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Bismuth triflate catalyzed Claisen rearrangement of allyl naphthyl ethers

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Abstract—Bismuth triflate was found to be an efficient catalyst for the Claisen rearrangement of allyl naphthyl ethers. The reaction proceeds smoothly with a catalytic amount of bismuth triflate (20 mol %) to afford the corresponding *ortho*-allyl naphthol in moderate to good yields in most cases.

ortho-Allyl naphthols are versatile intermediates in the synthesis of biologically active compounds as 1,4-naphthoquinones[1a] and anthracyclinones.[1b,c] The [3,3] sigmatropic shift (Claisen rearrangement) of allyl aryl ethers can provide convenient access to *ortho*-allyl naphthols.[2] Although the Claisen rearrangement provides an efficient synthetic route for the preparation of *ortho*-allyl naphthols, it usually requires high temperatures to proceed.[1] These forcing conditions lead to severe side reactions. Recently, synthetic methodologies involving rare earth triflates as catalysts for the Claisen rearrangement have been described.[3] High catalytic activity, low toxicity, moisture, and air tolerance of lanthanide triflates make them attractive catalysts. However, the high cost of these catalysts restricts their use. Clearly, there is a need for the development of new cheap Lewis acids that can promote the above reaction in a catalytic way.

Bismuth compounds have attracted recent attention due to low toxicity, low cost, and good stability.[4] Bismuth(III) salts have been reported as catalysts for epoxide opening,[5] imine allylation,[6] Mannich-type reactions,[7] Mukaiyama-aldol reactions,[8] formation and deprotection of acetals,[9] Friedel–Crafts reactions,[10] Fries rearrangement,[11] Diels–Alder reactions,[12] and intramolecular Sakurai cyclizations.[13] $Bi(OTf)_3$ is particularly attractive because it is commercially available or can easily be prepared from commercially available starting materials.[14]

Herein, we report an attractive method using bismuth(III) triflate hydrate ($Bi(OTf)_3{\cdot}xH_2O$, $2.5 < x < 4$)[4b] as a catalyst for the Claisen rearrangement of allyl naphthyl ethers.[15] Double rearrangement of di(allyloxy) naphthalenes is also reported. *ortho*-Allyl naphthols are obtained efficiently in the presence of 20 mol % $Bi(OTf)_3$. Among the various catalyst loadings tested, 20 mol % was found to give the rearrangement to occur with the best yield.

Initially, the Claisen rearrangement was screened on differently substituted allyl 1-naphthyl ethers (Table 1). The naphthol derivatives **1a**–**i** were first allylated according to the usual procedure (allyl bromide, Cs_2CO_3, DMF). The rearrangement occurs with 20 mol % $Bi(OTf)_3{\cdot}xH_2O$ in a polar coordinating solvent such as acetonitrile (Scheme 1). The corresponding *ortho*-allyl naphthols **3a**–**g** were isolated in moderate to good yields. Allyl 1-naphthyl ether **2a** afforded *ortho*-allyl naphthol **3a** with a moderate yield (**3a**, 64%; deprotected 1-naphthol **1a** was also isolated, 4%) (Table 1, entry 1). With various substituents on the naphthol ring, the reaction occurred smoothly to give the corresponding *ortho*-allyl naphthols **3a**–**e** (Table 1, entries 1–5). 1,5-Di(allyloxy)naphthalene **2f** could undergo a selective mono Claisen rearrangement to give compound **3f** with moderate yield (Table 1, entry 6). When a crotyl 1-naphthyl ether was used, a mixture of [3,3] and [1,3] products **3g** and **3g′** was obtained, with

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Keywords: Bismuth; Bismuth(III) triflate; Claisen; Rearrangement; Naphthol; Green chemistry.

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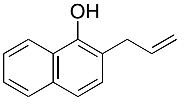
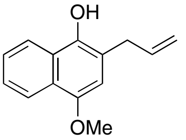
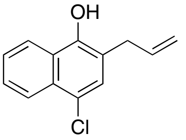
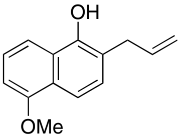
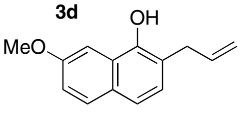
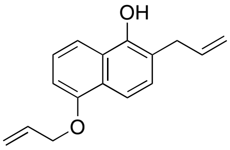
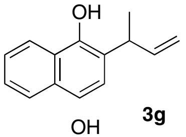
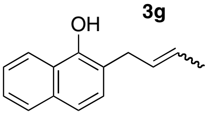
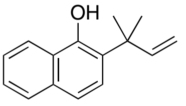
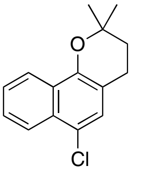
Table 1. $Bi(OTf)_3$ catalyzed *ortho*-Claisen rearrangement of allyl 1-naphthyl ethers

Entry	R^1	R^2	R^3	R^4	T^a (h)	Compound **3**	Yield **3**[b] (%)
1	H	H	H	H	24	 **3a**	64
2	H	4-OMe	H	H	1	 **3b**	85
3	H	4-Cl	H	H	40	 **3c**	57
4	5-OMe	H	H	H	24	 **3d**	61
5	7-OMe	H	H	H	40	 **3e**	62
6	$5\text{-}OCH_2CH{=}CH_2$	H	H	H	1.5	 **3f**	40
7	H	H	H	Me	6	 **3g**  **3g'** (**3g**/**3g'**: 91/9)	65[c]
8	H	H	Me	Me	24	 **3h**	—[d]
9	H	4-Cl	Me	Me	18	 **3i'**	80[e]

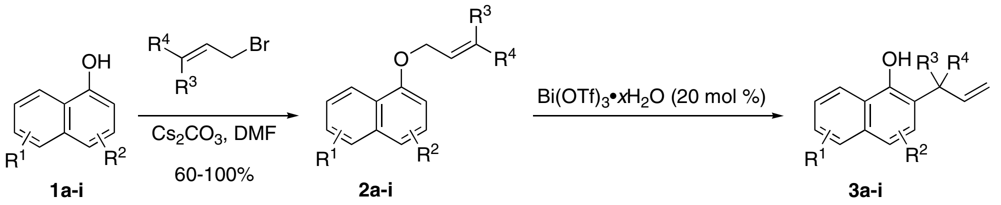
[a] Conditions: 20 mol % $Bi(OTf)_3 \cdot xH_2O$, MeCN, 82 °C, [allyl 1-naphthyl ether] = 0.1 M except 0.5 M for entry 6.

[b] Isolated yield.

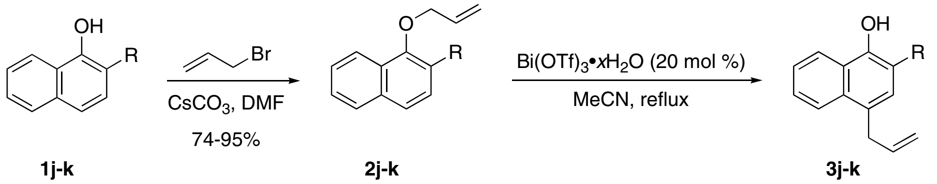
[c] Compounds **3g**/**3g′** ratio was determined by GC and ^1H NMR. Starting material **2g** was a 61/39 mixture of stereoisomers. Compound **3g′** was isolated as a 55/45 mixture of stereoisomers.

[d] Starting material **2h** was recovered.

[e] Reaction performed with 5 mol % $Bi(OTf)_3 \cdot xH_2O$, PhMe, 0 °C, 4 h, 22 °C, 19 h.



Scheme 1.

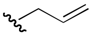


Scheme 2.

the expected Claisen rearrangement being the main pathway ([3,3]/[1,3] = 91:9) (Table 1, entry 7). No rearrangement was observed with the prenyl ether of 1-naphthol (**2h**), and the starting material was recovered (20 mol % $Bi(OTf)_3 \cdot xH_2O$, MeCN, reflux, 24 h) (Table 1, entry 8). However, the transfer of the allyl group in a [1,3] fashion was effective with 4-chloro naphthyl prenyl ether and was immediately followed by cyclization affording **3i′** in a good yield when slightly different conditions were applied (5 mol % $Bi(OTf)_3 \cdot xH_2O$, PhMe, 0 °C, 4 h, 22 °C, 19 h) (Table 1, entry 9). No [3,3] rearranged product was observed in that case. Such a sequential reaction involving a Claisen rearrangement followed by cyclization was already reported in a clay catalyzed rearrangement[16] and a $Sc(OTf)_3$ catalyzed rearrangement in ionic liquids.[17]

We hence further studied the scope and limitations of this reaction with differently 2-substituted allyl 1-naphthyl ethers (Scheme 2). Two examples of $Bi(OTf)_3 \cdot xH_2O$ catalyzed Claisen rearrangement are presented in Table 2. The corresponding *para*-allyl naphthols **3j** and **3k** were obtained in good to very good yields with 20 mol % of $Bi(OTf)_3 \cdot xH_2O$ in acetonitrile. In such case, the *para*-Claisen rearrangement products were obtained through a sequential *ortho*-Claisen rearrangement followed by a second [3,3] rearrangement.

Table 2. $Bi(OTf)_3$ catalyzed *para*-Claisen rearrangement of 2-substituted allyl 1-naphthyl ethers

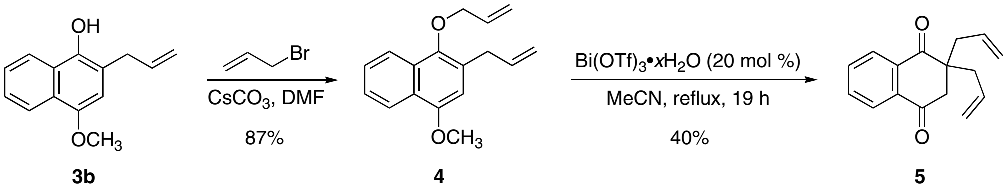
Entry	R	*T*[a] (h)	Compound **3**	Yield **3**[b] (%)
1	Me	0.5	**3j**	86
2		19	**3k**	76

[a] Conditions: 20 mol % $Bi(OTf)_3 \cdot xH_2O$, MeCN, 82 °C.

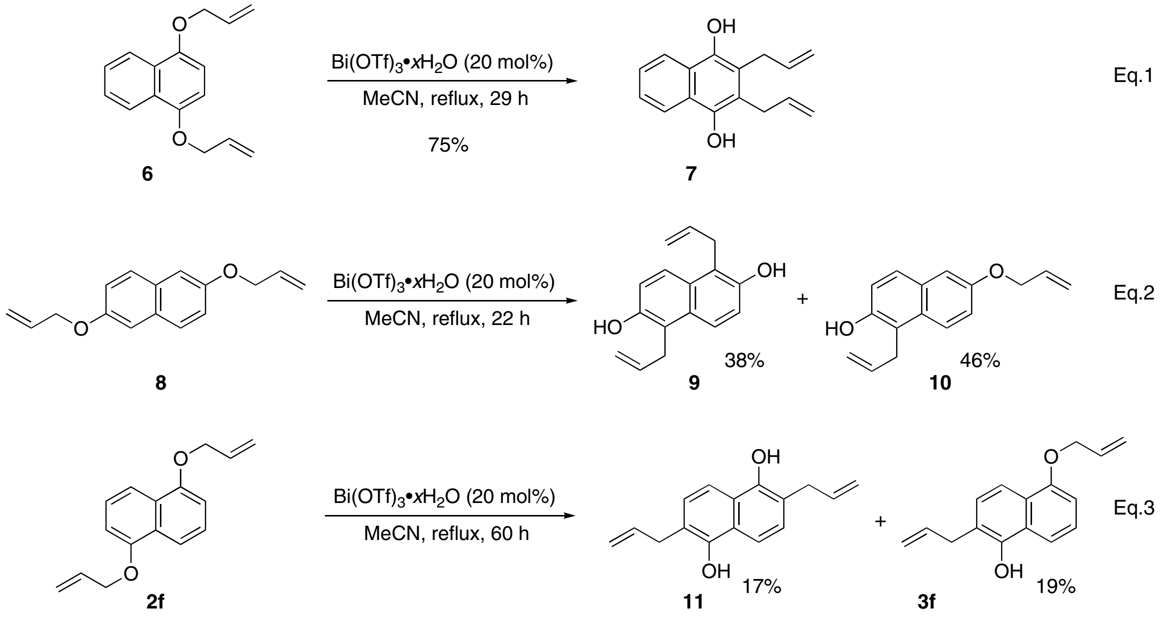
[b] Isolated yield.

When the rearrangement took place on 2,4-disubstituted allyl naphthyl ether **4**, only *ortho*-Claisen rearrangement could occur to yield 2,2-diallyl-2,3-dihydronaphthalene-1,4-dione **5**, presumably after acidic hydrolysis of the enol ether functionality (Scheme 3). Such formation of *ortho*-diallyl ketones was already reported in a microwave-assisted Claisen rearrangement of allyl naphthyl ethers.[18]

The same conditions were applied to various readily available diallyloxy naphthalenes as the corresponding doubly rearranged naphthols are known to be attractive precursors for anthracyclinones (Scheme 4).[1b] 1,4-Di(allyloxy)naphthalene **6** cleanly afforded the corresponding doubly rearranged product (Scheme 4, Eq. 1). 2,6-Di(allyloxy)naphthalene **8** reacted more slowly and a mixture of di- and mono-rearranged products was obtained (1,5-diallylnaphthalene-2,6-diol **9**, 38% and 1-allyl-6-(allyloxy)naphthalen-2-ol **10**, 46%) (Scheme 4, Eq. 2). Similarly, Claisen rearrangement occurred with 1,5-di(allyloxy)naphthalene **2f** leading to a mixture of di- and mono-rearranged products, **11** and **3f**, respectively (Scheme 4, Eq. 3). In this latter case, the conversion was not complete and 25% of the starting material **2f** was recovered. Interestingly, a 0.1 M concentration of starting material was necessary to get the doubly rearranged product **11**, along with **3f**, since a higher concentration (0.5 M) only led to the mono rearranged product **3f** (Scheme 1, Table 1).



Scheme 3.



Scheme 4.

Although the precise mechanism of the bismuth(III) catalyzed Claisen rearrangement has not been elucidated yet, we suppose that the reaction happens by formation of a Bi(III) naphtholate complex. Further investigations on the mechanism of this transformation are in progress.

In summary, we found that $Bi(OTf)_3 \cdot xH_2O$ is an efficient catalyst for the Claisen rearrangement of allyl naphthyl ethers.[19] An optimization of the catalyst amount showed that the reaction works best with a catalyst loading of 20 mol %. The method offers several advantages, including mild reaction conditions, use of a green catalyst, and no formation of decomposition products. Because of its various benefits, the $Bi(OTf)_3 \cdot xH_2O$ protocol should find utility in the synthesis of biologically active compounds. Development of other $Bi(OTf)_3 \cdot xH_2O$ catalyzed Claisen rearrangements and related mechanistic studies will be reported in due course.

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19. *Typical procedure for the* Bi(OTf)$_3$·xH$_2$O *catalyzed Claisen rearrangement of naphthyl allyl ethers* **2a**–**k**, **4**, **6**, and **8**. Under an inert atmosphere of argon, to a solution of allyl naphthyl ether **2** (1 mmol) in acetonitrile (10 mL) was added Bi(OTf)$_3$·xH$_2$O (0.20 mmol). The mixture was magnetically stirred and heated at 82 °C for 1–40 h. The reaction mixture was cooled to room temperature, evaporated, and, after addition of water, extracted with ethyl acetate, dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum (rotary evaporator). The residue was purified by column chromatography on silica gel using hexanes/ethyl acetate (93/7–90/10) as eluent. All the compounds were characterized by IR and ^{1}H NMR, and accord exactly with those previously reported in the literature. The spectral data for compounds **3a**–**b**, **3d**, **3g**–**g′**, **7**, **9**, and **11** accord exactly those reported in the literature.[1a,b,3b,20–24]
2-Allyl-4-chloro-naphthalen-1-ol (**3c**). Reagents: 1-allyloxy-4-chloronaphthalene (400 mg, 1.82 mmol) and Bi(OTf)$_3$·xH$_2$O (260 mg, 0.36 mmol). The reaction was stirred for 40 h and quenched according to the typical procedure. The crude product was purified by column chromatography on silica gel to afford 260 mg (57%) of **3c** as a reddish solid; mp 48–50 °C; R_f 0.31 (hexane/ethyl acetate = 93:7); IR (KBr): $\nu = 3511$ (br), 3081, 2920, 2865, 1622, 1596, 1571, 1505, 1458, 1426, 1264, 1229, 909, 763; ^{1}H NMR (CDCl$_3$): $\delta = 8.18$ (2H, m), 7.45 (2H, m), 7.32 (1H, s), 6.04 (1H, m), 5.55 (1H, s), 5.20–5.40 (2H, m), 3.55 (2H, d, $J = 2.3$ Hz); ^{13}C NMR (CDCl$_3$): $\delta = 145.1$, 131.7, 126.8, 124.4, 123.1, 122.3, 122.2, 120.5, 119.4, 113.9, 110.0, 31.8; HRMS: calcd for C$_{13}$H$_{11}$ClO (M$^+$) 218.0498, found 218.0503.
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