Barbier Reaction in the Regime of Metal Oxide: Carbonyl Allylation over β-SnO/Cu_2O and Surface Diagnostics

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A reagent combination of β-SnO and catalytic Cu_2O promotes the reaction of allyl halides with aldehyde, cyclic monoketone, 1,2-diketone, 1,3-diketone, and anhydride in DCM−H_2O, leading to corresponding homoallylic alcohols having exclusive γ-regioselectivity. Surface probing by XRD and XPS indicates that the reagent activates allyl halide preferentially via two kinds of binding interaction. The first one is characterized by an alkene−copper(I) interaction at the copper site, and the second a surface organometallic species at the tin site in which tin is in the +IV oxidation state.

Introduction

The reaction of a carbonyl compound and an organic halide in the presence of magnesium metal, trivially known as Grignard−Barbier reaction, has carved a distinct niche in synthetic and pharmaceutical chemistry.[1] In the hundred years since its original discovery,[2] this one-pot variant of Grignard reaction has been successfully demonstrated against a broad spectrum of zerovalent metals, and more recently using metal halides instead of a metal.[3,4] More recent demonstration of Barbier protocol in water alone provided renewed vigor to the field because of its relevance to quasi-nature catalysis.[5]

Carbonyl allylation reaction via organotin, like its alkali and alkaline-earth metal counterparts, is a useful reaction in the arsenal of an organic chemist. The product homoallylic alcohols are important synthons for further elaboration. Several recent reports demonstrate that reactivity of in-situ or ex-situ generated allylstannanes increases in aqueous or aqueous−organic medium.[6] A major question that continues to evoke interest is, How does water enhance the reactivity of organostannane? Formation of hydrated organometallic cations such as $[Bu_{3-n}(C_4H_7)Sn(OH_2)_m]^{n+}$ or allyl(hydroxy)tin species such as $(C_3H_5)Sn(OH)_3$ has been proposed.[7] Most recently, Li et al. speculated that an alkoxy or hydroxy pendant in "R−Sn(OH)$_3$" exerts electron donation to the vacant d orbital of tin, thereby stabilizing the species compared to an alkyl or halogen attached to the tin center, consequently enhancing its reactivity.[8]

Electronically, species SnY_2 (Y = H, Me, halogen, OR, SR, NR_2) are classified as stannylenes and characterized by a singlet ($^1A_1$) ground state, and the associated tin(II) chemistry is largely dominated by the bonding, energetics, and reactivity of the nonbonded pair of electrons.[9] In this context we were drawn by the bonding and structural similarity of tetragonal blue-black tin(II) oxide (hereafter β-SnO) with hydrated tin(II) halides

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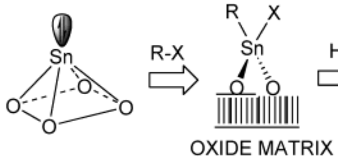


Figure 1. Organic halide activation over β-SnO: a working model.

and the trihalostannous ion. It is remarkable that the Sn−O bond distance in β-SnO (2.21 Å) is comparable to that in $SnCl_2(H_2O)_2$ (2.16 Å) and $Ph_3Sn(OH)$ (2.19 Å). Further, the Sn−Sn distance between metal atoms in the adjacent layer of β-SnO (3.70 Å) is indicative of considerable metal−metal interaction. The above similarities provided the first insight into the plausibility of an oxidative addition of an organic halide across β-SnO. We further reasoned that an oxidative addition, mediated in the presence of water, may generate intermediates that could be considered as surrogates of "R−Sn(OH)$_3$" (Figure 1). Could the new species be as reactive as previously known hydrated/hydroxy organotin species?

Keeping the above issues in view, we undertook to explore the β-SnO-mediated Barbier-like carbonyl allylation reaction. Initial studies clearly emphasized the poor ability of β-SnO alone to react with allyl halide and the necessity to add homogeneous catalysts of d^8/d^{10} metals, such as $PtCl_2(PPh_3)_2$ and $Pd_2(dba)_3$, to preactivate the allyl halide.[10] To deliver an all-oxide Barbier reagent, it was reasoned that a 3d transition metal oxide in low oxidation state capable of activating allyl halide would be required as a cocatalyst. Guided by our success with Sn(II)/Cu(II) and Sn(II)/Cu(I) reagents,[11,12] we selected a combination of β-SnO/catalytic Cu_2O to promote the carbonyl allylation reaction, the results of which are presented herein.

Result and Discussion

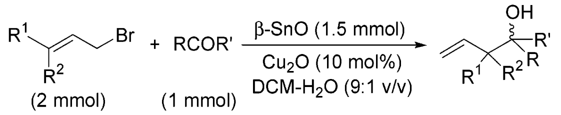
Reactivity of β-SnO/Cu₂O. Reaction of 3-bromopropene (2 mmol) and 4-chlorobenzaldehyde (1 mmol) over β-SnO (1.5 mmol) and Cu_2O (5 mol % with respect to carbonyl) in THF−H_2O (9:1 v/v) and under reflux afforded 52% of the desired homoallylic alcohol (Table 1, entry 2). The remarkable effect of catalyst and solvent is demonstrated by the fact that (a) reaction in THF−H_2O (9:1 v/v) but in the absence of Cu_2O gave only 9% of product (entry 1), while the reaction in the presence of Cu_2O but in dry THF gave 12% of the product (entry 4). Also Cu_2O alone fails to promote the carbonyl allylation. Following this initial success, a number of optimization experiments have been carried out, the major highlights of which are enumerated below. Solvent plays an important role in this reaction. Among the various solvents screened, DCM−H_2O appears to be the best choice compared to THF−H_2O, MeCN−H_2O, $CHCl_3$−H_2O, and dioxane−H_2O (entry 10). The optimized ratio of water to organic solvent is 9:1 (v/v). Remarkably, reactions conducted under anhydrous conditions either failed completely or gave very poor yields of product (entry 8). Reactions at ambient temperature are slow, indicating poor activation of the metal oxide surface (entries 6, 13). Further, the optimum loading of Cu_2O is 10 mol % (entries 9−12). While allyl chlorides were much slower in reactivity compared to allyl bromides, attempted activation of allyl alcohol failed. To further check if halide ions are responsible in the activation of oxide surface, the reaction was carried out in the presence of an equivalent amount of LiBr (with respect to β-SnO). The rate of reaction in the presence and absence of LiBr is found to be invariant, which rules out the possibility of oxide-surface activation by halide ion (compare entries 7, 11 with entries 6, 10). On the basis of the above results, we concluded that the best conditions are shown in Table 1, entry 10.

Table 1. β-SnO/Cu₂O-Promoted Carbonyl Allylation of 4-ClC₆H₄CHO with H₂C═CHCH₂Br: Effect of Solvent and Catalyst Loading[a]

no.	catalyst (mol %)	solvent	solvent:H_2O (v/v)	time (h)	yield (%)[b]
1	NIL	THF−H_2O	9:1	6	9
2	5	THF−H_2O	9:1	6	52
3	10	THF−H_2O	9:1	6	70
4	10	THF		5.5	12
5	10	THF−H_2O	3:2	5.5	55
6[c]	10	THF−H_2O	9:1	10	45
7[c,d]	10	THF−H_2O	9:1	10	41
8	10	DCM		10	13
9	5	DCM−H_2O	9:1	9	52
10	10	DCM−H_2O	9:1	7	80
11[d]	10	DCM−H_2O	9:1	7	80
12	20	DCM−H_2O	9:1	7	75
13[c]	10	DCM−H_2O	9:1	10	25

[a] Reaction conditions: β-SnO 1.5 mmol, 4-ClC_6H_4CHO 1 mmol, H_2C═$CHCH_2Br$ 2 mmol. [b] Isolated yields after chromatography based on aldehydes. [c] Reaction at room temperature. [d] Reaction in the presence of LiBr (1.5 mmol).

Scheme 1. Optimized Reaction Parameters



Aided by the above success, the reaction was extended to aldehydes and ketones to generate homoallylic alcohols by standard conditions (Scheme 1, 2, Table 2). All the reactions provide exclusively the γ-regioselective product. Presumably such regioselectivity arises via a six-membered cyclic transition state which is favored in solvents having higher dielectric constants. However the diastereoselectivities (*syn*:*anti* ratio) of the homoallylic alcohols are poor and varied from substrate to substrate (entries 1−4, 6). Heteroaromatic aldehydes are amenable for the reaction. For example, thiophene carboxaldehyde reacted with 1-bromobut-2-ene and

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Table 2. Allylation of Carbonyl Compounds RCOR′ with Allyl Bromides $R_1R_2C{=}CHCH_2Br$

	bromides		carbonyls				
no.	R_1	R_2	R	R′	time (h)	yield[a] (%)	ratio[b] (*syn*:*anti*)
1	Me	H	4-ClC_6H_4	H	6	78	50:50
2	Me	H	Ph	H	6.5	79	19:81
3	Me	H	$Me(CH_2)_5$	H	3	65	49:51
4	Me	H	$Me(CH_2)_8$	H	2	54	50:50
5	Me	H	$Me(CH_2)_6CH{=}CH$	H	3	57	
6	Me	H	2-thenyl	H	2	60	34:66
7	Me	H	$OCH(CH_2)_3CHO$		4	35	
8	Me	Me	2-thenyl	H	3	65	
9	^{n}Pr	H	$PhCH_2$	H	3	51	
10	H	H	Ph	PhCO	9	50	
11	H	H	Me	$EtOCOCH_2$	10	71	
12	H	H	Me	$MeCOCH_2$	12	40	
13	H	H	isobenzofuran-1,3-dione		6	41	
14	H	H	cyclohexanone		3	33	
15	H	H	Ph	Me	9		
16	H	H	Me	^{i}Bu	9		

[a] Isolated yield after chromatography. [b] *syn*:*anti* ratio determined from ^{1}H NMR.

Scheme 2. Carbonyl Selectivity of β-SnO/Cu_2O Reagent

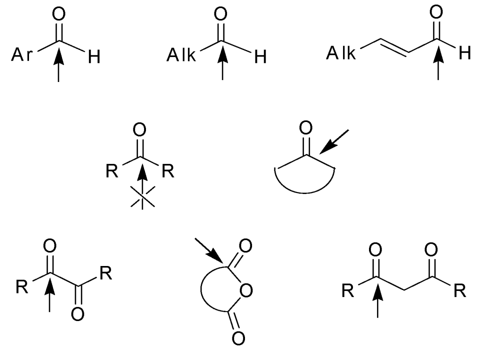

Table 3. XRD Data of β-SnO and Cu_2O before and after Treatment with 3-Bromopropene

sample	description	observed *d*-values (Å)[a]
A	β-SnO	3.03, 2.72, 2.44, 1.79
B	β-SnO/THF−H_2O/reflux	3.03, 2.72,2.44, 1.79
C	Cu_2O	2.48, 2.13, 1.51, 1.29
D	Cu_2O/THF−H_2O/reflux	2.48, 2.13, 1.51, 1.29
$\mathbf{S_{UTR}}$	β-SnO+Cu_2O/THF−H_2O/reflux	3.03, 2.72, 2.48, 2.44, 2.13, 1.51
$\mathbf{S_{TR}}$	β-SnO+Cu_2O+3-bromopropene/ THF−H_2O/reflux	3.29, 3.03, 2.48, 2.02, 1.72, 1.63

[a] JCPDS references: β-SnO: 6−0395; SnO_2: 21−1250; Cu_2O: 5−0667; CuO 80−1917; CuBr: 82−2118.

1-bromo-3-methylbut-2-ene, giving rise to 60% and 65% of the desired homoallylic alcohols, respectively (entries 6, 8). Interestingly, in the reaction of pentanedial with a 4-fold excess of 1-bromobut-2-ene, the bis-allylated product was isolated (entry 7). Unlike the aldehyde selectivity observed in general for allylstannanes,[3,6] the new reagent combination shows reactivity toward ketones and in particular 1,2- and 1,3-diketones. While reactions failed in the case of monoketones such as methyl isobutyl ketone and acetophenone, cyclic monoketone such as cyclohexanone reacts to give the corresponding monoallylated product (entry 14). Facile monoallylation only at one carbonyl center of 1,2- and 1,3-diketones is noteworthy (entries 10−12). Anhydride such as isobenzofuran-1,3-dione is also found to be reactive (entry 13).

Activation of Allyl Halide by β-SnO/Cu_2O: Surface Diagnostics. Barbier-like carbonyl allylation reaction using the present reagent combination is completely a heterogeneous phase reaction. In corroboration with this, several attempts to detect any soluble organotin or other intermediate species by in-situ ^{1}H and EIMS studies failed. Therefore, to diagnose the likely interactions/activation, we looked for the tools and techniques used in heterogeneous solid-supported reaction, in particular powder X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). XPS is an important tool for the diagnosis of surface and bulk characteristics, especially for metal oxides.[13] The BE of the valence electron is highly sensitive to the oxidation state and chemical environment of the atom. The major inquiries toward the above studies are as follows.

1. What is the role of catalytic Cu_2O during the reaction, and does it form any bimetallic association with β-SnO at the initial stage of the reaction?

2. Is a true Sn−C bond formed at the metal oxide surface?

Accordingly, XRD and XPS analyses were carried out for β-SnO−Cu_2O before and after treatment with 3-bromopropene. Sample $\mathbf{S_{TR}}$ was obtained by refluxing a mixture of β-SnO and Cu_2O in THF−H_2O (9:1 v/v) for 0.5 h under inert atmosphere followed by addition of 3-bromopropene. The mixture was further refluxed for 7 h, solvent was removed under reduced pressure, and the solid residue was dried completely under vacuum (0.001 Torr) for 6 h. Sample $\mathbf{S_{UTR}}$ was prepared under identical treatment as above but in the absence of 3-bromopropene.

XRD Analysis. XRD analysis was carried out on samples $\mathbf{S_{TR}}$, $\mathbf{S_{UTR}}$, β-SnO, and Cu_2O (Table 3). We observed that the XRD patterns of β-SnO, Cu_2O, or a combination of β-SnO and Cu_2O remain unaltered before and after refluxing in THF−H_2O. This rules out any preactivation of the oxide matrix by solvent alone, formation of any bimetallic association, and mixed oxide formation. This is also confirmed from the IR study. Sample $\mathbf{S_{TR}}$ shows peaks due to β-SnO and Cu_2O and new peaks at 3.29, 2.02, 1.72, and 1.63. These new peaks could be due to a species having a Cu(I)−X or −O−

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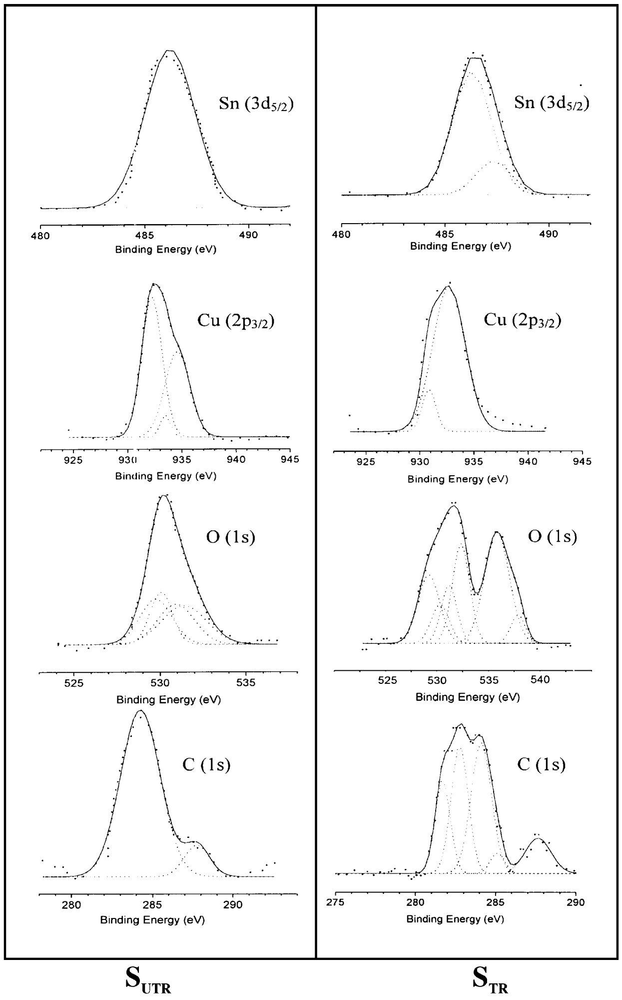

Figure 2. Narrow scan XPS of samples $\mathbf{S_{UTR}}$ and $\mathbf{S_{TR}}$ in the C(1s), O(1s), Cu(2p$_{3/2}$), and Sn (3d$_{5/2}$) regions.

Table 4. XPS Data BE (eV) of β-SnO/Cu$_2$O before (S_{UTR}) and after (S_{TR}) Treatment with 3-Bromopropene

entry	element	S_{UTR}	S_{TR}	β-SnO	Cu$_2$O
1	Sn (3d$_{5/2}$)	486.2	486.3, 487.3	486.1	
2	Cu (2p$_{3/2}$)	932.3, 933.5^a, 934.6^b	930.8, 932.5		932.5
3	O (1s)	529.7^c, 530.0, 530.9, 531.3^c	528.9, 530.0, 530.9, 532.0, 535.5, 537.6	530.0	530.4
4	C (1s)	284.4, 287.7	281.9,284.4, 283.6, 287.5		

Cu−X motif, the exact nature of which cannot be speculated.

XPS Analysis. Narrow scan XPS analyses were performed on samples $\mathbf{S_{TR}}$ and $\mathbf{S_{UTR}}$ following argon ion etching. The data, after multi-Gaussian peak fitting, were corrected with respect to the C(1s) BE of 284.4 eV. The binding energies (BE in eV) of O (1s), Sn (3d$_{5/2}$), Cu (2p$_{3/2}$), and C (1s) were compared to those in the literature to gain an understanding of the plausible species present (Figure 2, Table 4). The binding energy of the electron emitted from the 3d$_{5/2}$ level in tin is very informative regarding the chemical environment of the atom and increases from +II to the +IV state.[14-16] In the present case, the signals at 486.3 eV in sample $\mathbf{S_{TR}}$ and 486.2 eV in $\mathbf{S_{UTR}}$ are due to β-SnO (Table 4, entry 1). In $\mathbf{S_{TR}}$ the new signal at higher binding energy (487.3 eV) indicates the formation of a tin(IV) species, which compares well with organotin(IV) halides.[17] Therefore, we presume that the new species might arise from an oxidative interaction of allyl bromide at the tin site. The Cu (2p$_{3/2}$) signals at 932.3 in $\mathbf{S_{UTR}}$ and 932.5 in $\mathbf{S_{TR}}$ might be due to Cu$_2$O (Table 4, entry 2). In the sample $\mathbf{S_{TR}}$ a new signal appeared at a much lower BE (930.8) than commonly observed for Cu(I) compounds, emphasizing an increase in electron density around Cu$_2$O by additional linkage to other functional group(s). A suggestion pertaining to this is a probable interaction of allyl bromide on the Cu$_2$O surface, preferably via Cu(I)−olefin binding.[18] The XPS analyses in the the O(1s) and C(1s) regions further corroborate the above view (Table 4, entries 3, 4). Most noteworthy are the signals at 283.6 (C1s) and 532.0 (O1s) in $\mathbf{S_{TR}}$, which might be due to the proposed organotin(IV) species. In summary, the XPS study suggests plausible involvement of two kinds of binding interaction of allyl halide across β-SnO/Cu$_2$O. The first one is an alkene−metal interaction at the copper site, and the second one is an oxidative interaction of a carbon−halogen bond at the tin site. The two interactions just described between β-SnO, Cu$_2$O, and 3-bromopropene could be viewed as in Figure 3.

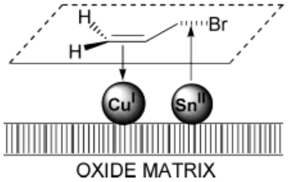

Figure 3. Plausible interaction of allyl halide over β-SnO/Cu$_2$O.

Plausible Mechanism of Allylation. While it is difficult to delineate the complete mechanistic sequence in the present all-oxide Barbier reaction, the results of XRD and XPS diagnostics, the catalytic effect of Cu$_2$O, and the known chemistry of σ-allyltin(IV) guided us to indicate the major bond-forming steps (Figure 4). Thus an initial activation of allyl halide at the copper site preferably through an alkene−copper interaction is a strong possibility (step a). Whether a π-allyl-like intermediate is involved is worthy of consideration as well. In the next step, an allyl transfer from the copper site to the tin site leading to a tin(IV) intermediate is presumed (step b). This would be akin to a redox-transmetalation pathway normally encountered in homogeneous reaction of d^8/d^{10} metal complexes with soluble tin(II) precursors. Finally, the new tin(IV) species will take part in a follow-up reaction with carbonyl (step c).

Concluding Remarks. Although carbon−carbon bond forming reactions over metal oxide (silica, alumina,

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(17) Sn (3d$_{5/2}$) BE (eV): Ph$_3$SnCl = 487.2; (PhCH$_2$)$_3$SnCl = 487.1; (PhCH$_2$)$_2$SnCl$_2$ = 487.8 (ref 16).

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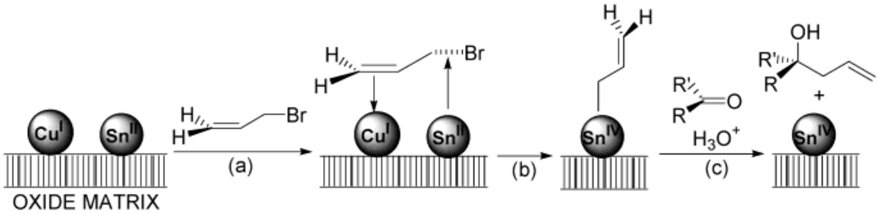

Figure 4. Carbonyl allylation by β-SnO/Cu$_2$O: major bond-forming steps.

zeolites, and others) are well known, examples of metal−carbon bond forming reactions are limited to polymerization reactions only.[19] Surface organometallic chemistry is an emerging area of current interest, which relies on the application of the tools and concepts of organometallic chemistry toward organic reactions over surfaces.[20] In the context of the present work, recently reported carbonyl metathesis of aldehydes over a TiO$_2$ surface, cyclotrimerization of alkynes and cyclization of diene over a modified silica surface, and Suzuki coupling over silver oxide are noteworthy.[21] Surface chemistry of metal oxides is majorly dictated by (a) the coordination environment of the surface atoms, (b) the redox properties of the oxide, and (c) the oxidation state of the surface.[22] In general, the above factors are equally pertinent to organometallic reactions. Moreover, the surface by itself can be considered as a “rigid ligand”. In the present work we demonstrated that the oxide reagent comprising β-SnO and Cu$_2$O is well suited toward the activation of an organic electrophile and in mediating a Grignard-like reaction with carbonyl compounds. The bimetallic nature of the reagent and the profound effect of water to promote the reaction is most noteworthy. Surface organometallic species have been indicated by XPS analysis; however, the detailed mechanistic rationale is yet to emerge. We presume that oxo-clusters of tin(II) and copper(I) could be the ideal model candidates to further probe the mechanism.

Experimental Section

General Methods. All reactions were performed under an inert atmosphere of argon. Substituted allyl bromides were prepared from the corresponding alcohols (Lancaster) using standard protocol. β-SnO and Cu$_2$O were prepared according to literature procedures. All the starting materials were >98% pure via NMR. ^{1}H NMR spectra were taken in CDCl$_3$ on a Bruker-200 spectrometer. EIMS (70 eV) spectra were recorded using VG MicroMass 7070H and VG Autospec M mass spectrometers. IR spectra were recorded on a Perkin-Elmer 883 instrument. X-ray powder diffraction data were obtained using a Phillips PW-1840 instrument using a Cu Kα target at 40 kV. X-ray photoelectron spectra were obtained on powdered samples pressed into gold foils by using a VG Escalab MKII spectrometer fitted with a Mg Kα X-ray source (1253.6 eV). Spectra were computer-fitted to 70% Gaussian line shapes, without using any constraints to the final fit, and the binding energies were reproducible to within 0.1 eV. The carbon 1s binding energy at 284.4 eV was used to calibrate the spectra.

Typical Procedure for the Synthesis of Homoallylic Alcohols using β-SnO and Cu$_2$O as Catalyst. A mixture of 4-chlorobenzaldehyde (140 mg, 1 mmol) and 1-bromobut-2-ene (270 mg, 2 mmol) in DCM (2 mL) was added slowly to a refluxing solution containing β-SnO (202 mg, 1.5 mmol) and Cu$_2$O as catalyst (14 mg, 0.1 mmol) in DCM−H$_2$O (2.5−0.5 mL) and under argon. The mixture was further refluxed for 6 h (TLC monitoring on silica gel, eluent: *n*-hexane−ethyl acetate, 9:1). An aqueous solution of ammonium fluoride (15%, 10 mL) was added to the reaction mixture, and the organic layer was extracted with diethyl ether (3 × 10 mL), washed with water (2 × 10 mL) and brine (2 × 10 mL), and dried over magnesium sulfate. Solvent removal followed by column chromatography (eluent: ethyl acetate−*n*-hexane 2% to 10%) afforded pure 1-(4-chlorophenyl)-2-methylbut-3-en-1-ol (153 mg, 78% with respect to aldehyde).

Sample Preparation for XRD and XPS Study. Sample $\mathbf{S_{TR}}$ was prepared in the following way: a mixture of β-SnO (606 mg, 4.5 mmol) and Cu$_2$O (86 mg, 0.6 mmol) was taken in THF−H$_2$O (9−1 mL) under an argon atmosphere. After the mixture was refluxed for 0.5 h, a mixture of 3-bromopropene (968 mg, 8 mmol) was added dropwise. The mixture was refluxed for 7 h. Solvent was removed under reduced pressure. The solid after drying under vacuum was subjected to further analysis. Sample $\mathbf{S_{UTR}}$ was prepared analogously but in the absence of 3-bromopropene.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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