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Bi(OTf)$_3$-catalyzed allylation of epoxides: a facile synthesis of homoallylic alcohols

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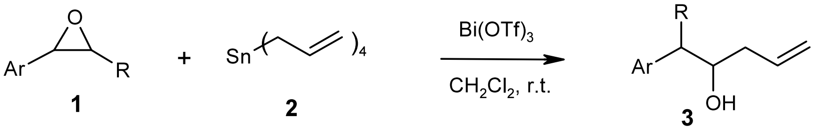
Abstract—Epoxides react smoothly with tetraallyltin in the presence of 2 mol% of Bi(OTf)$_3$ under mild reaction conditions to afford the corresponding homoallylic alcohols in excellent yields with high regioselectivity while aryl aziridines produce exclusively allyl amines in good yields under similar conditions.

The stereoselective addition of allylmetal reagents to aldehydes, imines and epoxides is one of the most important carbon–carbon bond forming reactions in organic synthesis.[1] In particular, Lewis acid catalyzed carbon–carbon bond forming reactions are of great significance in organic synthesis because of their high reactivity, selectivity and mild reaction conditions.[2] Epoxides and aziridines are versatile building blocks for the synthesis of many bioactive natural products.[3] They are well-known carbon electrophiles capable of reacting with various nucleophiles and their ability to undergo regioselective ring opening reactions contributes largely to their synthetic value.[4] Despite a number of methods that have been reported for the cleavage of epoxides and aziridines with various nucleophiles,[5] only a few methods are reported for the allylation of epoxides and aziridines with allylmetal reagents.[6] Moreover, many of these methods produce a mixture of products and thus the desired products are obtained in low to moderate yields. Therefore, the development of simple and novel reagents, which are more efficient and provide convenient procedures with improved yields, is needed.

Recently, bismuth(III) triflate has attracted the interest of synthetic organic chemists because it is inexpensive and can be easily prepared, even on multi-gram scale, in the laboratory from commercially available bismuth(III) oxide and triflic acid.[7] Owing to its unique catalytic properties, bismuth(III) triflate has been extensively used for a plethora of organic transformations[8] including rearrangement of oxiranes.[9] However, there have been no reports on the allylation of epoxides with allyltin reagents employing Bi(OTf)$_3$ as catalyst.

Herein, we wish to report the use of Bi(OTf)$_3$ as a remarkable Lewis acid for the allylation of aryl epoxides with tetraallyltin to produce the corresponding homoallylic alcohols under mild conditions (Scheme 1).

Accordingly, treatment of styrene oxide with tetraallyl tin in the presence of 2 mol% Bi(OTf)$_3$ afforded the corresponding 1-phenyl-4-penten-2-ol in 87% yield (entry **a**). In a similar fashion, various aryl substituted epoxides reacted smoothly with tetraallyl tin to give the correspnding homoallylic alcohols in excellent yields. Cycloalkyl oxiranes such as 1,2-dihydronaphthalene oxide and indene oxide also gave the corresponding homoallylic alcohols (entries **e**, **f**). Even the sterically hindered stilbene oxides and 2-naphthyl oxirane afforded the respective homoallylic alcohols in high



Scheme 1.

Keywords: bismuth triflate; allylation; oxiranes; homoallylic alcohols.

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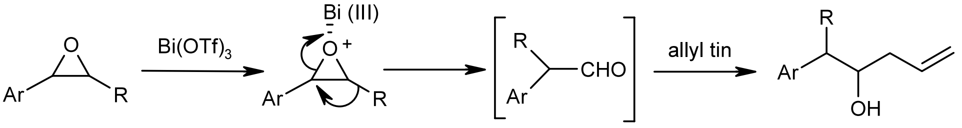
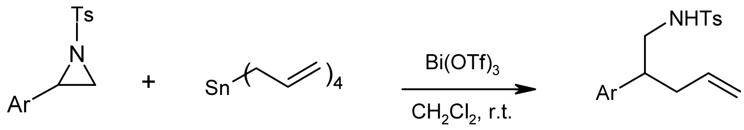
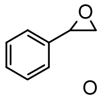
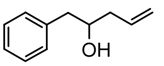
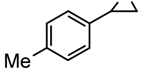
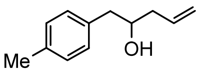
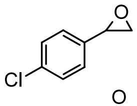
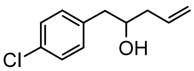
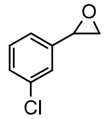
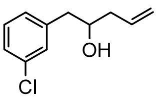
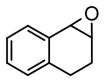
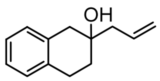
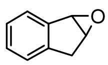
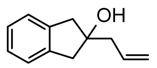
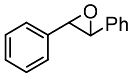
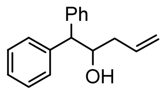
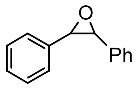
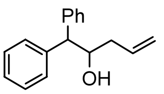
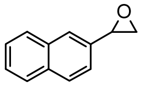
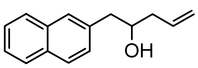
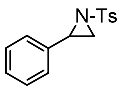
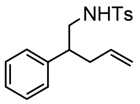
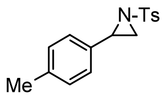
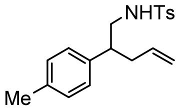
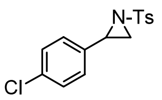
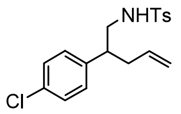


Scheme 2.



Scheme 3.

Table 1. Bi(OTf)$_3$-catalyzed allylation of epoxides and aziridines

Entry	Epoxide/aziridine	Product[a]	Yield (%)[b]	Time(h)
a			87	0.5
b			89	1.0
c			85	1.5
d			90	1.5
e			88	2.0
f			85	1.5
g			92	2.0
h			90	2.5
i			87	2.0
j			82	2.0
k			80	2.5
l			85	2.0

a:All products were characterized by ^{1}H NMR, IR and mass spectroscopy.
b:Yield refers to pure products after column chromatography.

yields (entries **g**, **h**, **i**). In all cases, the reactions proceeded rapidly at room temperature with high selectivity. No regioisomers were detected in the ^{1}H NMR spectrum of crude products. This clearly indicates that the oxiranes do not undergo cleavage with tetraallyltin under these reaction conditions. Initially, the epoxides undergo rearrangement in the presence of $Bi(OTf)_3$ to generate the corresponding aldehydes. These in situ formed aldehydes react rapidly with tetraallyl tin to afford the corresponding homoallylic alcohols (Scheme 2).

However, in the absence of catalyst, the reactions did not proceed even under reflux conditions after a long reaction time (8–12 h). Interestingly, a 2-phenylaziridine also underwent cleavage rapidly with tetraallyl tin in the presence of 2 mol% $Bi(OTf)_3$ to give the corresponding 2-phenyl-*N*-(*p*-toluenesulfonyl)-pent-4-en-1-amine in 82% yield (entry **j**). The allyl transfer occurred exclusively at the benzylic carbon to produce the γ-amino olefin (Scheme 3).

Similarly, *p*-methyl- and *p*-chlorophenylaziridines were opened with tetraallyl tin to generate the corresponding γ-amino olefin derivatives (entries **k**, **l**). The product obtained from *p*-chlorophenylaziridine is a key intermediate for the synthesis of the antispastic agent, Baclofen.[10] Arylaziridines underwent cleavage in a regioselective manner with preferential attack at the benzylic position. In the case of aryl aziridines, the reactions proceeded efficiently at room temperature with high regioselectivity. Among the various metal triflates such as $Bi(OTf)_3$, $Yb(OTf)_3$, $In(OTf)_3$ and $Ce(OTf)_3$ tested for this transformation, bismuth(III) triflate was found to be the most effective catalyst in terms of conversion and reaction rates. However, 5 mol% of scandium triflate also gave similar results under the present reaction conditions. As solvent, dichloromethane appeared to give the best results. Other allylating agents such as allyltributylstannane and allyltrimethylsilane also reacted smoothly with epoxides in the presence of 2 mol% $Bi(OTf)_3$, but the reactions took longer and the products were obtained in only moderate yields. The scope and generality of this process is illustrated with respect to various epoxides, aziridines and tetraallyl tin and the results are presented in Table 1.[11]

In summary, this paper describes a mild and efficient protocol for the allylation of aryl substituted epoxides and aziridines with tetraallyl tin using bismuth(III) triflate as a novel catalyst. This method is a useful and attractive strategy for the preparation of homoallylic alcohols from epoxides in a single operation.

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11. ***General procedure***: A mixture of the epoxide (2 mmol), bismuth triflate (0.05 mmol) and tetraallyltin (1 mmol) in dichloromethane (10 mL) was stirred at room temperature for the specified time (see Table 1). After completion of the reaction as indicated by TLC, the reaction mixture was quenched with water (15 mL) and extracted with dichloromethane (2×10 mL). Evaporation of the solvent followed by purification on silica gel (Merck, 100–200 mesh, ethyl acetate–hexane, 0.5–9.5) afforded the pure homoallylic alcohol. The spectroscopic data of all the products were identical with data reported in literature.[10,12] Spectral data for selected products: **3a**: ^{1}H NMR ($CDCl_3$) δ: 1.50–1.60 (br s, 1H, OH), 2.10–2.38 (m, 2H), 2.60–2.80 (m, 2H), 3.79–3.85 (m, 1H), 5.05 (dd, 1H, $J=1.9$, 10.2 Hz), 5.15 (dd, 1H, $J=1.9$, 17.3 Hz), 5.75–5.90 (tdd, 1H, $J=6.5$, 10.2, 17.3 Hz), 7.15–7.38 (m, 5H). IR (KBr): ν 3415, 2925, 2855, 1641, 1494, 1453, 1076, 1033, 915, 746 cm^{-1}. EIMS: *m*/*z*: 162 M$^+$, 121, 103, 92. HRMS calcd. for $C_{11}H_{14}O$: 162.1045. Found: 162.1019. **3f**: ^{1}H NMR ($CDCl_3$) δ: 1.95 (br s, 1H, OH), 2.50 (d, 2H, $J=6.4$ Hz), 2.90 (d, 2H, $J=17.5$ Hz), 3.05 (d, 2H, 17.5 Hz), 5.15 (dd, 1H, $J=1.8$, 10.3 Hz), 5.20 (dd, 1H, $J=1.8$, 17.3 Hz), 5.90–6.05 (tdd, 1H, $J=6.4$, 10.3, 17.3 Hz), 7.15–7.30 (m, 4H). IR (KBr): ν 3410, 3072, 2925, 1579, 1480, 1273, 1024, 915, 735 cm^{-1}. EIMS: *m*/*z*: 174 M$^+$, 155, 139, 131, 112, 103, 89, 76, 69, 52, 42. HRMS calcd. for $C_{12}H_{14}O$: 174.1044. Found: 174.1068. **3h**: ^{1}H NMR ($CDCl_3$) δ: 1.80 (br s, 1H, OH), 2.15–2.40

(m, 2H), 4.0 (d, 1H, $J=6.7$ Hz), 4.39–4.50 (m, 1H), 5.10 (dd, 1H, $J=1.7$, 10.2 Hz), 5.20 (dd, 1H, $J=1.7$, 17.3 Hz), 5.90–6.10 (tdd, 1H, $J=6.5$, 10.2, 17.3 Hz), 7.20–7.50 (m, 10H). IR (KBr) v: 3415, 2930, 1664, 1595, 1497, 1301, 1221, 1071, 757 cm^{-1} EIMS: m/z: 238 M^+, 196, 168, 152, 140, 112, 89, 65, 42. HRMS calcd. for $C_{17}H_{18}O$: 238.1357. Found: 238.1329.

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