Urea–Hydrogen Peroxide Complex

Compiled by Sandra Taliansky

Sandra Taliansky was born in Argentina and moved to Valencia (Spain) in 1992. She studied Chemistry at Universidad de Valencia where she got her degree in 2003. In 2001 she was an Erasmus student at Cambridge University, where she joined Prof. Ian Fleming’s research group. After receiving her BSc degree she joined the Instituto de Química Médica (CSIC) in Madrid where she is pursuing her PhD degree under the supervision of Dr. María Teresa Molina on the field of syntheses and reactions of quinones.

Instituto de Química Médica (CSIC), Juan de la Cierva 3, 28006 Madrid, Spain
E-mail: staliansky@iqm.csic.es

Introduction

The hydrogen bonded urea–hydrogen peroxide complex [CO(NH₂)₂H₂O₂, UHP] is a cheap and commercially available white crystalline solid (mp 84–86 °C, dec.) obtained by recrystallization of urea from commercially available 33% aqueous hydrogen peroxide. ¹

Its stability at room temperature, high hydrogen peroxide content (36.2%) and the potential for releasing it in a controlled manner,² as well as its solubility in organic solvents (alcohols, dichloromethane) makes it a good and safe substitute for anhydrous hydrogen peroxide (not available anymore) in most oxidation reactions.

UHP has been used for the epoxidation of a wide range of alkenes.³ It is capable of oxidizing a number of functional groups: nitriles to amides,⁴ oximes to nitroalkanes,⁵ sulfides to sulfoxides⁶ or sulfones,⁷ aldehydes to acids,⁸ etc. UHP has also been found useful for heteroatom oxidation reactions,⁹ as well as to carry out Baeyer–Villiger¹⁰ and related reactions. In recent years, UHP has proved to be effective in solid state reactions, both under heating¹¹ or microwave irradiation,¹² so becoming an interesting eco-friendly reagent.

Abstracts

(A) In the presence of anhydrides, alkenes are epoxidized with UHP through the in situ formation of peroxycarboxylic acids.¹ Large excess of UHP has to be used to avoid the build-up of high concentrations of diacyl peroxides. Phthalic anhydride supported on insoluble polystyrene-divinylbenzene (PS-DVB) and UHP allows the epoxidation of different alkenes in an efficient method where purification was limited to filtration, solvent change and evaporation.¹³

(B) Epoxidation of α,β-unsaturated ketones with UHP requires the presence of a base. N,N-dialkylimidazolium or N,N-dialkylanilinium cations) and UHP allows the epoxidation of different alkenes in an efficient method where purification was limited to filtration, solvent change and evaporation.¹³

(C) Regioselective epoxidation of monoterpenes in the liquid phase using titanoclasitcs TS-1 and TiAlb combined with UHP as an oxidant has been achieved.¹⁴ Epoxidation occurs exclusively at the more electron-rich bond. Hutchings et al.¹⁵ have also studied the influence of the hydroxy group in the regioselectivity of the epoxidation in linalool, geraniol and citronellol.

(D) Methyl trioxorhenium (MTO) has proved an efficient catalyst for regio- and stereospecific epoxidation of different substrates¹⁶ both in room temperature ionic liquids (based on N,N'-dialkylimidazolium or N,N'-alkylpyridinium cations)¹⁷ and in non-protic solvents such as dichloromethane.¹⁹ Diethyl ether as solvent and pyridine as the ligand gives the optimal results for epoxidation of cholesterol,²⁰ α-Hydroxy and α-siloxy esters are obtained from methyl trimethylsilyl ketene acetal through the corresponding epoxide under similar conditions.²¹
(E) Epoxidation of norbornene has been carried out over vanadium substituted phosphomolybdic acid catalysts with H$_2$O$_2$. UHP shows similar conversion rates as H$_2$O$_2$ but better selectivities (97% of the epoxide achieved) due to the slow and controlled release of hydrogen peroxide and the less acidic character of the reaction medium.\textsuperscript{22}

(F) Aromatic aldehydes are oxidized to the corresponding benzoic acids in good to excellent yields.\textsuperscript{9}

(G) The oxidation of sulfide to sulfoxide has been achieved using rhodium catalysts in non-aqueous media. Triphenylphosphine ligands in the catalyst proved to be effective to stop the reaction at the sulfoxide stage. A combination of UHP and trifluoroacetic anhydride in acetonitrile affords the sulfone in excellent yields.\textsuperscript{7} Solvent free oxidation of sulfides with UHP and tetrabutylammonium phosphomolybdate catalyst on fluorapatite was achieved at 4–25 °C by controlling the amount of UHP employed.\textsuperscript{23}

(H) The oxidation of unactivated C–H bonds with UHP has been reported. In the presence of catalytic amounts of a vanadium salt (Bu$_4$NVO$_3$) and pyrazine-2-carboxylic acid in acetonitrile, the hydroperoxide of cyclohexane was formed.\textsuperscript{24} Substituted toluenes were selectively oxidized to aldehydes with UHP in the presence of cobalt(II) acetate, acetic acid and an inorganic bromide source.\textsuperscript{25} Oxidation of cyclohexane with UHP in TFA gave the cyclohexyl trifluoroacetate in good yield.\textsuperscript{26}

(I) Oxidative halogenation of amines with UHP and iodine in ethyl acetate has been reported.\textsuperscript{27} Skulski et al. have also described an efficient solid state chlorination of iodoarenes with UHP affording dichloroiodoarenes in 64–98% yields after 15 minutes at 85 °C.\textsuperscript{28}

References