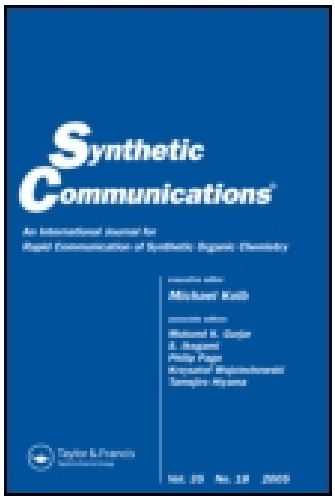

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TRANSFORMATION OF ALLYL STANNANES INTO ALLYL AMINES USING [*N*-(*p*-TOLUENESULFONYL)IMINO]-PHENYLIODINANE

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ABSTRACT

Reaction of allyl stannanes with PhI = NTs in the presence of 10 mol % of $Cu(OTf)_2$ provides a direct route for the preparation of *N*-tosylallyl amines in moderate yields.

The preparation of allyl amines has been an area of considerable activity in recent years due primarily to their key function as intermediates 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 allyl amines from alkene derivatives have been developed, but these require severe reaction conditions or several sequential reactions.[4] Synthetic methods for the preparation of allyl amines by nucleophilic allylic substitutions such as amination of allyl alcohols,[5] the Gabriel synthesis,[6] amination of allyl halides or acetates catalyzed by Pd,[7] Rh,[8] Ir,[9] etc, complexes, or direct

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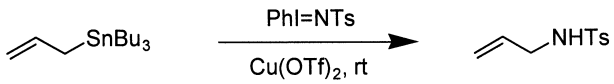
amination of dienes and allenes[10] met with varying degrees of success in the construction of allylic amines. Allyl amines were also obtained by allylic oxidation of simple alkenes using diimido- or imidoselenium reagents,[11] diimido-or imidosulfur reagent,[12] azodicarboxylates,[13] [*N*-(*p*-toluenesulfonyl)imino]phenyliodinane,[14] acyl nitroso compounds,[15] *N*-sulfinylcarbonate,[16] molybdenum oxaziridines,[17] peroxycarbamate,[18] catalytic molybdenum[19] or iron[20] complex as the catalysts and *N*-phenylhydroxyamine, as the nitrogen fragment donor. Other miscellaneous methods include amination of allyl phenyl tellurides with [*N*-(*p*-toluenesulfonyl)imino]phenyliodinane or chloramine-T,[21] the reaction of amine with allyl phenyl telluroxide which was prepared from allyl silane and benzenetellurinyl trifluoroacetate,[22] and the reaction of allyl silanes with (ethoxycarbonyl)nitrene.[23]

We have already demonstrated the transformation of allyl silanes into allyl amines using [*N*-(*p*-toluenesulfonyl)imino]phenyliodinane (PhI = NTs) as aminating agent.[24] We report here the preparation of allyl amines from allyl stannanes using PhI = NTs in the presence of $Cu(OTf)_2$ at room temperature. Amination of allyl stannanes with PhI = NTs did not proceed in the absence of $Cu(OTf)_2$. In the presence of 10 mol % of $Cu(OTf)_2$, a slight excess of the PhI = NTs (1.5 equiv.) reacted with allyl stannanes (the stoichiometrically limiting component except in entry 3) to form the *N*-tosylallyl amines. As shown in Table 1, the yields are moderate. Small amounts of the *p*-toluenesulfonamide were observed as contaminents. This is thought to arise from the decomposition of PhI = NTs under the reaction conditions. The reaction carried out in acetonitrile is much faster than in benzene (entries 1–3). 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 allyl stannanes using PhI = NTs.



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

EXPERIMENTAL

All reactions were carried out under nitrogen atmosphere. Acetonitrile and benzene were distilled from calcium hydride and stored over 4A°

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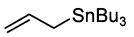
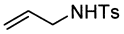
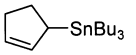
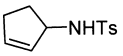
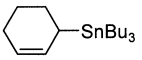
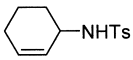
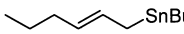
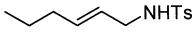
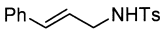
Table 1. Preparation of Allyl Amine from Stannes

entry	allyl stannane	solvent	time (h)	yield (%)[a]	products
1		CH_3CN	2.5	72	
2		C_6H_6	60	62	
3		C_6H_6	60	60[b]	
4		CH_3CN	2.5	58	
5		CH_3CN	2.5	65	
6		CH_3CN	2.5	51	
7		CH_3CN	2.5	26	
				32	

[a] Yields refer to isolated products.

[b] The reaction carried out using PhI=NTs (1 equiv) and excess of allyl stannane (5 equiv).

molecular sieves. ^1H and ^{13}C NMR were measured at 200 and 50 MHz respectively, in $CDCl_3$ with TMS as internal standard. Mass spectra were recorded on Shimadzu GC/MS QP5050 or Jeol HX 100/110. PhI = NTs was prepared according to the reported procedure.[25] Column chromatography was performed on Merck silica gel 60 (230–400 mesh).

General experimental procedure: To a stirred suspension of $Cu(OTf)_2$ (0.1 mmol), dry acetonitrile (5 mL) and PhI = NTs (1.5 mmol) was added allyl stannane (1 mmol) under dry nitrogen atmosphere. The resulting heterogeneous mixture was stirred for 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 chromatograpy to give *N*-tosylallyl amines.

***N*-(Allyl-*p*-toluenesulfonamide (3a)**.[7k] ^1H NMR ($CDCl_3$) δ7.70 (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; HRMS; calcd for $C_{10}H_{13}NO_2S$ 211.0667, found 211.0674.

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***N*-(Cyclopent-2-enyl)-*p*-toluenesulfonamide (3b)**. ^{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; HRMS: calcd for $C_{12}H_{15}NO_2S$ 237.0824, found 237.0831.

***N*-(Cyclohex-2-enyl)-*p*-toluenesulfonamide (3c)**.[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; HRMS: calcd for $C_{13}H_{17}NO_2S$ 251.0980, found 251.0975.

***N*-(Hex-2-enyl)-*p*-toluenesulfonamide (3d)**. ^{1}H NMR ($CDCl_3$) δ 7.75 (d, $J = 8.1$ Hz, 2H), 7.31 (d, $J = 8.1$ Hz, 2H), 5.60–5.45 (m, 1H), 5.43–5.20 (m, 1H), 4.50 (br, 1H), 3.53 (t, $J = 6.3$ Hz, 2H), 2.43 (s, 3H), 2.00–1.85 (m, 2H), 1.50–1.20 (m, 2H), 0.84 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 143.4, 137.8, 137.0, 134.5, 129.7, 129.4, 127.1, 124.4, 45.4, 37.6, 34.1, 22.0, 21.5, 13.6; HRMS: calcd for $C_{13}H_{19}NO_2S$ 253.1136, found 253.1130.

***N*-(1-Phenyl)allyl-*p*-toluenesulfonamide (3e)**. ^{1}H NMR ($CDCl_3$) δ 7.63 (d, $J = 8.2$ Hz, 2H), 7.40–7.05 (m, 7H), 5.98–5.80 (m, 1H), 5.20–5.05 (m, 2H), 4.94 (m, 1H), 4.76 (br, 1H), 2.39 (s, 3H), ^{13}C NMR ($CDCl_3$) δ 142.6, 139.5, 137.6, 134.4, 129.7, 128.5, 127.1, 126.5, 124.6, 52.3, 21.4; HRMS: calcd for $C_{16}H_{17}NO_2S$ 287.0980, found 287.0972

***N*-(3-Phenyl)allyl-*p*-toluenesulfonamide (3f)**. ^{1}H NMR ($CDCl_3$) δ 7.78 (d, $J = 8.1$ Hz, 2H), 7.33–7.24 (m, 7H), 6.45 (d, $J = 16.0$ Hz, 1H), 6.02 (dt, $J = 16.0$, 6.4 Hz, 1H), 4.50 (br, 1H), 3.76 (dt, $J = 6.4$, 1.2 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 143.6, 137.0, 136.0, 133.2, 129.8, 128.6, 128.0, 127.2, 126.4, 124.0, 45.5, 29.7; HRMS: calcd for $C_{16}H_{17}NO_2S$ 287.0980, found 287.0974.

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