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TRANSFORMATION OF ALLYLIC SILANES INTO ALLYLIC AMINES USING [N-(*P*-TOLUENESULFONYL)IMINO]PHENYLIODINANE

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Abstract : Reaction of allylic silanes with PhI=NTs in the presence of catalytic $Cu(OTf)_2$ provides a direct route for the preparation of allylic amines in moderate yields.

Allylic amines are an important class of compounds not only their utility as intermediate in organic synthesis but also because of their physiological properties[1] and their presence in several natural products.[2] A number of synthetic methods for the preparation of allylic amines from alkene derivatives have been developed, but these require severe reaction conditions or several sequential reactions.[3] Previously developed methods such as the Gabriel

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synthesis,[4] allylic displacement reaction using miscellaneous nitrogen nucleophiles,[5] themal and oxidative rearrangements,[6] and Pd(0)-catalyzed allylic amination[7] have met with varying degrees of success in the construction of allylic amines. Recently, allylic amines were also obtained by allylic oxidation of alkenes using diimidoselenium reagents,[8] diimidosulfur reagent,[9] azodicarboxylates,[10] acylnitroso compounds,[11] N-sulfinylcarbamate,[12] molybdooxaziridine complex,[13] catalytic molybdenum[14] or iron[15] complex as the catalysts with N-phenylhydroxylamine as the nitrogen fragment donor. Other micellaneous methods include allylic amination of alkene by [N-(*p*-toluenesulfonyl)imino]phenyliodinane,[16] amination of allylic phenyl tellurides with [N-(*p*-toluenesulfonyl)imino]phenyliodinane or chloramine-T,[17] the reaction of amine with allyl phenyl telluroxide which was prepared from allylic silane and benzenetellurinyl trifluoroacetate.[18]

Here we wish to report a transformation of allylic silanes into allylic amines. Allylic silane was treated with [N-(*p*-toluenesulfonyl)imino]phenyliodinane (PhI=NTs)[19] in the presence of Lewis acid at room temperature for 0.5~16 h. On work up allylic amines were isolated in moderate yields.

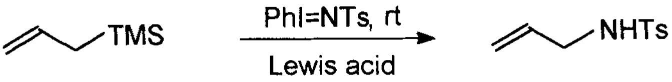
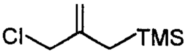
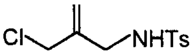
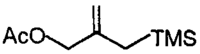
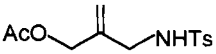
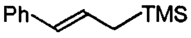
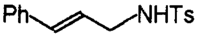


Table 1. Preparation of allylic amines from allylic silanes

entry	allylic silane	Lewis acid	solvent	time (h)	yields (%)	product
1		$Cu(OTf)_2$	CH_3CN	0.5	78	
2		$Cu(OTf)_2$	C_6H_6	16	62	
3		$BF_3.OEt_2$	CH_2Cl_2	12	56	
4		$Cu(OTf)_2$	CH_3CN	0.5	62	
5		$Cu(OTf)_2$	C_6H_6	16	59	
6		$Cu(OTf)_2$	CH_3CN	0.5	52	
7		$Cu(OTf)_2$	C_6H_6	16	37	

As shown in Table 1, the yields are moderate, however, small amounts of the *p*-toluenesulfonamide was observed. This is thought to arise by decomposition of PhI=NTs under the reaction conditions. Reaction carried out with $Cu(OTf)_2$ in acetonitrile afforded slightly higher yields than that carried out in benzene.(entry 1 and 2) Using acetonitrile as the solvent, the reactions were so fast than using benzene or methylene chloride.(entry 1~5) The yields when using catalytic

$Cu(OTf)_2$ (10 mol %) as the Lewis acid were higher than using 1 equiv. of $BF_3{\cdot}OEt_2$.(entry 1 and 3)

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

Experimental

All reactions were carried out under nitrogen atmosphere. Toluene, acetonitrile and benzene were distilled from calsium hydride and stored over 4A° molecular sieves. Products were characterized by comparison with authentic samples (^{1}H-NMR, ^{13}C-NMR, IR, and Mass spectrum). PhI=NTs was prepared according to the reported procedure.[19] Column chromatography was performed on Merck silica gel 60 (230-400 mesh).

The general experimental procedure : To a stirred suspension of $Cu(OTf)_2$ (36 mg, 0.1 mmol), dry acetonitrile (5 mL) and PhI=NTs (449 mg, 1.2 mmol) was added allylic silane (1 mmol) under dry nitrogen atmosphere. The resulting heterogeneous mixture was stirred for 0.5 h at room temperature. The reaction mixture was changed to clear solution, and then this mixture was filtered with silica gel. The filterate was concentrated *in vacuo*. The residure was purified by silica gel column chromatography to give N-tosyl allylic amines.

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