, V. K.; Imagawa, H.; Sugihara, T. *Org. Lett.* **2003**, *5*, 4563. (d) Fürstner, A.; Mamane, V. *Chem. Commun.* **2003**, 2112. (e) Reetz, M. T.; Sommer, K. *Eur. J. Org. Chem.* **2003**, 3485. (f) Mamane, V.; Hannen, P.; Fürstner, A. *Chem.—Eur. J.* **2004**, *10*, 4556. (g) Nevado, C.; Echavarren, A. M. *Synthesis* **2005**, 167. (h) Goj, L. A.; Gunnoe, T. B. *Curr. Org. Chem.* **2005**, *9*, 671. (i) Soriano, E.; Marco-Contelles, J. *Organometallics* **2006**, *25*, 4542. (j) Chernyak, N.; Gevorgyan, V. *J. Am. Chem. Soc.* **2008**, *130*, 5636. (k) Menon, R. S.; Findlay, A. D.; Bissember, A. C.; Banwell, M. G. *J. Org. Chem.* **2009**, *74*, 8901.

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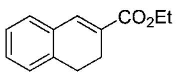
(9) (a) Ma, S.; Jiao, N.; Zhao, S.; Hou, H. *J. Org. Chem.* **2002**, *67*, 2837. (b) Zhu, X.-F.; Lan, J.; Kwon, O. *J. Am. Chem. Soc.* **2003**, *125*, 4716. (c) Shen, R.; Huang, X. *J. Org. Chem.* **2007**, *72*, 3961. (d) Tran, Y. S.; Kwon, O. *J. Am. Chem. Soc.* **2007**, *129*, 12632. (e) Castellano, S.; Fiji, H. D. G.; Kinderman, S. S.; Watanabe, M.; de Leon, P.; Tamanoi, F.; Kwon, O. *J. Am. Chem. Soc.* **2007**, *129*, 5843.



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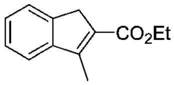
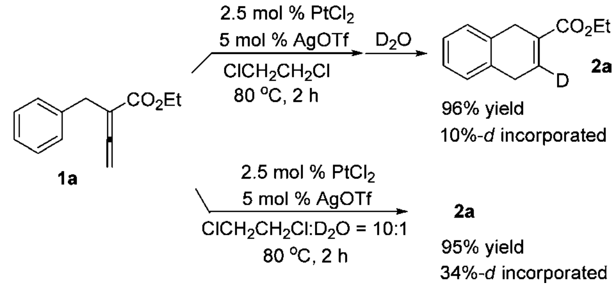


4

d-incorporation (Scheme 3). Also, addition of 10% D_2O as a cosolvent to $ClCH_2CH_2Cl$ provided **2a** in 95% yield with 34% *d*-incorporation, indicating that a vinylplatinum intermediate might be formed.[10]

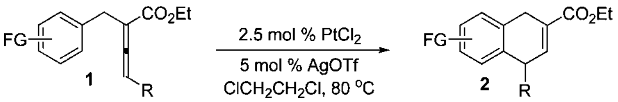
Scheme 3. Deuterium Incorporation in Pt-Catalyzed Hydroarylation

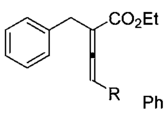
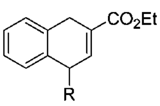
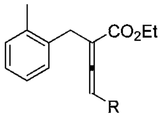
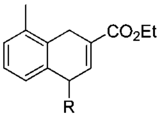
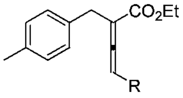
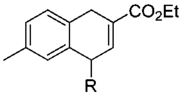
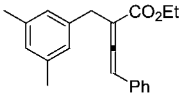
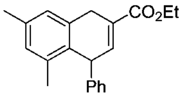
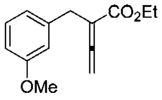
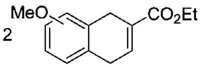
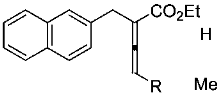
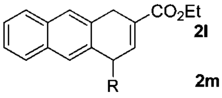
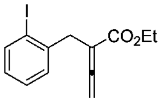
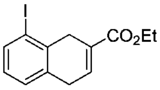
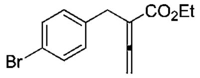
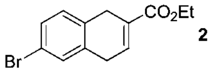
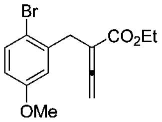
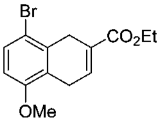


To demonstrate the efficiency and scope of the present method, we applied this catalytic system to a wide range of ethyl 2-benzyl-2,3-alkadienoates **1**. Intramolecular hydroarylation in the presence of a methyl and ethyl group on the terminal sp^2 carbon of the allenyl group proceeded smoothly to afford dihydronaphthalenes **2b** and **2c** in 90 and 88% yields, respectively (Table 2, entries 2 and 3). In the case of **1d**, 5 mol % of $PtCl_4$/20 mol % of AgOTf was superior, resulting in the formation of cyclic compound **2d** in 87% yield (entry 4). The presence of 2-methyl, 4-methyl, and 3,5-dimethyl groups on the phenyl ring exhibited little effect on either the reaction rate or product yield (entries 5−10). However, allenes **1g** and **1j** having a phenyl group on the terminal sp^2 carbon of the allene group were slightly less effective (76 and 82% yields, entries 7 and 10). Treatment of **1k** bearing a 3-methoxy group with 2.5 mol % of $PtCl_2$/5 mol % of AgOTf led to the mixtures of isomeric 1,4-dihydronaphthalenes, but the product (**2kb**) resulting from the 2-position predominates (entry 11). Under the optimum reaction conditions, naphthyl alkadienoates **1l** and **1m** were smoothly converted to 1,4-dihydroanthracenes **2l** and **2m** in 92 and 88% yields, respectively (entries 12 and 13). It was gratifying to obtain 1,4-dihydronaphthalenes **2n** and **2o** possessing iodide and bromide groups in 74 and 95% yields, respectively (entries 14 and 15). When ethyl 2,3-butadienoate bearing both a methoxy and a bromide group **1p** was subjected to the reaction conditions, the corresponding dihydronaphthalene **2p** was obtained in 78% yield (entry 16).

Next, two-fold intramolecular hydroarylations were briefly examined. When bisallenyl benzene **1q** was subjected to the standard condition, tetrahydroanthracene **2q** and tetrahydrophenanthrene **2r** were isolated in 52 and 32% yields, respectively (Scheme 4). The present method worked equally well with **1r**, producing 1,4,5,8-tetrahydroanthracene **2s** in 82% yield.

Table 2. Pt-Catalyzed Cyclization of Allenyl Esters



entry	allene	R		time (h)	product		yield (%)
1		H	**1a**	2		**2a**	93
2		Me	**1b**	2		**2b**	90
3		Et	**1c**	2		**2c**	88
4[a]		$PhCH_2$	**1d**	3		**2d**	87
5		H	**1e**	2		**2e**	94
6		Et	**1f**	2		**2f**	92
7		Ph	**1g**	3		**2g**	76
8		H	**1h**	2		**2h**	94
9		Me	**1i**	3		**2i**	92
10[b]			**1j**	3		**2j**	82
11		H	**1k**	2		**2ka** **2kb**	86 (1:1.6)[c]
12		H	**1l**	2		**2l**	92
13		Me	**1m**	2		**2m**	88
14[b]			**1n**	4		**2n**	74
15			**1o**	2		**2o**	95
16[b]			**1p**	4		**2p**	78

[a] Using 5 mol % of $PtCl_4$ and 20 mol % of AgOTf. [b] Using 5 mol % of $PtCl_2$ and 10 mol % of AgOTf. [c] Ratio of 2-ethoxycarbonyl-5-methoxy-1,4-dihydronaphthalene (**2ka**) and 2-ethoxycarbonyl-7-methoxy-1,4-dihydronaphthalene (**2kb**).

Finally, when ethyl 2-phenethyl-2,3-butadienoate (**1s**) was treated with Pt catalyst, seven-membered cyclic compound **2t** was selectively obtained in 64% yield. Apparently, intramolecular hydroarylation proceeded in a 7-*endo* mode without contamination of the 6-*exo* mode (Scheme 5).

Although the mechanism of the present reaction has not been established, a possible reaction mechanism for intramo-

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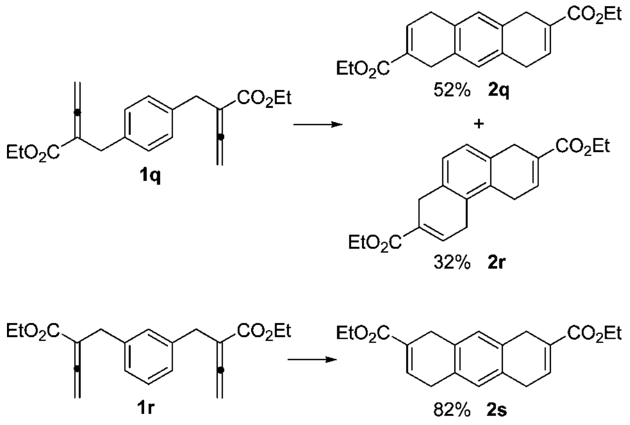
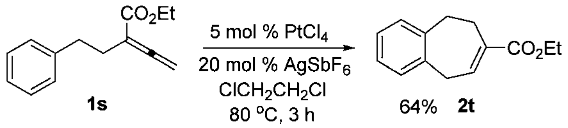
(10) Nelsen, D. L.; Gabne, M. T. *Organometallics* **2009**, *28*, 950.

Scheme 4. Two-Fold Intramolecular Hydroarylation Catalyzed by Platinum



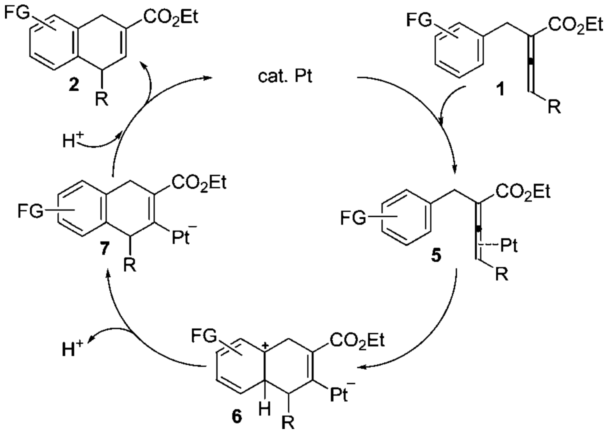
Scheme 5. Pt-Catalyzed Intramolecular Hydroarylation in 7-*endo* Mode



lecular Pt-catalyzed hydroarylation is shown in Scheme 6. The reaction would be initiated by activation of the allenyl group by platinum catalyst and followed by 6-*endo* cyclization to afford zwitterionic intermediate vinylplatinum **6**. Aromatization to vinylplatinum **7** and subsequent protonation would provide 1,4-dihydronaphthalene **2**. Deuterium incorporation (34%) shown in Scheme 3 indicates that the vinylplatinum **7** might be formed. The elucidation of the detailed reaction mechanism must wait further study.

In summary, we developed an efficient synthetic method of 1,4-dihydronaphthalenes having various alkyl groups on the 4-position and/or ethoxycarbonyl group on the 2-position through Pt-catalyzed 6-*endo* cyclohydroarylation of ethyl 2-benzyl-2,3-alkadienoates. The present method could be further extended to two-fold Pt-catalyzed 6-*endo* and 7-*endo* cyclizations. This method would pave a new way to synthetically valuable processes of a wide range of 1,4-dihydronaphthalene, 1,4,5,8-tetrahydroanthracene, and tetrahydrophenanthrene derivatives.

Scheme 6. Plausible Reaction Mechanism



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Supporting Information Available: Experimental procedure and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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