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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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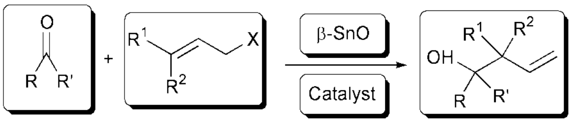
**Facile synthesis of homoallylic alcohols is achieved from allyl halides and aldehydes or ketones over an all-oxide heterogenous media involving $\beta$-SnO and catalytic Cu$_2$O.**

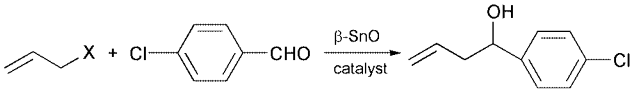
The reaction of a carbonyl compound and an organic halide in the presence of magnesium metal, trivially known as the Barbier reaction, has carved a distinct niche in synthetic organic and pharmaceutical chemistry.[1] In the hundred years, since its original discovery,[2] this one-pot variant of the Grignard 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 widespread[5] interest due to their chemo-, regio-, stereo-, and enantioselecivity aspects. Our continuing interest[6] 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 ($\beta$-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 $\beta$-SnO/catalytic Cu$_2$O 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 carbon–carbon 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 PtCl$_2$(PPh$_3$)$_2$ **4a** (0.01 mM) and $\beta$-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 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 $\beta$-SnO before and after treatment with THF–water, is indicated by XRD. Among the other catalysts screened, NiCl$_2$(PPh$_3$)$_2$, PdCl$_2$(PhCN)$_2$ and Pd$_2$(dba)$_3$·CHCl$_3$ are found unsatisfactory (< 25% yields), but PdCl$_2$(PPh$_3$)$_2$, Pd$_2$(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).



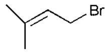
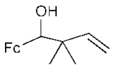
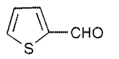
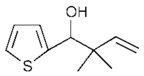
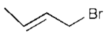
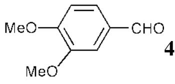
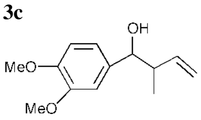
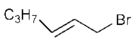
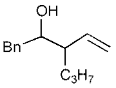
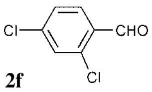
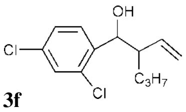
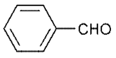
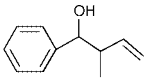
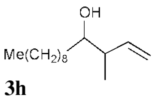
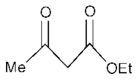
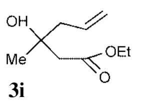
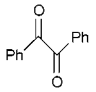
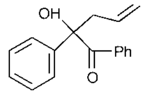
**Scheme 1**

**Table 1** $\beta$-SnO promoted carbonyl allylation: effect of catalyst



| # | X | 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$_2$O **4c** | DCM–H$_2$O | 80 |
| 6 | Cl | **4c** | DCM–H$_2$O | 52 |
| 7 | Br | CuCl **4d** | THF–H$_2$O | 33 |

**Table 2** Allylation of various carbonyl compounds with $\beta$-SnO/catalyst

| # | Halide | Carbonyl | Cat | Product | Yield (%) |
|---|---|---|---|---|---|
| 1 | <br>**1b** | Fc-CHO<br>**2b** | **4a** | <br>**3b** | 70 |
| 2 | **1b** | <br>**2c** | **4a** | <br>**3c** | 65 |
| 3 | <br>**1c** | <br>**2d** | **4a** | <br>**3d** | 63 |
| 4 | <br>**1d** | BnCHO<br>**2e** | **4b** | <br>**3e** | 53 |
| 5 | **1d** | <br>**2f** | **4b** | <br>**3f** | 76 |
| 6 | **1c** | <br>**2g** | **4c** | <br>**3g** | 79 |
| 7 | **1c** | Me(CH$_2$)$_8$CHO<br>**2h** | **4c** | <br>**3h** | 54 |
| 8 | **1a** | <br>**2i** | **4c** | <br>**3i** | 71 |
| 9 | **1a** | <br>**2j** | **4c** | <br>**3j** | 45 |

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† Electronic supplementary information (ESI) available: further experimental details, XRD and EIMS spectra. See http://www.rsc.org/suppdata/cc/b1/b104500h/

DOI: 10.1039/b104500h

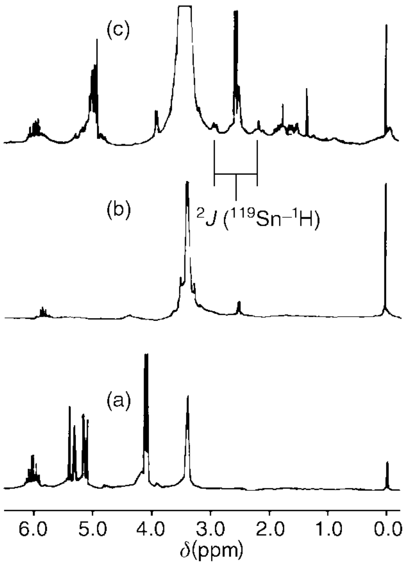


**Fig. 1** $^1$H NMR spectra in DMSO-d$_6$ of (a) allyl bromide; (b) residue from the reaction of β-SnO–allyl bromide; (c) residue from the reaction of β-SnO–allyl bromide–catalytic $Pd_2(dba)_3$ [dba = dibenzylideneacetone].

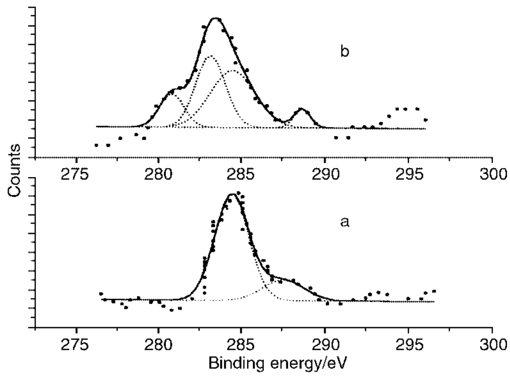
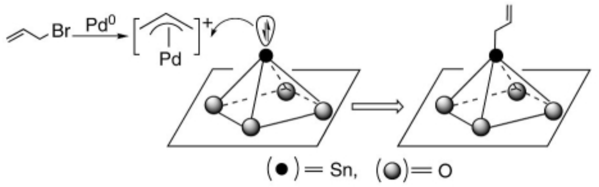


**Fig. 2** XPS spectra in the C-1s region of (a) untreated β-SnO/$Cu_2O$—peaks at 284.5, 287.6; (b) β-SnO/$Cu_2O$ after treatment with allyl bromide—peaks at 280.8, 283.2, 284.5, 288.9.

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 $Cu_2O$ 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 $Pd_2(dba)_3$ (0.02 mM) and allyl bromide (4 mM) in THF–$H_2O$ (99 : 1 v/v) was refluxed for 10 h. Following filtration under argon, and solvent removal, the residue was examined by $^1$H NMR. The spectrum (Fig. 1, spectrum c) showed the formation of a new σ-allyl tin species[9] characterized by allylic proton signals at 2.55 ppm [$^2J(^{119}\text{Sn}–^1\text{H})$ = 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 $Pd_2(dba)_3$ 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 $Cu_2O$, 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/$Cu_2O$ 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) 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.



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

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## Notes and references

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2 P. Barbier, *Competus Rendus*, 1898, **128**, 110; V. Grignard, *Competus Rendus*, 1900, **130**, 1322.

3 For representative examples, please see: T. H. Chan and Y. Yang, *J. Am. Chem. Soc.*, 1999, **121**, 3228; X.-H. Yi, Y. Meng, X-G. Hua and C. J. Li, *J. Org. Chem.*, 1998, **63**, 7472; A. Yanagisawa, S. Habaue, K. Yasue and H. Yamamoto, *J. Am. Chem. Soc.*, 1994, **116**, 6130; D. P. Curran, X. Gu, W. Zhang and P. Dowd, *Tetrahedron*, 1997, **53**, 9023; F. Dubner and P. Knochel, *Angew. Chem., Int. Ed.*, 1999, **38**, 379.

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5 For representative examples, please see: (*a*) G. E. Keck, K. H. Tarbet and L. S. Geraci, *J. Am. Chem. Soc.*, 1993, **115**, 8467; (*b*) A. Yanagisawa, H. Inoue, M. Morodome and H. Yamamoto, *J. Am. Chem. Soc.*, 1993, **115**, 10 356; (*c*) A. Ito, M. Kishida, Y. Kurusu and Y. Masuyama, *J. Org. Chem.*, 2000, **65**, 494; (*d*) J. P. Takahara, Y. Masuyama and Y. Kurusu, *J. Am. Chem. Soc.*, 1992, **114**, 2577; (*e*) T. H. Chan, Y. Yang and C. J. Li, *J. Org. Chem.*, 1999, **64**, 4452.

6 (*a*) P. Sinha, A. Kundu, S. Roy, S. Prabhakar, M. Vairamani, A. R. Sankar and A. C. Kunwar, *Organometallics*, 2001, **20**, 157; (*b*) A. Kundu and S. Roy, *Organometallics*, 2000, **19**, 105; (*c*) A. Kundu, S. Prabhakar, M. Vairamani and S. Roy, *Organometallics*, 1999, **18**, 2782; (*d*) A. Kundu, S. Prabhakar, M. Vairamani and S. Roy, *Organometallics*, 1997, **16**, 4796.

7 For chemistry of bivalent tin, please see: J. D. Donaldson, *Prog. Inorg. Chem.*, 1967, **8**, 287; P. J. Harrison, *Chemistry of Tin*, Blackie, New York, 1989, pp. 221–244.

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–$H_2O$ (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 $NH_4F$ (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 $Cu_2O$ as catalyst (14 mg, 0.1 mM), the solvent used was $CH_2Cl_2$–$H_2O$ (4.5 mL–0.5 mL).

9 For comparison with known σ-allyl tin NMR, please see: refs. 5*d*, 5*e* and 6*d*.

10 *The Organic Chemistry of Palladium*, ed. P. Maitilis, Vol. 1, 2, Academic Press, New York, 1971.

11 Direct injection of a reaction mixture into an EIMS probe results in major peaks at 351, 430, 478 corresponding to possible fragments $[(\text{allyl})_2\text{Sn}_2\text{O}_2 - \text{H}]^+$, $[(\text{allyl})_2\text{Sn}_2\text{O}_2\text{Br} - \text{H}]^+$, and $[(\text{allyl})_2\text{Sn}_2\text{Br}_2]^+$.

12 *Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Data for Use in XPS*, Perkin–Elmer Corporation Physical Electronics Division, 1979.

13 For olefin-Copper(I) interaction see: ref. 6*d*.