

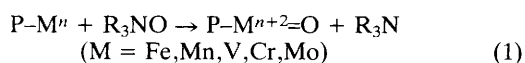
Copper(I) and Copper(II) mediated Two-electron Oxidations of Benzylic Alcohols and Diaryl Acetic Acids by Trimethylamine *N*-Oxide

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A novel ligand oxidation of Cu^I and Cu^{II} benzylic alcoholates and diaryl acetic carboxylates to carbonyl compounds by trimethylamine *N*-oxide gives support to the existence of cupryl (–Cu^{III}=O) intermediates, previously postulated in the reaction of Cu^I derivatives with dioxygen.

Tertiary amine *N*-oxides are known to transfer their oxygen atom to iron(II),¹ iron(III),² manganese(III),³ vanadium(IV),⁴ chromium(III),⁵ and molybdenum(IV)⁴ porphyrins or other complexes P, to provide high-valence reactive compounds [equation (1)]. To our knowledge, the only previous report of a copper(I)–amine oxide interaction describes an intramolecular diphenol oxidative coupling used in alkaloid synthesis.⁶



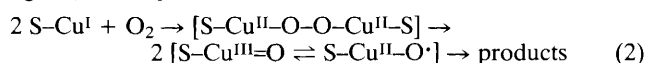
This Communication deals with the oxidation of Cu^I and Cu^{II} primary and secondary benzylic alcoholates and diaryl acetic carboxylates by trimethylamine *N*-oxide (TMAO) to carbonyl compounds; alcoholates present two-electron dehydrogenation and carboxylates undergo four-electron (2 successive two-electron) oxidative decarboxylation.

Each reaction (Scheme 1), carried out in dry acetonitrile at 60 °C, under anaerobic conditions, for 24 h, has been established to be a very slow process at room temperature, indicating that Cu^I and Cu^{II} salts are less reactive towards amine oxides than the aforementioned metal salts.

Copper(I) (A1a, A1b) and copper(II) (A3a) alcoholates are prepared *in situ* from the sodium alcoholates by metathesis with, respectively, Cu^ICl (as previously reported⁷) and Cu^{II}Cl₂. With such strong Cu^I and Cu^{II} chelating ligands as saligenols (B) no previous stoichiometric formation of copper salts is needed; for instance (B1d), Cu^ICl (1 equiv.), and trimethylamine *N*-oxide (TMAO; 4 equiv.) afford 4,6-di-*t*-butyl salicylaldehyde in quantitative yield. Copper(I) car-

boxylates (C1e) and (C1f) are prepared *in situ* either by reaction of acids with copper(I) oxide (0.5 equiv.) in acetonitrile or by metathesis of sodium carboxylates with Cu^ICl in the same solvent. Copper(II) diphenylacetate (C4e) is classically prepared by its sodium salt reaction with CuSO₄ in water. As shown in Table 1, Cu^I salts efficiently and selectively react with TMAO; transformations are quantitative or nearly so, and by-products are not detected, in contrast with Cu^{II} alcoholates which do not react at all (A3a, A4a) and saligenol (B3d) which affords carbonyl compound in moderate yield together with a significant quantity of unidentified by-products.

In previous studies concerning oxidations of phenols⁸ (tyrosine-like *o*-hydroxylation), alcohols^{7,9} (dehydrogenation), and carboxylic acids¹⁰ (oxidative decarboxylation) by Cu^I–dioxygen systems in acetonitrile, we have postulated that the homolytic cleavage of an early formed μ-peroxodicopper(II) intermediate affords reactive oxocopper(III) species (cupryl S–Cu^{III}=O, S being here alcoholate or carboxylate ligand), see equation (2).

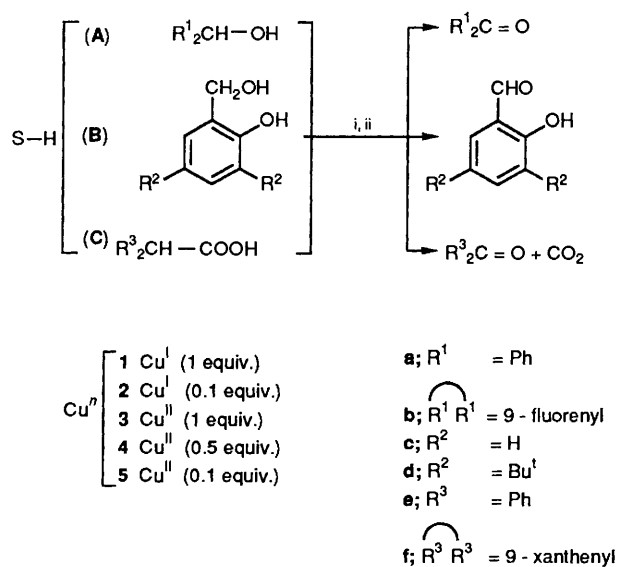


The TMAO/S–Cu^I or ^{II} interaction seems to provide an 'amine oxide shunt' to the S–Cu^I/O₂ system. Thus in TMAO reactions with Cu^I or Cu^{II} alcoholates or carboxylates, the same corresponding products are always formed suggesting that both reaction types may proceed by the same two-electron oxidant cupryl intermediates (Scheme 2) we have already discussed in previous papers.^{8–10}

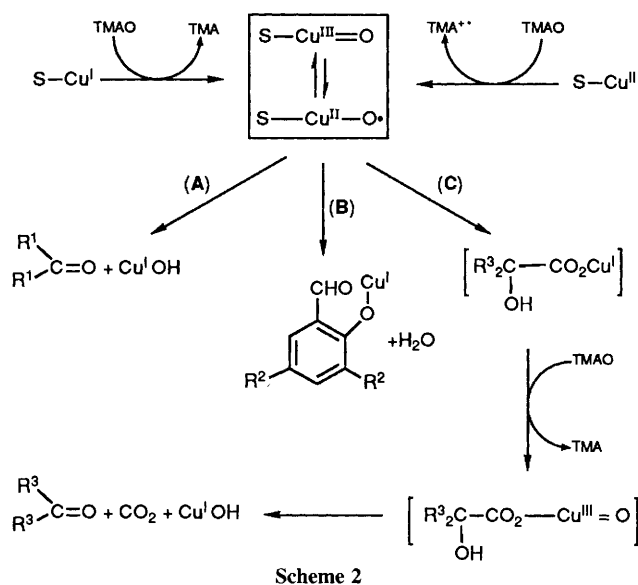
Table 1. Oxidation^{a,b} of Cu^I and Cu^{II} salts by TMAO.^c

S–H	Procedure	Carbonyl compounds	
		Conversion ^d /%	Yield ^d /%
Alcohols	A1a	38	100
	A1b	84	96
	A3a	0	0
	A4a	0	0
Saligenols	B1c	58	96
	B1d	100	100
	B2d	70	80
	B3d	100	40
	B5d	33	96
Acids	C1e	72	98
	C1f	94	94
	C4e	63	98

^a Copper salt (1 mmol substrate, 0.1–1 mmol Cuⁿ), excess TMAO (4 mmol) in dry MeCN (40 cm³), 60 °C, 24 h, N₂ atmosphere. ^b In preliminary experiments each copper derivative is obviously shown to be stable under the experimental conditions, without TMAO. ^c Obtained from TMAO·2H₂O by azeotropic distillation of its toluene solution. ^d Pure isolated (preparative TLC) products.



Scheme 1. Reagents and conditions: i, Cuⁿ, MeCN; ii, $\overline{O}NMe_3$ (4 equiv.), 60 °C.



Further chemical evidence is given by the isolation of minor amounts (2%) of the intermediate α -hydroxy acid (benzilic acid), trapped as its Cu^{II} salt and found in the recovered acid fraction from (C4e) oxidation runs, to be compared with the same observation in the corresponding Cu^{I} carboxylate reaction with dioxygen.¹⁰

In each reaction (Scheme 2) Cu^{I} is formed or reactivated, suggesting a catalytic ability in these systems, whenever the basicity of medium is strong enough (due to trimethylamine appearance) to allow copper-alcohol (or acid) linkage. Thus, in di-*t*-butyl saligenol catalytic oxidations (B2d) and (B5d),

turnover numbers of 7.0 and 3.3 are measured with respect to $\text{Cu}^{\text{I}}\text{Cl}$ and $\text{Cu}^{\text{II}}\text{Cl}_2$ under the same conditions.

Further interest in these catalytic systems is given by their high yields and selectivities, in particular $\text{Cu}^{\text{II}}\text{Cl}_2$ -catalysed oxidation (B5d) is a considerable improvement on the stoichiometric reaction (B3d). We are currently investigating these mechanisms in more detail, particularly the behaviour of the postulated aminium radical $\text{TMA}^{\bullet+}$ in $\text{Cu}(\text{II})$ -TMAO mediated oxidations. Together with the following Communication,¹¹ this preliminary report describes the first example of a copper(II) salt oxidation by an amine *N*-oxide.

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