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Ruthenium-Catalyzed Cycloaddition of Propargylic Alcohols with Phenol Derivatives via Allenylidene Intermediates: Catalytic Use of the Allenylidene Ligand as the C_3 Unit

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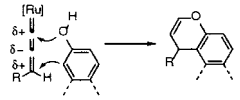
Transition metal allenylidene complexes ($M{=}C{=}C{=}CR_2$), which belong to a series of unsaturated carbene derivatives, have attracted a great deal of attention in recent years as a new type of organometallic intermediate.[1] Although remarkable developments of the reactivity of allenylidene complexes have been attained,[1,2] only a few examples of catalytic reactions via allenylidene intermediates have been reported until now.[3−5] As regards the catalytic activity of allenylidene complexes, we have recently disclosed the ruthenium-catalyzed propargylic substitution reactions of propargylic alcohols[6] with various heteroatom- and carbon-centered nucleophiles to afford the corresponding products in high yields with complete regioselectivities.[7] Interestingly, the reactions are only catalyzed by thiolate-bridged diruthenium complexes[8] such as [Cp*RuCl(μ_2-SR)$_2$RuCp*Cl] (Cp* = η^5-C_5Me_5; R = Me (**1a**)), but not by monomeric ruthenium complexes. A key step of these novel reactions is the selective attack of nucleophiles on the electrophilic C_γ atom in the allenylidene ligand at the thiolate-bridged diruthenium complexes.[7]

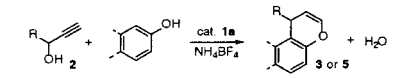
Some theoretical studies of the allenylidene complexes indicate that the C_α and C_γ carbon atoms of allenylidene ligands are the electrophilic centers, while the C_β carbon atom is a nucleophilic center.[9] In fact, a variety of nucleophiles stoichiometrically attack either the C_α or C_γ carbon atom of allenylidene ligands to afford Fischer-type carbenes or alkynyl complexes, respectively.[10] During our study, we have now found the novel unprecedented cycloaddition of propargylic alcohols with phenol derivatives catalyzed by **1** to afford naphthopyrans and benzopyrans with potential use for photochromic materials. In this reaction, both of the electrophilic C_α and C_γ carbon atoms in the allenylidene ligands are subjected to attack by nucleophiles (Chart 1). Preliminary results are described here.

Chart 1



Treatment of 1-phenyl-2-propyn-1-ol (**2a**) and 2-naphthol in $ClCH_2CH_2Cl$ in the presence of **1a**[11] (5 mol %) and NH_4BF_4 (10 mol %) at 60 °C for 1 h afforded 1-phenyl-1*H*-naphtho[2,1-*b*]pyran (**3a**) in 80% isolated (83% GLC) yield (Table 1; run 1). Neither other products nor regioisomers of **3a** were detected by GLC and ^{1}H NMR. The reaction proceeded even at room temperature, but a prolonged reaction time was required to produce **3a**. When 1-naphthol was used in place of 2-naphthol, a mixture of unidentified products was obtained.

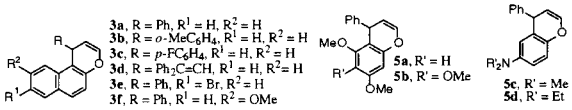
Table 1. Cycloaddition of Propargylic Alcohols with Phenol Derivatives Catalyzed by [Cp*RuCl(μ_2-SMe)$_2$RuCp*Cl] (**1a**)[a]



run	propargylic alcohol	phenol derivative	yield of product, %[b]
1	**2a**, R = Ph	2-naphthol	**3a**, 80 (83)[c]
2	**2b**, R = *o*-MeC_6H_4	2-naphthol	**3b**, 64
3	**2c**, R = *p*-FC_6H_4	2-naphthol	**3c**, 81
4	**2d**, R = $Ph_2C{=}CH$	2-naphthol	**3d**, 69
5	**2a**, R = Ph	6-bromo-2-naphthol	**3e**, 79
6[d]	**2a**, R = Ph	7-methoxy-2-naphthol	**3f**, 97
7[d,e]	**2a**, R = Ph	3,5-dimethoxyphenol (**4a**)	**5a**, 96
8[d,e]	**2a**, R = Ph	3,4,5-trimethoxyphenol (**4b**)	**5b**, 93
9[d,e]	**2a**, R = Ph	4-(dimethylamino)phenol (**4c**)	**5c**, 27
10[f]	**2a**, R = Ph	4-(diethylamino)phenol (**4d**)	**5d**, 50
11[d,g]	**2a**, R = Ph	3,4,5-trimethylphenol (**4e**)	**5e**, 50

[a] All the reactions of **2** (0.60 mmol) with phenol derivative (3.00 mmol) were carried out in the presence of **1a** (0.03 mmol) and NH_4BF_4 (0.06 mmol) in $ClCH_2CH_2Cl$ (15−30 mL) at 60 °C for 1 h. [b] Isolated yield. [c] GLC yield. [d] For 3 h. [e] 10 mol % of **1a** was used. [f] 20 mol % of **1a** was used. [g] For 19 h.

Reactions of various propargylic alcohols have been carried out in the presence of **1a**. Thus, the condensation of 1-aryl- and 1-alkenyl-substituted propargylic alcohols (**2b**−**d**) with 2-naphthol at 60 °C for 1 h proceeded smoothly to afford the corresponding 1-substituted 1*H*-naphtho[2,1-*b*]pyrans (**3b**−**d**) in moderate to high



yields (Table 1; runs 2−4). Unfortunately, the reaction of 1,1-diaryl-substituted propargylic alcohols such as $Ph_2C(OH)C{\equiv}CH$ did not proceed even after a prolonged reaction time (72 h), probably due to the steric bulkiness of two phenyl groups. 6-Bromo-2-naphthol and 7-methoxy-2-naphthol similarly reacted with **2a** to afford similar adducts (**3e** and **3f**) in high yields with complete selectivities (Table 1; runs 5 and 6).

The reactions of **2a** with 3,5-dimethoxyphenol (**4a**) and 3,4,5-trimethoxyphenol (**4b**) gave the corresponding 4*H*-1-benzopyrans (**5a** and **5b**) in excellent yields (Table 1, runs 7 and 8). The molecular structures of **3c** and **5a** were unambiguously clarified by X-ray analysis. When some 4-aminophenols (**4c** and **4d**) were used, the formation of the corresponding pyrans (**5c** and **5d**) was observed in moderate yields (Table 1, runs 9 and 10). A mixture of 4*H*-1-benzopyran (**5e**) and propargylic ether (**5f**) was formed in a 1 to 2 ratio by the reaction of **2a** with 3,4,5-trimethylphenol (**4e**) for 3 h (eq 1), but only **5e** was obtained (50% yield) by prolonging the reaction time to 19 h (Table 1, run 11). It is well-known that Claisen rearrangement of **5f** afforded not **5e** but **5g**. In fact, the *p*-TsOH-catalyzed reaction of 1,1-diarylpropargylic alcohols with

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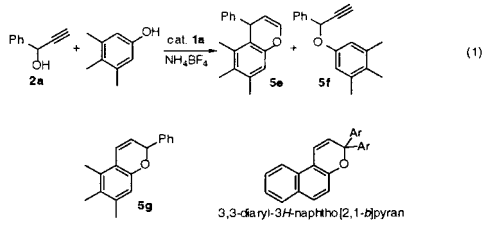
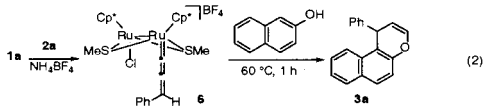


(1)

2-naphthol in the solid state has been reported recently, where only 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyrans, namely the regioisomers of 1,1-diaryl-1*H*-naphtho[2,1-*b*]pyrans (**3**), were obtained in only low to moderate yields via Claisen rearrangement of the initially produced propargylic ethers.[12] This result indicates that the novel reaction presented in this paper did not proceed via Claisen rearrangement of propargylic ethers. We consider that **5f** is transformed into **5e** via allenylidene intermediates (vide infra).

Starting propargylic alcohol (**2a**) was completely recovered in the reaction of **2a** with 1,2,3-trimethoxy- and 1,2,3-trimethylbenzenes. These results show that no propargylation of aromatic compounds occurs under the same reaction conditions. It is noteworthy that the cycloaddition of propargylic alcohols proceeds only when phenols bearing electron-releasing groups are employed. This is in contrast to the propargylic substitution reaction of **2a** where simple phenols are used to produce the corresponding phenyl propargylic ether.[7a]

Treatment of the allenylidene complex (**6**), which could be prepared from the reaction of **1a** with 1 equiv of **2a** in the presence of NH_4BF_4 in tetrahydrofuran (THF) at room temperature for 30 min,[7b] with 5 equiv of 2-naphthol in $ClCH_2CH_2Cl$ at 60 °C for 1 h led to the formation of **3a** in quantitative yield (eq 2). Furthermore,

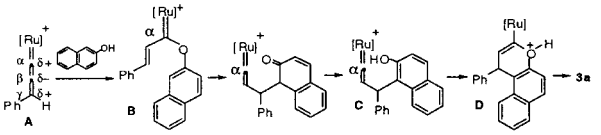


(2)

reaction of **2a** with 2-naphthol in the presence of 5 mol % of **6** at 60 °C for 1 h afforded **3a** in 74% yield. These results indicate that this catalytic reaction proceeds via allenylidene complexes such as **6**.

Because the C_α atom of the allenylidene complexes is favorably attacked by nucleophiles,[13] the catalytic formation of **3a** may occur by the reaction pathways shown in Scheme 1. Thus, the initial attack of the naphthol oxygen to the C_α atom of **A** results in the formation of a carbene complex **B**, which subsequently leads to a vinylidene complex **C** via Claisen rearrangement of **B**. Complex **C** is transformed into an alkenyl complex **D** by nucleophilic attack of the oxygen atom of the hydroxy group to the C_α atom of **C**. However, the possibility of a nucleophilic attack of the carbon atom at position 1 of 2-naphthol to the C_γ atom of the allenylidene complexes may not be excluded. Further investigations to elucidate the detailed reaction mechanism are currently in progress.

Scheme 1



Esteruelas and co-workers have already reported stoichiometric reactions of allenylidene complexes with organic molecules containg two nucleophilic heteroatoms such as pyrazole and 2-aminopyridine to give the corresponding alkenyl complexes with heterocyclic ligands,[14,15] but the cycloaddition described here is the first example of the use of the allenylidene ligands as a C_3 unit in the catalytic process.

In summary, we have found a novel ruthenium-catalyzed cycloaddition of propargylic alcohols with 2-naphthols and phenols bearing electron-donating groups to afford the corresponding 1*H*-naphtho[2,1-*b*]pyrans and 4*H*-1-benzopyrans, respectively, in moderate to excellent yields with a complete regioselectivity. This catalytic reaction provides a simple and efficient one-pot synthetic method for a new type of skeleton of photochromic naphthopyrans and benzopyrans.[16]

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Supporting Information Available: Experimental procedures and spectral data for all of the new compounds (**3** and **5**), and crystallographic data for **3c** and **5a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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