SYNLETT
Spotlight 222

The Use of Molecular Oxygen in Organic Synthesis

Compiled by Gaj Stavber

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Gaj Stavber was born in Ljubljana, the capital of Slovenia, in 1980. He studied chemistry at the Faculty of Chemistry and Chemical Technology, University of Ljubljana and obtained his B.Sc. degree in 2004. Gaj is currently working on his PhD thesis in the Laboratory of Organic and Bioorganic Chemistry, the joint laboratory of the Faculty of Chemistry and Chemical Technology, University of Ljubljana, and the 'Jozef Stefan' Institute, under the supervision of Professor Marko Zupan and Dr. Stojan Stavber. His research area is mainly focused on the halogenation of organic molecules with emphasis on the principles of green and sustainable chemistry.

Faculty of Chemistry and Chemical Technology, University of Ljubljana, Askerceva 5, 1000 Ljubljana, Slovenia
E-mail: gaj.stavber@fkkt.uni-lj.si

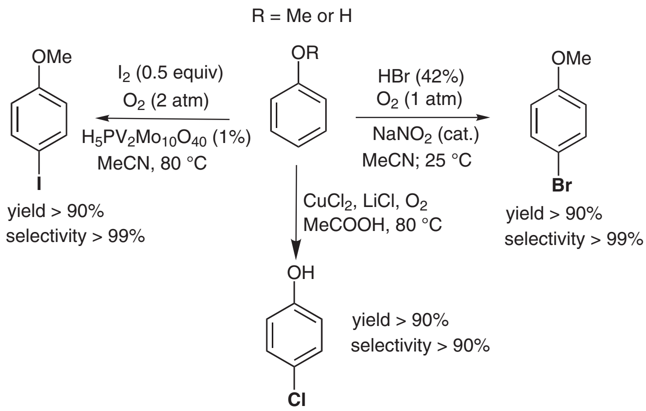
Introduction

The use of molecular oxygen for transformation of organic compounds is an attractive and challenging research subject which is especially interesting for industrial application. Molecular oxygen is inexpensive, readily available and ultimately produces benign byproducts such as water. The development of efficient protocols using O_2 as an oxidant is a subject of great importance also from the viewpoint of green approach to organic synthesis. Transformations of organic compounds with O_2 need catalysis in order to promote both the rate of reaction and the selectivity to partial oxidation products. The catalysts are usually transition metals, often as organometallic complexes[1] or as solid-supported species,[2] while $NaNO_2$ as non-metal catalyst for aerobic transformation of organic compounds was recently promoted.[3] From the green chemistry point of view the ideal system for oxidation is the use of O_2 together with a reusable catalyst in a non-toxic and non-volatile medium like water or ionic liquids or even under solvent-free conditions.[4]

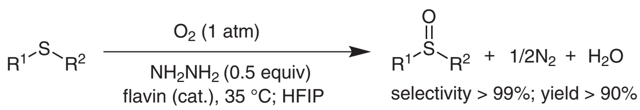
The present spotlight emphasises recent developments in the use of molecular oxygen for oxidation of benzene and its alkyl-substituted derivatives, alkenes, alcohols, sulphides and amines; special attention was also devoted to its application in oxidative halogenation of organic compounds.

Abstracts

(A) *Aerobic Oxidative Halogenation*
Efficient and regioselective aerobic oxidative bromination of various aromatic compounds and ketones using hydrobromic acid in the presence of sodium nitrite as catalyst was achieved.[5a] Aerobic oxidative chlorination of aromatic compounds under mild conditions in acetic acid using $CuCl_2$ as catalyst, chloride ions as halogenating agents (LiCl) and O_2 as the final oxidant was also reported.[5b,c] $H_5PV_2Mo_{10}O_{40}$ polyoxometalate, molecular iodine and O_2 as the final oxidant were found to be a very effective system for aerobic oxidative iodination of activated arenes.[5d]



(B) *Aerobic Selective Oxidation of Heteroatom Compounds*
Flavin-catalysed selective oxidation of sulfides or amines with O_2 in the presence of hydrazine monohydrate in a fluorous alcohols results in formation of sulfoxides or *N*-oxides.[6]



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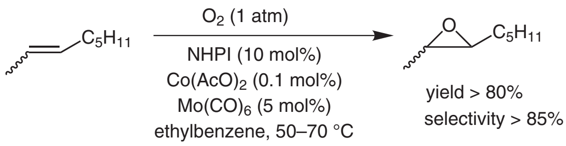
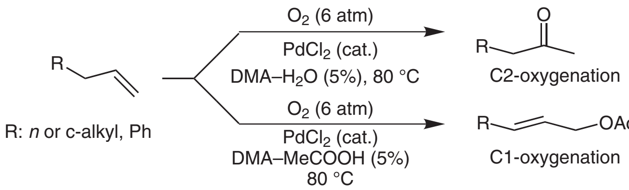
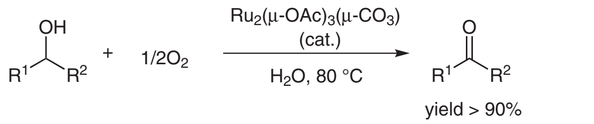
(C) *Stereoselective Epoxidation of Alkenes with Molecular Oxygen*
$Mo(CO)_6$-catalysed epoxidation of alkenes with hydroperoxides generated in situ by aerobic oxidation of ethylbenzene or tetraline in the presence of *N*-hydroxyphtalimide (NHPI) was established to be stereoselective.[7]



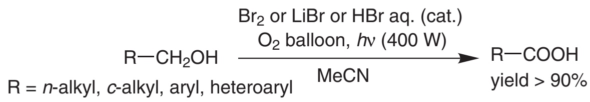
(D) *Wacker Oxyfunctionalisation of Terminal Olefins with O_2 as a Reoxidant*
Wacker oxidation of a wide range of terminal alkenes catalysed with $PdCl_2$ in DMA was reported. An oxygen atom can be efficiently and selectively incorporated at the C1 or C2 position of terminal alkenes by using an appropriate nucleophile (H_2O or AcOH) to form corresponding ketones or allylic acetates in high yields.[8]



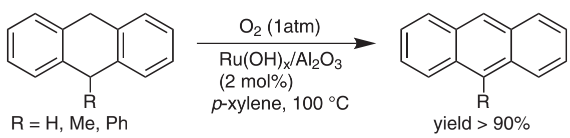
(E) *Selective Aerobic Oxidation of Alcohols in Water*
The efficient and selective aerobic oxidation of various types of alcohols can be performed in water in the presence of a catalytic amount of the water-soluble and recyclable acetate-bridged diruthenium complex under atmospheric pressure of O_2. This method, proceeding in water and with use of a recyclable catalyst, is important from economic and environmental viewpoints.[9]



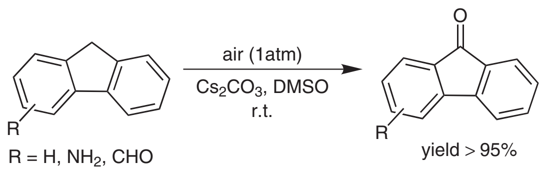
(F) *Aerobic Photo-Oxidation of Alcohols*
Photo-oxidation of various types of alcohols with molecular oxygen in the presence of catalytic amounts of an inorganic bromine source like LiBr, Br_2 or HBr was achieved and the corresponding carbocyclic acids were obtained in good yield.[10]

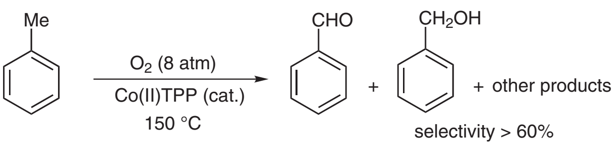


(G) *Dehydrogenation of Alkylarenes*
$Ru(OH)_x/Al_2O_3$ efficiently catalyses the heterogeneous aerobic oxidative dehydrogenation of alkylarenes to give the corresponding dehydrogenated products.[11]



(H) *Efficient and Selective Aerobic Oxidation of Arylalkanes*
Various arylalkanes (fluorenes, xanthene, anthrone, diphenylmethane) were effectively transformed into the corresponding arylketones with air oxygen in the presence of caesium carbonate, while easily oxidizable functionalities such as amino and aldehyde groups remained unchanged.[12]
Selective liquid-phase oxidation of toluene with air in the presence of catalytic amounts of cobalt tetraphenylporphyrin and in the absence of any solvents or promoters was reported. Compared with the present synthetic method for the preparation of benzaldehyde and benzyl alcohol which has been used in industry, this new method is cheaper and environmentally friendly.[13]





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