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Review

Recent advances in copper-catalyzed oxidation of organic compounds

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Abstract

The copper-catalyzed oxidation of organic compounds has made considerable progress in the recent years. Molecular oxygen, aqueous hydrogen peroxide, *tert*-butyl hydroperoxide and peroxyesters have been employed as terminal oxidants for this purpose. The use of polymer and solid-supported catalysts, ionic liquids and fluorous biphase systems (FBS) has been demonstrated to facilitate the recyclability of the catalysts. Efforts have been made for the aqueous oxidation processes employing water-soluble copper complexes. Chiral catalysts have been designed and developed for the enantioselective oxidative coupling of 2-naphthols, Baeyer–Villiger oxidation and Kharasch–Sosnovsky reaction with high enantioselectivity.
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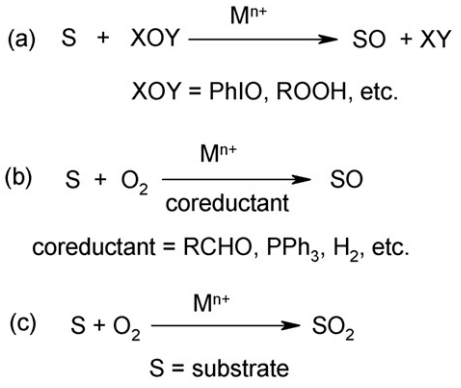
Keywords: Oxidation; Organic compounds; Copper catalysts; Molecular oxygen; Hydroperoxide; Peroxyester; Iodosylbenzene

1. Introduction

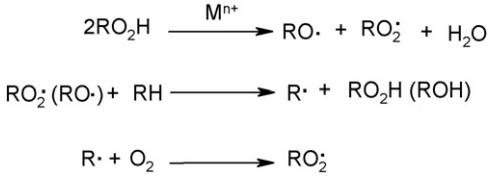
Catalytic oxidation is a key technology to transform the naturally available petroleum-based feed-stocks to more useful organic chemicals of a high oxidation state such as alcohols, alkenes and carbonyl compounds. Millions of tonnes of these compounds are annually produced world-wide and find applications in all areas of chemical industries, ranging from agrochemicals to large scale commodities [1–10]. The processes of bulk chemical industries predominantly use molecular oxygen as primary oxidant for economic reasons. Their success largely depends on the nature of the metal catalyst used to promote both the rate of reaction and the selectivity to partial oxidation products. While the fine chemical industries employ variety of oxidizing reagents such as permanganate and dichromate. However, these reagents are often required in stoichiometric quantities and generate unwanted hazardous by-products along with the target molecules demanding laborious work up procedure [11–34]. To circumvent this problem, there is currently considerable pressure to replace these antiquated technologies by cleaner, catalytic alternatives. A clean synthetic technology should proceed with a high atom-economy and the overall synthesis must be accomplished with low *E*-factor (by waste per kg product), thereby minimizing the cost of waste disposal [5].

The catalytic oxidations, irrespective of heterogeneous or homogeneous process, can be classified into three categories as follows:

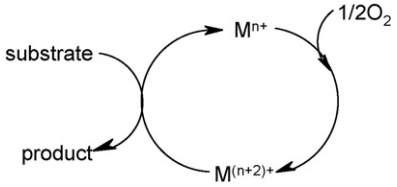
(i) *Catalytic oxygen transfer reactions*: in these processes, the substrates react with oxygen donor in the presence of a metal catalyst (Scheme 1) [14–19].
(ii) *Free radical oxidations*: this type involves the generation of chain-initiating radicals via the metal-catalyzed decomposition of alkyl hydroperoxide. These oxidations generally resemble autoxidation systems (Scheme 2) [20–23].
(iii) *Oxidations of a coordinated substrate by a metal ion*: in this oxidation, the oxidized form of the metal is subsequently regenerated by reaction of the reduced form with dioxygen (Scheme 3) [24,25,30].



Scheme 1.



Scheme 2.



Scheme 3.

This contribution reviews the copper-catalyzed oxidation of organic compounds. The oxidations of alkanes, alkenes, alcohols, arenes, benzylic substrates, ketones and sulfides have been studied in the presence of terminal oxidants such as molecular oxygen, hydrogen peroxide, *tert*-butyl hydroperoxide and peroxyester. Thus, section two is devoted to oxidations with molecular oxygen, while section three presents the oxidations using hydrogen peroxide. The reactions with *tert*-butyl hydroperoxide and peroxyester are discussed in sections four and five, respectively,

whereas section six gives a survey of the reactions with other oxidants. All the processes, which use copper catalysts have been considered.

Several books and review articles have appeared, which are wholly or partly devoted to copper-catalyzed oxidations [7]. Reviews and books devoted to more narrow topics will be cited later. Consequently, the present article emphasizes the work published during the past 10 years. Due to the vast literature, the reviews are cited rather than original publications in some cases. This review covers studies up to October 2006.

2. Reactions with molecular oxygen

Molecular oxygen is a cheap, ecologically benign and most readily available oxidant [34]. Thus, catalytic oxidation with molecular oxygen is particularly attractive [35]. Furthermore, the reactions with molecular oxygen generate water as only by-product in the absence of additives. This section covers copper-catalyzed reactions with molecular oxygen.

2.1. Epoxidation

Epoxides are versatile synthetic compounds, constituting convenient building blocks for the synthesis of many commodity and fine chemicals [36]. Several studies have focused on the preparation of these compounds employing transition metal catalysts in the presence of terminal oxidants such as NaOCl, PhIO, peracid, hydroperoxide and molecular oxygen. The reactions with molecular oxygen are attractive from the economic and environmental view point.

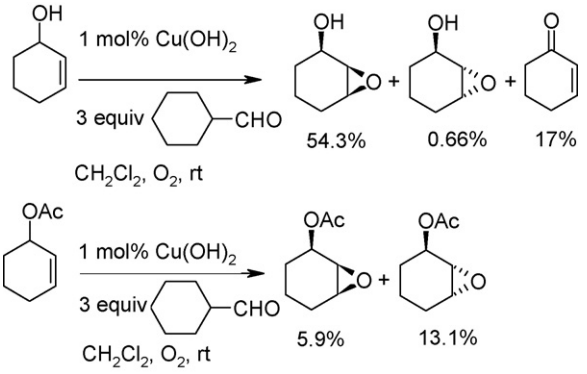
2.1.1. Reactions involving coreductants

Copper(II) salts, $Cu(OH)_2$, $Cu(OMe)_2$, $Cu(OAc)_2$ and $CuCl_2$, have been studied for the epoxidation of alkenes with molecular oxygen in the presence of aliphatic aldehydes (Table 1) [37a]. Internal alkenes are more reactive in comparison to terminal alkenes. *cis*-Alkenes are isomerized to afford a mixture *trans* and *cis* epoxides. Subsequently, copper(II) perchlorophthalocyanine **1** immobilized on HSi-MCM-41 [37b] has been used for the epoxidation of styrene, cyclohexene and 1-decene with high turnovers. No leaching of the metal complex is reported with these systems.

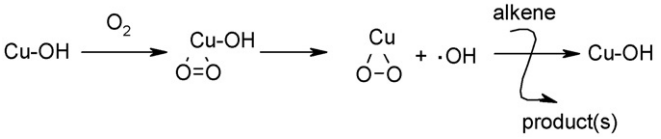
The oxidation of allylic alcohol and allylic acetate has also been studied [37a] (Scheme 4). Cyclohexen-1-ol is oxidized to afford *cis*-2,3-epoxy-1-cyclohexanol and *trans*-2,3-epoxy-1-cyclohexanol in a ratio of 98.8:1.2. Reverse of the *cis*/*trans* selectivity is observed, when hydroxy group is replaced by bulky acetoxy group. These results are similar to the reactions with peracid [37c], $Mo(CO)_6$-TBHP [37c] and $VO(acac)_2$-TBHP [37d].

2.1.2. Reactions without coreductants

The copper based aerobic epoxidations without coreductant have been studied for liquid as well as gas phase reactions. The oxidation of styrene and cyclohexene has been studied at 80 °C employing $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ as catalysts with molecular oxygen under air pressure (Scheme 5) [37e].



Scheme 4.



Scheme 5.

The epoxides are formed as minor products due to the oxidative cleavage as well as allylic oxidation processes. IR and EPR investigations suggest that the reactions proceed via the formation of peroxide and hydroxy radical species. In another study, the oxidation of propene to propene oxide has been reported using dispersed copper on silica (Cu/SiO_2). The best result available with system is 0.25% conversion and 53% selectivity [37f].

2.2. Oxidation of alkanes

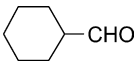
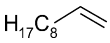
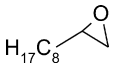
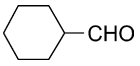
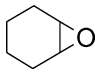
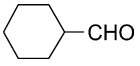
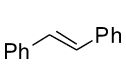
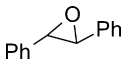
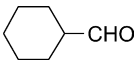
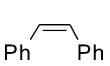
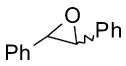
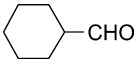
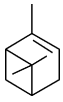
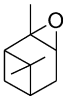
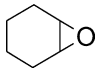
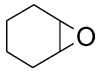
The selective transformation of hydrocarbons leading to oxygenated petrochemicals such as alcohols and carbonyl compounds is important utilization of petroleum and natural gas based resources [27–29]. The copper-catalyzed oxidation of alkanes with molecular oxygen is successful for the oxidation of higher alkanes affording the corresponding alcohols and ketones in high turnovers.

2.2.1. Reactions involving coreductants

Copper(II) based catalytic systems have been studied for the partial oxidation C_5–C_{10} alkanes (Scheme 6). Copper(II) hydroxide ($Cu(OH)_2$) has been used for the oxidation of *n*-pentane, *n*-decane, cyclohexane and methylcylohexane to give the respective alcohols and ketones in the presence of CH_3CHO under an oxygen atmosphere [38]. When the copper salt replaced by complexes, derived from CuX_2 (X = Cl and OAc) and 18-crown-6 **2** or CH_3CN, an enhancement in the efficiency of the oxidation was observed (Table 2). These reactions take place by a radical process to afford ketones as the major products in comparison to alcohols.

In extension to these reactions, the copper(II) complex **1** immobilized on NH_2-MCM-41 was subsequently investigated for the oxidation of cyclohexane to a 1:2 mixture of cyclohexanol and cyclohexanone with 297 TON in the presence of benzaldehyde [39]. While the copper(II) complex, formed from

Table 1
Copper-catalyzed epoxidation of alkenes with coreductants

Entry	Catalyst	Co-reductant	Substrate	Product(s)	TON[a]	Ref.
1	$Cu(OH)_2$				27	[37a]
2	$Cu(OH)_2$				79	[37a]
3	$Cu(OH)_2$				76	[37a]
4	$Cu(OH)_2$				64	[37a]
5	$Cu(OH)_2$			*trans: cis* = 22:3 	83	[37a]
6	**1**				645[b]	[37b]
7	**1**				798[b]	[37b]
8	**1**-MCM-41				3144[b]	[37b]
9	**1**-MCM-41				2532[b]	[37b]

[a] Reactions studied at ambient temperature.
[b] Reactions studied at 40 °C.

amine functionalized silica **3** (Me_2N-SiO_2) and $CuSO_4{\cdot}5H_2O$, has oxidized cyclohexane to a 3.3:1 mixture of cyclohexanol and cyclohexanone with 4.3% conversion (134 TON) in the presence of Zn in CH_3COOH [40]. The selectivity of cyclohexanol to cyclohexanone was further increased to 50:1 when the oxidation was studied using a combination of $Cu(OAc)_2$ and quinone (5:1) in CH_3CN in the presence of PPh_3 under irradiation [41] (Scheme 7). In this reaction, cyclohexylhydroperoxide formed first which on reaction with PPh_3 gives cyclohexanol and Ph_3PO.

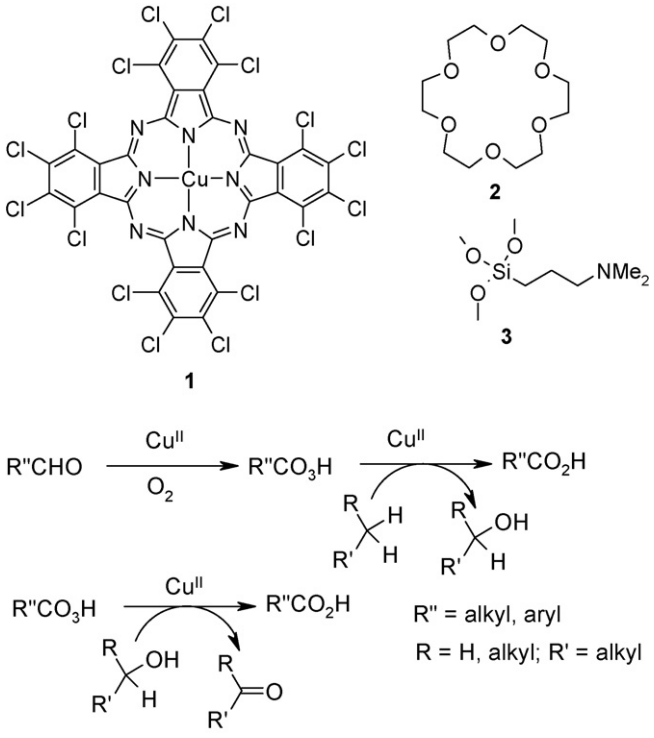
2.2.2. *Reactions without coreductants*

The oxidation of *n*-hexane to a mixture of hexanol and hexanal in 10.2% conversion catalyzed by the zeolite (NaY) supported copper-perchlorophthalocyanine **1** is reported under molecular oxygen (Scheme 8) [42]. Remarkably, the oxidation takes place only at the primary CH_3 group. This unusual product distribution weighs strongly against a free radical mechanism, which would normally be expected for a copper-catalyzed oxidation reaction.

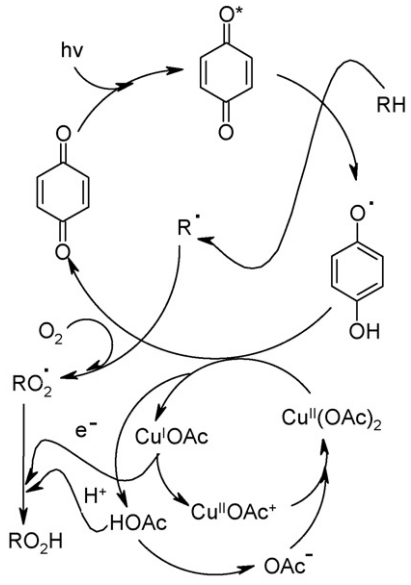
Table 2
Copper-catalyzed oxidation of alkanes with coreductants

Entry	Catalyst	Temperature (°C)	Coreductant	Substrate	Products (ratio)	TON[a]	Ref.
1	$CuCl_2$-**2**	70	CH_3CHO	Cyclohexane	Cyclohexanol (14), cyclohexanone (86)	16,200	[38b]
2	$Cu(OAc)_2/CH_3CN$	70	CH_3CHO	Cyclohexane	Cyclohexanol (43), cyclohexanone (57)	27,000	[38a]
3	NH_2-MCM-41-**1**	50	PhCHO	Cyclohexane	Cyclohexanol (32), cyclohexanone (68)	297[b]	[39a]
3	$CuSO_4{\cdot}5H_2O$-**2**	rt	Zn	Cyclohexane	Cyclohexanol (77), cyclohexanone (23)	134[b]	[40]
4	$CuCl_2$-**2**	70	CH_3CHO	Cyclooctane	Cyclooctanol (11), cyclooctanone (89)	18,600	[38b]
5	$CuCl_2$-**2**	70	CH_3CHO	*n*-Hexane	Hexan-2-ol (2.6), hexan-3-ol (2.6), hexan-2-one (46), hexan-3-one (48)	9,770	[38b]
6	$Cu(OH)_2$	rt	CH_3CHO	*n*-Decane	Decan-2-ol (20), decan-3-ol (20), decan-2-one (27), decan-3-one (27)	1.5	[37a]
7	$Cu(OH)_2$	rt	CH_3CHO	Adamandane	Adamantan-1-ol (27.7), adamantan-2-ol (1.6), adamantan-2-one (1)	9.6	[37a]

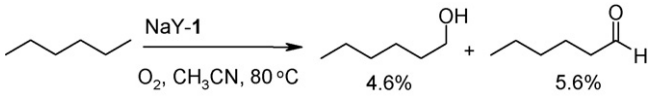
[a] Based on coreductant.
[b] Based on substrate.



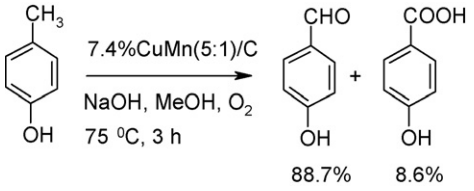
Scheme 6.



Scheme 7.



Scheme 8.



Scheme 9.

The use of $CuCl_2$ for the photocatalytic oxidation of cyclohexane was subsequently demonstrated with molecular oxygen [42b,c]. The reactions occurred with 50% conversion and 70% selectivity affording a mixture of cyclohexanol and cyclohexanone under visible light. In this system, the rate of oxidation of the starting cyclohexane is much greater in comparison to overoxidation of products, cyclohexanol and cylohexanone.

2.3. Benzylic oxidation

Benzylic oxidation is an important and fundamental functional transformation in industrial chemistry [34]. The copper based catalytic systems are used for the selective oxidation of the benzylic C–H bonds with molecular oxygen in excellent yields.

2.3.1. Reactions involving coreductants

The copper-catalyzed oxidation of benzylic substrates with molecular oxygen has been studied in the presence of aldehydes (Table 3) [38,43]. The oxidation of toluene, ethylbenzene, indane and tetralin is accomplished with excellent TON. These oxidations occurred selectively at the benzylic C–H bonds to afford a mixture of alcohol and ketone. No reactions were observed with the aromatic C–H bonds.

2.3.2. Reactions without coreductants

The copper(II) complex, derived from $CuCl_2{\cdot}2H_2O$ and $Me_2C{=}NOH$, has been employed for the oxidation of *p*-cresol to *p*-hydroxybenzaldehyde in 87% yield [44]. Subsequently, carbon supported copper and manganese bimetallic oxide, CuMn/C, was studied for this purpose with 95.6% selectivity for *p*-hydroxybenzaldehyde at 98.5% conversion of *p*-cresol (Scheme 9) [45]. This result is impressive in *p*-cresol oxidation and the catalyst, CuMn/C, is recyclable without loss of activity.

2.4. Aromatic C–H oxidation

Aromatic C–H oxidation is one of the most challenging problems in organic synthesis. The aromatic nucleus is resistant to oxidation because of its resonance stabilization, so oxygenation almost invariably requires a highly reactive oxidant under severe conditions [46]. Copper based catalytic systems with molecular oxygen have been successfully studied for this purpose.

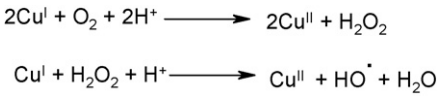
2.4.1. Benzene to phenol

Phenol, one of the important chemical intermediates in the broad industrial field, has been mainly manufactured using the cumene method by which selectivity for the phenol is high. How-

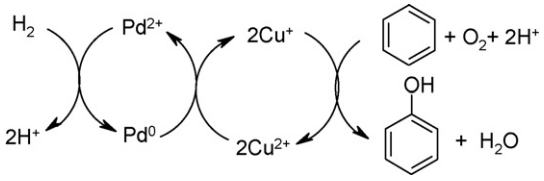
Table 3
Copper-catalyzed benzylic oxidation with coreductants [38b]

Entry	Catalyst	Coreductant	Substrate	Products (ratio)	TON[a]
1	$CuCl_2$-**2**	CH_3CHO	Ethylbenzene	1-Phenyethanol (13), acetophenone (87)	3,480
2	$CuCl_2$-**2**	CH_3CHO	Indane	1-Indanol (18), 1-indanone (82)	14,100
3	$CuCl_2$-**2**	CH_3CHO	Tetralin	α-Tetralol (14), α-tetralone (86)	14,800

[a] Based on coreductant. All the reactions have been studied at ambient temperature.



Scheme 10.



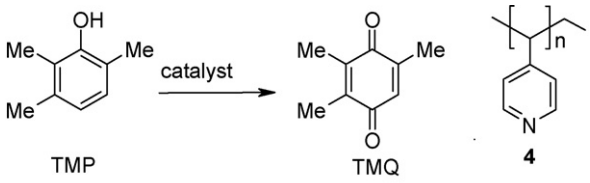
Scheme 11.

ever, this cumene process consists of three steps and produces acetone as a by-product. The one step-production of phenol by direct insertion of oxygen into the benzene ring is an attractive method from a practical as well as a synthetic view.

CuCl has been used for the oxidation of benzene to provide a 3:1 mixture of phenol and hydroquinone in 32% yield in the presence of molecular oxygen [47]. The active species is proposed to be a hydroxy radical generated as shown in Scheme 10. However the reaction proceeds catalytically when copper(II) is reduced to copper(I) by molecular hydrogen in the presence of a palladium co-catalyst (Scheme 11). More recently, copper(II) complexes immobilized on SiO_2, Al_2O_3, MCM-41, NaY, HZSM-5, $Ca_{10}(OH)_2(PO_4)_6$ and polyoxometalates were investigated for this purpose [49,50]. The catalysts prepared by co-precipitation and ion-exchange methods are more effective in comparison to the catalysts obtained by impregnation. The liquid phase reactions use ascorbic acid as reducing agent to obtain phenol with up to 9.2% conversion and 91.8% selectivity that corresponds to 25.8 TON [50a]. Some of these catalysts are effective for the gas phase oxidation where the formation of phenol (3.26%) observed with 65% selectivity [48c].

2.4.2. Phenol to quinone

Trimethyl-1,4-benzoquinone (TMQ) is a key intermediate in the vitamin E synthesis and the current method for its production in the industrial scale is *para*-sulfonation of 2,3,6-trimethylphenol (TMP) followed by oxidation with MnO_2. For its single step preparation, copper catalysts with molecular oxygen have been studied in depth [51–54]. The reactions with $CuCl_2 \cdot 2H_2O$ (10 mol%) are effective in the presence of co-catalysts (10 mol%) such as LiCl and amine salts [51]. The oxidation could be repeated several times by recycling the catalyst in the two-phase system, but the co-catalyst is to be added at every run to make up for the loss. In extension of these processes, recycling procedures have been subsequently studied by



Catalyst (mol%)	Temp. (°C)	Time (h)	Yield (%)
$CuCl_2$-[BMIm]Cl (2.5)	60	5	86
$CuCl_2$-**4** (10)	80	24	95

Scheme 12.

employing polymer-supported copper catalysts, $CuCl_2$-**4**, [52] and ionic liquids, $CuCl_2$-(BMIm)Cl (Scheme 12) [53]. These reactions occur efficiently and the catalysts are recyclable without loss of activity.

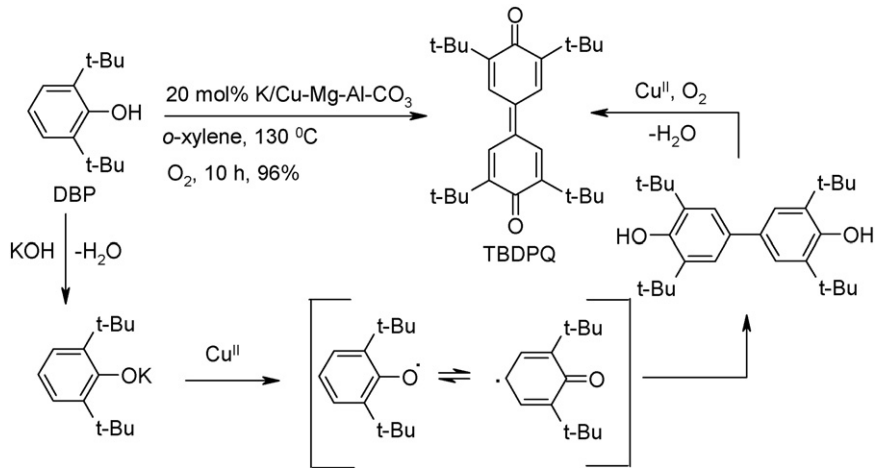
2.4.3. Oxidative coupling reactions

Carbon–carbon bond formation is one of the most important reactions in organic synthesis. In this context biaryl coupling occupies a prominent place [34]. The oxidative phenolic coupling is a reaction that has been actively pursued with synthetic and biosynthetic implications.

2.4.3.1. Reaction of phenol. 3,3′,5,5′-Tetra-*tert*-butyl-4,4′-diphenoquinone (TBDPQ) is a valuable raw material for highly functionalized photosensitizers [54]. The copper-catalyzed systems have been used for its single step preparation from 2,6-di-*tert*-butylphenol (DBP) with molecular oxygen. The presence of a strong base such as KOH is essential; in its absence the reactions are less active. Following the homogeneous copper(II) amine complexes catalyzed processes [55], copper(II) supported on poly(4-vinylpyridine) [56], mesoporous silicate MCM-41 [57] and Mg–Al hydrotalcite [58] have been studied as recyclable catalysts. The best result is available with the reaction employing hydrotalcite with 96% yield of TBDPQ (Scheme 13) [58]. In these reactions, the role of KOH is considered to be deprotonation of DBP into a K-phenolate species, which is subsequently oxidized by Cu^{II} to afford radical intermediates of carbon–carbon coupling. The resultant Cu^{I} is reoxidized to Cu^{II} by O_2.

2.4.3.2. Reaction of 2-naphthol. The copper(I) based oxidative coupling of 2-naphthols with molecular oxygen has made considerable progress [34]. They may be classified as reactions with achiral catalysts and enantioselective reactions.

2.4.3.2.1. Reactions with achiral catalysts. The copper complex, CuCl(OH).TMEDA **5**, [TMEDA = tetramethyl-



Scheme 13.

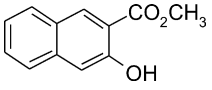
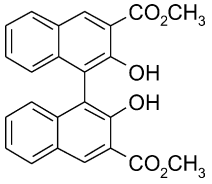
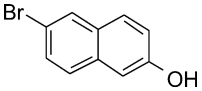
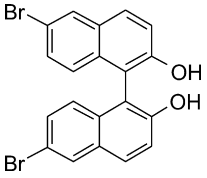
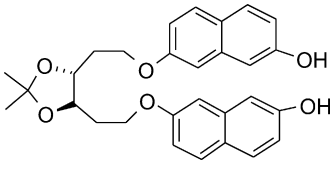
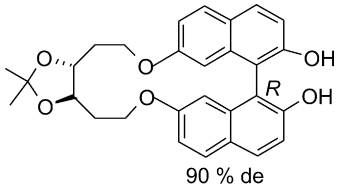
ethylenediamine] has been extensively used for the oxidative coupling of 2-naphthol to 1,1′-bi-2-naphthol (BINOL) in the presence of molecular oxygen [59–62]. Both inter- and intramolecular coupling is successfully accomplished. Chiral naphthols have been cyclized with high diastereoselectivity by intramolecular oxidative coupling. Representative examples are summarized in Table 4.

2.4.3.2.2. Enantioselective reactions. Chiral copper complexes bearing optically active amines **6** have been extensively studied for enantioselective reactions [63–65]. Homo- and cross coupling of 2-naphthols are successfully accomplished with up to 93% ee (Scheme 14). The substrates having an ester group at the 3-position have provided the highest enantioselectivity. Interestingly, BINOL having acetylene substituents are transformed to optically active π-conjugated binaphthyl polymers with good enantioselectivity (Scheme 15), where the asymmetric oxidative coupling of 2-naphthyl derivative has occurred in tandem with the acetylenic Glaser–Hay coupling [64b].

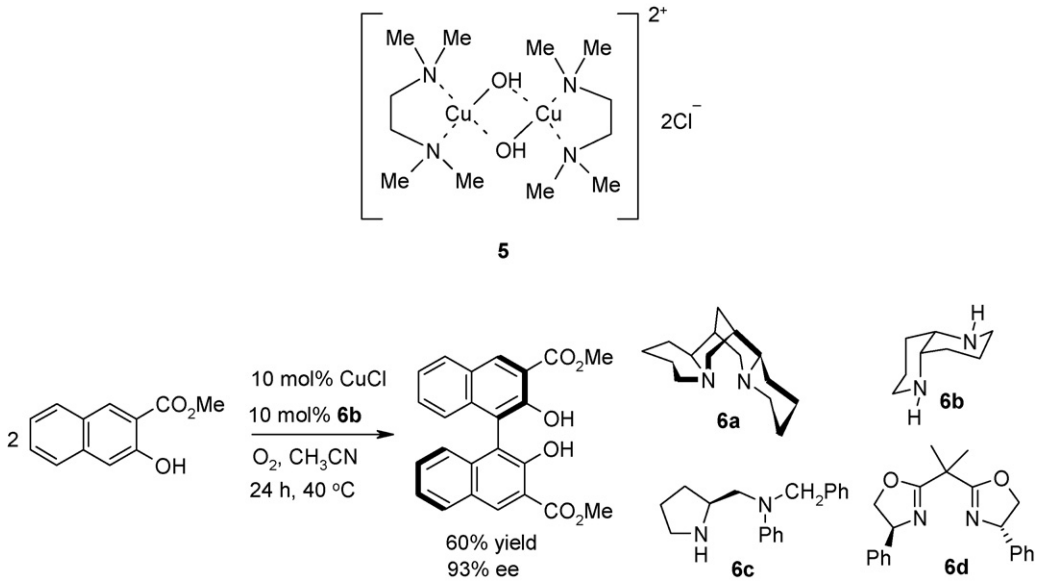
2.5. Glaser–Hay acetylenic coupling reactions

The oxidative coupling of terminal acetylenes is an important reaction in synthetic chemistry for the extension of linear scaffolds. In this context, CuCl·TMEDA **5** has been used for the synthesis of oligoacetylene moieties [66]. Yields are in the range of 70–75% in the synthesis of 1,4-bis(trimethylsilyl)buta-1,3-diyne, from trimethylsilylacetylene (Scheme 16).

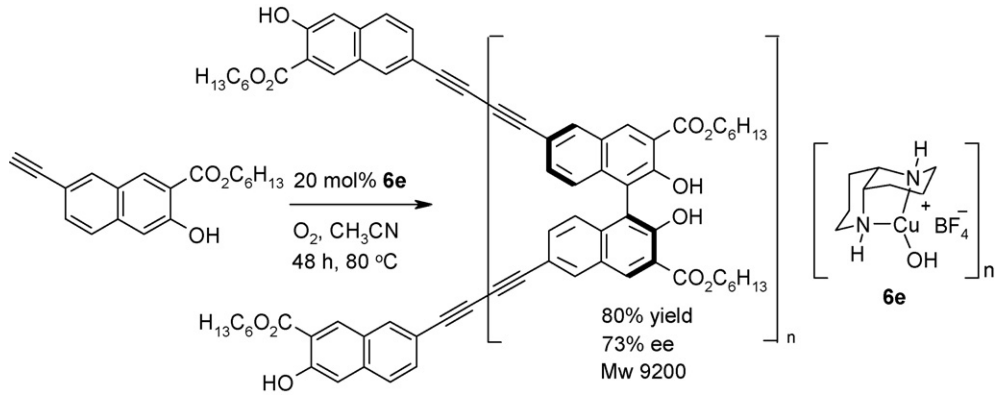
Table 4
CuCl(OH)·TMEDA-catalyzed oxidative coupling of 2-naphthols with molecular oxgyen[a]

Entry	Substrate	CuCl(OH)·TMEDA (mol%)	Time (h)	Product	Yield (%)	Ref.
1		1	96		99	[59]
2		1	24		80	[60]
3		8	–	 90 % de 12:1 = *R,R,R : R,R,S*	95	[62]

[a] Reactions are studied at ambient temperature.

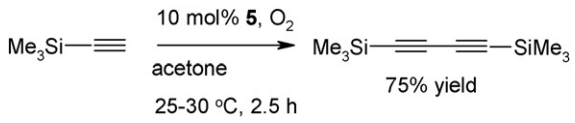


Scheme 14.

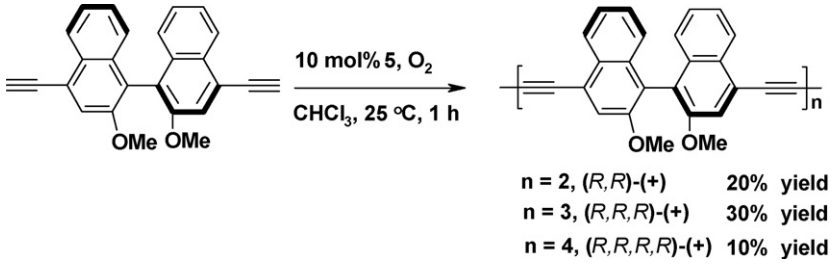


Scheme 15.

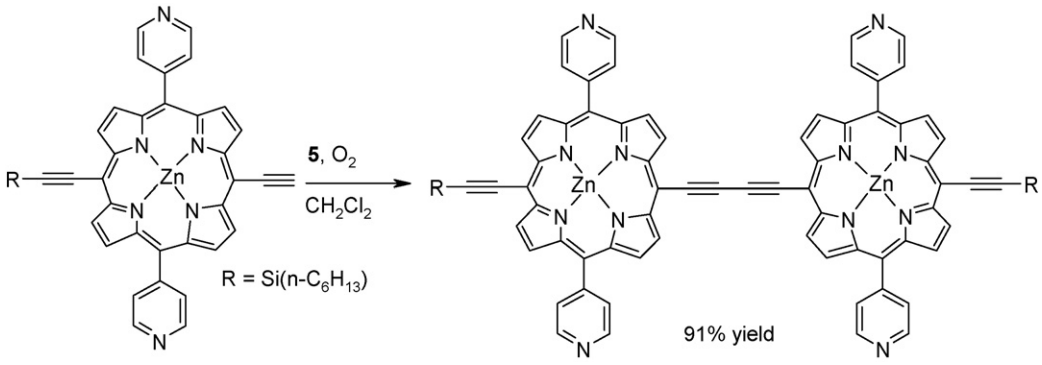
Molecules with very long π-systems are of intense interest as organic semiconductors, near-IR dyes and non-linear optical materials. The Glaser–Hay coupling has been successfully applied for the synthesis of π-conjugated macromolecules such as oligomers of BINOL [61], *meso*-porphyrin [67], phthalocyanine [68] and polycyclic cyclophane receptors [69]. For example, optically active diethynyl-binaphthyl is transformed to oligo-1,1′-bi-2-naphthalene in the form of a yellow fluorescent solid in moderate yield (Scheme 17). Likewise, *meso*-diethynylporphyrin [67] is transformed to the corresponding dimer in excellent yield (Scheme 18). Under similar conditions, the synthesis of the buta-1,3-diynediyl-linked macrotricyclic cyclophane receptor is accomplished by a critical ring closure reaction in 42%



Scheme 16.



Scheme 17.



Scheme 18.

yield (Scheme 19) [69]. No by-product is formed in this reaction.

2.6. Alcohol oxidation

The oxidation of alcohols is among the most routinely used functional transformation in synthetic chemistry. Several methods and reagents are available for this purpose [24]. However, these reagents are often required in stoichiometric amounts and generate inorganic salt containing effluent along with the target molecules demanding laborious work-up procedure. To overcome this problem, catalytic systems have been recently studied.

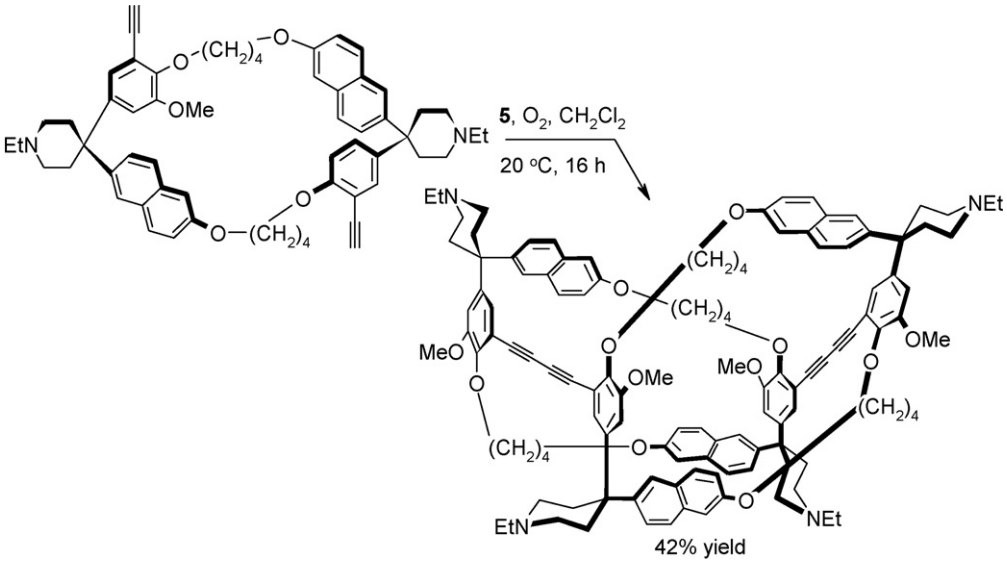
2.6.1. Reactions to aldehydes and ketones

Copper catalysts have been extensively studied for the oxidation of alcohols to aldehydes and ketones (Table 5). The reactions more effective when copper catalysts are employed in combination with either 2,2,6,6-tertramethyl-piperidyl-1-oxy (TEMPO) [70–72] or metal oxides such as (n-Pr_4N)RuO_4 [73], OsO_4 [74] and $MoO_2(acac)_2$[75]. Subsequently, the Ru–Cu–Al-hydrotalcite [77a], Cu/NaZSM-5 [77b], ionic liquid **7** [76a], fluorous biphase system (FBS) **8** have been used for this purpose to recycle the catalysts [76b]. The oxidation of activated alcohols (allylic and benzylic) is more successful. The aliphatic alcohols especially primary alcohols are less reactive affording the aldehydes in moderate yields.

While Marko and coworkers employed CuCl-1,10-phenanthroline (phen) **9** for this purpose in the presence of azodicarboxylates under molecular oxygen [78,79]. These reactions proceed *via* hydrogen transfer from the alcohol *via* aza derivative such as DBAD (DBAD=^{t}BuO$_2$C–N=N–CO$_2{}^t$Bu) to molecular oxygen, as in the case of Ru/quinine/Co systems (Scheme 20) where K_2CO_3/^{t}BuOK acts as a support, as a base and as a water scavenger. These systems are effective for the oxidation of all kinds of substrates including primary aliphatic alcohols (Table 6).

2.6.2. Selective oxidation of alcohols to aldehydes

The selective oxidation of primary alcohols to aldehydes is one of the more important processes in the fine chemical industry. Copper complexes containing copper(II)-phenoxyl **10–15**, having a structure around the copper(II) ion similar to that in galactose oxidase (GO) [80], have been studied as functional models of GO for the oxidation of alcohols with molecular oxygen [81–87]. The catalytic activity of these complexes is mostly



Scheme 19.

Table 5
Copper-catalyzed aerobic oxidation of alcohols in combination with TEMPO or other metal salts

Entry	Catalyst	Temperature (°C)	Substrate	Product (yield, %)	Ref.
1	CuCl-TEMPO	25	Benzyl alcohol	Benzaldehyde (97)	[70]
2	$Cu(ClO_4)_2$-TEMPO	25	Benzyl alcohol	Benzaldehyde (98)	[72]
3	CuCl-OsO_4	100	4-Methylbenzyl alcohol	4-Methylbenzaldehyde (78)	[74]
4	CuCl-**7**	50	Geraniol	Geranial (98)	[76a]
5	CuBr-**8**-TEMPO	90	Decanol	Decanal (73)	[76b]

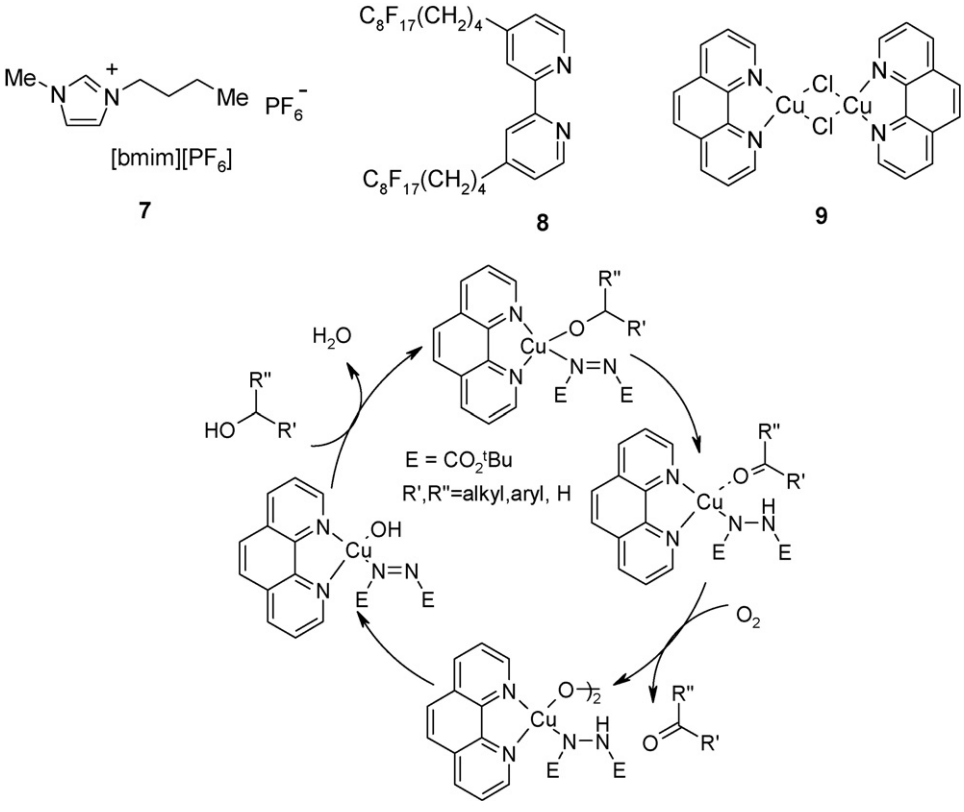
Table 6
CuCl-Phen-catalyzed oxidation of alcohols with molecular oxygen

Reaction Conditions	Substrates	Additives[a]	Product (%, yield)	Refs.
5 mol% CuCl·Phen; 2 equiv. K_2CO_3, O_2; toluene, 90 °C, h	Decanol, 2-decanol	5 mol% DBAD-H_2; 5 mol% DBAD	Decanal (65); 2-decanone (88)	[78]
5 mol% CuCl·Phen; 5 mol% ^{t}BuOK, O_2; C_6H_5F, 70–80 °C, h	Decanol	5 mol% DBAD; 5 mol% DBAD/5 mol% DMAP[a]; 5 mol% DBAD/10 mol% DMAP; 5 mol% DBAD/7 mol% NMI[b]	Decanal (60); decanal (80); decanal (100); decanal (100)	[79]

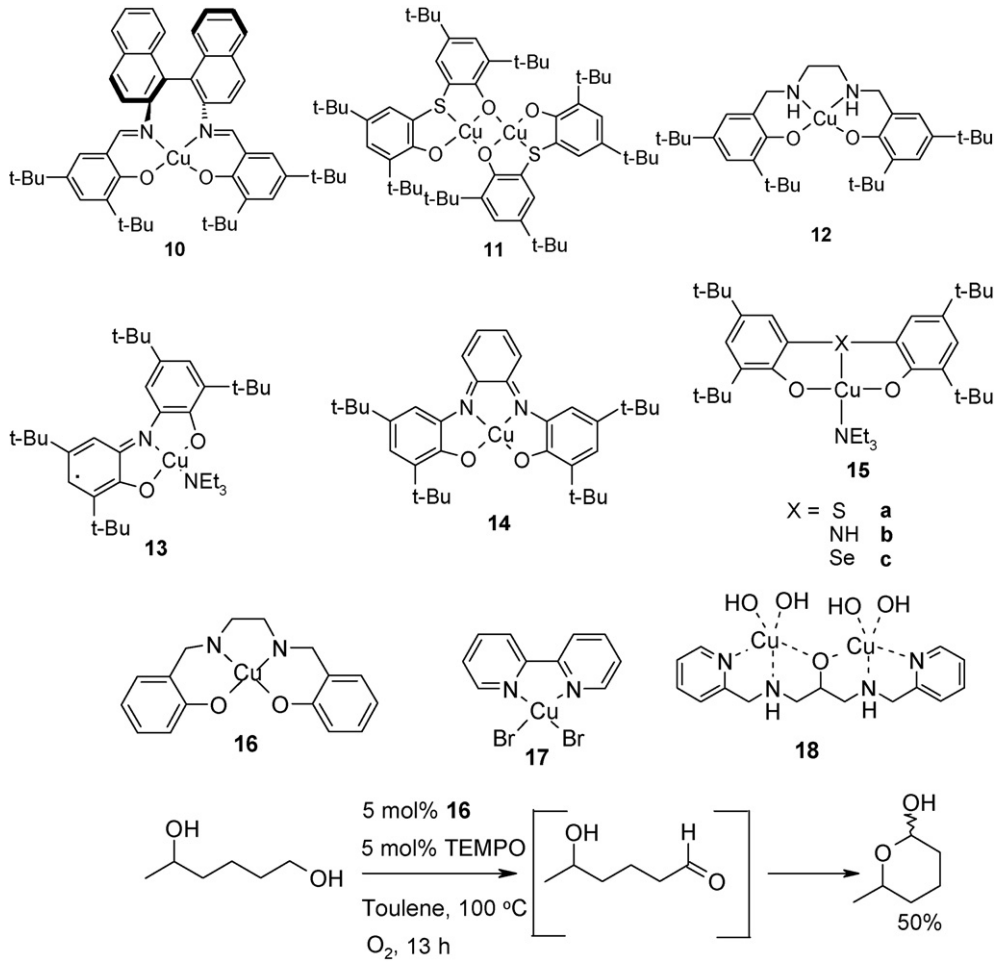
[a] DMAP = *N*,*N*-dimethylaminopyridine.
[b] *N*-Methylimidazole.

limited to activated (e.g., benzylic and allylic) primary alcohols (Table 7). Mechanistic studies involving the GO enzyme clearly indicate that the dioxygen molecule is actually activated by the copper(I) species.

Copper(II) complexes **16**–**17** in combination with TEMPO were subsequently used for this purpose [88–90]. These systems catalyze the less reactive aliphatic primary alcohols efficiently with high yields. The oxidation of secondary alcohols is inert which has been shown by the chemoselective oxidation of hexan-1,5-diol to the formation of lactone in moderate yield (Scheme 21). The proposed transition states **19** for this selectivity focused on the unfavoured steric repulsion between the



Scheme 20.



Scheme 21.

methyl group of TEMPO and substituents of alcohols. Detailed study of these reactions bears a close resemblance to the accepted mechanism for analogues oxidation mediated by galactose oxidase and mimics thereof.

2.7. Baeyer–Villiger oxidation

Baeyer–Villiger oxidation is a frequently used synthetic tool for the conversion of cycloalkanones to lactones. Usually, this transformation is carried out by peroxy compounds such as peracids [91] and ROOH [92]. Acids, bases, enzymes and metal containing reagents are known to catalyze Baeyer–Villiger oxidation [93].

Table 7
Copper(II)-catalyzed oxidation of alcohols with molecular oxygen

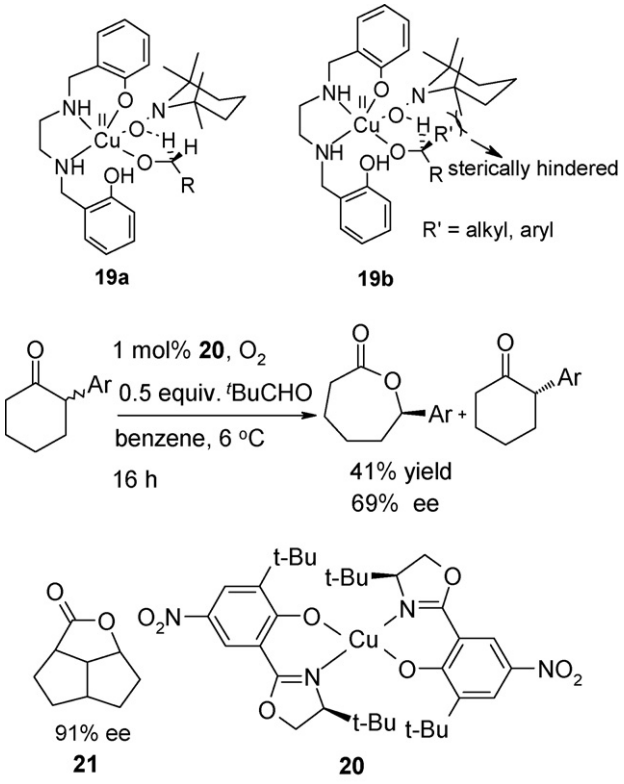
Entry	Catalyst	Substrate	Product	TON	Ref.
1	**10**	Benzyl alcohol	Benzaldehyde	1300	[82]
2	**14**	Ethanol	Acetaldehdye	5000	[83]
2	**15b**	Ethanol	Acetaldehyde	2593	[84]
3	**15a**	Benzyl alcohol	Benzaldehyde	90	[85]
4	**15c**	Cinnamyl alcohol	Cinnamaldehyde	27	[85]

Bolm and coworkers have employed copper catalysts with molecular oxygen for this purpose in the presence of benzaldehyde [94]. The reactions of cyclic ketones are successful. Soon after, these authors studied enantioselective oxidation employing chiral complex **20** in the presence of pivaldehyde. Thus, the racemic 2-phenylcyclohexanone were transformed to optically active lactone in 41% yield with 69% ee and the unreacted ketone shows *S*-configuration (Scheme 22). Under these conditions, chiral cyclobutanones are oxidized with up to 95% ee (Table 8). Prochiral cyclobutanones also give optically active lactones, the enantioselectivity in this process, however, is only moderate (up to 44% ee). The only exception observed is the oxidation of Kelly et al's tricyclic ketone [94e], which afforded lactone **21** in 91% ee.

2.8. Sulfoxidation

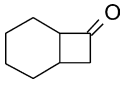
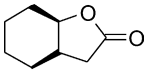
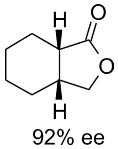
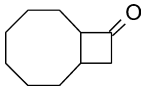
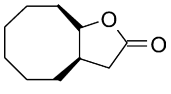
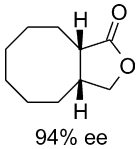
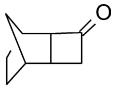
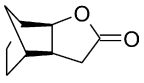
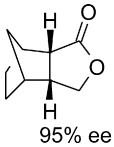
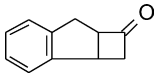
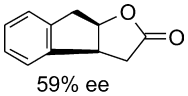
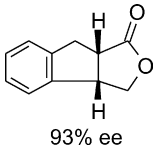
The oxidation of sulfides to sulfoxides has been extensively studied due to their importance as useful intermediates in organic synthesis and some play key roles in the activation of enzymes [95]. Many oxidants are available to perform this key transformation [96].

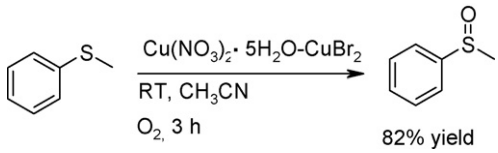
Copper salts have been used for this purpose with molecular oxygen. $CuCl_2$ is used for the air oxidation of sulfides for



Scheme 22.

Table 8
Chiral copper(II) complex **20** catalyzed enantioselective Baeyer–Villiger reaction

Entry	Substrate	Products	
		Normal lactone	Abnormal lactone
1		 67% ee	 92% ee
2		 61% ee	 94% ee
3		 76% ee	 95% ee
4		 59% ee	 93% ee



Scheme 23.

the purification of the petrol fuel (Cu 6 mmol/L, 140°, 5 mPa, 20 min) [97]. The sulfoxides are formed with up to 60% yield and 100% selectivity. Activation of this catalytic system with 0.4 mol% AcOH/L increased the sulfoxide yield to 70%, but decreased the selectivity to 98%, while the combined use of $Cu(NO_3)_2$ and $CuBr_2$ has catalyzed the oxidation of sulfides to sulfoxides in high yields at ambient temperature (Scheme 23) [98]. In another example, $Cu(OH)_2$ and $Cu(OAc)_2$ were used in the presence of isovaleraldehyde where the sulfoxides have formed along with sulfones in moderate yields [99].

3. Reactions with hydrogen peroxide (H_2O_2)

H_2O_2 is an attractive oxygen source for liquid-phase reactions [100]. It can oxidize organic compounds with atom efficiency of 47% generating water as the only co-product. It is relatively cheap and particularly useful for the synthesis of high-value fine chemicals, pharmaceuticals, agrochemicals and electronic materials, which require high chemical purity. This section covers the copper-catalyzed reactions with H_2O_2.

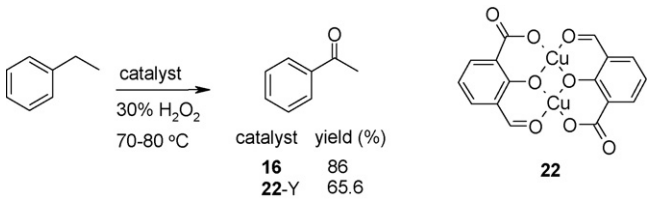
3.1. Oxidation of alkanes

The selective oxidation of methane is a potential route to obtain a feedstack for the chemical industry from natural gas. Copper salts have been studied for this purpose using in situ generated H_2O_2 from H_2 and O_2 over 5% Pd/C at 50 °C in a 4:1 mixture of trifluoroacetic acid (TFA) and trifluoroacetic anhydride (TFAA) [101]. Reaction with $Cu(OAc)_2$ provided the best result of having CF_3COOMe (78%) and HCOOH (22%).

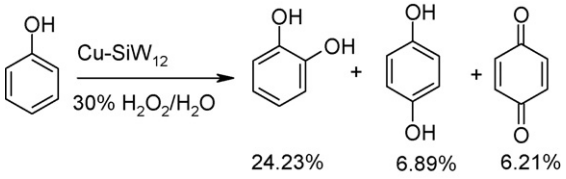
The copper based catalytic system with 30% H_2O_2 was also studied for the oxidation of cyclohexane. Reaction with copper(II) complex immobilized on amine functionalized MCM-41 (NH_2-$(CH_2)_3$-Si-MCM-41) provided cyclohexanol and cyclohexanone with 20 TON [102], while the multinuclear copper complex $[OCu_4(tea)_2(BOH)_4(BF_4)]_2$ [tea = triethanol-amine] catalyzed the reaction affording a 2:1 mixture of cyclohexanol and cyclohexanone with 31% conversion at ambient temperature [103].

3.2. Benzylic oxidation

The copper based catalytic system with aqueous H_2O_2 was used for the oxidation of the substrates having secondary benzylic C–H bonds. These reactions operate in 70–80 °C to afford the corresponding ketones in high yields. Reactions using copper(II) complex **16** were shown to catalyze the oxidation of butylbenzene, ethylbenzene, methyl phenylacetate and tetralin to the corresponding ketones in 86–89% yields (Scheme 24)



Scheme 24.



Scheme 25.

[104], while the copper(II) complex **22** encapsulated on Y zeolite oxidized ethylbenzene to acetophenone in 65.6% conversion [105]. The latter is recyclable and no leaching of the metal species is reported.

3.3. Phenol oxidation

The oxidation of phenol was studied with 30% H_2O_2 in the presence of copper(II) catalysts. The reaction employing the recyclable copper-12-silicotungstic acids ($CuSiW_{12}$) transformed phenol to catechol, hydroquinone and benzoquinone with 39% conversion in water (Scheme 25) [106]. Copper hydroxyphosphate $Cu_2(OH)PO_4$ oxidized 2,3,6-trimethylphenol(TMP) to trimethyl-1,4-benzoquinine(TMQ) (54.6%) along with trimethylbenzo-quinone (27.9%) in 51.1% conversion (474 TOF) at 55 °C in CH_3CN [107].

3.4. Alcohol oxidation

The oxidation of alcohols was accomplished with excellent selectivity by copper-catalyzed oxidation in the presence of aqueous H_2O_2 (Table 9). Regarding the oxidation of primary alcohols, the product selectivity aldehyde versus carboxylic acid depends on the reaction conditions. The catalytic systems employing copper(II) complex **22** encapsulated on zeolite (Y) (**22**-Y) [105] and binuclear copper(II) complex, $Cu_2(O_2CC_6H_{10}CO_2)_2{\cdot}H_2O$, [108] selectively provided aldehydes, while reactions with copper(II) complex **16** led to carboxylic acids in quantitative yields [109].

3.5. Sulfoxidation

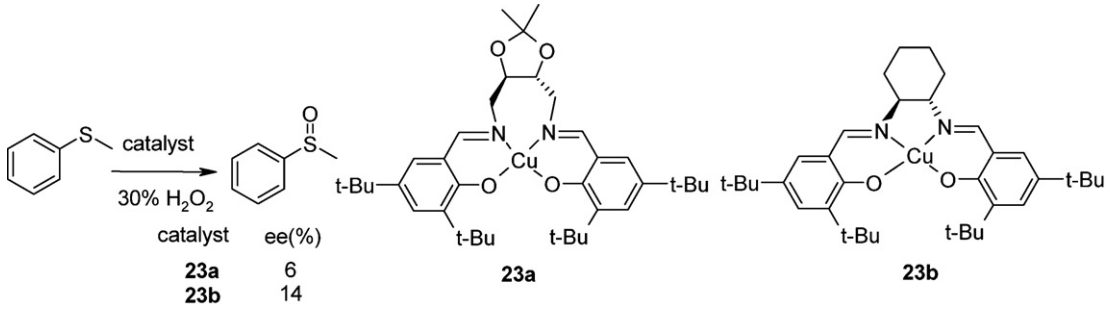
The oxidation of alkyl aryl sulfides was studied using chiral as well as achiral complexes in the presence of 30% H_2O_2 at ambient temperature. The complex **16** was used for the oxidation of a wide range of sulfides to provide the corresponding sulfoxide in high yields [110]. The chiral complexes **23** were employed for the oxidation methyl aryl sulfide with 14% ee (Scheme 26) [111]. All these reactions were studied at ambient temperature and over oxidation to sulfone is not reported.

4. Reactions with *tert*-butyl hydroperoxide (TBHP)

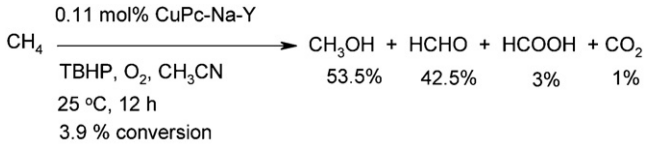
TBHP is one of the best sources of oxygen atoms for a variety of organic oxygenations. It has good thermal stability ($t_{1/2} \simeq 520$ h at 130 °C for a 0.2 M solution in C_6H_6) and leads

Table 9
Copper(II)-catalyzed oxidation of alcohols with 30% H_2O_2

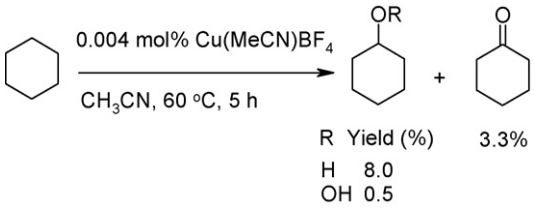
Entry	Catalyst	Substrate	Product (selectivity)	TON	Refs.
1	$Cu_2(O_2CC_6H_{10}CO_2)_2{\cdot}H_2O$	Benzyl alcohol	Benzaldehyde (>99)	12	[108]
2	**22**-Y	Benzyl alcohol	Benzaldehyde (>99)	–	[105]
3	**16**	Benzyl alcohol	Benzoic acid (>99)	92	[109]
4	$Cu_2(O_2CC_6H_{10}CO_2)_2{\cdot}H_2O$	2-Propanol	Acetone (>99)	35	[108]
5	$Cu_2(O_2CC_6H_{10}CO_2)_2{\cdot}H_2O$	1-Octanol	1-Octanal (>99)	4.1	[108]
6	$Cu_2(O_2CC_6H_{10}CO_2)_2{\cdot}H_2O$	Cyclohexanol	Cyclohexanone (>99)	9.1	[108]
7	**16**	Cyclohexanol	Cyclohexanone (>99)	99	[109]



Scheme 26.



Scheme 27.



Scheme 28.

to selective oxidation after activation by an appropriate transition metal complex [112]. It is very soluble in non-polar solvents and generates *tert*-butanol as co-product after the use of peroxygen atom. This is easy to separate by distillation and can be recycled or used for other industrial process. This section reviews the copper-catalyzed oxygenation of organic compounds with TBHP.

4.1. Oxidation of alkanes

The oxidation of alkanes with TBHP catalyzed by copper catalysts have been focused on liquid phase reactions. The oxidation of methane to a mixture of methanol and formaldehyde was performed employing zeolite (Y) encapsulated Cu(II)-Pc (Pc = phthalocyanine) in the presence of TBHP (Scheme 27) [113a]. Subsequently, Cu(II)-Pc encapsulated in Y Faugasite, CuPcY-3 [39c], $Cu(CH_3CN)_4BF_4$ [114a] and $((CH_3)_3COO)_2Cu$ [114b] were used for the oxidation of cyclohexane to cyclohexanol and cyclohexanone as major products. The solid catalyst is recyclable and no leaching is reported. These reactions are effective affording products with up to 2200 TON (based on TBHP) (Scheme 28).

4.2. Benzylic oxidation

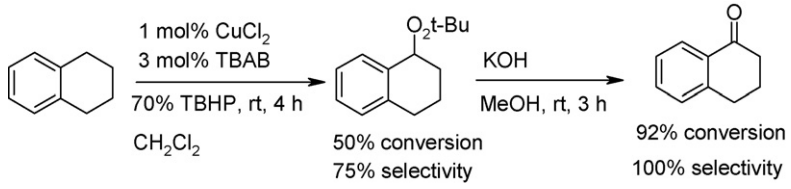
By the combined use of $CuCl_2$-TBAB [TBAB = tetrabutylammonium bromide] the oxidation of benzylic substrates was studied in the presence of 70% aqueous TBHP in CH_2Cl_2 at ambient temperature. This reaction functions in a two-phase system where TBAB acts as a phase transfer catalyst [115a] and involves a free radical process generating benzyl *tert*-butylperoxide as the major product (Scheme 29). This, on reaction with KOH in methanol at ambient conditions, provides the corresponding ketones with 100% selectivity. More recently, zeolite-Y encapsulated copper(II) aza macrocyclic complexes were studied for the oxidation of ethylbenzene in the presence of TBHP. This reaction provided acetophenone (98%) along with a trace of *o*/*p*-hydroxyacetophenone (2%) in 44.4% conversion (67 TOF) (Scheme 30) [115b].

4.3. Phenol to quinone

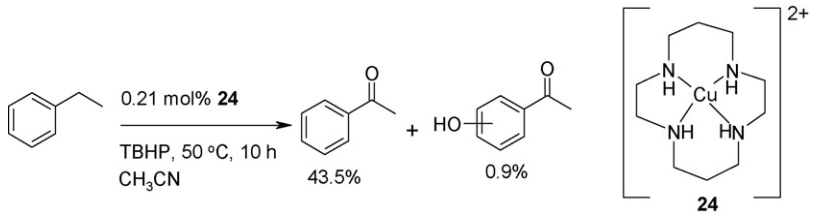
Copper based catalytic systems with TBHP were used for the single step oxidation of 2,3,6-trimethylphenol (TMP) to trimethyl-1,4-benzoquinone (TMQ) in high yield. The homogeneous process involving $CuCl_2$-NH_2OH·HCl catalyzed the oxidation with 80% yield in CH_3COOH [116]. Solid-supported catalyst, Cu-MCM-41, was subsequently studied for this purpose with 88% yield [117]. The latter is recyclable without loss of activity and no leaching is reported.

4.4. Allylic oxidation

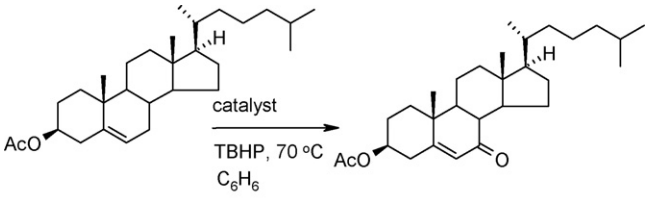
Allylic oxidation is a fundamental organic reaction of significant interest with applications in areas ranging from agricultural products to pharmaceuticals [118,119]. Copper based catalysts



Scheme 29.



Scheme 30.



Catalyst (mol%)	Time (h)	Yield (%)
CuI(2.6)	24	80
25 (6)	48	72

Scheme 31.

[Cu, $CuCl_2$, CuX (X = Cl, Br, I) and **25**] were studied with TBHP for the oxidation of Δ^5 steroids to provide 5-en-7-ones, known to be inhibitors of sterol biosynthesis and with some use in cancer chemotherapy [120]. These systems can be used for the oxidation of variety of substrates to give the corresponding α,β-carbonyl compounds in 70–84% yields (Scheme 31) [121,122].

A few studies focused on the use of α-TiCuAs [123], $Cu(NTB)Cl_2{\cdot}4H_2O$ [NTB = *tris*(2-benzimidazolylmethyl)amine] [124] and Schiff base complexes **26–27** supported on SiO_2 [125] and Al_2O_3 [126] for the oxidation of cyclohexene. These reactions provided a mixture of cyclohexenone and cyclohexenol as major products along with a trace of hydroperoxide in moderate yield (Scheme 32). The solid-supported catalysts are recyclable and no leaching is reported.

4.5. Alcohol oxidation

By the combined use of $CuCl_2$-TBAB (TBAB = tetrabutylammonium bromide) the oxidation of primary and secondary alcohols was carried out at ambient conditions in the presence of 70% aqueous TBHP in CH_2Cl_2 (Table 10) [127a,b]. This reaction functions in aqueous-organic biphase system where TBAB acts as a phase transfer catalyst. The proposed mechanism for this reaction involves a dehydrogenation process and no radical intermediate is involved. Subsequently, copper(II) complex **28b** was used with aqueous TBHP for the oxidation of secondary alcohols to ketones in aqueous medium [127c]. The oxidation of a variety of heterocyclic alcohols has been demonstrated in high yields.

Solid based catalysts were subsequently studied for solvent free reactions. For example, $[Cu(bpy)]^{2+}$-bentonite was shown to catalyze the oxidation of benzyl alcohol, hexanol and cylohexanol in 42–98% yields [128a]. Under similar conditions, the polystyrene supported copper(II) complex **28** oxidized benzyl alcohol to benzaldehdye with 72% yield and 93.8% selectivity [128b], while the copper(II) layered double hydroxide (LDH) transformed benzyl alcohol to a mixture of benzaldehyde (74.9%), benzoic acid (6.6%) and benzyl benzoate (18.5%) in 51.3% conversion. These catalysts are recyclable without loss of activity [129].

4.6. Sulfoxidation

The chiral copper(II) salen complex **29** immobilized on MCM-41 was studied for the oxidation of methyl phenyl sulfide in the presence of TBHP (Scheme 33) [130]. The sulfoxide has formed with 87% conversion (490 TOF) and 96% selectivity. The enantioselectivity reported for this system is 5% ee and the catalyst is recyclable without loss of activity.

5. Reactions with peroxyester

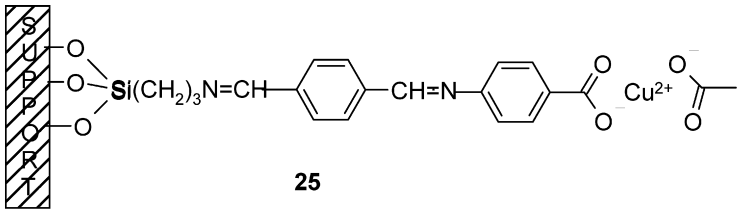
The copper-catalyzed oxidation of organic substrates with peroxyesters (Kharasch–Sosnovsky reaction) is one of the more powerful reactions in synthetic chemistry [131]. Since its invention in 1958, numerous synthetic and mechanistic investigations have been reported [131–133]. With respect to the recent progress, the allylic oxidation of alkenes was extensively studied (Scheme 34). Since these results have been recently reviewed [132–133], this section deals only briefly with the studies, which have appeared more recently.

5.1. Reactions with achiral catalysts

The copper-catalyzed allylic acyloxylation of alkenes with peroxyesters is a well-explored reaction (Scheme 34). In an extension, recent studies focused on the use of solid-supported catalysts, aqueous and fluorous phases to recycle the catalysts (Table 11). Sartori and coworkers studied the allylic oxidation of alkenes employing recyclable Cu(II)-exchanged zeolite, Cu-Na-HSZ-320, in the presence of *t*-butyl perbenzoate [134]. Subsequently, the copper complex formed from $Cu(CH_3CN)_4BF_4$ [135] and **30** [136] was shown to catalyze the oxidation of alkenes in water. The aqueous phase containing the catalyst can be recycled without loss of activity. In another example, Cu_2O in combination with perfluorodecanoic acid and *t*-butyl perbenzoate was used for this purpose in hex-

Table 10
Copper(II)-catalyzed oxidation of alcohols with TBHP

Entry	Catalyst	Substrate	Product (%)	Selectivity (%)	Ref.
1	$Cu(bpy)^{2+}$/bentonite	Benzyl alcohol	Benzaldehyde (55)	100	[128a]
2	**28a**	Benzyl alcohol	Benzaldehyde (72)	93.8	[128b]
3	Cu-Cr-LDH	Benzyl alcohol	Benzaldehyde (38)	74.9	[129]
4	$Cu(bpy)^{2+}$/bentonite	Hexanol	Hexanal (42)	100	[128a]
5	$Cu(bpy)^{2+}$/bentonite	Cyclohexanol	Cyclohexanone (98)	100	[128a]



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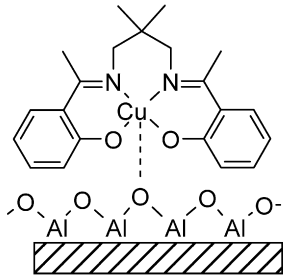

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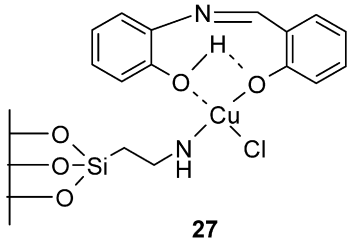

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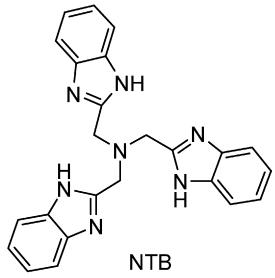
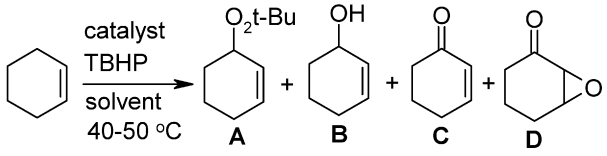
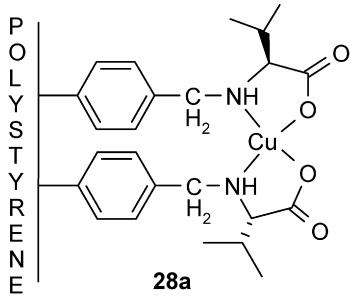


NTB



Catalyst (mol%)	Yield (%)			
	A	B	C	D
26 (1)	7.09	11.17	41.82	-
27 (0.01)	-	17.38	58.46	3.16
$Cu(NTB)Cl_2.\ 4H_2O$ (1)	-	9.00	48.00	-
α-TiCuAs (2)	-	1.5	0.14	2.7

Scheme 32.



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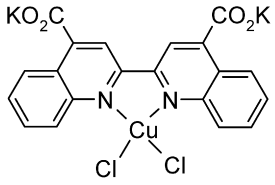

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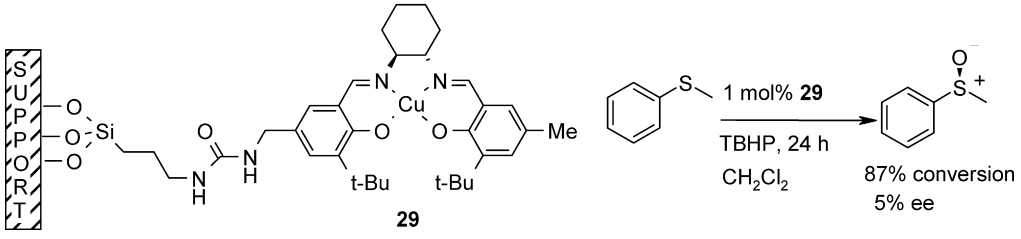

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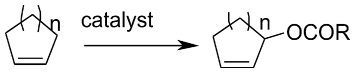
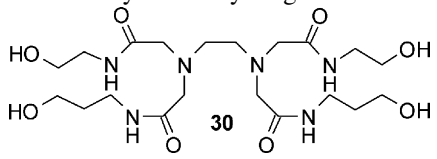
Scheme 33.

Table 11
Copper-catalyzed allylic oxidation with peroxyesters



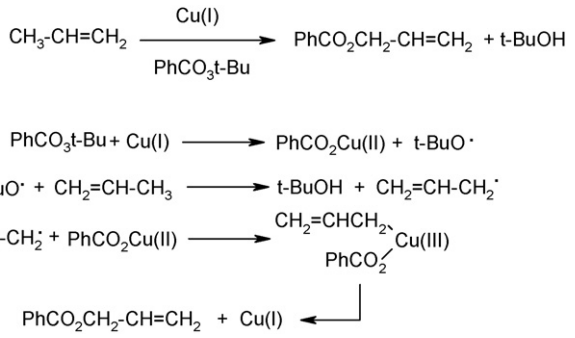
Entry	*n*	Catalyst	Solvent	Temperature (°C)	Yield (%)	Refs.
1	2	Cu-Na-HSZ-320 [Cu (% wt): 2.8]	Neat	45	70	[134]
2	1	Cu-Na-HSZ-320 [Cu (% wt): 2.8]	Neat	45	60	[134]
3	4	Cu-Na-HSZ-320 [Cu (% wt): 2.8]	Neat	45	68	[134]
4	2	$Cu(MeCN)_4BF_4$, **30**	Water	80	67	[136]
5	3	$Cu(MeCN)_4BF_4$, **30**	Water	80	64	[136]
6	4	$Cu(MeCN)_4BF_4$, **30**	Water	80	42	[136]
7	2	Cu_2O, $Cu_{11}F_{23}CO_2H$	$(CF_3)_2CHOH$	59	30	[137]
8	4	Cu_2O, $Cu_{11}F_{23}CO_2H$	$(CF_3)_2CHOH$	59	20	[137]

afluoroisopropanol [137]. In this reaction, the recovered catalyst had enhanced reactivity after recycling.



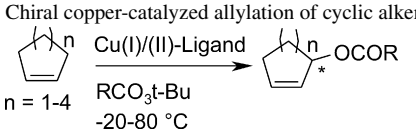
5.2. Enantioselective reactions

Chiral copper-catalyzed enantioselective allylic oxidation with peroxyesters has made remarkable progress in recent years. Numerous chiral ligands **31–40** have been designed and developed for this purpose [138–163]. The oxidation of cyclic



Scheme 34.

Table 12
Chiral copper-catalyzed allylation of cyclic alkenes with peroxyesters

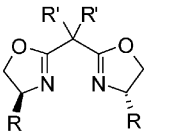


Entry	Cu(I)/C(II)	Ligand	R	*n*	Yield (%)	ee (%)	Configration	Refs.
1	Cu(I)	**31a**	Ph	1	61	84	*S*	[138]
2	Cu(I)	**31a**	Ph	2	64	77	*S*	[138]
3	Cu(I)	**31b**	4-NO_2-C_6H_4-	1	41	99	*S*	[139]
4	Cu(I)	**31d**	4-NO_2-C_6H_4-	2	44	96	*S*	[139]
5	Cu(I)	**32a**	Ph	2	80	71	*S*	[138]
6	Cu(II)	**33**	Ph	1	30	93	*S*	[141]
7	Cu(II)	**33**	Ph	2	4	72	*S*	[141]
8	Cu(I)	**34**	Ph	1	58	70	–	[143]
9	Cu(II)	**35**	Ph	2	63	65	*R*	[144]
10	Cu(II)	**31c**	4-NO_2-C_6H_4-	2	52	85	–	[140]
11	Cu(I)	**34**	Ph	2	58	38	*R*	[145]
12	Cu(II)	**37**	Ph	2	45	91	*S*	[146]
13	Cu(II)	**38**	Ph	2	48	78	*S*	[142]
14	Cu(I)	**39**	4-NO_2-C_6H_4-	2	76	73	*S*	[155]
15	Cu(II)	**40**	Ph	2	35	82	*R*	[156]

Table 13
Copper-catalyzed anaerobic oxidation of alcohols

Entry	Reaction conditions	Substrate	Product (yield, %)	Ref.
1	5 mol% CuCl; 5 mol% 1,10-phenanthroline; 1 equiv. DBAD; 10 mol% K_2CO_3; toluene, 70 °C, 3 h	Decanol	Decanal (79)	[164]
2	5 mol% CuCl; 5 mol% 1,10-pheanthroline; 1 equiv. DBAD; 10 mol% K_2CO_3; toluene, 70 °C, 3 h	2-Undecanol	2-Undecanone (84)	[164]
3	Cu/Al_2O_3; 1 equiv. styrene; toluene, 90 °C, 4 h	2-Octanol	2-Octanone (100)	[165]

alkenes is successful affording enantioselectivity up to 99% ee (Table 12). Of the various ligands studied, the bisoxazoline based ligands showed the highest enantioselectivity. These results compliment the catalytic epoxidation and dihydroxylation methods that occur with high selectivity.



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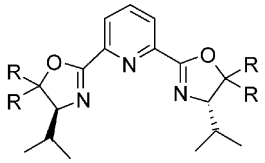
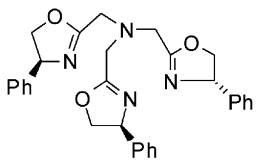


32 R
a H
b Ph



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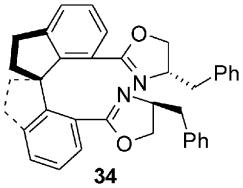

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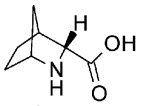

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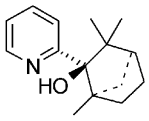

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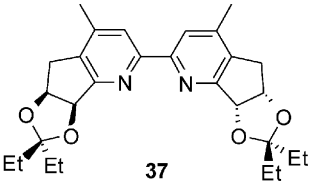

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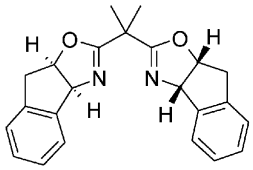

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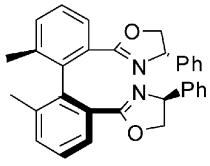
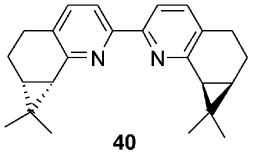


39



40

(DBAD=^{t}BuO$_2$C–N=N–CO$_2$^{t}Bu) catalyzed the oxidation of primary and secondary alcohols in excellent yield [164], while the use of recyclable solid-supported catalysts, Cu/SiO_2 and Cu/Al_2O_3, with styrene was successful with the oxidation of secondary alcohols [165]. Under these conditions primary alcohols are less reactive providing the aldehydes in very low yield.

6. Miscellaneous

The copper-catalyzed oxidation of organic substrates was also investigated employing other commonly used oxidants such as sodium hypochlorite (NaOCl), iodosylbenzene (PhIO) and *m*-chloroperbenzoic acid (mCPBA). This section reviews those studies.

6.1. Epoxidation

The epoxidation of alkenes was studied employing copper complexes in the presence of PhIO, NaOCl and *m*-CPBA as oxidants [160–163]. The reactions with *m*-CPBA are more effective in comparison to PhIO and NaOCl transforming alkenes to the corresponding epoxides in good yields [163]. Functional groups such as aldehyde, acetal and silyl ether are compatible with this system.

6.2. Alcohol oxidation

The oxidation of alcohols was successfully demonstrated employing copper catalysts in the presence of dehydrogenating reagents (Table 13). The reactivity of the substrates, primary versus secondary, depends on the reaction conditions. Marko's procedure employing CuCl/1,10-phenanthroline with DBAD

7. Conclusion

The foregoing sections clearly demonstrated the impressive progress made in the area of copper-catalyzed oxidation of organic compounds. The methodologies described have clearly opened up new avenues for a major growth in the area of oxidation chemistry. The oxidation of alcohols, arenes, carbon–carbon triple bonds and Kharasch–Sosnovsky reactions has made remarkable progress, while the oxidation of alkanes, benzylic substrates and Baeyer–Villiger reaction has been extensively explored. Many of these reports demonstrated the use of polymer and solid-supported catalysts, ionic liquids, aqueous and fluorous biphase systems to facilitate the recyclability of the catalysts. In addition, the enantioselective oxidation of biaryl coupling, Baeyer–Villiger oxidation and Kharasch–Sosnovsky reaction accomplished excellent enantioselectivity. Thus, the success has opened avenues for future growth in accessing oxidized organic molecules using copper catalysts. Efforts in this area should fo culminate in tackling the major issues pertaining to environmentally acceptable technologies for the future.

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