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Pd^0/Sn^{II} promoted Barbier-type allylation and crotylation of sulfonimines

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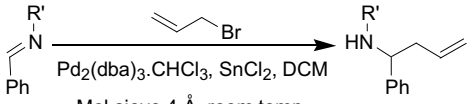
Abstract—A one-pot Barbier protocol is described for the facile formation of homoallyl sulfonamides from sulfonimines and allyl or crotyl bromide in the presence of $SnCl_2$, and catalytic $Pd_2(dba)_3{\cdot}CHCl_3$ at room temperature.

Addition of allyl, propargyl or allenylstannanes to organic electrophiles such as aldehydes, imines and epoxides is a well-known tool for carbon–carbon bond formation in organic chemistry. The far-reaching utility of these reagents have led to the development of Barbier-like protocols wherein reactive organostannanes are generated in situ from Sn(0/II/IV).[1] It is now well demonstrated that the generation of allyltin(IV) from Sn(II) in a Barbier fashion is considerably easier in the presence of a catalytic d^8/d^{10} transition metal.[2] A major event in the catalytic cycle involves facile allyl transfer from the transition metal to tin. We and others have successfully delineated the strategy for regioselective allylation, propargylation and allenylation of carbonyls and epoxides.[2–4] In this communication we demonstrate the further utility of the concept in Barbier-like allylations of conjugatively stabilized imines in general, and sulfonimines in particular, under ambient conditions leading to the corresponding homoallylamine derivatives.

Homoallylamines are important building blocks for the preparation of synthetically and biologically important compounds such as β-amino acids, 1,3-amino alcohols, 1-amino-3,4-epoxides, pyrrolidines and piperidines.[5] The most frequently employed methodology for the synthesis of homoallylamines is the allylation of imines with an allyl-metal reagent.[6,7] To our knowledge, there are only very few reports of facile one-pot, Barbier-like imine allylations using an allyl halide, the metal reagent being Mg(0), Zn(0), In(0), Ga(0), Sm(0) or Zn(0)/In(III).[8] However, there are no such reports in the realm of tin chemistry.

Initially we attempted to allylate a set of *N*-substituted imines derived from benzaldehyde (Scheme 1). The reactions were conducted in a one-pot Barbier fashion utilizing the reagent combination of catalytic $Pd_2(dba)_3{\cdot}CHCl_3$, allyl bromide and $SnCl_2$ in dry DCM at room temperature. The reaction of *N*-benzylbenzaldimine **1a** led to the isolation of the desired *N*-benzyl homoallylamine **2a** in only 11% yield, along with 68% of the corresponding homoallyl alcohol and traces of *N*,*N*-diallyl benzylamine. On the other hand *N*-phenylbenzaldimine **1b** yielded 33% of homoallylamine **2b** besides homoallyl alcohol (40%), and *N*,*N*-diallyl aniline (trace). Similar reaction of *N*-(4-nitrophenyl)benzaldimine **1c** yielded 39% of homoallylamine **2c** along with homoallyl alcohol (30%). Gratifyingly, the reactions of *N*-benzoylbenzaldimine **1d**, and *N*-tosylbenzaldimine **1e**, were facile and free from side reactions, and were complete within 14 h. Work-up gave the desired homoallyl benzamide **2d**, and homoallyl sulfonamide **2e** in 81% and 89%



1

1a, R' = $PhCH_2$-
1b, R' = Ph-
1c, R' = *p*-NO_2Ph-
1d, R' = PhC(O)-
1e, R' = *p*-$TolSO_2$-

2

2a, 11%
2b, 33%
2c, 39%
2d, 81%
2e, 89%

Scheme 1. Allylation of *N*-substituted benzaldimines.

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Table 1. One-pot Barbier allylation of sulfonimine **1e**: effect of catalyst[a]

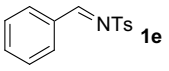
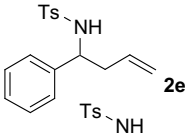
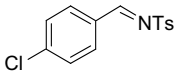
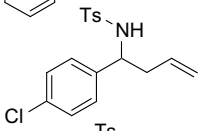
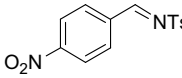
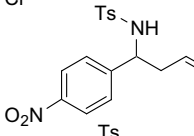
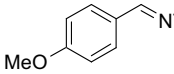
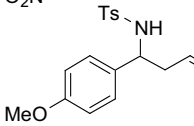
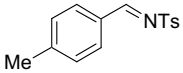
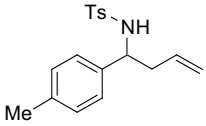
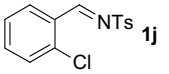
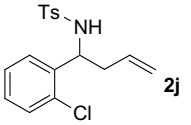
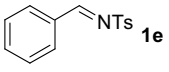
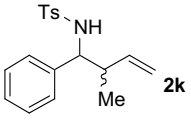
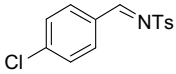
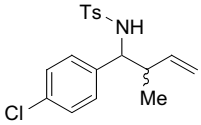
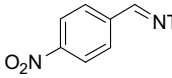
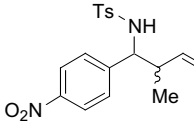
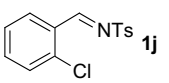
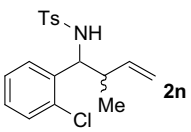
Entry	Catalyst	Yield of **2e** (%)
1	$Pd_2(dba)_3{\cdot}CHCl_3$	89
2	$Pd(dba)_2$	71
3	$PdCl_2$	Trace
4	$Pd(PPh_3)_4$	35
5	$PdCl_2(MeCN)_2$	17
6	$PdCl_2(PPh_3)_2$	21
7	$NiCl_2(PPh_3)_2$	0
8	$PtCl_2(PPh_3)_2$	25
9	$CuCl(SMe_2)$	36

[a] Reagents and conditions: allyl bromide (2 mmol), $SnCl_2$ (1.5 mmol), catalyst (1 mol %), mol sieve 4 Å, sulfonimine (1 mmol).

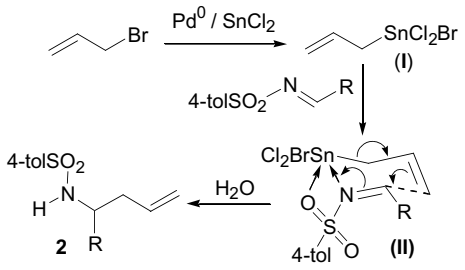
yields, respectively. The above results indicate that conjugatively stabilized imines are better tuned for the present Barbier allylation reaction. Due to their ease of preparation and hydrolytic stability, henceforth we chose sulfonimines for further study.

From the screening of various late transition metal catalysts for the allylation of sulfonimine **1e** (Table 1), $Pd_2(dba)_3{\cdot}CHCl_3$ was adjudged to be the best. Also in our case, dichloromethane was found to be a better solvent than THF, benzene, diethyl ether, and DCE. Attempted reaction with $SnCl_2$ dihydrate gave 56% of **2e**, while reaction in DCM–water (1:1 v/v) led to the formation of homoallyl alcohol as the major product.

Table 2. One-pot Barbier allylation and crotylation of sulfonimines[a]

Entry	Sulfonimine	Product	% Yield (*syn*/*anti*)
1	 **1e**	 **2e**	89
2	 **1f**	 **2f**	83
3	 **1g**	 **2g**	88
4	 **1h**	 **2h**	80
5	 **1i**	 **2i**	84
6	 **1j**	 **2j**	82
7	 **1e**	 **2k**	76 (61/39)
8	 **1f**	 **2l**	72 (71/29)
9	 **1g**	 **2m**	70 (46/54)
10	 **1j**	 **2n**	65 (70/30)

[a] Reagents and conditions: bromide (2 mmol), $SnCl_2$ (1.5 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (1 mol %), mol sieve 4 Å, sulfonimine (1 mmol).



Scheme 2. Proposed pathway for the allylation of sulfonimines.

Using the optimized parameters, the reaction of allyl bromide was tested with various sulfonimines (Table 2). The reactions were complete in 13–17 h. Sulfonimines **1e**–**j** derived from substituted aromatic aldehydes gave the corresponding homoallylamines **2e**–**n** as the exclusive products, and in good to excellent yields (entries 1–10). It should be noted that both electron donating and withdrawing substituents on the aromatic ring are amenable to the reaction. The reaction of crotyl bromide with sulfonimines **1e**–**g** and **1j** resulted in formation of the corresponding homoallylamines **2k**–**n** with 100% γ-regioselectivity, but in varying *syn*/*anti* ratios (entries 7–10).

While mechanistic explorations are warranted, a suggestion is postulated in Scheme 2. Prior formation of allyltrihalostannane **I** from allyl bromide and Pd(0)/Sn(II) occurs via the well-known pathway involving oxidative addition of allyl bromide across palladium and insertion of $SnCl_2$, followed by reductive elimination.[2] Subsequently, the allyltin(IV) species could be activated by the sulfonimine via N-, and O-coordination as in six-membered transition state **II**.[9] Concomitant S_E2' attack followed by hydrolysis would furnish the homoallylamine.

In summary, we have presented a Pd(0)/$SnCl_2$ mediated Barbier-type allylation of imines.[10] Due to the operational simplicity and mild conditions, this one-pot allylation is expected to be attractive, and useful. Investigations are underway to broaden the scope using other conjugated imine systems possessing donor atoms.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.07.201.

References and notes

1. Reviews: (a) Li, C.-J. *Chem. Rev.* **2005**, *105*, 3095–3165; (b) Denmark, S. E.; Fu, J. *Chem. Rev.* **2003**, *103*, 2763–2793; (c) Marshall, J. A. *Chem. Rev.* **2000**, *100*, 3163–3185.
2. (a) Thoonen, S.; Deelman, B. J.; Koten, G. V. *Tetrahedron* **2003**, *59*, 10261–10268; (b) Takahara, J. P.; Masuyama, Y.; Kurusu, Y. *J. Am. Chem. Soc.* **1992**, *114*, 2577–2586.
3. Selected references: (a) Tan, X.-H.; Shen, B.; Deng, W.; Zhao, H.; Liu, L.; Guo, Q.-X. *Org. Lett.* **2003**, *5*, 1833–1835; (b) Tan, X.-H.; Shen, B.; Liu, L.; Guo, Q.-X. *Tetrahedron Lett.* **2002**, *43*, 9373–9376; (c) Imai, T.; Nishida, S. *J. Chem. Soc., Chem. Commun.* **1994**, 277–278; (d) Masuyama, Y.; Takahara, J. P.; Kurusu, Y. *Tetrahedron Lett.* **1989**, *30*, 3437–3440; (e) Masuyama, Y.; Takahara, J. P.; Kurusu, Y. *J. Am. Chem. Soc.* **1988**, *110*, 4473–4474.
4. (a) Roy, U. K.; Roy, S. *Tetrahedron* **2006**, *62*, 678–683; (b) Banerjee, M.; Roy, U. K.; Sinha, P.; Roy, S. *J. Organomet. Chem.* **2005**, *690*, 1422–1428; (c) Banerjee, M.; Roy, S. *Org. Lett.* **2004**, *6*, 2137–2140; (d) Sinha, P.; Roy, S. *Organometallics* **2004**, *23*, 67–71; (e) Banerjee, M.; Roy, S. *Chem. Commun.* **2003**, 534–535; (f) Kundu, A.; Prabhakar, S.; Vairamani, M.; Roy, S. *Organometallics* **1999**, *18*, 2782–2785; (g) Kundu, A.; Prabhakar, S.; Vairamani, M.; Roy, S. *Organometallics* **1997**, *16*, 4796–4799.
5. (a) Felpin, F.-X.; Girard, S.; Vo-Thanh, G.; Robins, R. J.; Villieras, J.; Lebreton, J. *J. Org. Chem.* **2001**, *66*, 6305–6312; (b) Wright, D. L.; Schulte, J. P., II; Page, M. A. *Org. Lett.* **2000**, *2*, 1847–1850; (c) Laschat, S.; Kunz, H. *J. Org. Chem.* **1991**, *56*, 5883–5889.
6. Reviews: (a) Enders, D.; Reinhold, U. *Tetrahedron: Asymmetry* **1997**, *8*, 1895–1946; (b) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207–2293.
7. Selected recent references on imine allylation under non-Barbier conditions: allyl-Mg/Zn: (a) Jain, R. P.; Williams, R. M. *J. Org. Chem.* **2002**, *67*, 6361–6365; (b) Sluis, M. V. D.; Dalmolen, J.; Lange, B. D.; Kaptein, B.; Kellogg, R. M.; Broxterman, Q. B. *Org. Lett.* **2001**, *3*, 3943–3946; (c) Jones, P.; Knochel, P. *J. Org. Chem.* **1999**, *64*, 186–195; (d) El-Shehawy, A. A.; Omara, M. A.; Ito, K.; Itsuno, S. *Synlett* **1998**, 367–368; allyl-B: (e) Wada, R.; Shibuguchi, T.; Makino, S.; Oisaki, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2006**, *128*, 7687–7691; (f) Solin, N.; Wallner, O. A.; Szabo, K. J. *Org. Lett.* **2005**, *7*, 689–691; (g) Itsuno, S.; Yokoi, A.; Kuroda, S. *Synlett* **1999**, 1987–1989; allyl-Si: (h) Rabbat, P. M. A.; Valdez, S. C.; Leighton, J. L. *Org. Lett.* **2006**, *8*, 6119–6121; (i) Friestad, G. K.; Korapala, C. S.; Ding, H. *J. Org. Chem.* **2006**, *71*, 281–289; (j) Shimizu, M.; Itou, H.; Miura, M. *J. Am. Chem. Soc.* **2005**, *127*, 3296–3297; (k) Yamasaki, S.; Fujii, K.; Wada, R.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2002**, *124*, 6536–6537; (l) Billet, M.; Klotz, P.; Mann, A. *Tetrahedron Lett.* **2001**, *42*, 631–634; (m) Wang, D.-K.; Zhou, Y.-G.; Tang, Y.; Hou, X.-L.; Dai, L.-X. *J. Org. Chem.* **1999**, *64*, 4233–4237; (n) Nakamura, K.; Nakamura, H.; Yamamoto, Y. *J. Org. Chem.* **1999**, *64*, 2614–2615; allyl-Sn: (o) Colombo, F.; Annunziata, R.; Benaglia, M. *Tetrahedron Lett.* **2007**, *48*, 2687–2690; (p) Li, G.-I.; Zhao, G. *Synthesis* **2006**, 3189–3194; (q) Wallner, O. A.; Olsson, V. J.; Eriksson, L.; Szabo, K. J. *Inorg. Chim. Acta* **2006**, *359*, 1767–1772; (r) Szabo, K. J. *Synlett* **2006**, 811–824; (s) Das, B.; Laxminarayana, K.; Ravikanth, B.; Ramarao, B. *Tetrahedron Lett.* **2006**, *47*, 9103–9106; (t) Yin, Y.; Zhao, G.; Li, G.-L. *Tetrahedron* **2005**, *61*, 12042–12052; (u) Fernandes, R. A.; Stimac, A.; Yamamoto, Y. *J. Am. Chem. Soc.* **2003**, *125*, 14133–14139; (v) Aspinall, H. C.; Bissett, J. S.; Greeves, N.; Levin, D. *Tetrahedron Lett.* **2002**, *43*, 323–325; (w) Fang, X.; Johannsen, M.; Yao, S.; Gathergood, N.; Hazell, R. G.; Jorgensen, K. A. *J. Org. Chem.* **1999**, *64*, 4844–4849; (x) Nakamura, H.; Nakamura, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4242–4243.

8. For imine allylation under Barbier conditions, see: (a) Law, M. C.; Cheung, T. W.; Wong, K.-Y.; Chan, T. H. *J. Org. Chem.* **2007**, *72*, 923–929; (b) Sun, X.-W.; Xu, M.-H.; Lin, G.-Q. *Org. Lett.* **2006**, *8*, 4979–4982; (c) Vilaivan, T.; Winotapan, C.; Banphavichit, V.; Shinada, T.; Ohfune, Y. *J. Org. Chem.* **2005**, *70*, 3464–3471; (d) Andrews, P. C.; Peatt, A. C.; Raston, C. L. *Tetrahedron Lett.* **2004**, *45*, 243–248; (e) Yanada, R.; Negoro, N.; Okaniwa, M.; Ibuka, T. *Tetrahedron* **1999**, *55*, 13947–13956; (f) Negoro, N.; Yanada, R.; Okaniwa, M.; Yanada, K.; Fujita, T. *Synlett* **1998**, 835–836; (g) Wang, D.-K.; Dai, L.-X.; Hou, X.-L.; Zhang, Y. *Tetrahedron Lett.* **1996**, *37*, 4187–4188; (h) Estevam, I. H. S.; Bieber, L. W. *Tetrahedron Lett.* **2003**, *44*, 667–670.
9. For chelation assisted allylation of *N-tert*-butylsulfinyl aldimines, see: (a) Foubelo, F.; Yus, M. *Tetrahedron: Asymmetry* **2004**, *15*, 3823–3825; (b) Cogan, D. A.; Liu, G.; Ellman, J. *Tetrahedron* **1999**, *55*, 8883–8904.
10. *General procedure*: The procedure given below was followed in all cases. All products show satisfactory ^{1}H, ^{13}C NMR, and HRMS data, which are given in the Supplementary data. *Synthesis of N-[1-(4-Methoxyphenyl)-but-3-enyl]-4-methyl-benzenesulfonamide* (**2h**): Allyl bromide (242 mg, 2 mmol, 0.17 mL), $Pd_2(dba)_3{\cdot}CHCl_3$ (10 mg, 0.01 mmol) and activated molecular sieves 4 Å (100 mg) were mixed in 3 mL of dry DCM and stirred for 5 min at room temperature. Anhydrous $SnCl_2$ (285 mg, 1.5 mmol) and *N*-tosyl anisaldimine **1h** (289 mg, 1 mmol) were added to the resulting solution sequentially and the reaction was allowed to stir for 15 h at room temperature (TLC monitoring: silica gel, eluent: *n*-hexane–EtOAc 8:2). Upon completion, the molecular sieves were filtered off, DCM was removed, and aq NH_4F (10%, 5 mL) was added, followed by saturated aq sodium bicarbonate until the mixture was slightly alkaline. The organic product was extracted with ethyl acetate, washed with water, brine, and dried over anhydrous sodium sulfate. Solvent removal under reduced pressure followed by column chromatography over silica gel 60–120 (gradient elution with EtOAc–hexane 8% to 12%) afforded the desired *N*-[1-(4-methoxyphenyl)-but-3-enyl]-4-methyl-benzenesulfonamide **2h** (265 mg, 80% with respect to *N*-tosyl anisaldimine **1h**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 3H), 2.40–2.48 (m, 2H), 3.75 (s, 3H), 4.31 (dd, 1H, $J = 13.2$ Hz, $J = 6.8$ Hz), 5.04 (br d, 3H, $J = 12.4$ Hz), 5.45–5.55 (m, 1H), 6.69 (d, 2H, $J = 8.4$ Hz), 6.98 (d, 2H, $J = 8.4$ Hz), 7.15 (d, 2H, $J =$ 8.4 Hz), 7.55 (d, 2H, $J = 8$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.44, 41.81, 55.2, 56.66, 113.65, 119.06, 127.13, 127.72, 129.26, 132.36, 133.25, 137.46, 142.97, 158.79; HRMS (ESI): calcd for $C_{18}H_{21}NO_3SNa$ $[M+Na]^+ =$ 354.1140; found, 354.1144.