fresh zeolites undoped with aminopropylsilyl groups did not develop the characteristic purple color.

Independently, a piece of thin glass ($18 \times 18$ mm$^2$) was treated with [3-(2,3-epoxypropoxy)propyl]trimethoxysilane (2 mM) in toluene (10 mL, 110 °C, 1 h) under argon to assemble a layer of 3-(2,3-epoxypropoxy)propylsilyl groups on the glass surface (see Scheme 1B). The presence of surface-bound terminal epoxy groups attached on the glass was confirmed by pale-red coloration of the surface when treated with an aminated azo dye (Fat Brown RR) at 110 °C in toluene.[14] The UV/Vis spectrum of the glass showed a broad band with the absorption maximum at ≈440 nm. Undoped glasses gave negligible intensities in the ≈440 nm region.

The coated glass plate was inserted into a suspension of 3-aminopropylsilyl-coated zeolite powders in toluene (0.1 g, 10 mL) and the mixture was refluxed (> 1 h) under argon (see Scheme 1C). The zeolite-coated opaque glass was then removed from the reaction mixture and washed extensively with toluene. The zeolite-coated glass was subsequently sonicated in toluene for 20 s to remove physisorbed zeolite crystals on the chemically bound first layer.

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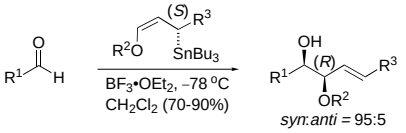
# Addition of Enantioenriched γ-Oxygenated Allylic Stannanes to *N*-Acyl Iminium Intermediates: A New Synthesis of *syn*-Amino Alcohol Derivatives**

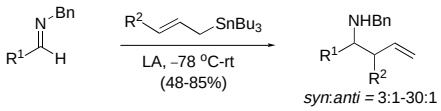
James A. Marshall,* Kevin Gill, and Boris M. Seletsky

Some years ago we discovered a facile route to monoprotected *syn*-1,2-diol derivatives through $BF_3$-promoted addition of enantioenriched γ-oxygenated allylic stannanes to aldehydes (Scheme 1).[1] We had hoped to extend these




Scheme 1. A facile route to monoprotected *syn*-1,2-diol derivatives. $R^1$ = alkyl, alkenyl; $R^2$ = methoxymethyl (MOM), tributylsilyl (TBS), benzyloxymethyl (BOM); $R^3$ = alkyl.

additions to imines, along the lines reported by Keck and Enholm (Scheme 2),[2] but were unsuccessful in these attempts. No detectable β-amino ether adducts were formed, even at room temperature. We attributed these failures to the lower reactivity of oxygenated allylic stannanes relative to their nonoxygenated allyl and crotyl counterparts.[3]




Scheme 2. Addition of allylic stannanes to imines. $R^1$ = *c*-$C_6H_{11}$, Ph, *s*Bu, *i*Pr; $R^2$ = H, Me; Lewis acid LA = $BF_3 \cdot OEt_2$, $TiCl_4$. Bn = benzyl, rt = room temperature.

A report by Yamamoto and Schmid, describing the addition of a γ-OMOM allylic stannane to several *N*-acyliminium intermediates from Hiemstra and Speckamp[4] (Scheme 3), prompted our examination of this alternative route to β-amino alcohol derivatives.[5] In fact, addition of the racemic (*Z*)-γ-oxygenated allylic stannanes **2a** and **2b**[1] to the *N*-acyliminium precursor **1**, derived from isovaleraldehyde,[5] proceeded in high yield to afford the desired adducts (Table 1). Unfortunately, a mixture of *syn* and *anti* isomers **3** and **4** was obtained from these additions.

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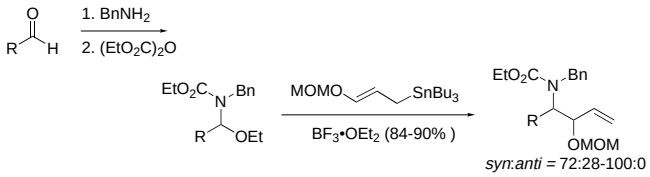
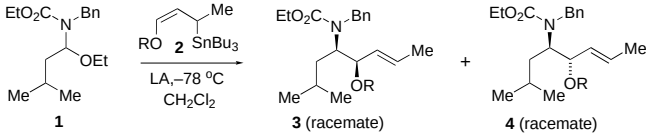



Scheme 3. Addition of $\gamma$-OMOM allylic stannanes to *N*-acyliminium intermediates. R = *i*Pr, *i*Bu.

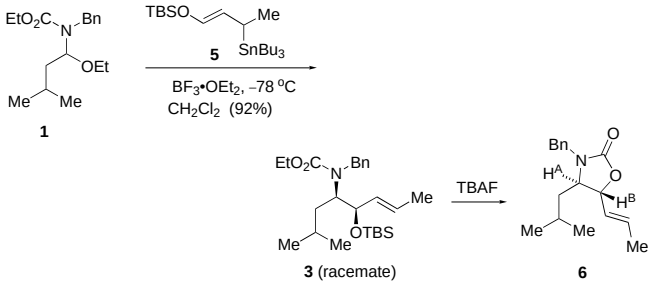
Table 1. Additions of racemic allylic stannanes **2** to **1**, the *N*-benzyl-*N*-carbethoxyiminium salt of isovaleraldehyde.




| R | LA | Yield [%][a] | **3**:**4** |
|---|---|---|---|
| TBS (**2a**) | $BF_3 \cdot OEt_2$ | 72 | 86:14 |
| MOM (**2b**) | $BF_3 \cdot OEt_2$ | 72 | 84:16 |
| MOM (**2b**) | $BF_3 \cdot OEt_2$ | 92[b] | 84:16 |
| MOM (**2b**) | $TiCl_4$ | 82 | 86:14 |

[a] Yield of **3** and **4**. [b] Lewis acid added to premixed stannane and carbamate.

Interestingly, the racemic (*E*)-$\gamma$-OTBS allylic stannane **5** afforded only the *syn* adduct **3** when treated with the ethoxy carbamate **1** (Scheme 4).[6] The relative stereochemistry of this adduct is assigned by analogy with related additions to aldehydes and in consideration of the coupling constant ($J_{A,B} = 5.9$ Hz)[7] of the indicated *trans*-oxazolidinone protons of **6**,[5] into which **3** is readily converted. While this result was encouraging, it failed to meet our needs for a route to enantioenriched amino alcohol adducts, as we have not yet been able to devise a synthesis of enantioenriched (*E*)-$\gamma$-oxygenated allylic stannanes such as **5**.

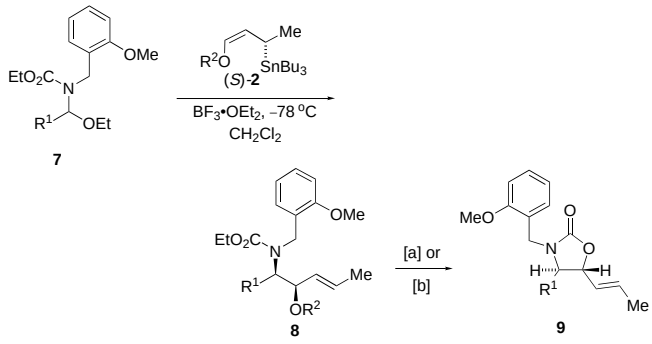



Scheme 4. Reaction of (*E*)-$\gamma$-OTBS allylic stannane **5** with ethoxy carbamate **1**. For product **6**, $J_{A,B} = 5.9$ Hz. TBAF = tetrabutylammonium fluoride.

We next examined additions of the racemic (*Z*)-$\gamma$-OTBS allylic stannane **2a** to the ethoxy carbamate derived from isovaleraldehyde and (*R*)-$\alpha$-phenethylamine in the hopes of effecting a kinetic resolution by using a twofold excess of the stannane.[8] The result was a nearly 1:1 mixture of the diastereomeric *syn* adducts and a modest 8% enantioenrichment of the recovered stannane, favoring the *R* enantiomer (*R*)-**2a**. Interestingly, the *syn*:*anti* ratio of the diastereomeric adducts was found to be 98:2, as opposed to 86:14 previously observed with the benzyl analogue **1** of the *N*-$\alpha$-phenethyl carbamate. Thus it appeared that branching at the benzylic center caused a marked improvement in the diastereoselectivity of the addition.

Supposing that this improvement was the consequence of increased bulk or restricted rotation of the *N*-benzylic group in the *N*-acyliminium intermediate, we examined the *o*-methoxybenzyl derivative **7a** and the enantioenriched (*S*)-$\gamma$-silyloxy allylic stannane **2a** (Table 2, entry 1). The results were quite promising: the *syn* adduct **8aa** predominated over the *anti* adduct by over 95:5. The relative stereochemistry of the *syn* adduct was confirmed through its one-step conversion into the *trans*-oxazolidinone **9a**.[5] The OMOM adduct **8ab** afforded the identical oxazolidinone (entry 2) by a two-step procedure involving sequential treatment with aqueous acid followed by base. The absolute configuration of the adducts was initially assigned by analogy to the well-studied additions of stannanes **2a** and **2b** to aldehydes.[1]

Table 2. Additions of enantioenriched allylic stannanes (*R*)-**2a** and **2b** to *N*-acyliminium salts.




| Entry | $R^1$ | $R^2$ | Yield [%] **8** | Yield [%] **9** |
|---|---|---|---|---|
| 1 | *i*Bu (**7a**) | TBS (**2a**) | 90 (**8aa**) | 91 (**9a**) |
| 2 | *i*Bu (**7a**) | MOM (**2b**) | 91 (**8ab**) | 88 (**9a**) |
| 3 | $C_6H_{13}$ (**7b**) | TBS (**2a**) | 71[c] (**8ba**) | 93 (**9b**) |
| 4 | $C_6H_{13}$ (**7b**) | MOM (**2b**) | 66 (**8bb**) | 82 (**9b**) |
| 5 | *c*-$C_6H_{11}$ (**7c**) | TBS (**2a**) | 67[d] (**8ca**) | 94 (**9c**) |
| 6 | *c*-$C_6H_{11}$ (**7c**) | MOM (**2b**) | 78 (**8cb**) | 72 (**9c**) |
| 7 | 2-furyl (**7d**) | TBS (**2a**) | 73 (**8da**) | 94 (**9d**) |
| 8 | 2-furyl (**7d**) | MOM (**2b**) | 65 (**8db**) | decomp. |

[a] For $R^2$ = TBS: TBAF, THF. [b] For $R^2$ = MOM: 1. HCl, $H_2O$, THF, 2. KOH, THF, MeOH. [c] $R^2$ = H. [d] A mixture was used: 42% of $R^2$ = H and 25% of $R^2$ = TBS.

Additions to the *N*-acyliminium intermediates from carbamates **7b**–**7d** were equally selective (entries 3–8). The diastereomeric *anti* adducts made up less than 5% of the product, based on GC analysis. This analysis also revealed that the *ee* value of adduct **9a** was over 95%. We were unable to separate the enantiomers of adducts **9b**–**9d** by this technique or by HPLC on several columns. However, we were able to determine *ee* values (>95%) of adducts **9b** and **9c** through removal of the *N*-*o*-methoxybenzyl groups with ceric ammonium nitrate[9] and conversion of the derived oxazolidinones to the *N*-*tert*-butoxycarbonyl (BOC) amino alcohols by addition of $(BOC)_2O$ and cleavage of the resulting *N*-BOC oxazolidinones with aqueous $K_2CO_3$.[10] The *N*-BOC alcohols

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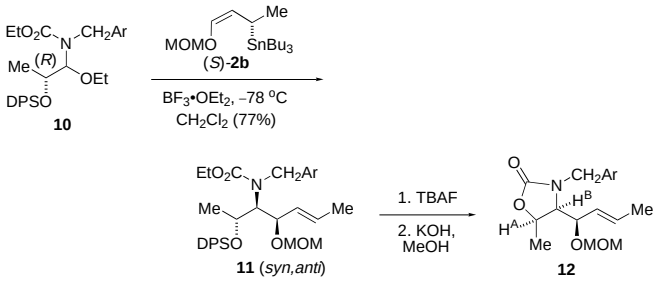
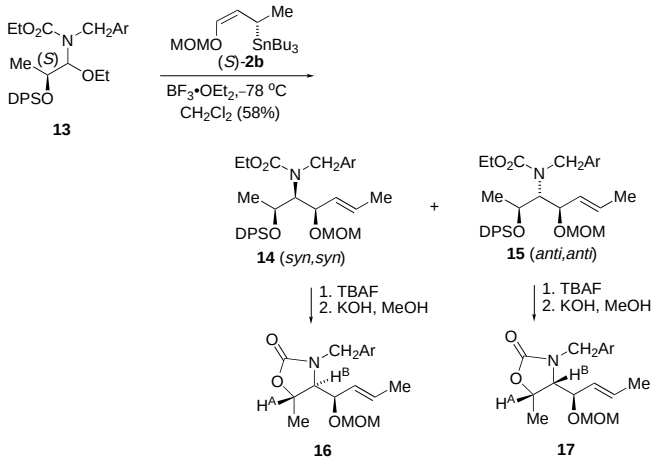
obtained through this sequence were analyzed as their *O*-methyl mandelic esters.[11] The $^1$H NMR spectra of the *R* and *S* derivatives confirmed both the *ee* values (> 95 %) and the assigned absolute configuration of these compounds.

The matching/mismatching characteristics of the addition were examined with the OMOM allylic stannane (*S*)-**2b**[12] and the *N*-(*o*-methoxybenzyl)carbamates **10** and **13** derived from the DPS ether derivatives of (*R*)- and (*S*)-lactic aldehyde (Schemes 5 and 6; DPS = Si*t*BuPh$_2$).[13] As expected from



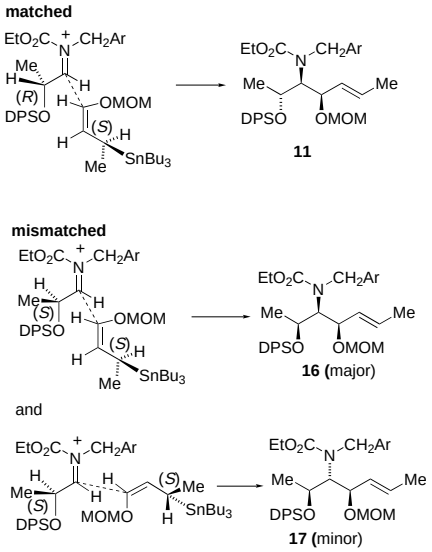

Scheme 5. Reaction of **2b** with **10**. For product **12**, $J_{A,B} = 7.2$ Hz. Ar = *o*-MeOC$_6$H$_4$.




Scheme 6. Reaction of **2b** with **13**. Adducts **14** and **15** are formed as a 60:40 mixture. For product **16**, $J_{A,B} = 3.6$ Hz. For product **17**, $J_{A,B} = 7.5$ Hz. Ar = *o*-MeOC$_6$H$_4$.

analogous additions to aldehydes,[1] the *R*/*S* combination is the matched pairing and affords the *syn*,*anti* adduct **11** as the exclusive product (Scheme 5). The *S*/*S* combination led to a 60:40 mixture of the *syn*,*syn* and *anti*,*anti* adducts **14** and **15** (Scheme 6). The relative stereochemistry of these adducts was confirmed through $^1$H NMR analysis of the derived oxazolidinones **12**, **16**, and **17**. The observed diastereoselectivity is consistent with a preferred antiperiplanar acyclic transition state (Scheme 7).

The present findings extend the utility of nonracemic $\gamma$-oxygenated allylic stannanes to the preparation of enantioenriched *syn*-$\beta$-amino alcohol derivatives.[14] These products are potential precursors of $\alpha$-amino-$\beta$-hydroxy acids, $\beta$-amino-$\alpha$-hydroxy acids, amino and aza sugars, and related natural products of biological interest.[15] The reason for the unprecedented enhanced diastereoselectivity of the *o*-methoxybenzyl derivatives is at present obscure. Neither steric nor




Scheme 7. Possible transition states for matched and mismatched pairing of allylic stannane (*S*)-**2a** and the Speckamp iminium intermediates from ODPS-protected lactic aldehyde.

electronic factors offer likely explanations, as reactions with the *o*-methyl- or *p*-methoxybenzyl analogues of **7** both gave approximately 80:20 mixtures of *syn* and *anti* adducts. The issue is a complex one and may depend upon *E*/*Z* preferences of the intermediate acyliminium ion.[4] It is also possible that internal hydrogen bonding between the *o*-methoxy oxygen atom and the acidic acyliminiun hydrogen atom gives rise to a rotationally restricted transition state.[16] Further studies with other nucleophilic reagents and *ortho*-substituted benzylic imines are clearly warranted. However, mechanistic rationale aside, the influence of *ortho*-methoxy substitution on diastereoselectivity is unexpected and of significant practical import to the success of the present methodology. It is worth noting that although other routes to enantioenriched $\beta$-amino alcohols are known,[17] few proceed with simultaneous creation of a carbon–carbon bond and two contiguous stereogenic centers.[18, 19]

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[10] **9b** or **9c** → (1. CAN, MeCN, $H_2O$; 2. $(BOC)_2O$, DMAP; 3. $K_2CO_3$, MeOH; 4. (*R*)- or (*S*)-PhCH-(OMe)$CO_2$H) → BOC, NH, $R^1$, Me, $OR^2$

Scheme 8. $R^1 = C_6H_{13}$ or *c*-$C_6H_{11}$; $R^2$ = (*R*)- or (*S*)-PhCH(OMe)CO. CAN = cerium ammonium nitrate, BOC = butoxycarbonyl, DMAP = dimethylaminopyridine.

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## Sterically Controlled Pathways in the Reaction of 2,4,6-Tris(isopropyl)benzenesulfonyl Azide and $[Pd_2Cl_2(dppm)_2]$**

Gábor Besenyei,* László Párkányi, Isabella Foch, and László I. Simándi

Organic azides often react with metal complexes with extrusion of $N_2$, affording imido (nitrene) derivatives.[1] The azide moiety is not necessarily cleaved, however, as illustrated by earlier studies on hydridoosmium and dimeric molybdenum complexes.[2] Several aryl and cyclohexyl azide complexes revealing various modes of coordination have recently been characterized structurally and chemically.[3]

Our previous work on the phosgene-free synthesis of isocyanates has shown that arenesulfonyl azides react with $[Pd_2Cl_2(dppm)_2]$ (**1**, dppm = bis(diphenylphosphanyl)methane), resulting in the formation of arylsulfonylimido A-frame adducts.[4, 5] These novel reactions show good selectivities with most sulfonyl azides, except for the 2-nitro derivative, which gave $[Pd_2Cl_2(dppm)_2(N_3SO_2C_6H_4\text{-}2\text{-}NO_2)]$ as a by-product.[5a] To elucidate the steric effects of azide ligands, we conducted studies with 2,4,6-tris(isopropyl)benzenesulfonyl azide ($TipSO_2N_3$, **2**). The results of these investigations, together with crystallographic data on the parent azide **2**, are presented here.

Reaction of $[Pd_2Cl_2(dppm)_2]$ with **2** affords the azide complex **3** and the nitrene complex **4** in 75 and 25% yield, respectively [Eq. (1); $^1H$ NMR, see the Experimental Section], involving a very bulky bridging imido ligand. The

$$2\,[Pd_2Cl_2(dppm)_2] \;(\mathbf{1}) + 2\,TipSO_2N_3\;(\mathbf{2}) \xrightarrow{-N_2} [Pd_2Cl_2(dppm)_2(\mu,\eta^1\text{-}N_3SO_2Tip)]\;(\mathbf{3}) + [Pd_2Cl_2(dppm)_2(\mu\text{-}NSO_2Tip)]\;(\mathbf{4}) \quad (1)$$

molecular structures of the complexes formed are shown in Figures 1 and 2. The products are typical A-frame adducts with an extended boat conformation of the $Pd_2P_4C_2$ ring. The Pd–Pd distances are about 0.6 Å longer than in $[Pd_2Br_2(dppm)_2]$, ruling out metal–metal bonding.[6]

The redistribution of valence electrons induced by coordination can be best visualized by comparing bond lengths in free and coordinated sulfonyl azide. Although N3 is disordered in **2** (structure not shown, the numbering corresponds to that of **3**), the short N1–N2 and N2–N3 bonds (1.213(3) and 1.14 Å) indicate multiple bonding, in line with structural data for other sulfonyl azides.[7] Decreased bond orders as a result of complexation are clear from the N2–N3 and N1–N2 distances of 1.248(5) and 1.340(5) Å in **3**. The structural features of **3** are consistent with **2** reacting as a 1,3-dipole ($Ar\text{–}SO_2\text{–}N^-\text{–}N{=}N^+$), producing a zwitterionic structure with the negative charge delocalized on the N1–N2 and N1–S1 bonds. The azide-to-sulfonyl electron transfer shortens the

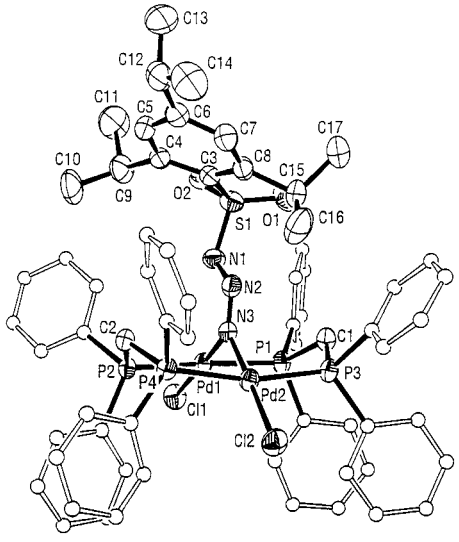


Figure 1. Molecular structure of **3** without hydrogen atoms. Selected interatomic distances [Å] and angles [°]: Pd1···Pd2 3.315(1), Pd1-N3 1.984(4), Pd2-N3 1.972(4), N2-N3 1.248(5), N1-N2 1.340(5), N1-S1 1.627(4), S1-C3 1.808(5), S1-$O_{av}$ 1.437; Pd1-N3-Pd2 113.8(2), Pd1-N3-N2 126.0(3), Pd2-N3-N2 120.2(3), N1-N2-N3 114.7(4); C–H···O close contacts: H9···O2 2.325, C9–H9··O2 114.4, H15···O1 2.205, C15–H15···O1 125.2.

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