Lewis Acid-Catalyzed Allylic Amination of Allylsilanes and Allylstannanes with [*N*-(*p*-Toluenesulfonyl)imino]phenyliodinane

Dae Young Kim,* Hee Suk Kim, Eun Ju Park, Joo Yang Mang, and Kilsung Lee†

Department of Chemistry, Soonchunhyang University, Asan P. O. Box 97, Chungnam 336-600, Korea
†Cheil Industries Inc. Euiwang, Kyoungki 437-010, Korea
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The preparation of allylic amines has been an area of considerable activity in recent years due primarily to their key function as intermediate in organic synthesis,[1] as well as their biological properties[2] and their presence in several natural products.[3] A number of synthetic methods for the preparation of allylic amines are now known.[4] Some representative examples include nucleophilic allylic substitutions[5] and allylic amination of alkenes.[6]

In the course of our studies on the development of new synthetic methods using hypervalent iodine compounds, we have reported the synthetic method for the preparation of β-keto phosphonates from silyl enol ethers using iodosobenzene,[7] allylation of aromatic compounds by the reaction of allylsilane with aromatic compounds using hypervalent iodine compound,[8] aziridination of vinylphosphonates using [*N*-(*p*-toluenesulfonyl)imino]phenyliodinane (PhI=NTs),[9] and transformation of allylsilanes into allylic amines using PhI=NTs.[10] Herein we report the transformation of allylsilanes and allylstannanes into allylic amines using PhI=NTs as amination reagent in more details.

Table 1 shows that the Lewis acid catalyzed amination of allylsilanes and allylstannanes with PhI=NTs provided moderate yields of allylic amines in both polar and nonpolar media. The reaction rate and the efficiency are enhanced when more polar solvent, such as acetonitrile, is employed. In solvents of lower polarity such as methylene chloride and benzene, the reactions are substantially slower and some cases provide lower yields of products.

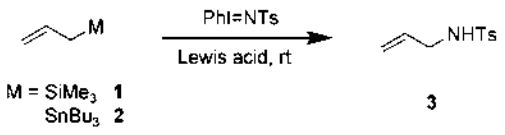
Amination of allylsilanes and allylstannanes with PhI=NTs did not proceed in the absence of $Cu(OTf)_2$. The yields when using catalytic $Cu(OTf)_2$ (10 mmol) as the Lewis acid were higher than using 1 equiv. of $BF_3 \cdot OEt_2$ (entry 1 and 3). In the presence of 10 mol % of $Cu(OTf)_2$, a slight excess of the PhI=NTs (1.5 equiv.) reacted with allylsilanes and allylstannanes (the stoichiometrically limiting component except in entry 3) to form the *N*-tosylallyl amines. The use of 10 mol % of $Cu(OTf)_2$ in acetonitrile at room temperature was found to be the optimal catalyst load-solvent combination for the amination of allylstannanes using PhI=NTs. As shown in Table 1, the yields are moderate, however, small amounts of the *p*-toluenesulfonamide were observed. This is thought to arise from the decomposition of PhI=NTs under the reaction conditions.

Table 1. Preparation of allylic amines from allylsilanes and allylstannanes

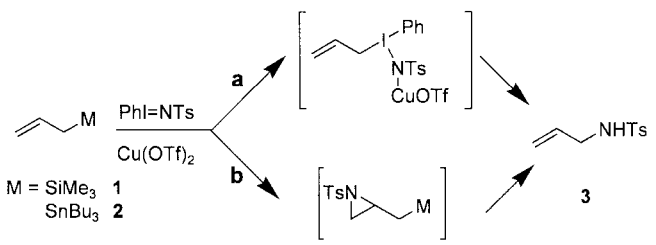
entry	allyl reagents	Lewis acid	solvent	time (h)	yield (%)[a]	products
1		$Cu(OTf)_2$	CH_3CN	0.5	**3a**, 78	
2		$Cu(OTf)_2$	C_6H_6	16	**3a**, 62	
3		$BF_3 \cdot OEt_2$	CH_2Cl_2	12	**3a**, 56	
4		$Cu(OTf)_2$	CH_3CN	0.5	**3b**, 62	
5		$Cu(OTf)_2$	C_6H_6	16	**3b**, 59	
6		$Cu(OTf)_2$	CH_3CN	0.5	**3c**, 52	
7		$Cu(OTf)_2$	CH_3CN	2.5	**3a**, 72	
8		$Cu(OTf)_2$	C_6H_6	60	**3a**, 62	
9		$Cu(OTf)_2$	C_6H_6	60	**3a**, 60[b]	
10		$Cu(OTf)_2$	CH_3CN	2.5	**3d**, 58	
11		$Cu(OTf)_2$	CH_3CN	2.5	**3e**, 65	

[a]Yields are isolated ones. [b]The reaction carried out using PhI=NTs (1 equiv) and excess allylstannane (5 equiv).

On the basis of these results, we speculated that the reaction proceeds *via* allyliodine(III) intermediate (Scheme 2, a). The first step of the reaction is presumable the nucleophilic



Scheme 1



Scheme 2

attack of the allylic metals on electron deficient iodine atom of the activated PhI=NTs, yielding the reactive allyliodine intermediate followed by 1,2-shift of nitrogen to allylic amines. Another plausible mechanism of the reaction is route b in Scheme 2. The first addition product is the aziridine which undergo desilylation (destannulation) to afford the allylic amines.

In summary, we have developed a new synthetic procedure for the preparation of allylic amines from allylsilanes and allylstannanes using PhI=NTs in the presence of $Cu(OTf)_2$ as the catalyst.

Experimental Section

General. ^{1}H NMR spectra were recorded on a Bruker AC 200 spectrometer using tetramethylsilane as an internal standard. Chemical shifts are measured in part per million(δ) and coupling constants, J, are reported in Hz. Multiplicity was simplified such as s = singlet, br = broad, d = doublet, t = triplet, dt = double triplet, and m = multiplet. All reactions were carried out under nitrogen atmosphere. Acetonitrile and benzene were distilled from calcium hydride and stored over 4 Å molecular sieve. Methylene chloride was refluxed and distilled from phosphorus pentoxide. Column chromatography was performed on Merck silica gel 60 (230-400 mesh). PhI=NTs was prepared according to the reported procedure.[11]

The General Experimental Procedure. To a stirred suspension of $Cu(OTf)_2$ (36 mg, 0.1 mmol), dry acetonitrile (5 mL), 4 Å molecular sieve (100 mg), and PhI=NTs (560 mg, 1.5 mmol) was added allylsilane or allylstannane (1.0 mmol) under dry nitrogen atmosphere. The resulting heterogeneous mixture was stirred for 0.5-2.5 h at room temperature. The reaction mixture was filtered with silica gel pad. The filtrate was concentrated in vacuum. The residue was purified by silica gel column chromatography to give *N*-tosylallyl amines.

***N*-Allyl-*p*-toluenesulfonamide (3a)**.[5e] ^{1}H NMR ($CDCl_3$) δ 7.70 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 5.70-5.59 (m, 1H), 5.20-5.00 (m, 2H), 4.52 (br, 1H), 3.62-3.55 (m, 2H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 143.5, 136.9, 132.9, 129.7, 127.1, 117.7, 45.8, 21.5.

***N*-(2-Chloromethyl)allyl-*p*-toluenesulfonamide (3b)**. ^{1}H NMR ($CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 5.17 (s, 1H), 5.06 (s, 1H), 4.65 (br, 1H), 4.02 (s, 2H), 3.70 (d, J = 6.5 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 145.6, 140.5, 136.7,129.8, 125.7, 110.2, 50.1, 45.8, 21.6.

***N*-(2-Acetoxymethyl)allyl-*p*-toluenesulfonamide (3c)**. ^{1}H NMR ($CDCl_3$) δ 7.75 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 5.10-5.30 (m, 2H), 4.49 (s, 2H), 3.57-3.60 (m, 2H), 2.42 (s, 3H), 2.02 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 175.4, 148.7, 140.9, 136.8,129.7, 127.4, 110.4, 71.5, 45.7, 21.4, 17.8.

***N*-(Cyclopent-2-enyl)-*p*-toluenesulfonamide (3d)**. ^{1}H NMR ($CDCl_3$) δ 7.75 (d, J = 7.8 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H), 5.30-5.71 (m, 2H), 4.39 (br, 1H), 3.50-3.62 (m, 1H), 2.43 (s, 3H), 2.40-2.20 (m, 2H), 2.20-1.95 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 134.2, 133.5, 130.9,129.7, 127.1, 125.4, 45.4, 31.9, 29.7, 21.5.

***N*-(Cyclohex-2-enyl)-*p*-toluenesulfonamide (3e)**.[1b] ^{1}H NMR ($CDCl_3$) δ 7.89 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 5.80-5.61 (m, 1H), 5.43-5.30 (m, 1H), 5.11 (br, 1H), 4.78 (br, 1H), 2.41 (s, 3H), 1.91-1.48 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 143.2, 138.3, 131.2,129.5, 127.0, 126.9, 48.9, 30.1, 24.4, 21.4, 19.3.

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