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Barbier reaction in the regime of metal oxide: the first example of carbonyl allylation mediated by tetragonal tin(II) oxide[†]

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Facile synthesis of homoallylic alcohols is achieved from allyl halides and aldehydes or ketones over an all-oxide heterogenous media involving β -SnO and catalytic Cu₂O.

The reaction of a carbonyl compound and an organic halide in the presence of magnesium metal, trivially known as the Barbier reaction, has carved a distinct niche in synthetic organic and pharmaceutical chemistry.¹ In the hundred years, since its original discovery,² this one-pot variant of the Grignard reaction has been demonstrated solely with zerovalent metals, and metal halides.3 With specific reference to carbonyl allylation via tin reagents,4 both preformed as well as in situ generated allylstannanes continue to evoke widespread⁵ interest due to their chemo-, regio-, stereo-, and enantioselecivity aspects. Our continuing interest⁶ in organotin chemistry and recent interest in heterobimetallic reagents, prompted us to explore a gateway into the Barbier reaction via metal oxides. We are delighted to disclose herein a facile carbonyl allylation reaction over tetragonal tin(II)oxide (β -SnO)⁷ and catalytic Pt(II), Pd(II), Pd(0), Cu(I) salts/complexes in organic-aqueous or aqueous medium (Scheme 1). Further extension to β -SnO/ catalytic Cu₂O affords an all-oxide reagent in Barbier allylation. We believe that the results provide new directions in the synthetic and mechanistic issues of Grignard type carboncarbon bond forming reactions across metal oxides.

The model reaction of 1-bromoprop-2-ene **1a** (2 mM) and 4-chlorobenzaldehyde **2a** (1 mM) in the presence of catalytic PtCl₂(PPh₃)₂ **4a** (0.01 mM) and β -SnO (1.5 mM) in THF–water (9:1 v/v) at 70 °C for 6 h gives rise to the desired homoallylic alcohol 1-(4-chlorophenyl)but-3-ene-1-ol **3a** in 96% isolated



Table 1 β -SnO promoted carbonyl allylation: effect of catalyst

//	×	+ СІСНС) β-SnO catalyst	OH CI
#	Х	Catalyst	Solvent	Yield (%)
1	Br	NIL	THF-H ₂ O	15
2	Br	PtCl ₂ (PPh ₃) ₃ 4a	THF	15
3	Br	4a	THF-H ₂ O	96
4	Br	$Pd_2(dba)_3$ 4b	THF-H ₂ O	76
5	Br	Cu_2O 4c	$DCM - \tilde{H}_2O$	80
6	Cl	4c	DCM-H ₂ O	52
7	Br	CuCl 4d	THF-H ₂ O	33

† Electronic supplementary information (ESI) available: further experimental details, XRD and EIMS spectra. See http://www.rsc.org/suppdata/ cc/b1/b104500h/ yield (Table 1, entry 3).⁸ Under identical conditions, uncatalyzed reaction affords < 15% of the product. Also important is the remarkable effect of water: reaction in the presence of catalyst **4a** but in dry THF yields <15% of the product, while reaction in water alone gives rise to 55% of the desired alcohol. That there is no phase change of β -SnO before and after treatment with THF–water, is indicated by XRD. Among the other catalysts screened, NiCl₂(PPh₃)₂, PdCl₂(PhCN)₂ and Pd₂(dba)₃·CHCl₃ are found unsatisfactory (<25% yields), but PdCl₂(PPh₃)₂, Pd₂(dba)₃, and CuCl afford moderate to excellent yields of product. The generality of the reaction has been successfully tested with aliphatic, aromatic and heteroaromatic aldehydes and substituted allyl bromides (Table 2, entry 1–5).

Table 2 Allylation of various carbonyl compounds with β-SnO/catalyst

#	Halide	Carbonyl	Cat	Product	Yield (%)
1	Br	Fc-CHO	4a	OH Fc	70
2	1b 1b	2b	4 a		65
3	Br) 4a	MeO OH	63
	1c	2d		3d OH	
4	1d	BnCHO 2e	4b	С ₃ Н ₇ Зе	53
5	1d	сі— Сно	4b		76
6	1c	2f сі Драгосно 2g	4c	3f OH	79
7	1c	Me(CH ₂) ₈ CHO	4c	OH Me(CH ₂) ₈	54
8	1a	2n Me OEt	4c	OH Me 3i	71
9	1a	Ph Ph	4c	OH Ph	45
		2j		3ј	



Fig. 1 ¹H NMR spectra in DMSO-d₆ of (a) allyl bromide; (b) residue from the reaction of β -SnO-allyl bromide; (c) residue from the reaction of β -SnO-allyl bromide-catalytic Pd₂(dba)₃ [dba = dibenzylideneacetone].



Fig. 2 XPS spectra in the C-1s region of (a) untreated β -SnO/Cu₂O—peaks at 284.5, 287.6; (b) β -SnO/Cu₂O after treatment with allyl bromide—peaks at 280.8, 283.2, 284.5, 288.9.

Triggered by the success as above, we wished to attempt *an all-oxide reagent* for carbonyl allylation. The reagent combination of β -SnO and catalytic Cu₂O in refluxing DCM–water (9:1 v/v) is adjudged to be the best (Table 1, entry 5–6; Table 2, entry 6–9).

While mechanistic studies are underway in our laboratory, preliminary experiments clearly establish the formation of new tin-carbon bonded species during the course of the reaction. Thus, a mixture of β -SnO (2 mM), catalytic Pd₂(dba)₃ (0.02 mM) and allyl bromide (4 mM) in THF-H₂O (99:1 v/v) was refluxed for 10 h. Following filtration under argon, and solvent removal, the residue was examined by ¹H NMR. The spectrum (Fig. 1, spectrum c) showed the formation of a new σ -allyl tin species⁹ characterized by allylic proton signals at 2.55 ppm $[^{2}J(^{119}Sn-^{1}H) = 154 Hz]$, as compared to that of allyl bromide at 4.1 ppm (spectrum a). No such species was detected in the reaction without catalyst (Fig. 1, spectrum b). On the other hand, reaction of allyl bromide with Pd₂(dba)₃ alone, showed signals due to known π -allylpalladium intermediate.¹⁰ We conclude that the latter assists the formation of the σ -allyl tin species (Scheme 2).¹¹

Unlike the above, we could not detect any soluble organotin species in the reaction of allyl bromide with β -SnO/catalytic Cu₂O, thereby indicating that the incipient metal–carbon intermediate is formed in the solid phase. To test this hypothesis, narrow scan XPS analysis was performed for β -SnO/Cu₂O before and after its reaction with allyl bromide. Formation of new species is indicated by major shifts in the binding energies of Sn (3d_{5/2}, 3d_{3/2}), Cu (2p_{3/2}, 2p_{1/2}), O (1s)



Scheme 2 π -Allylpalladium attacks tetragonal tin(II) oxide.

and C (1s) peaks.¹² Multi-Gaussian peak analysis of carbon-1s spectra shows two new peaks at 280.8 and 283.2 eV (Fig. 2, spectrum b) indicative of metal–carbon bonded species. Prior interaction of alkene with copper(I) is likely to promote the formation of an allyltin intermediate.¹³ We hope to address this and related mechanistic issues in future studies.

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- 8 Typical procedure: a mixture of **1a** (242 mg, 2 mM) and **2a** (140 mg, 1 mM) in THF (2 mL) was added slowly to a refluxing solution containing β -SnO (202 mg, 1.5 mM) and **4a** (8 mg, 0.01 mM) in THF–H₂O (2.5 mL–0.5 mL) and under argon. Upon completion (TLC monitoring: silica gel, eluent: *n*-hexane–EtOAc 9:1), an aqueous solution of NH₄F (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), brine (2 × 10 mL) and dried over magnesium sulfate. Solvent removal followed by column chromatography (eluent *n*-hexane–ethyl acetate 9:1) afforded pure **3a** (175 mg, 96% w.r.t. aldehyde). Similar procedure as above was followed for reactions with Cu₂O as catalyst (14 mg, 0.1 mM), the solvent used was CH₂Cl₂–H₂O (4.5 mL–0.5 mL).
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