Facile homopropargylation of aldehydes by propargyl bromides over tetragonal tin(II)oxide and catalytic palladium(0) occurs which is proposed to involve the prior formation of dimuclear allenylpalladium followed by redox transmetalation to β-SnO.

The organic reactivity of allenyl and propargyl metal reagents continues to evoke widespread interest due to their chemo, regio, stereo and enantioselectivity aspects.1 Like their allyl counterpart, these reagents can be synthesized from organic halides, esters or ketones by Barbier and Grignard methodologies.2,3 The metalloc tropic rearrangement between propargyl and allenyl organometallics often result in poor regioselection in the end organic product for example in the case of reaction with carbonyl compounds and other electrophiles. In this context recent approaches to tune the selectivity toward either acetylenic or allene end organic product is noteworthy.4,5

One of our research programs is in the area of metal oxide mediated organic synthesis (MOMOS).6 We reasoned that metalloc tropic rearrangement might be arrested/attenuated if an organometallic fragment is appended to an oxide matrix, the latter acting as a restricted scaffold. The present communication describes our endeavour toward this goal for the reaction of homopropargyl alcohols with aldehydes mediated by tetragonal tin(II) oxide (β-SnO) and catalytic palladium(0) or palladium(II) complexes. Tetragonal blue–black tin(II) oxide was chosen due to its conceptual similarity to stannylenes: SnY2. Moreover the Sn–Sn distance between metal atoms in adjacent layers in β-SnO (3.70 Å) is similar to that in elemental tin.7 The above features are expected to promote oxidative-addition or oxidative transmetalation across β-SnO.

The model reaction of 3-bromo-3-methylbut-1-yn-2-ol 1a (2 mM) and 4-chlorobenzaldehyde 2a (1 mM) in the presence of catalytic Pd2(dba)3 (0.01 mM) and β-SnO (1.5 mM) in THF–H2O (9:1 v/v) at 70 °C for 16 h gives rise to the corresponding homopropargyl alcohol 3 in 81% yield (Scheme 1). Under identical conditions, uncatalyzed reaction affords <5% of the product. Also important is the effect of water: reaction in dry THF yields 57% of the product. Other solvent systems such as THF, DCM, DCM–H2O (9:1 v/v), MeOH–H2O (9:1 v/v) are also found to be less effective. The order of efficiency is NiCl2(PPh3)2 < PdCl2(PPh3)4 < PbCl2(PPh3)2 < PdCl2(PhCN)2 < Pd2(dba)3. Since the reaction takes place in a heterogeneous solid–liquid interface, we assumed that surface characteristics might influence the reactivity. Indeed cubic–β-SnO (SnO-A, Fig. 1) is found to be more reactive than other morphological forms (SnO-B, Fig. 1).8 Thus reaction of 3-chloroprop-1-yn-2-ol with SnO-A gives rise to 8 in 52% isolated yield after 12 h. Under similar conditions, SnO-B affords only 30% of the product.

The reaction is extended to propynyl bromides bearing terminal alkynes and aldehydes (Table 1) affording the product. Also important is the effect of water: reaction in dry THF yields 57% of the product. Other solvent systems such as THF, DCM, DCM–H2O (9:1 v/v), MeOH–H2O (9:1 v/v) are also found to be less effective. The order of efficiency is NiCl2(PPh3)2 < PdCl2(PPh3)4 < PbCl2(PPh3)2 < PdCl2(PhCN)2 < Pd2(dba)3. Since the reaction takes place in a heterogeneous solid–liquid interface, we assumed that surface characteristics might influence the reactivity. Indeed cubic–β-SnO (SnO-A, Fig. 1) is found to be more reactive than other morphological forms (SnO-B, Fig. 1).8 Thus reaction of 3-chloroprop-1-yn-2-ol with SnO-A gives rise to 8 in 52% isolated yield after 12 h. Under similar conditions, SnO-B affords only 30% of the product.

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corresponding homopropargyl alcohols 4–10 in 43–74% isolated yields. Substitution at the 3-position retards the activity, as in the case of 3-phenylprop-2-ynyl bromide (entry 8). The reaction is also chemoselective towards aldehyde over ketone.

Activation of propargyl halides and esters by Pd(0) has been the subject of intense investigation. With reference to carboxyl propargylation, Tamura, Marshall and others have recently shown that facile reductive transmetalation can occur between allenylpalladium to zinc or indium. We anticipated that a similar pathway involving reductive transmetalation from allenylpalladium to zinc or indium.4 We anticipated that a good first order fit for the disappearance of the halide concentration of individual species. Treatment of the data yields ratio of peak area in each case provides a measure of the relative concentration of individual species. A good first order fit for the disappearance of the halide 1c with a half-life value of 2.2 h\(^{-1}\) (Fig. 2). Interestingly the data for the appearance of allenylpalladium do not respond to first-order; instead they are representative of slow conversion of one allenyl isomer to another. Taking hints from the recent work of Ogoshi et al.,10 we propose a tentative mechanism involving isomerization of a mononuclear allenylpalladium I to dinuclear species II. The latter can undergo reductive transmetalation reaction with \(\beta\)-SnO to afford allenyl-Sn intermediate III (Scheme 2). Ex-situ IR studies indeed support such a process. Untreated \(\beta\)-SnO shows absorptions at 315, 500 and 802 cm\(^{-1}\). A sample of \(\beta\)-SnO, 1c and Pd\(_2\)(dba)\(_3\) (2 mol %) in THF is refluxed for 12 h, filtered, dried under vacuum. The IR spectrum of 1c-Sn.Sn.O thus treated shows new peaks due to allenylmetal at (cm\(^{-1}\)): 2920 (\(\delta\)CH stretching), and 1619 (\(\delta\)C=O stretching), 1030 (\(\delta\)CH out-of-plane bending), and 1580 (\(\delta\)C=C wagging), 1030 (\(\delta\)CH out-of-plane bending), 1619 (\(\delta\)C=C stretching), and 2920 (\(\delta\)CH stretching). Further work is underway to characterize the intermediate and extend the scope of the present reaction.

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Notes and references


Fig. 2 \(^1\)H NMR monitoring for the reaction of 1a with Pd\(_2\)(dba)\(_3\). Plot showing peak area ratio (A/A\(_{\text{ref}}\)) against time (A), and corresponding logarithmic plot (B). Allenic proton (\(\gamma\)).