Palladium(0) catalyzed regioselective carbonyl propargylation across tetragonal tin(II) oxide *via* redox transmetallation†

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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 dinuclear allenylpalladium followed by redox transmetallation 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 carbonates by Barbier and Grignard methodologies.[2,3] The metallotropic 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 allenic 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 metallotropic 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 propargyl halides 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: SnY_2. 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 transmetallation across β-SnO.

The model reaction of 3-bromo-3-methylbut-1-yne **1a** (2 mM) and 4-chlorobenzaldehyde **2a** (1 mM) in the presence of catalytic $Pd_2(dba)_3$ (0.01 mM) and β-SnO (1.5 mM) in THF–H_2O (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–H_2O (9:1 v/v), MeOH–H_2O (9:1 v/v) are also found to be less effective . The effect of various catalysts has been studied for the carbonyl propargylation reaction. The order of efficiency is $NiCl_2(PPh_3)_2$ < $Pd(PPh_3)_4$ < $PtCl_2(PPh_3)_2$ < $PdCl_2(PPh_3)_2$ < $PdCl_2(PhCN)_2$ < $Pd_2(dba)_3$. 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-yne and **2a** over 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
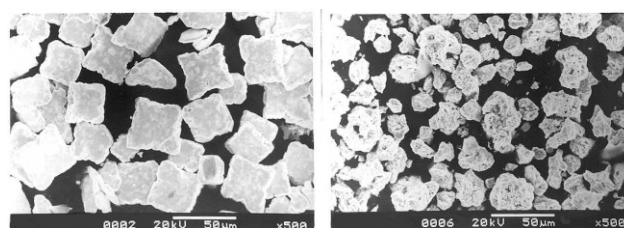

Fig. 1 SEM micrograph of two morphologies of β-SnO. The cubic form (**SnO-A**) is most reactive towards homopropargylation.

Table 1 Propargylation of various carbonyl compounds mediated by β-SnO and catalytic $Pd_2(dba)_3$ (1 mol%) in THF–H_2O

No	Halide	Carbonyl	Product	Time/ h	Yield (%)[a]
1	**1b**	**2a**	**4**	10	63
2	**1b**	**2b**	**5**	14	74
3	**1b**	**2c**	**6**	12	54
4	**1a**	**2d**	**7**	16	48
5	**1c**	**2a**	**8**	12	60
6	**1c**	**2e**	**9**	14	55
7	**1c**	**2f**	**10**	16	43
8	**1d**	**2a**		24	0

[a] Refers to isolated yield.

Scheme 1

† Electronic supplementary information (ESI) available: general method and experimental procedure and spectroscopic data for compounds **3–10**. See http://www.rsc.org/suppdata/cc/b2/b211555g/

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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.[9] With reference to carbonyl propargylation, Tamaru, Marshall and others have recently shown that facile redox transmetallation can occur between allenylpalladium to zinc or indium.[4] We anticipated that a similar pathway involving redox transmetallation from allenylpalladium to β-SnO could be responsible in our case. ^{1}H NMR monitoring of a solution of Pd$_2$(dba)$_3$ (9.14 mg, 0.01 mM) and **1c** (2.38 mg, 0.02 mM) in CDCl$_3$ at regular time intervals show the slow disappearance of peaks due to **1c** (δ 2.5, t, 1H and δ 3.9, t, 2H). Concomitant appearance of a peak due to allenylpalladium is observed (δ 4.1–4.3, m, 3H). The integrated ratio of peak area in each case provides a measure of the relative concentration of individual species. Treatment of the data yields 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 isomerisation of a mononuclear allenylpalladium I to dinuclear species II. The latter can undergo redox transmetallation reaction with β-SnO to afford allenyl-Sn intermediate III (Scheme 2). *Ex-situ* IR studies indeed support such a process. Untreated β-SnO shows absorptions at 315, 500 and 802 cm^{-1}. A sample of β-SnO, **1c** and Pd$_2$(dba)$_3$ (2 mol%) in THF is refluxed for 12 h, filtered, washed several times with THF to remove the catalyst, and dried under vacuum. The IR spectrum of β-SnO thus treated show new peaks due to allenylmetal at (cm^{-1}): 820 (=CH$_2$ wagging), 1030 (=CH out-of-plane bending), 1619 (–C=C=C– stretching), and 2920 (=CH stretching). Further work is underway to characterize the intermediate and extend the scope of the present reaction.
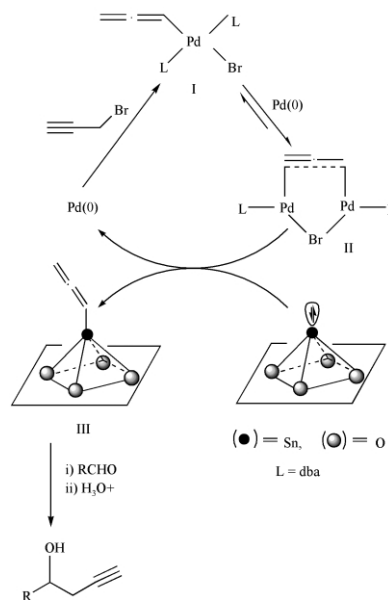
Scheme 2

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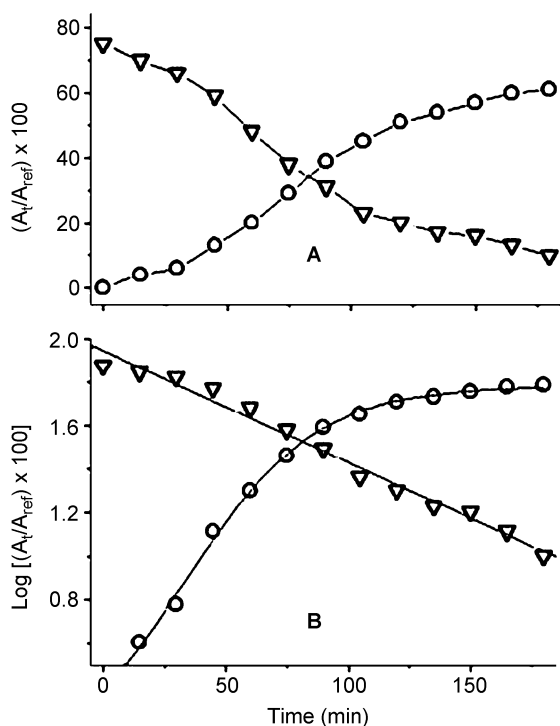
Fig. 2 ^{1}H NMR monitoring for the reaction of **1a** with Pd$_2$(dba)$_3$. Plot showing peak area ratio (A_t/A_{ref}) against time (A), and corresponding logarithmic plot (B). Acetylenic proton ($\triangledown$). Allenic proton ($\circ$).