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Synthesis of Naphthalenyl Acetate by Platinum-Catalyzed [1,5]-Sigmatropic Hydrogen Shift of Propargylic Esters

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The [1,5]-sigmatropic hydrogen shift is a useful tool in organic synthesis[1] which has stimulated many mechanistic studies[2] and has found numerous applications in complex molecules synthesis.[3] In cyclic systems,[1c,4] this process has also been proved efficiently by using acyclic dienes and its derivates,[1c,5] such as *cis*-1,3-dienes,[5a,b] *cis*-1-alkyl-2-vinylcyclopropanes[5c,d] and *cis*-1-allen-4-enes[5e,f] [Eq. (1–3)]. However, in the alkyne area this reaction mechanism has not been observed until Liu and co-workers recently reported that *cis*-3-en-1-ynes did undergo the [1,5]-sigmatropic hydrogen shift via ruthenium–vinylidene intermediates [Eq. (4)].[6] Consequently, reactions of the [1,5]-hydrogen shift in the alkyne chemistry are still largely unexplored.

As a special of alkynes, readily available propargylic esters have continued to attract the interest of different research groups.[7] The metal–allene complexes, which are formed during the reaction, are considered common intermediates, that further react with various functional groups resulting in astonishingly diverse products under platinum and gold catalysis.[7,8] We envisioned that this type of allenyl esters **B** could realize the [1,5]-hydrogen shift process, although the nucleophilic attack on the C2 position still remains virtually unknown[9] compared with C1[8h,i] and C3[8j–l] positions [Eq. (5)]. Herein, we report the first examples of [1,5]-sigmatropic hydrogen shift reaction of propargylic esters.

Optimization studies of this transformation began with propargylic ester **1a** (0.3 mmol) with various catalysts. Among the platinum catalysts used (Table 1, entries 1–4), $PtCl_2$ (10 mol%) with CO (1 atm) gave the best result (Table 1, entry 4). Low-catalyst loading led to the poor yield of **2a**, whereas a similar result was obtained when 20 mol% of $PtCl_2$ were added (Table 1, entries 5 and 6). The changes in solvent and temperature did not give better results (Table 1, entries 7–10). Gold catalysts could also catalyze this cyclization, however, no superior results were obtained (entries 11–14). Thus, the use of $PtCl_2$ (10 mol%) and CO (1 atm) in toluene (2 mL) at 85 °C was found to be most efficient, which was subsequently used as the standard reaction condition.

Under these optimal conditions, we studied the scope of this cyclization as shown in Table 2. Besides the phenyl group, various aryl substituents were tolerated at the propargylic position (entries 1–4). The vinyl group also gave moderate yields of **2e** (entry 5). When the furyl substituent was used, uneliminated product **3a**[10] was isolated in 81% yield

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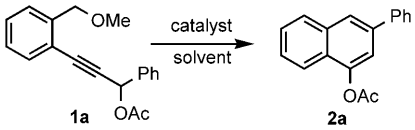
Table 1. Optimization of reaction conditions for the cyclization of **1a**.[a]

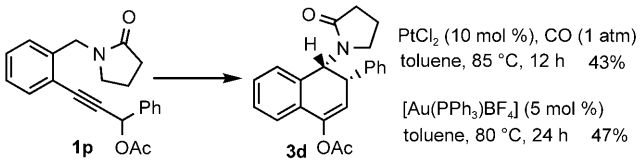


Entry	Catalyst [mol%]	Conditions	Yield [%][b]
1	$PtCl_2$ (10)	toluene, 85°C, 24 h	trace
2	$PtCl_2$ (10), COD (40)	toluene, 85°C, 24 h	52
3	$PtCl_2$ (10), O_2 (1 atm)	toluene, 85°C, 24 h	trace
4	$PtCl_2$ (10), CO (1 atm)	toluene, 85°C, 6 h	87
5	$PtCl_2$ (5), CO (1 atm)	toluene, 85°C, 24 h	78
6	$PtCl_2$ (20), CO (1 atm)	toluene, 85°C, 5 h	85
7	$PtCl_2$ (10), CO (1 atm)	CH_3CN, 85°C, 24 h	trace
8	$PtCl_2$ (10), CO (1 atm)	DCE, 85°C, 4 h	26
9	$PtCl_2$ (10), CO (1 atm)	toluene, 60°C, 24 h	63
10	$PtCl_2$ (10), CO (1 atm)	toluene, 100°C, 6 h	72
11	$AuCl_3$ (2)	toluene, 85°C, 24 h	trace
12	AuCl (2)	toluene, 85°C, 24 h	37
13	$Au(PPh_3)Cl$ (2), $AgBF_4$ (2)	toluene, 85°C, 24 h	43
14	$Au(PPh_3)Cl$ (2), AgOTf (2)	toluene, 85°C,24 h	trace

[a] Unless noted, all reactions were carried out using **1** (0.3 mmol). [b] Isolated yield.

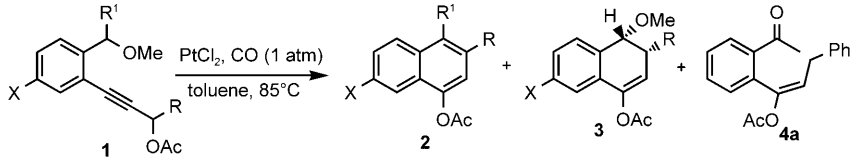
Furthermore, various protective groups of benzyl alcohols were investigated, which always resulted in moderate to high yields of desired products (Table 3). Among these, the best attractive one might belong to the group of TBS, as the singly uneliminated product **3c** and [1,7]-sigmatropic hydrogen shift product **4a** were obtained in high yields from the respective substrates (entries 5 and 6).

Interestingly, when the benzyl position was substituted by N-containing groups such as lactams, this tandem process also proceeded smoothly under optimal conditions to afford **3d**[10] in 43% yield. A similar result was obtained by using $[Au(PPh_3)BF_4]$ as the catalyst [Eq. (6)].



(6)

Table 2. Pt^{II}-catalyzed [1,5]-H shift reactions of propargylic esters.[a]

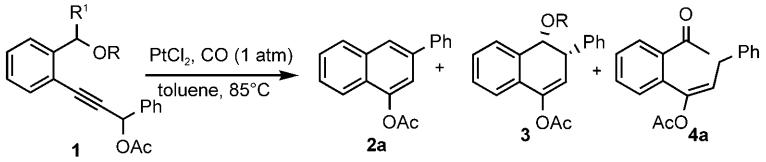


Entry	Substrate	*t* [h]	Product (yield [%])[b]
1	R = Ph, X = R^1 = H (**1a**)	6	**2a** (87)
2	R = p-ClC_6H_4, X = R^1 = H (**1b**)	6	**2b** (88)
3	R = p-$CH_3C_6H_4$, X = R^1 = H (**1c**)	4	**2c** (68)
4[c]	R = 2,3-methylenedioxy, X = R^1 = H (**1d**)	18	**2d** (96)
5	R = vinyl, X = R^1 = H (**1e**)	7	**2e** (56)
6	R = 2-furanyl, X = R^1 = H (**1f**)	1	**3a** (81)
		4	**2f** (52)[d]
7	R = Ph, X = Cl, R^1 = H (**1g**)	4	**2g** (93)
8	R = Ph, X = H, R^1 = Ph (**1h**)	5	**2h** (87)
9	R = Ph, X = H, R^1 = CH_3 (**1i**)	6	**2i** (55)
			4a (32)

[a] Unless noted, all reactions were carried out using **1** (0.3 mmol) with 10 mol% of $PtCl_2$ under CO (1 atm) in toluene (2 mL) at 85°C. [b] Isolated yield. [c] 20 mol% of $PtCl_2$ was used. [d] H_2O (1 equiv) was added.

The deuterium-labeling experiments (Scheme 1) showed that the deuterium on the benzyl position transferred into the β-position of the ester after reaction ([D_1]-**2i** and [D_1]-**4a**). However, the shift of deuterium on the methyl group was only observed in the product [D_3]-**4a**[11]. This observation is consistent with our proposed mechanism, as depicted in Scheme 1. The Pt^{II}-promoted [1,3]-OAc shift lead to the formation of allenyl esters **A**,[7] which undergoes a [1,5]-H shift process[5] to form intermediates **B**. Subsequent 6π cyclization[12] of compounds **B** afford cyclization with high *cis*-selectivity, whereas 1 equiv of H_2O led to a complete transformation (entry 6). However, for R = H or alkyl groups, the desired products were not detected. Substituents on the benzene as well as benzyl positions did not affect the reactivity (entries 7–9). However, when the methyl group was introduced in the benzyl position, the [1,7]-sigmatropic hydrogen shift product **4a** was also isolated (entry 9).

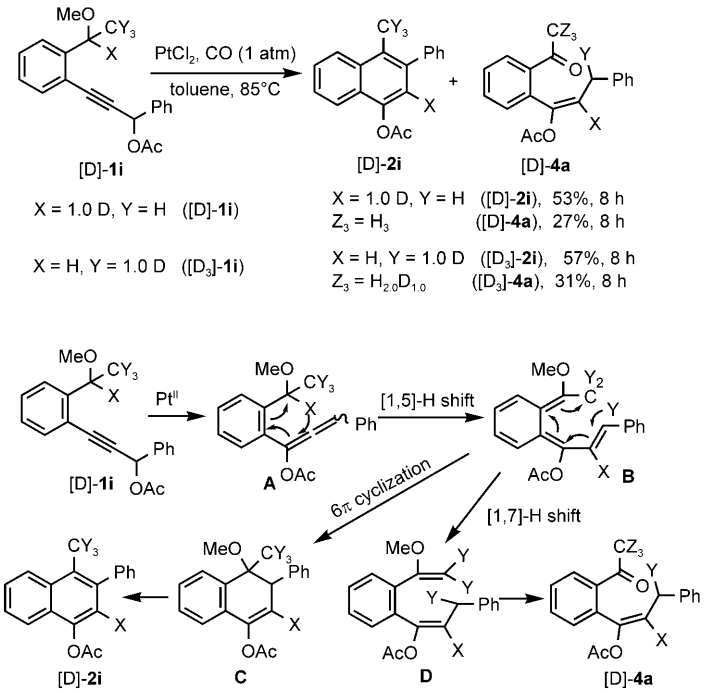
Table 3. Affects of different protective groups.[a]



Entry	Substrate	*t* [h]	Product (yield [%])[b]
1	R = allyl, R^1 = H (**1j**)	3	**2a** (91)
2	R = Ph, R^1 = H (**1k**)	5	**2a** (65)
3	R = THP, R^1 = H (**1l**)	4	**2a** (53)
4	R = Bn, R^1 = H (**1m**)	3	**2a** (14) **3b** (84)
		13	**2a** (94)
5[c]	R = TBS, R^1 = H (**1n**)	12	**3c** (93)
6	R = TBS, R^1 = CH_3 (**1o**)	5	**4a** (81)

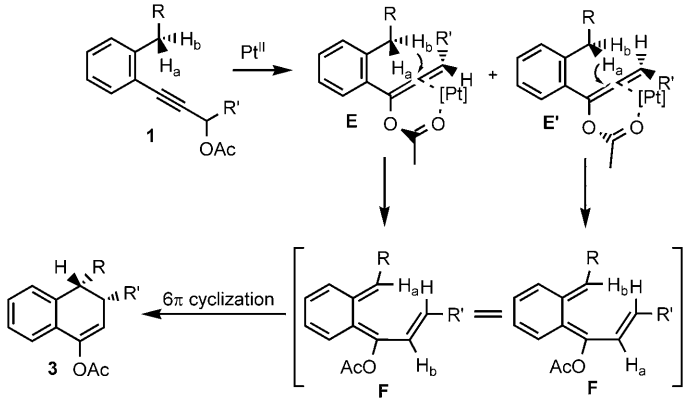
[a] Unless noted, 0.3 mmol of 1 and 10 mol% of $PtCl_2$ was used. [b] Isolated yield. [c] DCE was used.

products **C**, which further eliminated to give products [D_1]-**2i**. At the same time, the intermediates **B** might also undergo a [1,7]-H shift[13] to afford compound **D**, which could be easily transformed into ketone [D_1]-**4a** by enolization.



Scheme 1. Deuterium-labeling experiments and proposed mechanism.

Additionally, the platinum catalyzed domino process is stereospecific, as explained in Scheme 2. Platinum-promoted rearrangement of propargylic esters affords two isomers of allene complex. The configurational orientation of the acyloxy group away from the large substituents led to the formation of a platinum-coordinated six-membered ring[14] opposite to R′ group, which prevents the H-shift process. Based on this, path H_b in compounds **E** and path H_a in compounds **E**' are favored. Both afford the same intermediates **F**.[5f] Further high stereoselective 6π cyclization transforms **F** into *cis* products **3**.[12a,d]



Scheme 2. Stereospecificity study.

In conclusion, we have reported a novel platinum-catalyzed transformation of 3-(2-alkyl)phenyl-propynyl acetate to naphthalenyl acetate. The deuterium-labeling experiments show that the reaction might include the [1,3]-OAc shift, [1,5]-sigmatropic hydrogen shift and 6π cyclization processes. The high stereoselectivity of this tandem reaction was also disclosed.

Experimental Section

General produce for the platinum catalyzed tandem reactions of propargylic esters 1: $PtCl_2$ (8.0 mg, 10 mol %) was added under CO atmosphere (1 atm) at 85 °C to a stirred solution of propargylic esters **1** (0.30 mmol) in toluene (2.0 mL). When the reaction was considered complete as determined by TLC analysis, the reaction mixture was diluted with ethyl acetate (20 mL) and evaporated under reduced pressure. The residue was purified by column/flash chromatography on silica gel to afford corresponding products.

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Keywords: Hydrogen shift · homogeneous catalysis · naphthalenyl acetate · platinum · propargylic ester

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