

Tuning the reactivity of organotin(IV) by LiOH: allylation and propargylation of epoxides via redox transmetalation

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Abstract

In presence of catalytic Pd(0) or Pt(II), a reagent combination of SnCl₂–LiOH promotes the reaction of organic halides and epoxides in dichloromethane leading to the regioselective formation of corresponding homoallyl and homopropargyl alcohols in good yields. This 2-carbon extension strategy adds to the repertoire of Barbier reactions via metal salts and reinforces views on the enhanced reactivity of organotin having –OH pendant.

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1. Introduction

Addition of allyl, propargyl or allenylstannanes to organic electrophiles like aldehydes, imines, and epoxides is a well-known tool for carbon–carbon bond forming strategy in organic chemistry [1–3]. Far-reaching utility of these reagents have led to the development of Barbier-like protocols wherein reactive organostannanes are generated in-situ from tin(0/II/IV) partner. Along with others, we have been exploring a bimetallic strategy which involves oxidative-addition of an organic halide (RX) across catalytic d⁸/d¹⁰ metal [M], followed by redox-transmetalation of R–[M]–X to tin(II) to generate R–Sn(IV) in-situ. Successful delineation of the strategy for carbonyl allylation and propargylation [4] prompted us to extend the same for the nucleophilic addition of organotin(IV) to epoxide in one-pot. During the investigation, we have observed a dramatic effect of lithium hydroxide in promoting the reactivity of organotin lead-

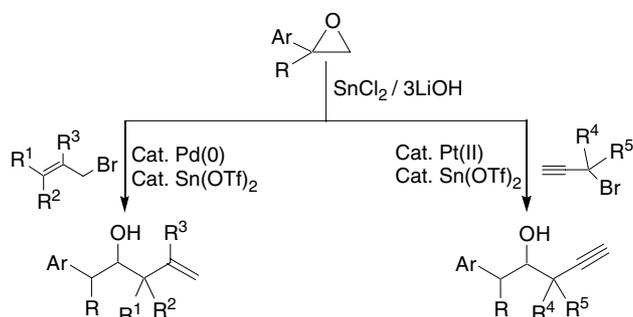
ing to homoallyl and homopropargyl alcohols via tandem rearrangement-carbonyl addition reaction (Scheme 1). As elaborated later, the study also reinforces earlier views on the enhanced reactivity of the potential intermediate “R–Sn(OH)₃”.

2. Results and discussion

Reaction of styrene oxide **2a** and 3-bromopropene **1a** in presence of stannous chloride and catalytic Pd₂(dba)₃ in dichloromethane under reflux led to the formation of 1-phenyl-pent-4-en-2-ol **3a** and 1-phenyl-ethane-1,2-diol in 15% and 70% yield, respectively. On the other hand, reaction in absence of catalyst afforded unreacted epoxide **2a** along with the diol. No further improvement was possible by varying the solvent, catalyst, tin(II) precursor, temperature, mode of addition or by adding water. Since it is well established that the reagent combination of Pd(0/II)/SnCl₂/allyl bromide generates allyltrihalo stannane [5], we ascribe the above failure due to the poor nucleophilicity of the allylating agent. Concurrent to this observation, we were enthused with the recent

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Scheme 1. Tandem epoxide rearrangement – allylation/propargylation.

suggestion by Li and co-workers [6] that an alkoxy or hydroxy pendant as in $\text{RSn}(\text{OH})_3$ and $\text{RSn}(\text{OR}')_3$ exerts electron donation to the vacant d-orbital of tin, thereby stabilizing the species and consequently enhancing its reactivity. In view of this we desired to generate the potential allylating agent $\text{C}_3\text{H}_5\text{Sn}(\text{OH})_3$ in non aqueous medium. True to this expectation, addition of lithium hydroxide (3 equiv.) led to dramatic improvement in yield of **3a** from 15% to 35% [7]. Further enhancement of yield to 69% was achieved by using stannous triflate as Lewis acid catalyst. Results from various optimization studies are accrued in Table 1, from which we conclude that the best condition is as shown in entry 5.

The generality of the reaction was further tested with substituted allyl bromides and epoxides (Table 2). 3-Substituted allyl bromides **1b–1e** afforded exclusively the γ -regioselective products **3b–3e**. Reaction of 2-bromomethyl(ethyl)acrylate **1g** with **2b** resulted in tandem lactonization leading to 6-methyl-3-methylene-6-phenyl-tetrahydropyran-2-one **3g**. To test if steric crowding is tolerated, α -methylstyrene epoxide **2b** was reacted with allyl bromides **1b** and **1f**. In each case the reactions proceed smoothly to afford the products **3h** and **3i** in moderate to good yields. However, epoxides bearing only aliphatic substituents, for example cyclohexane epoxide gave negligible yield of product.

Table 1
Reaction of styrene oxide **2a** with allyl bromide **1a**/SnCl₂/LiOH: effect of catalyst and Lewis acid^a

#	Catalyst (2 mol%)	LA (10 mol%)	Yield (%)
1	None	Sn(OTf) ₂	21
2	PtCl ₂ (PPh ₃) ₂	Sn(OTf) ₂	49
3	PdCl ₂ (PPh ₃) ₂	Sn(OTf) ₂	54
4	Pd(PPh ₃) ₄	Sn(OTf) ₂	35
5	Pd ₂ dba ₃	Sn(OTf) ₂	69
6	Pd ₂ dba ₃	None	35
7 ^b	Pd ₂ dba ₃	Cu(OTf) ₂	47
8 ^b	Pd ₂ dba ₃	Zn(OTf) ₂	42
9	Pd ₂ dba ₃	Sc(OTf) ₂	55

^a Unless otherwise mentioned, all reactions were run for 9 h.

^b Reaction time 45 h.

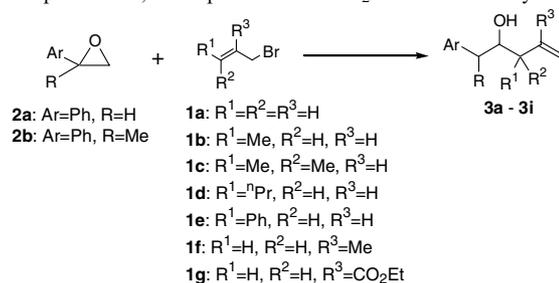
The scope of the reaction has been successfully extended to the propargylation of epoxides in which PtCl₂(PPh₃)₂ was found to be most efficient among the catalysts screened. Thus reaction of 3-bromo-but-1-yne **4b** and styrene oxide **2a** in presence of catalytic PtCl₂(PPh₃)₂ yielded 92% of 3-methyl-1-phenyl-pent-4-yn-2-ol **5c** (Table 3, entry 6). Similar reaction of propargyl bromide and substituted propargyl bromides with styrene oxide **2a** and α -methyl styrene oxide **2b** afforded moderate to good yields of the corresponding homo-propargyl alcohols (Table 4). Most strikingly no allenic alcohol is obtained in any of the cases suggesting that under the reaction condition metallotropic rearrangement between the propargyltin(IV) and allenyltin(IV) is completely inhibited.

The first issue concerning the mechanism of the reaction relates to the formation of homoallyl and homo-propargyl alcohols as end-organic product, which clearly suggests that the reaction proceed via epoxide rearrangement to give an aldehyde in-situ. Control experiments with styrene oxide confirmed that under our reaction condition such rearrangement indeed take place by tin(II) but not the transition metal partner, the order of efficiency being Sn(OTf)₂ > SnCl₂ [8d]. A mechanism is proposed as shown in Scheme 2, which is analogous to InCl₃ catalyzed rearrangement of arylepoxide to carbonyl compounds [8d].

The second issue relates to the identity of the reactive organotin(IV) species in the present case, which was investigated for the allylation reaction. According to the well-established redox-transmetalation sequence, the reaction proceeds via a Pd(0)/Pd(II) catalytic cycle with the initial formation of a π -allylpalladium(II) intermediate [5]. Insertion of tin(II) followed by reductive transmetalation leads to allyltrichlorostannane (Scheme 3).

Pronounced effect of lithium hydroxide in promoting the reaction suggests that a more reactive intermediate other than **I** is the actual reacting species. To test this assumption, in-situ ¹H NMR diagnosis was carried out in which the chemical shift (δ , ppm) and ²J_{117,119Sn-H} values of characteristic methylene doublet were inspected (Fig. 1). The spectrum of authentic allyl-SnCl₃ (**a**) shows methylene peak at 3.15 (²J_{Sn-H} = 120 Hz, Sn-CH₂) along with signals at 5.35 (m, =CH₂), and 5.92 (dtd, J = 1.8 Hz, J = 8.3 Hz, J = 18.5 Hz, =CH-). Upon reacting allyl-SnCl₃ with LiOH (3 equiv.) in DCM at 40 °C for 5 h a residue was obtained after centrifugation/concentration. NMR of the residue (**b**) confirmed the formation of a new σ -allyltin(IV) species, in which the methylene doublet shifts upfield to 2.50 ppm (²J_{Sn-H} = 144 Hz, Sn-CH₂), along with other signals at 4.9 ppm (m, =CH₂), and 5.98 ppm (dtd, J = 1.7 Hz, J = 8.4 Hz, J = 18.5 Hz, =CH-). The spectrum of allyltin (**c**) generated in-situ from allyl bromide, anhydrous SnCl₂ and catalytic Pd₂(dba)₃ in CDCl₃ after stirring

Table 2

Reaction of allyl bromides **1a–1g** with epoxides **2a, 2b** in presence of SnCl₂/LiOH and catalytic Sn(OTf)₂/Pd₂(dba)₃ at 40 °C

#	Bromide	Epoxide	Product	Pdt. No.	Time (h)	Yield (%)	Syn: Anti
1	1a	2a		3a	9	69	–
2	1b	2a		3b	3	76	42:58
3	1c	2a		3c	3	56	–
4	1d	2a		3d	3	56	44:56
5	1e	2a		3e	4	12	0:100
6	1f	2a		3f	3	52	–
7	1g	2b		3g	3	45	–
8	1b	2b		3h	2	80	69:31
9	1f	2b		3i	2	52	38:62

at 40 °C for 5 h shows methylene peak at 3.19 ppm ($^2J_{\text{Sn-H}} = 120$ Hz, Sn–CH₂), which is similar to (**a**) and therefore is most likely to be allyl-SnCl₂Br. Addition of 3 equivalent LiOH to the in-situ generated allyltin results in decrease in peak at 3.19 and concomitant appearance of a new methylene peak at 2.78 ppm ($^2J_{\text{Sn-H}} = 118$ Hz, Sn–CH₂). Comparing (**b**) and (**d**), we propose the new organotin species to be a σ -allyl(halo)(hydroxy)tin(IV) intermediate. Several attempts to isolate the said intermediate remain unsuccessful so far.

Using ¹H and ¹¹⁹Sn NMR monitoring Blunden et al. [9] have shown that base treatment of RSnCl₃ (R = Me, Bu) results in the formation of pH-dependent hydroxy species, and at 1:6 ratio the formation of RSn(OH)₃ is suggested. Tagliavini and co-workers [10] proposed the formation of hydrated organotin(IV) cations in aqueous solution of organotin halides. Enhanced reactivity of ArSn(OH)₃, Ar₃Sn(OMe), ArBi(OH)₂ over the corresponding halo derivatives in arylation reactions is further noteworthy [6,11]. One may also note that while existence of silanetriols RSi(OH)₃ is fully established

Table 3
Reaction of styrene oxide **2a** with propargyl bromide **4b**/SnCl₂/LiOH: effect of catalyst^a

#	Catalyst (2 mol%)	L.A. (10 mol%)	Yield (%)
1	None	None	15
2	[RhCl(COD)] ₂	Sn(OTf) ₂	28
3	[IrCl(COD)] ₂	Sn(OTf) ₂	36
4	NiCl ₂ (PPh ₃) ₂	Sn(OTf) ₂	21
5	PtCl ₂ (PPh ₃) ₂	None	43
6	PtCl ₂ (PPh ₃) ₂	Sn(OTf) ₂	92
7	PdCl ₂ (PPh ₃) ₂	Sn(OTf) ₂	57
8	Pd ₂ (dba) ₃	Sn(OTf) ₂	73
9	Pd(PPh ₃) ₄	Sn(OTf) ₂	61

^a All reactions were run for 15 h.

(vide isolation and X-ray structure), the analogous stan-nanetriols still await such confirmation [12].

A plausible mechanism (Scheme 4) of the present reaction involves (a) formation of R–SnXCl₂ **I** vide

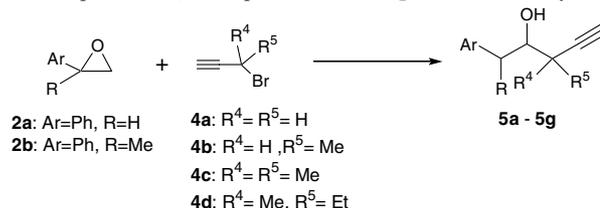
Scheme 3, (b) reaction of lithium hydroxide with **I** to generate RSnX_n(OH)_{3–n} **II** in solution, (c) tandem rearrangement of arylepoxide to benzylic aldehyde **III** by tin(II), and (d) carbonyl addition via S_E2' attack of organotin(IV) intermediate **II** to aldehyde **III** to furnish the end-organic product.

In conclusion, we demonstrated here the allylation and propargylation of aryl substituted epoxides under Barbier-like protocol to afford corresponding homoallyl and homopropargyl alcohols with two carbon extension, and with 100% γ -regioselectivity in all cases. Further light on the enhanced organometallic reactivity of hydroxytin(IV) species is demonstrated.

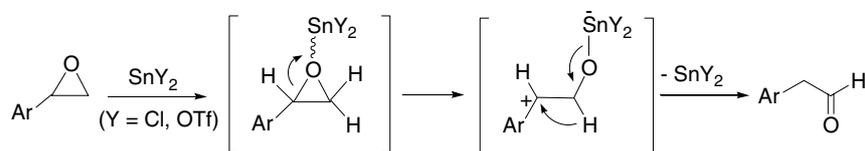
3. Experimental

¹H (200 MHz) NMR spectra were recorded on a BRUKER-AC 200 MHz. Spectrometer. Chemical shifts

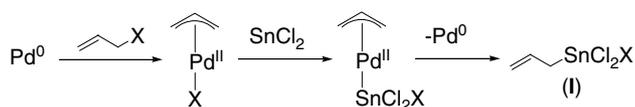
Table 4
Reaction of propargyl bromides **4a–4d** with epoxides **2a, 2b** in presence of SnCl₂/LiOH and catalytic Sn(OTf)₂/PtCl₂(PPh₃)₂ at 40 °C



#	Bromide	Epoxide	Product	Pdt. No.	Time (h)	Yield (%)	Syn: Anti
1	4a	2a		5a	18	51	–
2	4a	2b		5b	22	43	45:55
3	4b	2a		5c	15	92	72:28
4	4b	2b		5d	14	78	100:0
5	4c	2a		5e	18	73	–
6	4c	2b		5f	16	48	55:45
7	4d	2a		5g	20	55	54:46



Scheme 2. Plausible route to benzylic aldehyde from arylepoxide via catalytic Sn(II).



Scheme 3. Redox transmetalation from allyl-Pd(II) to allyl-Sn(IV).

are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuteriochloroform: δ 7.27 ppm). Data are reported as follows:

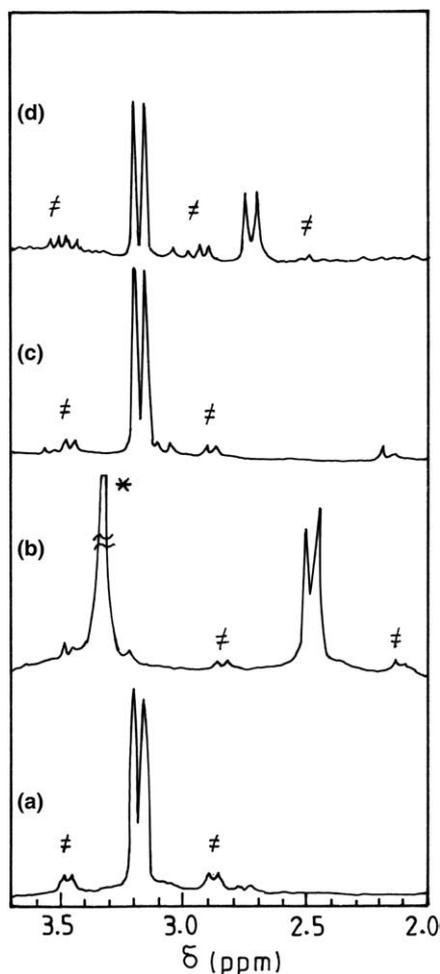
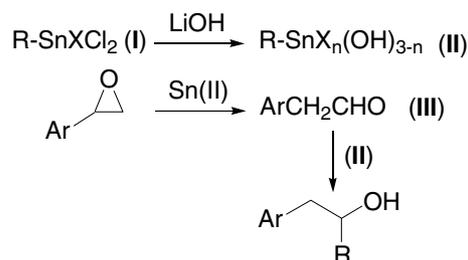


Fig. 1. NMR profile of intermediates in the chemical shift region of the methylene doublet. **a**: authentic allyltrichlorostannane in CDCl_3 ; **b**: product from reaction of **a** with 3 equiv. LiOH in DMSO-d_6 ; **c**: allyltrihalostannane generated *in-situ* from allyl bromide/ SnCl_2 / $\text{Pd}(0)$ in CDCl_3 ; **d**: after addition of 3 equiv. LiOH to **c**; \neq indicates peaks due to $^2J_{\text{Sn-H}}$ and * denotes peak due to residual proton in DMSO-d_6 .

Scheme 4. Tandem rearrangement of epoxide to aldehyde and carbonyl addition of organotin(IV) in presence of LiOH .

chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constant (Hz). ^{13}C (54.6 MHz) NMR spectra were recorded on a BRUKER-AC 200 MHz. Spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuteriochloroform: δ 77.0 ppm). EIMS (70 eV) spectra and HRMS were taken using a VG Autospec M and Waters LCT mass spectrometer. Elemental analyses were carried out using a CHNS/O Analyzer Perkin Elmer 2400 Series II instrument.

All reactions were carried out under an argon atmosphere in flame dried glassware using Schlenk techniques. Chromatographic purifications were done with either 60–120 or 100–200 mesh silica gel (SRL). For reaction monitoring, precoated silica gel 60 F_{254} TLC sheets (Merck) were used. Petroleum ether refers to the fraction boiling in the range 60–80 °C.

3.1. General procedure

The procedure given below was followed in all cases. All products showed satisfactory spectral and analytical data.

3.2. Allylation of epoxide

1-Bromo-3-methyl-but-2-ene **1c** (224 mg, 1.5 mmol) was added dropwise to a mixture of anhydrous SnCl_2 (189 mg, 1 mmol) and $\text{Pd}_2(\text{dba})_3$ (9 mg, 0.01 mmol) in dry DCM (3 ml) under argon atmosphere at a bath temperature of 40 °C, and was allowed to stir (5 h). LiOH (75 mg, 3 mmol) was added to the mixture and further stirred for 1 h. Finally, a solution of styrene oxide **2a** (0.06 ml, 0.5 mmol) in dry DCM

(1 ml) was added followed by Sn(OTf)₂ (21 mg, 0.05 mmol). Upon completion (TLC monitoring silica gel, eluent: *n*-hexane-EtOAc 9:1), the reaction was quenched with 2(N) HCl (5 ml), and aq. NH₄F (10%, 5 ml). Organic product was extracted with diethyl ether, washed with water, brine, and dried over anhydrous magnesium sulfate. Solvent removal under reduced pressure followed by column chromatography over silica gel 60–120 (gradient elution with EtOAc-hexane 2–10%) afforded 3,3-dimethyl-1-phenylpent-4-en-2-ol **3c** (54 mg, 56% with respect to epoxide). ¹H NMR (200 MHz, CDCl₃): δ 1.03 (s, 6H), 1.53 (brs, 1H), 2.31–2.43 (m, 1H), 2.77–2.85 (dd, 1H, *J* = 11, 2 Hz), 3.39–3.35 (dd, 1H, *J* = 11, 11 Hz), 4.97–5.06 (m, 2H), 5.78–5.92 (m, 1H), 7.16–7.26 (m, 5H). ¹³C NMR (50.3 MHz, CDCl₃): δ 22.80, 38.39, 41.42, 79.31, 112.96, 126.21, 128.25, 129.23, 139.83, 145.25. EIMS *m/z* (rel. abundance): 190 (M⁺, 2), 173 [(M–OH)⁺, 8], 157 (60), 131 (46), 121 (42), 117 (30), 91 (100), 77 (38), 69 (52), 65 (22). Anal. (C₁₃H₁₈O) calcd. C: 82.06, H: 9.53; found, C: 81.77, H: 9.89.

3.3. Propargylation of epoxide

Following identical method as above using the reagents 3-bromo-3-methyl-but-1-yne **4c** (221 mg, 1.5 mmol), anhydrous SnCl₂ (228 mg, 1.2 mmol), PtCl₂(PPh)₂ (8 mg, 0.01 mmol), LiOH (86 mg, 3.6 mmol), styrene oxide **2a** (0.06 ml, 0.5 mmol), and Sn(OTf)₂ (21 mg, 0.05 mmol) afforded 3,3-dimethyl-1-phenyl-pent-4-yn-2-ol **5e** (69 mg, 73% with respect to epoxide). ¹H NMR (200 MHz, CDCl₃): δ 1.25 (s, 6H), 1.63 (s, 1H), 2.15 (s, 1H), 2.56 (dd, 1H, *J* = 10.5, 13.8 Hz), 3.02 (dd, 1H, *J* = 13.8, 2.1 Hz), 3.51 (dd, 1H, *J* = 10.5, 2.1 Hz), 7.13–7.27 (m, 5H). ¹³C NMR (50.3 MHz, CDCl₃): δ 24.64, 25.57, 36.70, 38.80, 70.10, 78.76, 89.44, 126.38, 128.50, 129.29, 139.21. ESI-MS: for C₁₃H₁₆O [M], [M + H]⁺ = 189.14, [M–OH]⁺ = 171.12. HRMS calculated for the fragment C₁₃H₁₅ [M–OH]⁺ = 171.1174 found 171.1190. Anal. (C₁₃H₁₆O) calcd. C: 82.94, H: 8.57; found, C: 82.81, H: 8.69.

3.4. Rearrangement of epoxide

Styrene oxide **2a** (0.06 ml, 0.5 mmol) was added to a mixture of anhydrous Sn(OTf)₂ as catalyst (21 mg, 0.05 mmol, 10%) in dry DCM (3 ml) under argon atmosphere at a bath temperature of 40 °C, and was allowed to stir (6 h). Upon completion (TLC monitoring silica gel, eluent: *n*-hexane-EtOAc 9:1), the solvent was evaporated in vacuum and the residue was extracted with diethyl ether. The organic layer was washed with water, brine, and dried over anhydrous magnesium sulfate. Solvent removal under reduced pressure followed by column chromatography over silica gel 60–120 (elution

with EtOAc-hexane 1:99) afforded phenylacetaldehyde (36 mg, 60% with respect to epoxide), which was compared and found to identical with an authentic sample.

Under identical condition as above, but with SnCl₂ as catalyst (9.5 mg, 0.05 mmol, 10%), the yield of phenylacetaldehyde was 18 mg (30% with respect to epoxide).

Under identical condition as above, but with catalytic Pd₂(dba)₃ (46 mg, 0.05 mmol, 10%), the yield of phenylacetaldehyde was <2% (vide NMR).

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Appendix A. Supplementary data

General procedure, spectral and analytical data of products. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorgchem.2004.12.008.

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