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The dehydrogenative oxidation of aryl methanols using an oxygen bridged [Cu–O–Se] bimetallic catalyst†

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Herein, we report a new protocol for the dehydrogenative oxidation of aryl methanols using the cheap and commercially available catalyst $CuSeO_3{\cdot}2H_2O$. Oxygen-bridged [Cu–O–Se] bimetallic catalysts are not only less expensive than other catalysts used for the dehydrogenative oxidation of aryl alcohols, but they are also effective under mild conditions and at low concentrations. The title reaction proceeds with a variety of aromatic and heteroaromatic methanol examples, obtaining the corresponding carbonyls in high yields. This is the first example using an oxygen-bridged copper-based bimetallic catalyst [Cu–O–Se] for dehydrogenative benzylic oxidation. Computational DFT studies reveal simultaneous H-transfer and Cu–O bond breaking, with a transition-state barrier height of 29.3 kcal mol^{-1}.

The selective and controlled oxidation of organic compounds to generate new functional groups and modify existing functional groups in molecules is a significant area in organic synthesis.[1,2] Hence, oxidation reactions are at the heart of many important transformations pertaining to chemical synthesis.[3] Reactions are widely undertaken in the chemical industry using organic peroxide (ROOH) and molecular oxygen (O_2) as terminal oxidants.[4] Traditional homogeneous methods use Cr/Mn/Os/V metals as stoichiometric oxidants with defined ligands and at high temperature; this in turn can produce undesirable side products and waste, thus increasing purification costs and pollution.[5] Hence, clean technology is much appreciated by industry in view of *E*-factor considerations.[6,7] Transition metal catalysts capable of using molecular oxygen (O_2)[8] as a stoichiometric oxidant are appealing for alcohol oxidation, but only a handful of reports is available detailing the presence of activator nitroxyl radicals such as TEMPO, AZADO, ABNO, and NMI.[9] Over the decades, major advances have been made in the development of catalytic methods for the aerobic oxidation of alcohols using different transition metals.[7–11]

Among the transition metals used, copper is very cheap and a suitable choice of metal for alcohol oxidation in the presence of nitroxyl radicals, organic peroxide, and molecular oxygen.[12–14] Markó *et al.* have demonstrated a Cu(I)-phen-(DABDH$_2$) system for alcohol oxidation with O_2 in toluene,[13] whereas Sthal *et al.* have established a Cu/TEMPO-based catalyst for the aerobic oxidation of alcohols using ambient air as an oxidant.[14] In addition to Cu-based catalysts for alcohol oxidation,[15] SeO_2 is historically well-known for allylic oxidation *via* the Se(IV)–Se(II) cycle.[16] For example, Sharpless *et al.* were able to convert cyclohexene to cyclohex-2-enol in 20% yield with 39% of the side-product cyclohexyl *t*-butyl ether.[17]

It is evident that both selenium and copper are very good oxidizers. We considered the effects on alcohol oxidation if both the metal (Cu) and metalloid (Se) are joined through an oxygen bridge [Cu–O–Se] (Fig. 1). Being inspired in our continuous effort to explore oxygen-bridged [M–O–M] bimetallic catalyst for organic reactions,[18] we investigated the oxidation of 1-(furan-2-yl)

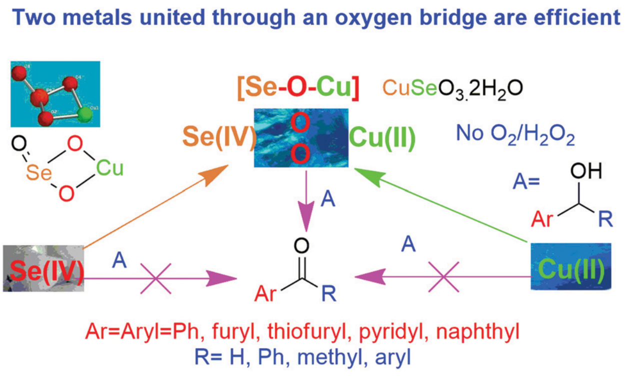

Fig. 1 Designing a [Cu–O–Se] oxo-bridged bimetallic catalyst for alcohol oxidation.

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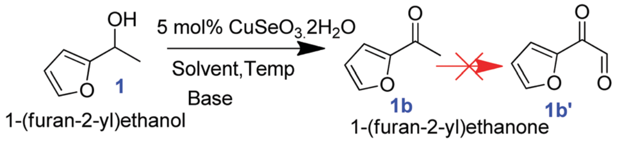
Table 1 Results for the oxidation of 1-(furan-2-yl)ethanol under different conditions

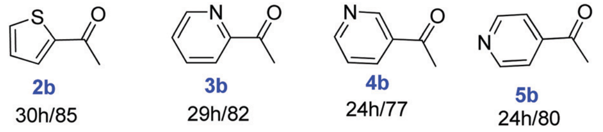


Entry	Catalyst	Base	Solvent	Yield[ab] (%)
1	$CuSeO_3{\cdot}2H_2O$	NaOH	Toluene	20
2	$CuSeO_3{\cdot}2H_2O$	KOH	Toluene	91/95[f]
3	$CuSeO_3{\cdot}2H_2O$	KOH	Toluene	30[c]
4	$CuSeO_3{\cdot}2H_2O$	KO*t*-Bu	Toluene	70
5	$CuSeO_3{\cdot}2H_2O$	Na_2CO_3	Toluene	20
6	$CuSeO_3{\cdot}2H_2O$	K_2CO_3	Toluene	30
7	$CuSeO_3{\cdot}2H_2O$	Pyridine	Toluene	45
8	$CuSeO_3{\cdot}2H_2O$	KOAc	Toluene	40
9	$CuSeO_3{\cdot}2H_2O$	KOH	CH_3CN	80
10	$CuSeO_3{\cdot}2H_2O$	KOH	Dioxane	60
11	$CuSeO_3{\cdot}2H_2O$	KOH	DMF	55
12	$CuSeO_3{\cdot}2H_2O$	KOH	*t*-BuOH	40
13	$CuSO_4{\cdot}2H_2O$	KOH	Toluene	10
14	$CuCl_2{\cdot}2H_2O$	KOH	Toluene	10
15	SeO_2	KOH	Toluene	0
16	CuO	KOH	Toluene	10
17	—	KOH	Toluene	0[d]
18	$CuSeO_3{\cdot}2H_2O$	—	Toluene	0[e]

[a] Alcohol (1 mmol), catalyst (5 mol%, 11 mg), and base (1.5 equiv.) were refluxed in a 25 ml flask in 2 ml of solvent for 28 h. [b] Isolated yield. [c] 80 °C. [d] No catalyst. [e] No base. [f] Crude NMR yield using an internal standard.

ethanol with the readily and commercially available $CuSeO_3{\cdot}2H_2O$ catalyst (purchased from Sigma-Aldrich). To our delight, 30% of the desired product 1-(furan-2-yl) ethanone (**1b**) (Table 1) was formed upon employing 5 mol% catalyst with 1 equiv. KOH in toluene solvent at 80 °C after 20 h. Moreover, we did not observe any allylic oxidation to 1-(furan-2-yl)-2-oxoacetaldehyde (**1b′**), even though selenium(IV) is present. A further examination of the reaction conditions (see the ESI†) revealed that the highest yield of **1b** obtained was 91% after 28 h, with 5 mol% catalyst and the use of 1.5 equiv. KOH under reflux conditions in toluene solvent.[19] The preliminary results indicated that bimetallic $CuSeO_3{\cdot}2H_2O$ is capable of promoting alcohol oxidation without the use of peroxide/nitroxyl radicals/O_2.

Other bases such as Na_2CO_3, K_2CO_3, KOAc, and pyridine provided 20–40% yields, whereas only the base KO*t*Bu provided 70% yield of the desired product (Table 1, entries 4–8). Among the solvents screened, *t*-BuOH, 1,4-dioxane, and DMF afforded 40–60% yields, whereas the solvent CH_3CN was very effective, providing 80% yield under these conditions (Table 1, entries 9–12). Under optimal conditions, catalysts other than $CuSeO_3{\cdot}2H_2O$, such as $CuSO_4{\cdot}2H_2O$, $CuCl_2{\cdot}2H_2O$, CuO, and SeO_2, barely provided the desired product under the same conditions (Table 1, entries 13–16). It is noteworthy that blank reactions without the catalyst $CuSeO_3{\cdot}2H_2O$ or base KOH did not afford any product (Table 1, entries 17 and 18). With the optimized conditions in hand, we subsequently examined the generality of the method using a range of heteroaryl secondary alcohols (Scheme 1). For example, 1-(furan-2-yl)ethanol, 1-(thiophene-2-yl)ethanol, 1-(pyridin-2-yl)ethanol, 1-(pyridin-3-yl)ethanol, and 1-(pyridin-4-yl)ethanol (**2a–5a**, respectively) were oxidized to the corresponding ketones (**2b–5b**) in 75–85% yields within 24–30 h. The highest yield was obtained for 1-(furan-2-yl)ethanol among the secondary heteroaryl alcohols (Scheme 1).



Scheme 1 The oxidation of secondary heteroaromatic ethanols, with reaction times (h) and yields (%).[a,b] [a] Alcohol (1 mmol), $CuSeO_3{\cdot}2H_2O$ catalyst (5 mol%, 11 mg), and KOH (1.5 equiv.) were refluxed in 2 ml of toluene. [b] Isolated yield.

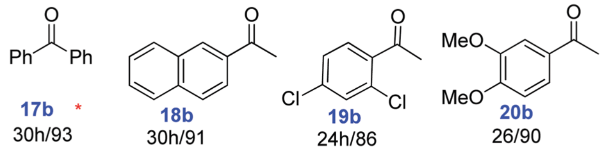
We next investigated the reactivities of *ortho*-, *para*-, and *meta*-substituted aryl secondary alcohols (**6–16a**) under optimal conditions. 1-(Phenyl)-ethanol (**6a**) underwent oxidation to 1-(phenyl)-ethanone (**6b**) in 82% yield (Scheme 2). Among the p-substituted halogenated aryl alcohols, the reactivity follows the order F > Cl > Br > I, with 70–88% yields (Scheme 2, **7b–10b**). Electron-donating 1-(4-methoxy phenyl)ethanol and 1-(4-methyl phenyl)ethanol let to 93% and 87% yields, respectively, (Scheme 2, **11b–12b**).

Similarly, the *ortho*-substituted secondary aryl alcohols 1-(2-fluoro phenyl)ethanol and 1-(2-methoxy phenyl)ethanol were oxidized to the corresponding ketones **13b** and **14b** in 87–88% yields (Scheme 2). It is noteworthy that 1-(2-bromo phenyl)ethanol did not result in any product, which can be attributed to steric effects at the *ortho*-position. The *meta*-substituted aryl ethanols (3-nitrophenyl)ethanol and 1-(3-aminophenyl)ethanol underwent oxidation with 88% and 82% yields, respectively (Scheme 2, **15b** and **16b**).

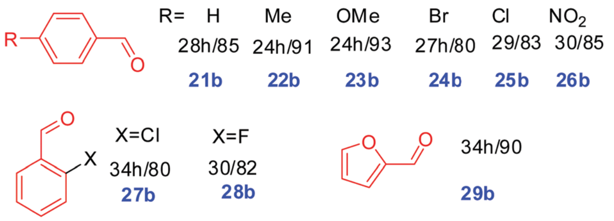
Diphenylmethanol and 1-(2-naphthyl)ethanol were oxidized to benzophenone and 1-(2-naphathyl)ethanone in 91–93% yields (Scheme 3, **17b–18b**). Disubstituted 1-(2,4-dichlorophenyl)ethanol and 1-(3,4-dimethoxy phenyl)ethanol resulted in 86–90% yields of the desired oxidized products (Scheme 3, **19b–20b**). The product **17b** was isolated with a TON of 510 (1 mol% catalyst and 20 mmol of diphenyl methanol after 40 h).[6]

Further, we investigated the oxidation of primary benzylic alcohols under the optimal conditions (Scheme 4). Benzyl-, 4-methyl benzyl-, and 4-methoxy benzyl-alcohol underwent oxidation to the corresponding ketones **21b–23b** in 85–93% yields (Scheme 4). *para*-Halobenzyl alcohols were oxidised to the

Scheme 2 The oxidation of *o*-, *m*-, and *p*-substituted secondary benzylic alcohols, with reaction times (h) and yields (%).[a,b] [a] Alcohol (1 mmol), $CuSeO_3{\cdot}2H_2O$ catalyst (5 mol%, 11 mg), and KOH (1.5 equiv.) were refluxed in 2 ml of toluene. [b] Isolated yield.



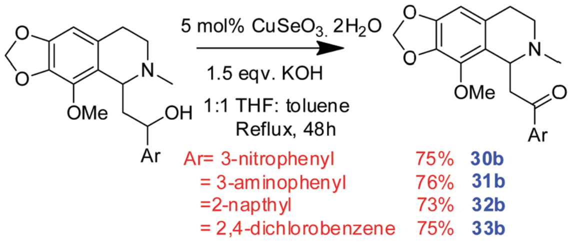
Scheme 3 The oxidation of some secondary aryl alcohols, with reaction times (h) and yields (%).[a,b] [a] Alcohol (1 mmol), $CuSeO_3{\cdot}2H_2O$ catalyst (5 mol%, 11 mg), and KOH (1.5 equiv.) were refluxed in 2 ml of toluene. [b] Isolated yield. *TON for **17b** is **28** (0.3 mol% cat. and 12 mmol of diphenylmethanol).



Scheme 4 The oxidation of primary aryl methanols, with the reaction times (h) and yields (%).[a,b] [a] Aryl methanol (1 mmol), catalyst (5 mol%), and base (1.5 equiv.) were refluxed in 2 ml of toluene. [b] Isolated yield.

corresponding aldehydes in 80–83% yields (**24b–25b**). 4-Nitrobenzyl alcohol underwent oxidation to 4-nitrobenzyl aldehyde with 80% yield under optimal conditions. 2-Chloro- and 2-fluorobenzyl alcohols afforded 80–82% yields, whereas heteroaryl 2-furfuryl alcohol underwent oxidation to 2-furylethanone (**29b**) in 90% yield (Scheme 4). It is noteworthy that oxidation stops at the aldehyde stage without further oxidation to acids. Primary aryl methanols react faster than secondary aryl methanols in the first 4 h, and then the reaction proceeds smoothly until the end.

Under these conditions, the catalyst $CuSeO_3{\cdot}2H_2O$ is not able to oxidise aliphatic secondary and primary alcohols. For example, 1-hexanol, 1-octanol, cyclohexanol, and cyclopentanol did not undergo oxidation and the starting materials could be recovered. Finally, the $CuSeO_3{\cdot}2H_2O$ catalyst is employed for the oxidation of synthetically important molecules with cotarnine skeletons, such as the 2-(4-methoxy-6-methyl-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5]-isoquinolin-5-yl)-1-arylethanols **30–33a**, which have a broad range of anti-cancer and antitussive properties (Scheme 5).[19] It is noteworthy that the oxidation reactions proceeded smoothly, affording the corresponding carbonyl products **30–33b** in 73–76% yields without any side products using THF and toluene solvents in a 1 : 1 ratio.

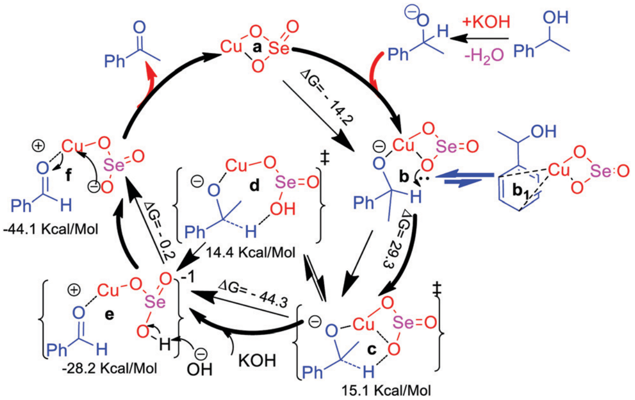


Scheme 5 The oxidation of antitussive cotarnine skeletons.[a,b] [a] Aryl methanol (1 mmol), $CuSeO_3{\cdot}2H_2O$ catalyst (5 mol%, 11 mg), and KOH (1.5 equiv.) were refluxed in 2 ml of solvent (1 : 1, THF : toluene). [b] Isolated yield.

A plausible mechanism

Furthermore, we investigated the mechanism of the $CuSeO_3{\cdot}2H_2O$-catalyzed oxidation reaction (Scheme 6). From Table 1 and Schemes 1–5, it is evident that the catalyst is very good at benzylic alcohol oxidations but poor at oxidising aliphatic alcohols. Se(VI) is most abundant at pH 8, whereas Se(IV) will be more available in the presence of KOH (pH = 12). In basic solution, the Se(IV)/Se(0)/Se(II) reduction potentials are very low ($Se^{6+}/Se^{4+} = 0.03$ V, $Se^{4+}/Se^{0} = -0.30$ V, and $Se^{0}/Se^{2-} = -0.67$ V).[20] In that case, copper ($E_{red} = 0.33$ V) will act as the oxidizing centre.[15,21] Hence, in the case of $CuSeO_3{\cdot}2H_2O$, copper is believed to play an important role along with selenium for the dehydration of aryl methanols.[22–24]

DFT calculations suggest that the alcohol forms a precursor complex (**b**) with the $CuSeO_3$ catalyst (**a**) with $\Delta G = -14.2$ kcal mol^{-1}. There is simultaneous hydrogen transfer and Cu–O bond breaking in the transition state with a barrier height of 29.3 kcal mol^{-1} from **b** to **c**. Complex **c** may adopt structure **d** with a broken Cu–O bond, with a difference of −0.7 kcal mol^{-1} in the Gibbs free energies (Fig. 2). Subsequently, it forms complex **e** through precursor **d.** The catalyst is regenerated after the elimination of the oxidised product from the successor complex **e/f.**[21] Catalyst selectivity for aryl methanols in



Scheme 6 A plausible mechanism for the oxidation of aryl methanols.

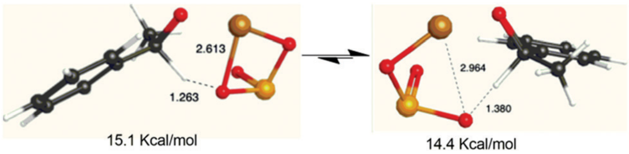


Fig. 2 TSs of simultaneous H-transfer and Cu–O bond breaking with a difference of −0.7 kcal mol^{-1} in Gibbs free energy. Relative G values (kcal mol^{-1}) are calculated using M06L/6-31G(d)/auto-geometry optimization, followed by M06-2x/6-311+G(2d,p)/SDD single-point calculations including SMD/toluene. Orange = Se; gold = Cu; red = O; black = C; and white = H.

comparison to aliphatic alcohols is anticipated to arise due to stabilization *via* Cu–π interactions.

Conclusions

In conclusion, we report here a new and relatively inexpensive oxygen-bridged bimetallic $CuSeO_3 \cdot 2H_2O$ catalyst with [Cu–O–Se]-type bonds for the first time for the oxidation of aryl methanols to carbonyl compounds. The catalyst is able to oxidize a diverse array of primary, secondary, aromatic, and hetero-aromatic aryl methanols to the corresponding carbonyl compounds without over-oxidation to the corresponding acids. The reaction does not need any additives. It is anticipated that the oxygen-bridged bimetallic catalyst [Cu–O–Se][25] has inherent properties that are responsible for making the reaction successful in comparison to the monometallic Se(IV) and Cu(II) salts. The concept is further supported by computational DFT studies.

Conflicts of interest

There are no conflicts to declare.

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