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Rhenium-catalyzed regioselective synthesis of 1,2-disubstituted naphthalenes

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ABSTRACT

Rhenium-catalyzed coupling reaction of alkynes with phenylacetaldehyde dimethylacetal in the presence of H_2O regioselectively afforded the corresponding 1,2-disubstituted naphthalenes.

The polysubstituted naphthalene compounds constitute an attractive class of compounds from the view points of chemical, biologically active molecules, and materials science. Numerous synthetic procedures have been developed for the preparation of polysubstituted naphthalenes.[1] The traditional regioselective construction methods of polysubstituted naphthalenes are the stepwise introduction of a substituent through an electrophilic substituent reaction[2] or transition metal-catalyzed coupling reaction to naphthalene framework.[3] Recently, new and efficient synthetic methods of polysubstituted naphthalenes have been accomplished, that is, (i) the annulations via Fischer carbene complexes, called the Dötz reaction,[4] (ii) the transition metal-catalyzed reaction of alkynes with benzynes generated in situ,[5] (iii) the ring expansion reaction of cyclopropane and cyclobutanes,[6] (iv) transition metal-catalyzed intramolecular cyclization of *o*-substituted arenes,[7] (v) Au- and Cu-catalyzed [4+2] benzannulation between *o*-alkynylbenzaldehydes and alkynes,[8] (vi) X^+ (X = I, Br, or PhSe)-assisted intermolecular electrophilic cyclization of alkynes,[9] and (vii) Lewis acid-, such as gallium trichloride[10] and gold trichloride/$AgSbF_6$,[11] catalyzed or titanium tetrachloride[12]-assisted reaction of alkynes and phenylacetaldehyde or styrene oxide.

The catalytic use of rhenium complexes in organic synthesis has shown a tremendous potential in the past few decades.[13] Recently, a novel and efficient synthetic method of aromatic cyclic compounds by the rhenium-catalyzed coupling reaction of aldimine with various organic compounds bearing carbon–carbon or carbon–heteroatom unsaturated bonds has been reported.[13a,14] In these reports, these authors have proposed a reaction mechanism including (i) the coordination of a nitrogen atom of the imines to the rhenium center, (ii) C–H bond activation, (iii) insertion of carbon–carbon or carbon–heteroatom unsaturated bonds into the rhenium–carbon bond of the arylrhenium intermediate, (iv) intramolecular nucleophilic attack of the formed alkyl- and alkenylrhenium moiety on a carbon atom of the imine, and (v) reductive elimination and 1,3-rearrangement of the hydrogen atom.

This report describes the first rhenium-catalyzed regioselective synthesis of 1,2-disubstituted naphthalenes by the reaction of phenylacetaldehyde dimethylacetal with alkynes. For the reaction, it was suggested that the reaction pathway might involve the electrophilic substituted reaction of the vinyl cation intermediate, which was formed by the addition of an aldehyde generated in situ by the hydrolysis of the acetal to the carbon–carbon triple bond of alkynes in the presence of the rhenium complex, on the aromatic ring.[15]

When phenylacetaldehyde dimethyl acetal (**1a**) was allowed to react with 1-phenyl-1-butyne (**2a**) in the presence of a catalytic amount of rhenium bromopentacarbonyl, $ReBr(CO)_5$, (5 mol %) in 1,2-dichloroethane solvent at 80 °C for 20 h, 2-ethyl-1-phenylnaphthalene (**3a**) was formed in 31% yield without the formation of the regioisomer, 1-ethyl-2-phenylnaphthalene (Table 1, entry 1). During the reaction, the formation of phenylacetaldehyde, which was a hydrolysis product of **1a**, was observed by GC and GC–MS analyses during the initial stage of the reaction. Based on this, it was suggested that the formation of phenylacetaldehyde is the one of the key steps of the reaction. In order to smoothly form the phenylacetaldehyde in situ, two equivalent amounts of H_2O were added to the reaction. The yield of **3a** was significantly improved without affecting the selectivity and **3a** was obtained in 73% yield (entry 2). Decreasing the amount of **1a** led to the decreasing yield of **3a** (entries 3 and 4). The yield

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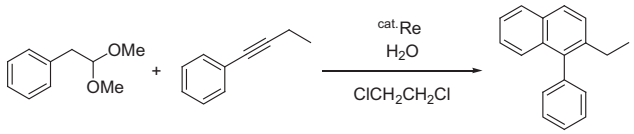
Table 1
Reaction of phenylacetaldehyde dimethylacetal (**1a**) with 1-phenyl-1-butyne (**2a**)[a]

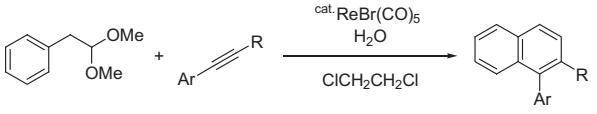


1a **2a** **3a**

Entry	**1a** (mmol)	Catalyst	*T* (°C)	Yield[b] (%)
1[c]	1.0	$ReBr(CO)_5$	80	40
2	1.0	$ReBr(CO)_5$	80	73 (70)
3	0.50	$ReBr(CO)_5$	80	42
4	0.75	$ReBr(CO)_5$	80	61
5	1.0	$ReBr(CO)_5$	40	Trace
6	1.0	$ReBr(CO)_5$	60	54
7	1.0	$ReCl(CO)_5$	80	72
8[d]	1.0	$Re_2(CO)_{10}$	80	23
9[d]	1.0	Re_2O_7	80	12
10	1.0	$ReCl_5$	80	19
11	1.0	None	80	0

[a] Reaction conditions: **1a**, **2a** (0.50 mmol), Re catalyst (5 mol %), H_2O (1.0 mmol), $ClCH_2CH_2Cl$ (2.0 mL), 80 °C, 20 h.
[b] GC yield based on **2a**. The number in parenthesis shows the isolated yield based on **2a**.
[c] H_2O was not added.
[d] Rhenium complex (2.5 mol %) was used.

Table 2
Reaction of phenylacetaldehyde dimethylacetal (**1a**) with various aryl substituted alkynes **2**[a]



1a **2** **3**

Entry	Ar	R	Yield[b] (%)
1	C_6H_5	H	**3b**, 14
2	C_6H_5	CH_3	**3c**, 50
3	C_6H_5	C_2H_5	**3a**, 70
4	C_6H_5	*n*-C_3H_7	**3d**, 62
5	1-$C_{10}H_7$	*n*-C_3H_7	**3e**, 75
6	2-$C_{10}H_7$	*n*-C_3H_7	**3f**, 53
7	2-$CH_3C_6H_4$	*n*-C_3H_7	**3g**, 69
8	3-$CH_3C_6H_4$	*n*-C_3H_7	**3h**, 63
9	4-$CH_3C_6H_4$	*n*-C_3H_7	**3i**, 59
10	4-$CH_3C_6H_4$	*n*-C_3H_7	**3j**, 66
11	2-FC_6H_4	*n*-C_3H_7	**3k**, 43
12	4-FC_6H_4	*n*-C_3H_7	**3l**, 58
13	4-BrC_6H_4	*n*-C_3H_7	**3m**, 30
14	2-Thienyl	*n*-C_3H_7	**3n**, 54
15	C_6H_5	C_6H_5	**3o**, 15
16	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	**3p**, 43
17	2-$C_{10}H_7$	2-$C_{10}H_7$	**3q**, 26

[a] Reaction conditions: **1a** (1.0 mmol), **2** (0.50 mmol), $ReBr(CO)_5$ (5 mol %), H_2O (1.0 mmol), $ClCH_2CH_2Cl$ (2.0 mL), 80 °C, 20 h.
[b] Isolated yield based on **2**.

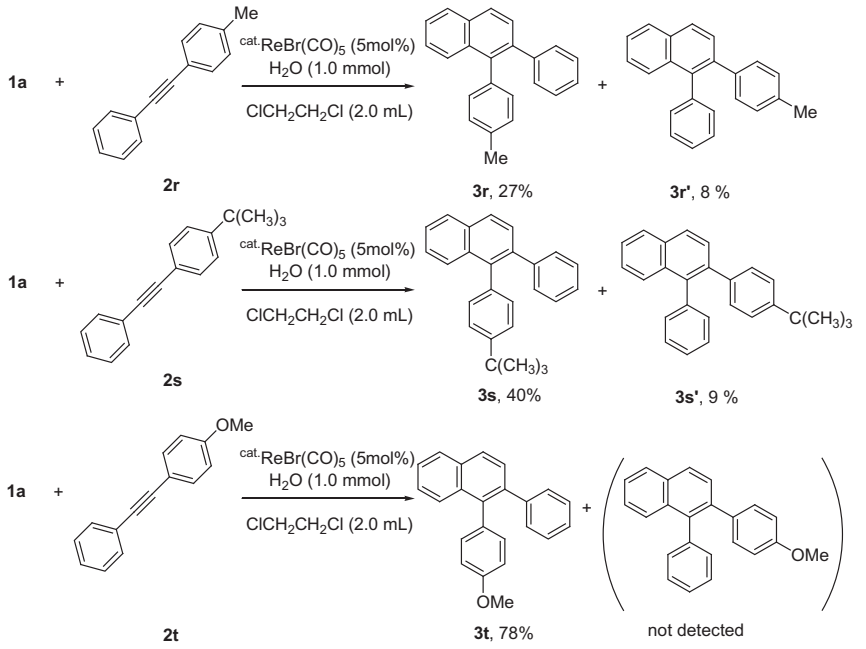
of **3a** was also diminished at lower reaction temperatures (40 and 60 °C) (entries 5 and 6). For the reaction, other rhenium complexes, such as $ReCl(CO)_5$, $Re_2(CO)_{10}$, Re_2O_7, and $ReCl_5$, are effective (entries 7–10). A better yield of **3a** was obtained using the rhenium halo pentacarbonyl complexes, $ReBr(CO)_5$ and $ReCl(CO)_5$ (entries 4 and 7). In the absence of the rhenium complex, **3a** was not formed and the starting materials **1a** and **2a** were recovered (entry 11).

The results of the reaction of phenylacetaldehyde dimethyl acetal (**1a**) with various alkynes are shown in Table 2. For the terminal acetylene, the yield of 1-phenylnaphthalene (**3b**) decreased due to the formation of various by-products (entry 1). When **1a** was allowed to react with 1-phenyl-1-propyne, 1-phenyl-1-butyne, and 1-pheny-1-pentyne in the presence of H_2O and a catalytic amount of $ReBr(CO)_5$ at 80 °C for 20 h, the 2-methyl-, 2-ethyl-, and 2-propyl-1-phenylnaphthalenes **3a**,**c**,**d** were obtained in 50%, 70%, and 62% yields, respectively (entries 2–4). Similarly, the reaction of **1a** with the 1-(1-naphthyl)- and 1-(2-naphthyl)-1-pentyne efficiently proceeded to give 1-(1-naphthyl)- and 1-(2-naphthyl)-2-propylnaphthalenes **3e**,**f** in 75% and 53% yields, respectively (entries 5 and 6). Also, the reaction of **1a** with the 1-aryl-1-propyne substituted electron donating groups, such as methyl and methoxy groups, bromo, and fluoro groups on the aromatic ring gave the corresponding 1-aryl-2-propyl naphthalenes **3g–m** in moderate to good yields (entries 7–13). In the case of 1-(4-nitrophenyl)-1-butyne, only uncharacterized products were observed. The 1-(2-thienyl)-2-propylnaphthalene (**3n**) was prepared by the rhenium-catalyzed reaction of **1a** with 1-(2-thienyl)-1-propyne (entry 14). For all alkyl aryl acetylenes, other regioisomers were not detected by the ^1H NMR and GC analyses of the crude reaction mixtures (entries 1–14). One-pot synthesis of the 1,2-diaryl substituted naphthalenes **3o–q** was achieved by the reaction of **1a** with the 1,2-diaryl alkynes (entries 15–17). However, when the aliphatic alkynes were used, no formation of the corresponding naphthalenes was observed.

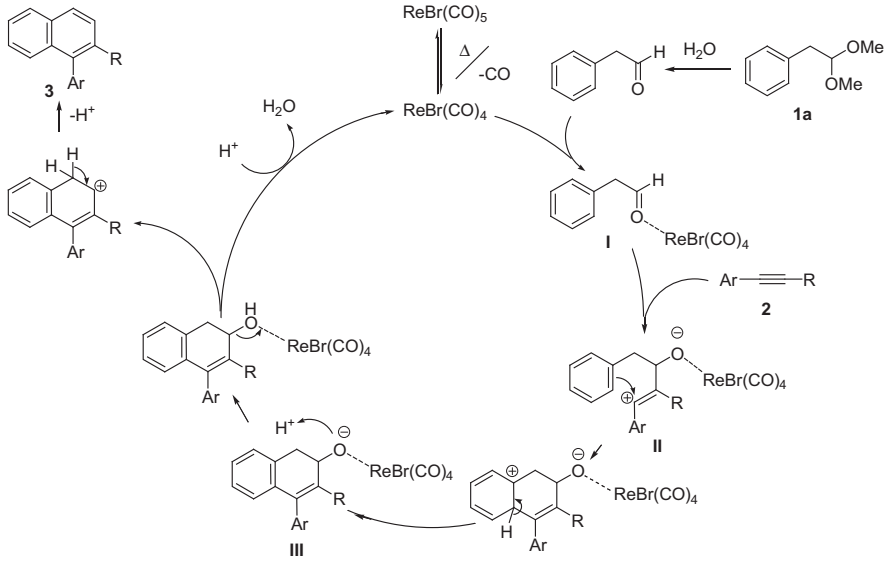
To elucidate the reaction pathways for the regioselective synthesis of the 1,2-disubstituted naphthalenes by the reaction of alkynes and phenylacetaldehyde dimethylacetal (**1a**) in the presence of H_2O, some experiments were carried out. When phenylacetaldehyde was allowed to react with 1-phenyl-1-butyne (**2a**), 2-ethyl-1-phenylnaphthalene (**3a**) was formed in 31% yield without the formation of a regioisomer. Next, in order to clarify the selectivity of the reaction, we carried out the reaction of **1a** with unsymmetrical diaryl acetylenes (Scheme 1). When phenylacetaldehyde dimethyl acetal (**1a**) was treated with 1-(4-methylphenyl)- and 1-(4-*tert*-butylphenyl)-2-phenyl acetylenes, **2r** and **2s**, the 1,2-diaryl substituted naphthalenes **3r**,**s** were predominantly formed together with a small amount of the regioisomers, **3r′**,**s′**. For the 1-(4-methoxyphenyl)-2-phenyl acetylene (**2t**) having methoxy group as the strong electron donating group, it is interesting to note that the reaction proceeded with a regioselectivity to give the 1-(4-methoxyphenyl)-2-phenylnaphthalenes (**3t**) as a single isomer in 78% yield.

Based on the above observations, one of the possible reaction pathways is shown in Scheme 2. First, the decarbonylation of $ReBr(CO)_5$ to form $ReBr(CO)_4$, which is the coordinative unsaturated 16-electron complex, is the first step of the catalytic reaction.[16] The coordination on the phenylacetaldehyde, which is generated in situ by the hydrolysis of acetal **1a** with H_2O, followed by the regioselective electrophilic addition of the Re-aldehyde complex **I** to C2 of the alkynes **2** forms the alkenyl cation **II**. Intramolecular electrophilic attack of **II** on the aromatic ring followed by elimination of a proton generates the cyclization product **III**, which aromatizes to form the naphthalene derivatives **3** and regenerate the catalytic active species. For the reaction of unsymmetrical diaryl acetylenes, it was suggested that the stability of the alkenyl cation intermediate **II** played an important role in the selectivity of the products.

In conclusion, we have developed a rhenium complex-catalyzed reaction of phenylacetaldehyde dimethylacetal (**1a**) with alkynes **2** in the presence of H_2O, giving the corresponding 1,2-disubstituted naphthalenes in moderate to good yields. The application of the reaction and the investigation of the reaction mechanism are now in progress.



Scheme 1. Reaction of **1a** with unsymmetrical diaryl acetylenes **2r**-**t**.



Scheme 2. A possible reaction pathway of **1a** with alkyne **2**.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.10.123.

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