

Review

Recent Advances in Homogeneous Metal-Catalyzed Aerobic C–H Oxidation of Benzylic Compounds

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Abstract: Csp^3 -H oxidation of benzylic methylene compounds is an established strategy for the synthesis of aromatic ketones, esters, and amides. The need for more sustainable oxidizers has encouraged researchers to explore the use of molecular oxygen. In particular, homogeneous metal-catalyzed aerobic oxidation of benzylic methylenes has attracted much attention. This account summarizes the development of this oxidative strategy in the last two decades, examining key factors such as reaction yields, substrate:catalyst ratio, substrate scope, selectivity over other oxidation byproducts, and reaction conditions including solvents and temperature. Finally, several mechanistic proposals to explain the observed results will be discussed.

Keywords: oxidation; molecular oxygen; metal catalysts; aryl ketones; benzoate esters; benzamides

1. Introduction

Aryl ketones, benzoate esters, and benzamides are ubiquitous structures found in natural and biologically active compounds (e.g., hypericin [1–3], acetosyringone [4,5], oxcarbazepine [6,7], daidzein [8,9], sitaxentan [10,11], radicicol [12,13], arnamial [14–16], epicatechingallate [17], Rucaparib [18–21], and Leucine-rich repeat kinase-2 (LRRK2) [22,23], Figure 1). In addition, such carbonyl compounds are also extensively used in advanced materials [24–28] and as key intermediates for the synthesis of fine chemicals, including structurally complex compounds. [29–31]. Among the many synthetic procedures devised for the preparation of aromatic ketones, esters and amides [32–37], including Friedel–Crafts acylation, esterification and amidation of benzoic acid derivatives [38–46], the oxidation of benzylic methylene compounds stands out as a simple approach that has attracted much attention in the last decades. Many reagents ($KMnO_4$, iodine(V) species, $tBuOOH$, m -CPBA, H_2O_2 , $NHPI$, inter alia) can oxidize the activated benzylic position of aromatic alkanes, benzyl ethers, and amines to provide the corresponding arylcarbonyl moiety (Scheme 1) by a process opposite to Clemmensen, Wolf–Kisnerr and related reduction reactions [47–61]. Although good yields and selectivities have been obtained in most cases, stoichiometric amounts of relatively harmful or unsafe oxidizing agents are required. For safety and environmental reasons, molecular oxygen is the oxidant of choice in most oxidative transformations, and an increasing number of reports concerning oxidation of arylmethylene compounds under aerobic conditions can be found in the literature [62–78]. Interestingly, although a theoretically easier catalyst–product separation has boosted research on heterogeneous catalysts (e.g., polymer- or montmorillonite clay-supported catalysts, Pd, Au, or Co nanoparticles) [79–93], leaching problems and efficiency or selectivity issues [79,85,86,90,93] have encouraged investigations on the development of new homogeneous catalyst systems. This review will cover recent literature from 2000 on the use of homogenous metal catalysts for the aerobic benzylic methylene C–H oxidation leading to aromatic ketones, esters, and amides, with a focus on

relevant parameters such as reaction yields, substrate:catalyst ratio, selectivity towards target carbonyl compounds, reaction media, and other experimental conditions. Considering that metal complexes and combination of metal salts and ligands have been described as catalysts or precatalysts in this field, this review is organized according to the metal core involved in the reaction. Although mechanism for this transformation is far from being completely elucidated, several proposals will be discussed.

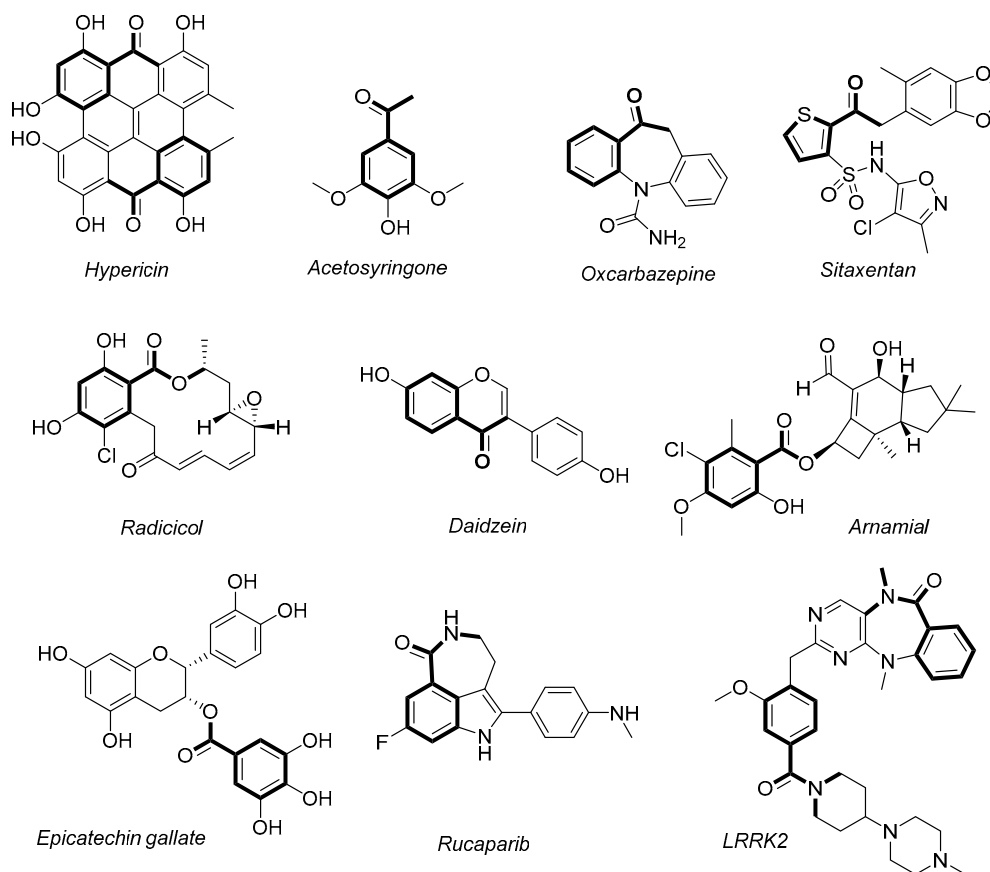
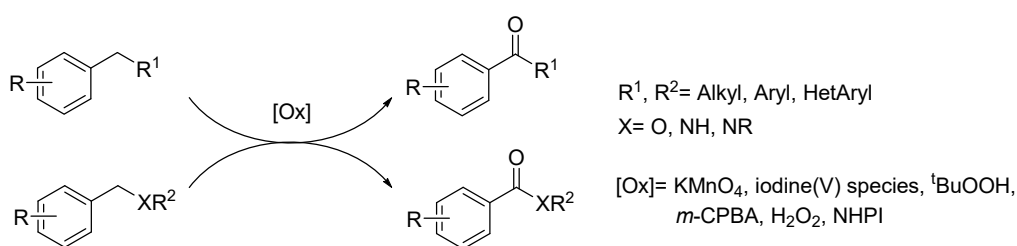


Figure 1. A selection of biologically relevant aromatic ketones and esters.



Scheme 1. Benzylic C–H oxidation with oxidants other than molecular oxygen.

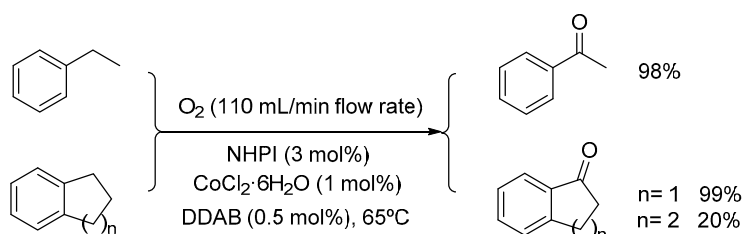
2. Cobalt Catalysts

2.1. Co(II)-NHPI

Following the pioneering works by Ishii [63–66], cobalt(II) salts combined with *N*-hydroxyphthalimide (NHPI) derivatives have been amply used for the aerobic C–H oxidation of methylene compounds at atmospheric pressure. An in situ-generated phthalimide-*N*-oxyl radical (PINO) is proposed to play a key catalytic role as hydrogen atom abstracting species in the reaction, and other *N*-hydroxylated ligand/additives prone to form related radical species have also been evaluated and compared with NHPI. Among other transition metals, cobalt salts have been defined as promoters

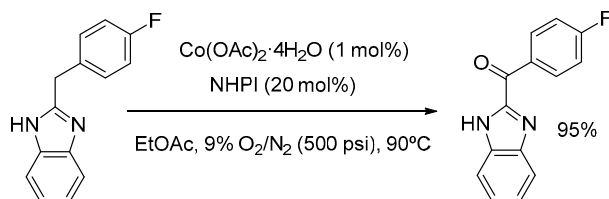
for the formation of PINO. Nolte and coworkers published the use of 0.5 mol% of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ combined with NHPI (10 mol%) in acetic acid to perform benzylic oxidation of 2-(hetero)arylacetic esters to the corresponding α -ketoesters at relatively low temperatures (40–80 °C). Lower yields (<30%) were obtained from some *o*-alkoxylated and brominated substrates, as well as from all the heteroaromatic esters. Finally, with regard to the oxidation of ethylbenzene to acetophenone, several *N*-hydroxy-phthalimides were evaluated as co-catalysts, achieving good conversion rates (except for nitro-substituted NHPIs) and relatively good acetophenone:1-phenylethanol ratios (59–88:2–5) [94].

The solvent-free oxidation of several alkylbenzenes to the corresponding ketones using di-*n*-decyl-di-methyl ammonium bromide (DDAB) and other phase transfer agents was explored by Patil et al. A 0.5 mol% of the latter quaternary ammonium salt was required along with NHPI (3 mol%) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1 mol%) to perform the oxidation under oxygen gas flow rate of 110 mL/min at 65 °C, although other metal sources ($\text{MnCl}_2(\text{H}_2\text{O})_4$ and $\text{CrCl}_3(\text{H}_2\text{O})_6$) and ammonium phase transfer catalysts (TBAB and TOAB; CTAB and Aliquat 336) were also tested and provided poorer results in most cases ($\text{CrCl}_3(\text{H}_2\text{O})_6$ performed better with tetralin). Excellent selectivity was observed for ethylbenzene and indane, but other oxidation products (17–20%) were detected from tetralin (Scheme 2). Catalyst–product separation by vacuum distillation is described along with upscaling of the reaction leading to acetophenone [95].



Scheme 2. Solvent-free oxidation of alkylbenzenes by Patil et al.

In addition to a new electrochemical NHPI-catalyzed oxygenation of methylene compounds, Stahl and coworkers reported the Co/NHPI co-catalyzed benzylic C–H oxidation of a number of alkyl(hetero)arenes, including several di(hetero)arylmethanes precursors of pharmacologically active compounds. After observing selectivity problems (side-products from overoxidation or oxidative cleavage of the alkyl chain, among others), a careful optimization of the reaction conditions led to a procedure involving a greener solvent, *n*-butyl acetate (Scheme 3). In some cases pyridine was added as co-solvent (7:3 proportion) in order to minimize the above side-reactions. They also showed that the presence of certain heterocyclic moieties could inhibit the radical oxygenation reaction, probably by chelation with the metal catalyst. In those cases the aforementioned electrochemical procedure can be used as a valid alternative. (Benzoimidazol-2-yl)(4-fluorophenyl)methanone, precursor to a clinical candidate for schizophrenia, was prepared in 2 g scale by a variation of the procedure that involved the use of 500 psi of a mixture ($\text{O}_2:\text{N}_2$ 9:91) in order to maintain the concentration of molecular oxygen below the limiting oxygen concentration of EtOAc (Scheme 3) [96].



Scheme 3. Synthesis of a clinical candidate for the treatment of schizophrenia by Stahl and col.

Wang et al. prepared an analog to NHPI (Py-NHPI, Figure 2) and used it for the oxidation of *N*-benzyl-acetamides, -propionamides, and -benzamides to the corresponding imides as well as for the synthesis of several aromatic ketones and esters by oxidation of isochomane and alkylarenes. Under 1

atm of molecular oxygen, $\text{Co}(\text{PF}_6)_2$ (1 mol%) and Py-NHPI (5 mol%) catalyzed the above oxidations at 65 °C using for the first time a ionic liquid as solvent ($[\text{bmim}][\text{PF}_6]$) [97]. A Diels–Alder cycloaddition was the key for the preparation of several chiral anthrone-derived NHPI derivatives performed by Shen and Tan. Ethylbenzene, 1,2-dihydroacenaphthylene, and 2-methoxy-2-phenyl-2,3-dihydroindene were reacted with molecular oxygen (1 atm) in the presence of $\text{Co}(\text{OAc})_2$ (5 mol%) and one of the above chiral anthrone-derived *N*-hydroxyphthalimides (10 mol%) in acetonitrile at 60 °C. Mixtures of monohydroxylated product along with the corresponding ketone were obtained for the first two substrates, and 2-methoxy-2-phenyl-2,3-dihydroindene-1-one was isolated in a 48% yield (Scheme 4). Enantiomeric excesses for chiral products ranged from 4 to 13% [98].

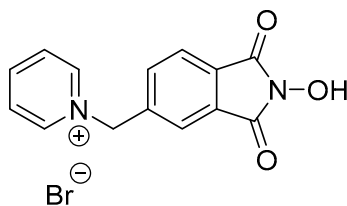
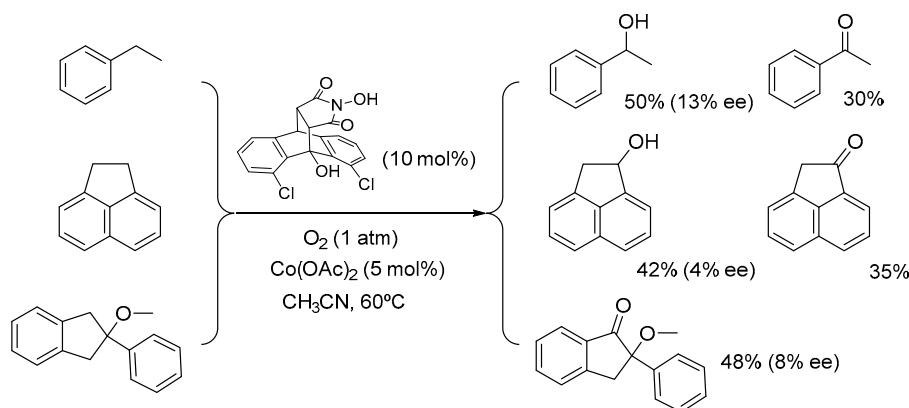
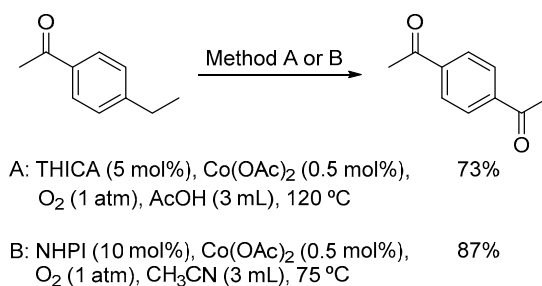


Figure 2. Structure of Py-NHPI prepared by Wang et al.



Scheme 4. Aerobic oxidation of several alkylbenzenes in the presence of a chiral NHPI derivative.

As an alternative to NHPI-based catalysts, Sheldon and coworkers reported the use of NHS (*N*-hydroxysaccharin) (10 mol%) for the oxidation of ethylbenzene. A 0.5 mol% of $\text{Co}(\text{OAc})_2$ or $\text{Co}(\text{acac})_2$ were tested as co-catalysts in four different solvents (AcOH , CH_3CN , PhCF_3 , and BuOAc) at 100 °C and 85 °C, and the results compared with those obtained with 10 mol% of NHPI. Higher conversion rates and selectivities were observed in the NHPI-co-catalyzed reactions, and only when benzoic acid (5 mol%) was added to the NHS-catalyzed reaction performed in BuOAc , the conversion rate and selectivity towards acetophenone improved to 71% and 90%, respectively [99]. Among other oxidations of the alkyl group of alkylacetophenones, the group of Ishii reported the molecular oxygen-mediated oxidation of 4-ethylacetophenone by using $\text{Co}(\text{OAc})_2$ (0.5 mol%) and a 5 mol% of *N,N',N''*-trihydroxyisocyanuric acid (THICA) in acetic acid. Although 1,1'-(1,4-phenylene)*bis*(ethan-1-one) was obtained by this method, a higher yield was observed when *N*-hydroxy imide THICA was replaced with NHPI (10 mol%) as catalyst for the generation of carbon radicals from the methylene sp^3 C–H bonds (Scheme 5) [100].



Scheme 5. THICA- or NHPI-co-catalyzed benzylic oxidation of 4-ethylacetophenone.

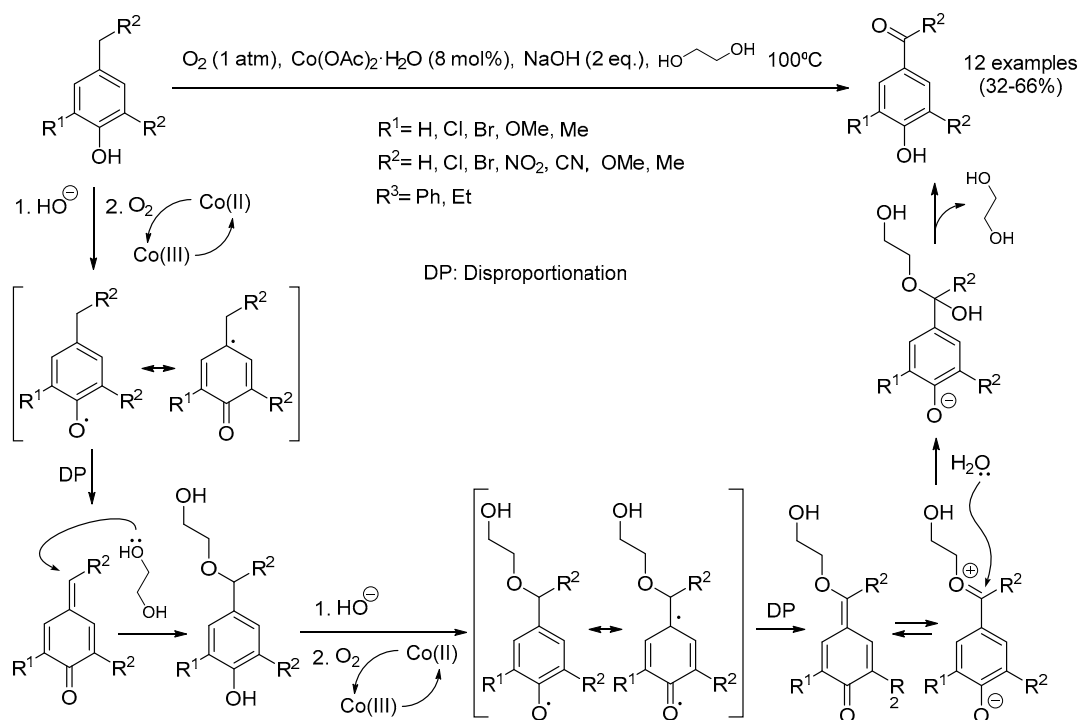
2.2. Co(II) without Hydroxyimides

Shaabani et al. carried out the oxidation of several benzylic methylene compounds to the corresponding ketones employing cobalt(II) phthalocyanine (5 mol%) in an ionic liquid ([bmim]Br) at 100 °C under oxygen at one atmospheric pressure. Good yields were obtained, and recycling of the catalyst–solvent system was also reported, as after several cycles no decrease in the catalytic activity was observed. The authors propose a radical pathway which starts with hydrogen abstraction by superoxocobalt(III) species [101]. Activation of molecular oxygen by metalloporphyrins toward hydrocarbon oxidation was proposed by Wang et al. as the key for the Co(II) tetraphenylporphyrin (CoTPP)-catalyzed solventless oxidation of alkylaromatics under the special temperature control method (reaction initiation at high temperatures and progress at lower temperatures). Depending on the substrate, the reaction mixture containing 10^{-3} mol% of CoTPP and 1 atm of O_2 was initially heated to 136–200 °C for 1 min, and then heating was continued at 130 °C for 12 h. Moderate yields (<50%) and selectivities for target ketones were observed in most cases [102].

A Co(II)/Mn(II) co-catalyzed aerobic oxidation of ethylbenzene was performed in a gas–liquid continuous flow reactor. Different reaction parameters (flow rates, temperature, reaction time, etc.) were optimized (CoBr_2 (2.5 mol%), $\text{Mn}(\text{OAc})_2$ (2.5 mol%) in AcOH, 0.6 mL/min for the liquid stream and 100 mL/min for the synthetic air flow, 12 atm, 100 °C, ~20 min) in order to get an 84% of acetophenone mixed with small proportions of benzoic acid (5%), phenylethanol (2%), benzaldehyde (1%), 1-phenylethyl acetate (2%), and 2-bromoacetophenone (5%) by a comparatively fast oxidative transformation. Higher temperatures (150 °C) provoked oxidative cleavage of ethylbenzene to benzoic acid [103]. It should be pointed out that the reaction conditions were close to those for the industrial oxidation of *p*-xylene to terephthalic acid.

Medium-pressure oxidation of ethyl benzene and other alkylbenzenes such as *n*-propylbenzene, tetraline, 1,2-dihydroacenaphthylene, and fluorene is described in the report by Wang and He. The authors propose that $\text{Co}(\text{OAc})_2$ acts not only as an initiator for generating polyethylene glycol (PEG) radicals but also as a promoter of the decomposition of intermediate hydroperoxides into the product, in a similar way to the radical reactions performed in the presence of the couple NHPI/ $\text{Co}(\text{OAc})_2$. High-pressure CO_2 is introduced in the system in order to “expand” PEG so that lowered melting points, raised diffusion rates and lowered solvent viscosity are achieved. Although oxidation of ethylbenzene to acetophenone performed at 120 °C (2 mol% of $\text{Co}(\text{OAc})_2$, 36 mol% of PEG-1000, 24.7 atm O_2 , 69 atm CO_2 , 12 h) provided target ketone with a 65% yield, a lower temperature (100 °C) was chosen in order to explore the generality of the procedure. Moderate to good yields ranging from 13 to 83% were obtained [104]. Another polyol (ethylene glycol) is the solvent of the procedure described by Ji and coworkers. A number of 4-benzyl- and 4-ethylphenols were oxidized to the corresponding 4-hydroxybenzophenones and 4-hydroxyacetophenones by the basic conditions displayed in Scheme 6. On the basis of the comparison of the yields obtained from 4-benzyl- and 4-ethyl derivatives and of the isolation and/or reactivity of presumed intermediates, the authors propose a mechanistic path initiated by a phenoxy radical formed by single electron transfer between the phenoxide and dioxygen-induced Co(III) species. Disproportionation or hydrogen abstraction leads to a benzoquinone methide which undergoes conjugate addition by ethylene glycol, and after

formation of the corresponding phenoxy radical and subsequent benzoquinone methide, hydrolysis provides target ketone (Scheme 6) [105].

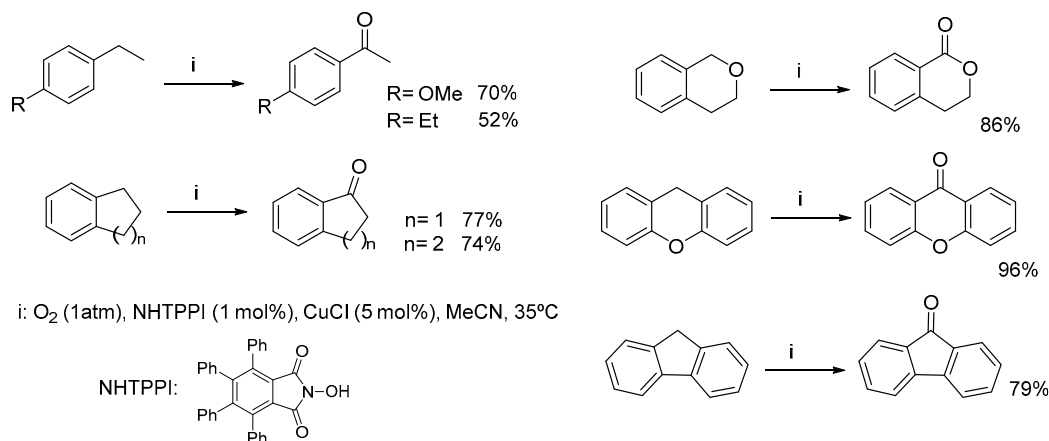


Scheme 6. Oxidation to 4-hydroxybenzophenones and 4-hydroxyacetophenones.

3. Copper Catalysts

3.1. Cu-NHPI

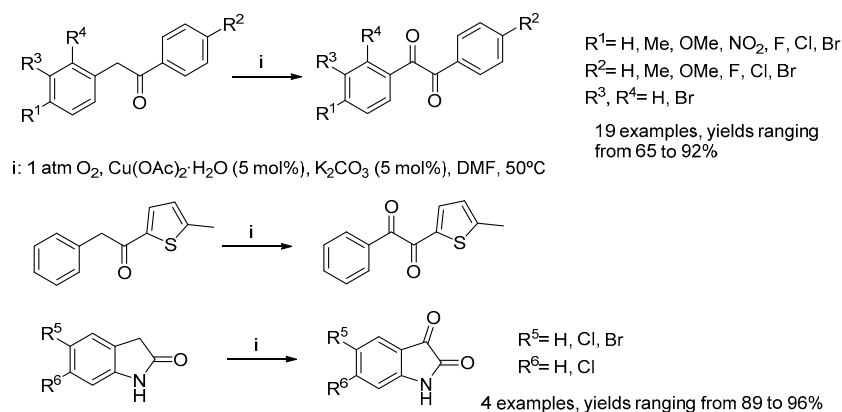
In comparison with the Co(II)-NHPI system, a notable smaller number of reports on molecular oxygen-mediated benzylic C–H oxidation in the presence of copper-imide co-catalysts can be found in the literature. Following previous research by Orlinska and Romanowska on aerobic oxidation of cumene derivatives [106], Chen et al. published the medium pressure (11.8 atm of O_2) oxidation of tetralin using a 10 mol% of NHPI and 2.5 mol% of CuCl_2 in CH_3CN . 1-Tetralone was produced with a selectivity of 46% over other undetermined oxidation products. An in situ generation of PINO radical from NHPI through the redox reaction of copper salts is suggested by the authors as the key step of the reaction mechanism [107]. Several chiral and achiral *N*-hydroxyimides were evaluated as co-catalysts for the aerobic oxidation of indane to 1-indanone published by Einhorn and coworkers. *N*-hydroxy-3,4,5,6-tetraphenylphthalimide (NHTPPI) resulted very convenient for the latter transformation performed with O_2 at atmospheric pressure at 35°C in MeCN. The reaction scope was then extended to other alkylbenzenes bearing benzylic methylene groups, providing the results displayed in Scheme 7. In addition to the mild conditions employed, the relatively high conversion rates (69–98%) and the high selectivities observed (1–3% of the corresponding partially alcohol derivatives were detected), the procedure was also efficient, as only a 1 mol% of NHTPPI and 5 mol% of CuCl were required. Such enhanced catalytic activity may be due to the higher stability of the NHTPPI-derived radical [108].



Scheme 7. NHTPPI-CuCl co-catalyzed oxidation of alkylbenzenes at 35 °C.

3.2. Additive-Free Procedures

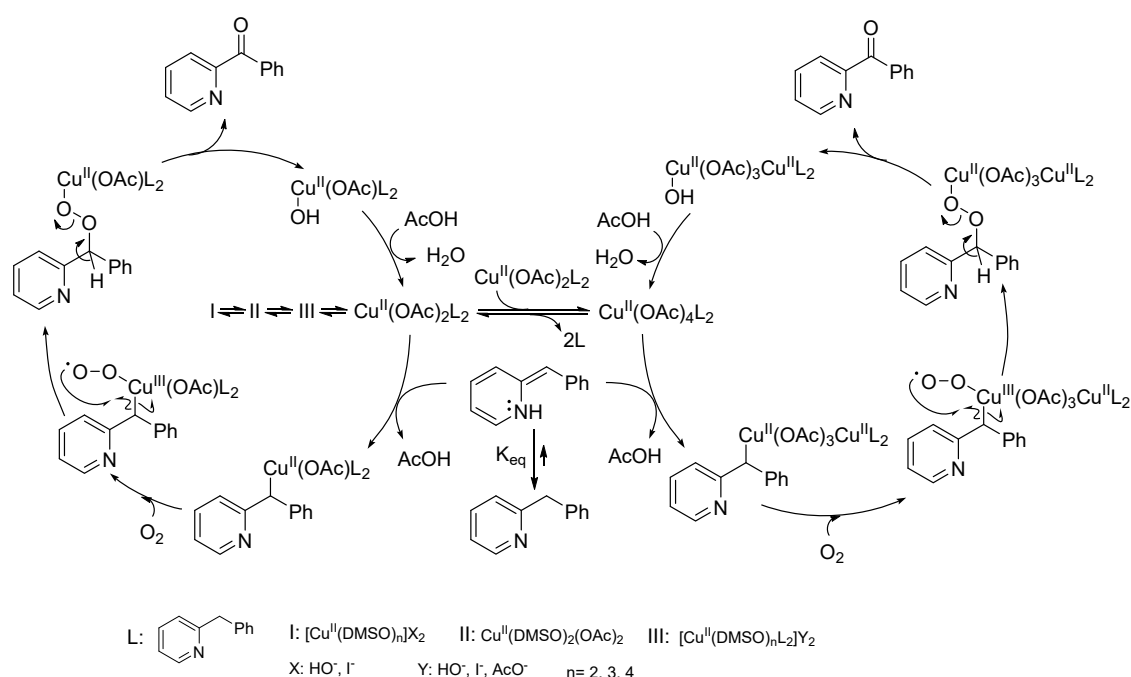
A simple catalyst system comprising CuCl₂·2H₂O (10 mol%) was enough to catalyze the oxidation at atmospheric pressure of the benzylic methylene unit of 4-ethylpyridine, 4-benzylpyridine and 2-benzylpyridine to the corresponding ketones. DMSO was the best solvent for the presented procedure, as model reaction in other reaction media provided negligible results. In contrast with 4-ethylpyridine, good conversion rates and selectivity towards ketones was observed for the latter benzyl derivatives [109]. The additive- and ligand-free procedure described by Ji and coworkers provides *m,m'*-disubstituted *p*-hydroxyaryl ketones from *m,m'*-disubstituted *p*-alkylphenols by treatment with 1 atm of air in the presence of 1 mol% of Cu(OAc)₂ in ethylene glycol at 50 °C. In order to explain this process, a mechanistic path akin to the one proposed for the cobalt-catalyzed oxidation under similar conditions [105] was postulated by the authors [110]. A rather specific benzylic oxidation was observed by Chiba and coworkers during the addition of Grignard reagents to *o*-cyanodiarylmethanes. The authors described the aerobic oxidation of the benzylic methylene unit to the corresponding ketone by using Cu(OAc)₂ (10 mol%) in DMF, and suggested that complexation of the copper catalyst to the so-formed *o*-carboximino group enables an anchimeric assistance leading to *o*-acylbenzophenone derivatives [111]. A copper-catalyzed and carbonate base-accelerated oxidation of deoxybenzoins and oxindoles to benzils and isatins was reported by Yung et al. Dimethylformamide was found to be the best solvent for the reaction, which involves the use of the conditions displayed in Scheme 8. On the basis of a radical trapping experiment with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) the authors propose the participation of a benzyl radical, that after trapping with oxygen and hydrogen abstraction undergoes dehydration to provide target diketones/ketoamides [112].



Scheme 8. Oxidation of deoxybenzoins and oxindoles to benzils and isatins.

3.3. With Ligand and/or Additives

Following their initial research on the oxidation of the methylene group of aryl(di)azinylmethanes [113], an extensive mechanistic study designed to understand the parameters governing the copper-catalyzed aerobic oxidation of a number of benzylpyridines and other benzylheterocycles (2-benzylbenzoxazoles, -benzothiazoles, and -imidazoles, inter alia) was performed by Maes and coworkers. As a result, a direct correlation between calculated imine–enamine tautomerization equilibrium constants of the substrates (DFT calculations) and the yields of the obtained ketones was found, so that K_{eq} values serve as tool to predict if a substrate can be oxidized by the optimized procedure (O_2 (1 atm), CuI (10 mol%) AcOH (Equation (1)), DMSO, 100 °C). In addition, it was also demonstrated that benzyl alcohol is not an intermediate but a side-product, and that mononuclear and less active dinuclear catalytic species are involved in a relatively complex catalytic cycle (Scheme 9) [114].

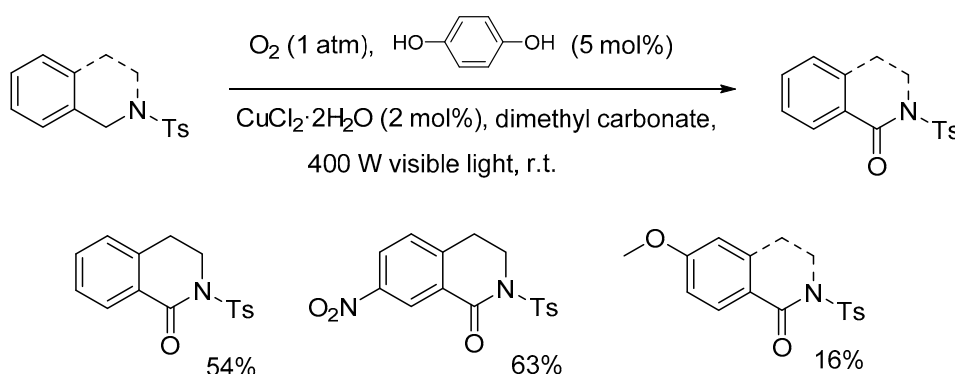


Scheme 9. Postulated mechanism for the oxidation of 2-benzylpyridine using O_2 /CuI/AcOH/DMSO.

The benefits of introducing other activating groups for the oxidation of aliphatic C–H bonds of *N*-heterocyclic compounds with molecular oxygen to produce *N*-heterocyclic ketones were explored by Liu et al. They found that ethyl chloroacetate (Equation (1)) combined with O_2 (1 atm), $CuCl_2 \cdot 2H_2O$ (10 mol%) in DMF at 130 °C could effectively promote the selective oxidation of a number of *N*-heterocyclic methylene compounds, including pyridines, quinolines, benzoquinolines, quinoxalines, benzimidazoles, and benzothiazoles. A number of experiments (isotopic labeling, kinetic, byproduct isolation, electron paramagnetic resonance, etc.) led them to propose that *N*-alkylation of heterocyclic nitrogen with ethyl chloroacetate activates the benzylic methylene unit for a catalytic hydrogen abstraction, and the resulting benzyl radical interacts with dioxygen to generate a hydroperoxide, that upon dehydration and copper induced reduction, provides target ketone along with ethyl acetate [115].

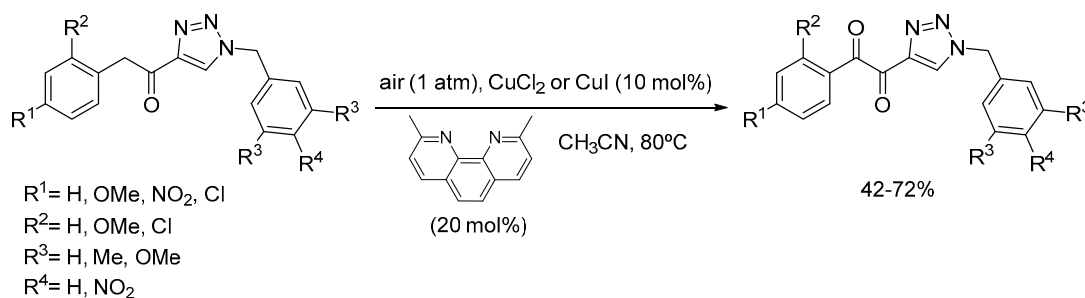
An efficient oxidation of ethylbenzene, tetraline, and indane was reported under medium pressure by Murahashi and coworkers. Acetaldehyde (2.5 mol%) was added to the reaction mixture containing the benzylic methylene compound and $Cu(OAc)_2$ (6×10^{-4} mol%) in a mixture of acetonitrile and dichloromethane under O_2 (1 atm)/ N_2 (8 atm). The in situ formation of peracetic acid was proposed by the authors to explain the oxidation results. However, selectivity towards the corresponding

ketones was poor, as mixtures with the partially oxidized benzylic alcohol were obtained in all cases [116]. The increase in oxidizing ability of quinones upon irradiation with visible light was exploited by Finney et al. in order to perform the benzylic C–H oxidation of a number of isochromanes, phthalans and other benzyl ethers, benzyltosylamines and diarylmethanes. 1,4-Hydroquinone, readily available from the naturally occurring β -D-glucopyranoside Arbutin was employed (5 mol%) as precursor of benzoquinone and thus as a pre-oxidant, along with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (2 mol%) as an electron transfer mediator and molecular oxygen as the thermal oxidant in dimethyl carbonate at 25–30 °C. Although minor selectivity issues were encountered (e.g., oxidation of 5-methoxyphthalan or of 1-methoxy-4-(methoxymethyl)benzene), it should be pointed out the access to benzamides by this more sustainable method (Scheme 10) [117].



Scheme 10. Visible light-mediated oxidation of *N*-benzyltosylamides.

Goggiamani and coworkers found that the previously reported DABCO/air oxidation of deoxybenzoins failed when applied to some of their diarylethanones. Accordingly, they devised a more reliable procedure for the copper-catalyzed aerobic oxidation of deoxybenzoins that provided the corresponding benzils. Indeed, moderate to good yields (45–95%) were obtained for a number of benzils bearing methyl, methoxy, cyano, acetyl, methoxycarbonyl, chloro, bromo, and iodo functionalities using $\text{Cu}(\text{OAc})_2$ (15 mol%) and PPh_3 (30 mol%) in 1,2,4-trimethylbenzene at 100 °C under air (1 atm) [118]. Structurally related α,β -diketotriazoles were selectively prepared by aerobic oxidation of α -ketotriazoles, with the 1-alkyl-1,2,3-triazol-4-yl moiety acting as an intramolecular assisting group. The 1-Alkyl group (benzyl group in most cases) remained untouched under the reaction conditions (Scheme 11). The authors propose active participation of both the substrate carbonyl oxygen and triazolyl N3-nitrogen in the reaction mechanism as copper(II) chelating positions that favor interaction with dioxygen [119]. Navarro's group reported the evaluation of two discrete Cu(II) imidazolyl complexes as catalysts for the oxidation of tetralin. Under the optimized reaction conditions (air (35 atm), Cu complex (0.14 mol%), 100 °C), α -tetralone was obtained with a moderate selectivity over α -tetralol (39–43:13) with a moderate conversion yield (52–57%) [120].



Scheme 11. Aerobic oxidation to α,β -diketotriazoles.

4. Iron Catalysts

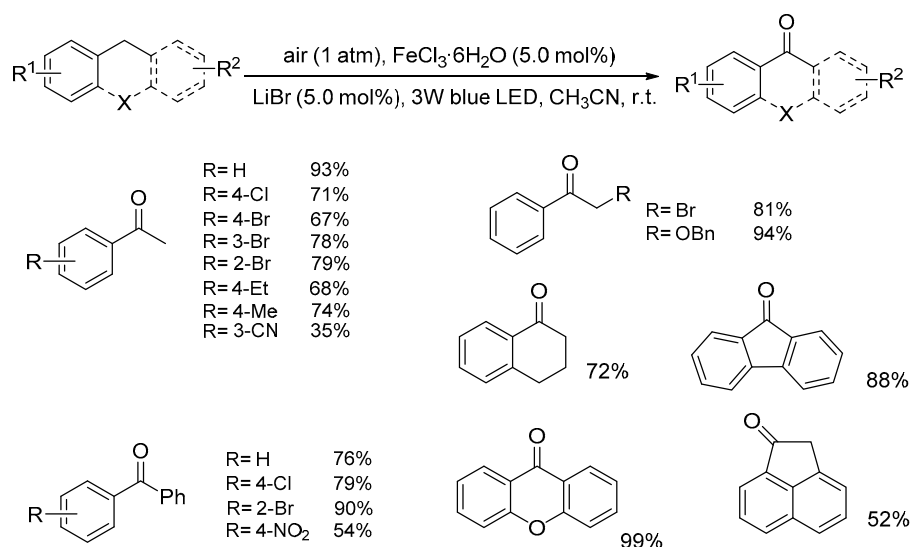
4.1. Fe-NHPI

Up to 15 benzylic methylene compounds were oxidized by the system $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8 mol%)/NHPI (10 mol%) in acetonitrile under 1 atm of O_2 at 25 °C. Sun and coworkers performed a series of experiments in order to get information on the reaction mechanism. As a result, they concluded that substrates bearing electron-donating groups have a higher oxidation rate, and proposed a catalytic cycle involving hydrogen abstraction by PINO to generate a benzylic radical followed by interaction with dioxygen and nitrate anions [121].

4.2. Light-Induced Oxidations

Several photochemical approaches to the iron-catalyzed benzylic C–H oxidation can be found in the recent literature. Thus, Pasau and coworkers described the flow synthesis of benzylic ketones using a combination of riboflavin tetraacetate (10 mol%) as the photocatalyst, $\text{Fe}(\text{ClO}_4)_2$ (5 mol%) as an additive to avoid photocatalyst bleaching, a flow of molecular oxygen of 1.0 mL/min and 106 W UV lamp for the mesofluidic C–H oxidation process of benzylic methylene compounds. Moderate to good conversions were obtained for substrates bearing amide, cyano, acetyl, carboxyl and halogen groups. When a 24 W 240-nm blue LED light was employed conversion dropped to 32%. The reaction mechanism is supposed to be initiated by a benzylic hydrogen abstraction with the photoactivated riboflavin tetraacetate catalyst aided the iron salt. The so-formed benzyl radical upon incorporation of singlet oxygen provides target ketones [122]. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (10 mol%) is the additive chosen by Tang et al. to perform the photocatalytic activation of C–H bonds using riboflavin tetraacetate (10 mol%) and *N*-hydroxysuccinimide (20 mol%) organophotocatalysts and a 90 W 450-nm LED light at room temperature. Tetralin, *n*-butylbenzene, *n*-propylbenzene, and three ethylbenzene derivatives were oxidized in moderate to good yields by this method [123].

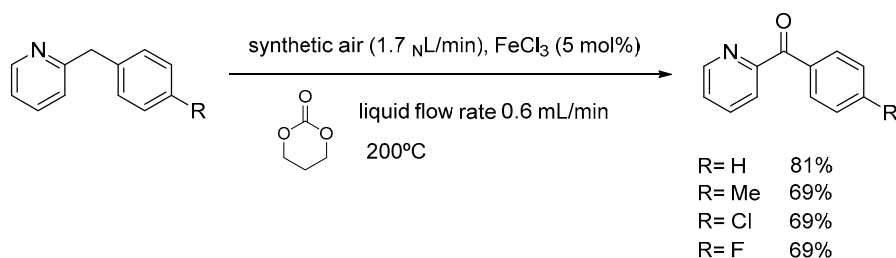
A photochemical aerobic oxidation of a number of alkylbenzene derivatives was performed in the presence of FeCl_3 (5.0 mol%), LiBr (5.0 mol%) in MeCN at 25 °C. Irradiation with 3 W blue LED light under 1 atm of air induced selective methylene C–H oxidation to the corresponding ketones (Scheme 12). Good yields were obtained in most cases, although the presence of nitro or ciano electron-withdrawing groups in the arene moiety resulted in a decrease a yield (34–55%). The authors postulated that an excited iron complex related to $\text{Li}(\text{FeCl}_3\text{Br})$ driven by visible light oxidize benzylic methylene compounds through a single-electron transfer process [124].



Scheme 12. Visible light-induced oxidation of methylene compounds by Quio and coworkers.

4.3. Other Approaches

After an initial report on the oxidation of aryl(di)azinylmethanes using the $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ /AcOH/DMSO system [113], Maes' group reported a further investigation on extension of the substrate scope (including benzoannulated azines and diazines, papaverine, or the total synthesis of antimalarial agent Mefloquine), chemoselectivity, alternative solvents, and trace metal analysis. In addition, an extensive comparison with alternative copper catalysts discovered by the same group [114] is made, revealing that oxidation for 2-benzylpyridine derivatives under the optimized conditions (O_2 (1 atm), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (10 mol%), AcOH (Equation (1)), DMSO, 100–130 °C) provided comparable and in some cases superior results [125]. A high-temperature/pressure gas–liquid continuous flow approach to 2-arylpyridines was described by Pieber and Kappe. As shown in Scheme 13, several 2-benzylpyridines were quickly (13 min) oxidized in propylene carbonate, a high-boiling point solvent alternative to traditional aprotic polar solvents such as dimethyl sulfoxide or *N*-methylpyrrolidone. In addition, this procedure avoids the need of stoichiometric amounts of additives such as AcOH [126].

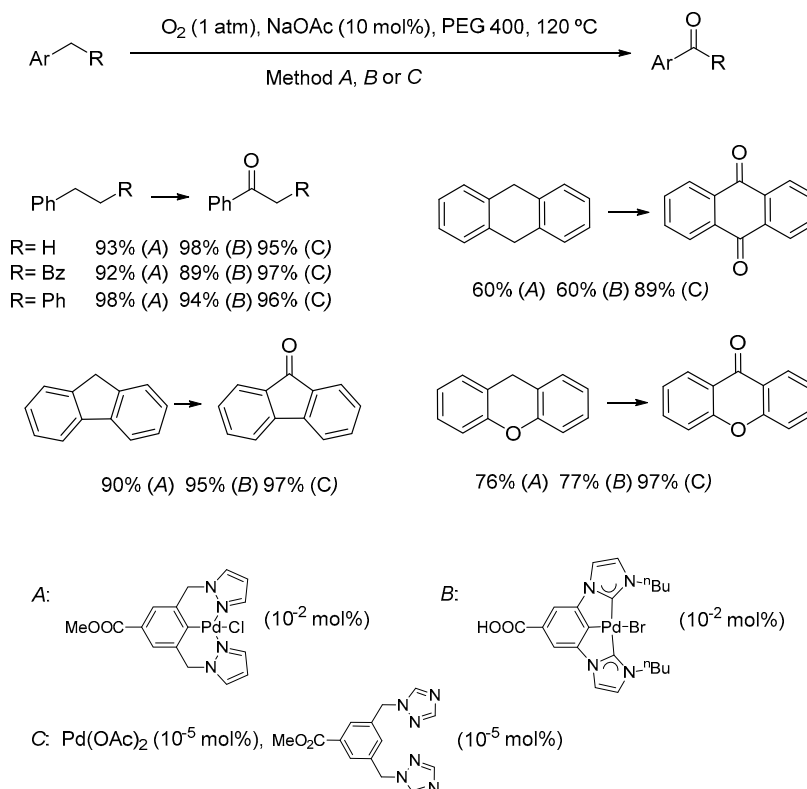


Scheme 13. Oxidation of 2-benzylpyridines under high-temperature/pressure gas–liquid continuous conditions.

Several alkylbenzenes were oxidized to the corresponding ketones at room temperature by using substoichiometric amounts of an additional oxidant along with molecular oxygen. Li and Wang reported a system comprising O_2 (1 atm), chloramine-T (1 mmol) and $\text{Fe}(\text{TPP})\text{Cl}$ (5 mol%) in acetonitrile (TPP *meso*-tetrakisphenyl porphyrin). Good to excellent yields were obtained in all cases with excellent selectivity [127]. Feringa's group published the results from the oxidation of ethylbenzene under 1 atm of molecular oxygen using a 0.1 mol% of different non-heme iron complexes. Initial temperature of 30 °C was increased to 80 °C in order to enhance the catalytic activity. However, the reactions showed a poor selectivity towards acetophenone over 1-phenylethanol [128].

5. Palladium Catalysts

In addition to their investigation with copper catalysts (see Section 3.3), Navarro and coworkers evaluated the catalytic activity of a palladium bis-imidazolyl complex (0.14 mol%) for the medium-pressure (35 atm) aerobic oxidation of tetralin at 100 °C. A low (30%) conversion rate was observed for a mixture (22:8) of α -tetralone and α -tetralol respectively [119]. Two palladium NCN and CNC tricoordinated complexes were tested as catalysts for the benzylic C–H oxidation of several alkylbenzenes under 1 atm of molecular oxygen. Good to excellent yields were obtained in all cases with complete selectivity towards the corresponding ketones, and the procedure allowed the use of unusually low catalyst loadings (10^{-2} mol%) [129]. Later the same group published similar results with a more simple palladium system comprising a combination of $\text{Pd}(\text{OAc})_2$ and a bis-triazolyl ligand (Scheme 14). A further improvement in efficiency had been achieved, as catalyst amounts as low as 10^{-5} mol% were enough to catalyze the reaction in an environmentally friendly solvent, polyethylene glycol [130].



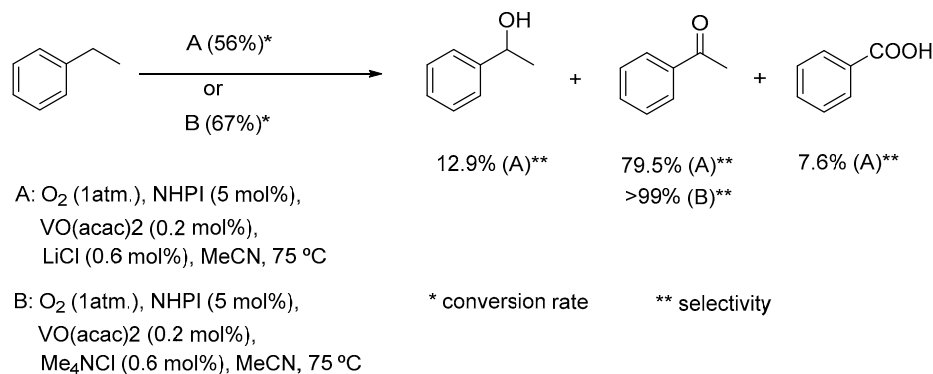
Scheme 14. Benzylic C–H oxidation of methylene compounds by SanMartin and coworkers.

A base-mediated (Cs_2CO_3 , Equation (1)) oxidation of 2-benzylbenzothiazole and 2-benzylbenzimidazole derivatives under air atmosphere was presented by Dos Santos et al. and the results were compared with those from the oxidation using palladium catalysis ($\text{Pd}(\text{OAc})_2$ (10 mol%) or $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ (10 mol%), CsOPiv (Equation (1)), DMF, 90°C). Both methods turned out to be complementary, as in some cases, depending on the substrate, only one of them provided the target 2-arylbenzothiazole or 2-arylbenzimidazole with acceptable yields [131].

6. Other Metal Catalysts

6.1. Mg/V-NHPI

Xu's group explored the use of alkali-earth metal salts as promoters for the formation of PINO radical, key intermediate for NHPI-catalyzed oxidations. After evaluating the results from different alkali-earth metal chlorides, they found that MgCl_2 gave better conversion rates and selectivities in the oxidation of ethylbenzene. Other Mg(II) salts were also tested, providing inferior results. In addition to ethylbenzene, fluorene, tetralin, and diphenylmethane were submitted to the optimized reaction conditions (O_2 (3 atm), MgCl_2 (2.5 mol%), NHPI (10 mol%), CH_3CN , 90°C) to afford the corresponding ketones with moderate to good conversion rates (47–93%) and selectivities (75–99%) over other oxidation products such as benzyl alcohol and hydroperoxide derivatives [132]. A lower pressure of molecular oxygen (1 atm) was employed by Figiel and Sobczak to perform the NHPI/ $\text{VO}(\text{acac})_2$ -co-catalyzed oxidation of ethylbenzene. Depending on the chloride additive (LiCl or Bu_4NCl) two procedures were devised and applied to several alkanes, including ethylbenzene. As shown in Scheme 15, a better conversion rate and selectivity was observed for the latter Bu_4NCl -based procedure [133].



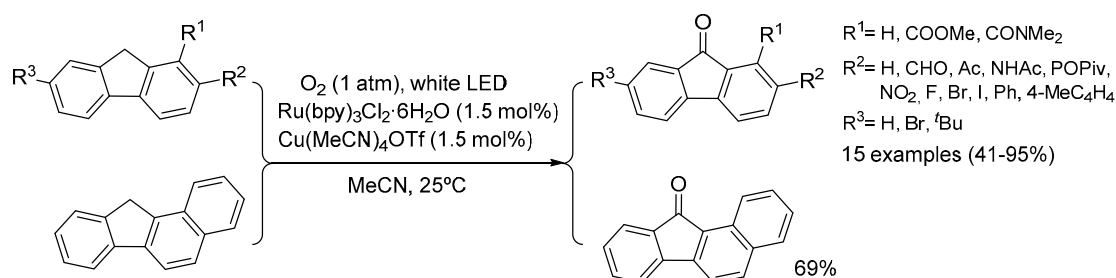
Scheme 15. NHPI/VO(acac)₂-co-catalyzed oxidation of ethylbenzene.

6.2. Other Approaches

A manganese(II) catalyst (MnCO₃) proved to be active for the medium-pressure (PO₂: 10 atm) oxidation of ethylbenzene. When the latter alkylbenzene was submitted to the optimized conditions (MnCO₃ (0.5 mol%), 190 °C) a mixture of acetophenone (26%) and 1-phenylethanol (7%) was detected and quantified by gas chromatography-mass spectroscopy (GC-MS). Gao et al. propose that high-valence Mn species, formed from MnCO₃ in the presence of oxygen, can activate aromatic hydrocarbons to the corresponding radical intermediates [134]. A more efficient solvent-free oxidation of ethylbenzene, tetralin, and diphenylmethane was carried out at lower temperatures (120 °C) in the presence of O₂ (1 atm), [Cp*IrCl₂]₂ (1.6 × 10^{−3} mol%), Cp* = pentamethylcyclopentadienyl, picolinic acid (3 × 10^{−3} mol%) as nitrogen ligand and iodobenzene (1.9 mol%) as radical initiator. Although good to excellent TON values are reported, moderate selectivity was achieved from ethylbenzene (73:27 acetophenone/1-phenylethanol) and tetralin (61:39 α-tetralone/α-tetralol). A radical oxidation mechanism initiated by decomposition of iodobenzene under the reaction conditions to generate phenyl radical is postulated by the authors [135].

Following their research on palladium-catalyzed aerobic oxidations [129,130], Urgoitia et al. found that a combination of NiBr₂ (10^{−5} mol%), triazole ligands (10^{−5} mol%), and sodium acetate (10^{−1} mol%) could promote the selective oxidation of seven alkylarenes (ethylbenzene, diphenylmethane, 2-phenylacetonitrile, 4-benzylpyridine, fluorene, 9,10-dihydroanthracene, and xanthene) to the corresponding ketones at 120 °C under 1 atm of molecular oxygen in polyethylene glycol. Yields ranged from 50 to 98% with reaction times of 48–72 h [136].

A ruthenium catalyst system was devised by Kojima, Oisaki and Kanai for the selective photooxidation of fluorene derivatives at room temperature in acetonitrile. As shown in Scheme 16, Cu(MeCN)₄OTf was employed as a metal additive, and this copper additive along with tris(bipyridyl)ruthenium(II) dichloride and irradiation with visible white LED light were essential to get the target transformation. A high compatibility with a number of functional groups was observed, and the authors discarded any autooxidation process after examining the results from several experiments performed under limited irradiation time, then in the dark [137].



Scheme 16. Synthesis of 9-fluorenones by aerobic photooxidation of fluorenes.

7. Conclusions

As in many other fields of synthetic chemistry, the molecular oxygen-mediated C–H oxidation of benzylic methylene compounds has witnessed a clear evolution towards more sustainable procedures. Starting from the need of lower pressures of the terminal oxidant or reagent itself (O₂, air in some cases), more active and selective homogeneous metal catalysts have been discovered, thus rivaling other strategies based on heterogeneous or metal-free approaches. Indeed, although chemoselectivity under oxidation conditions and product selectivity towards the carbonyl compound (ketone, ester or amide, depending on the starting material) are still issues to be addressed, a substantial decrease in the catalyst amount can be easily noticed by comparison with earlier literature data. In addition to procedures with a wider substrate scope, some more specific methods applicable to certain compounds (e.g., benzylazine derivatives) have been devised. Moreover, new protocols involving visible light induction and alternative, greener solvents have been introduced. Some of the above methods allow reaction performance under mild conditions, or by continuous flow technology. Considering also that a number of synthetic intermediates for pharmacologically active compounds have been prepared by this aerobic strategy, and although research is needed to improve selectivity and efficiency in some reactions, it can be concluded that the use of homogeneous metal catalyst for this benzylic C–H oxidation has reached a mature state.

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