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A preliminary study on microwave assisted metal-free epoxidation of cyclic olefins by hydrogen peroxide – trifluoroethanol system.

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Abstract

Preliminary results of microwave assisted epoxidation of cyclic alkenes with hydrogen peroxide – trifluoroethanol system were presented.

Keywords

Epoxidation, alkenes, hydrogen peroxide, fluorinated alcohols, 2,2,2-trifluoroethanol, 1,1,1,3,3,3-hexafluoro-2-propanol, TFE, HFIP, microwave irradiation, green chemistry

Introduction

Hydrogen peroxide seems to be very promising as the oxidant of organic molecules in terms of non-toxic side products (i.e. water) and high oxidation potential. The catalytic epoxidation of olefins with hydrogen peroxide is an important synthetic method. In fact, oxidation reaction of many organic compounds (included alkenes) by H₂O₂ required some kind of activation. Many catalysts systems based on d-metals, e.g. titanium, manganese, molybdenum, vanadium, tungsten or rhenium, or non-metal e.g. selenic or arsenic organocompounds have been studied [1 and references cited there]. Recently it was shown that perfluorinated alcohol solvent such as 2,2,2-trifluoroethanol (TFE) and particularly 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) are able to activate of H₂O₂ for the epoxidation of olefins [2]. Perfluorinated alcohols are inert (can be oxidized only with difficulty) and easy to recycle low boiling point solvents. The strong electron-withdrawing properties of fluorine along with the hydrogen bonding properties of the O-H hydrogen atom lead to formation of an electrophilically activated, polar hydrogen peroxide intermediate (Fig. 1).

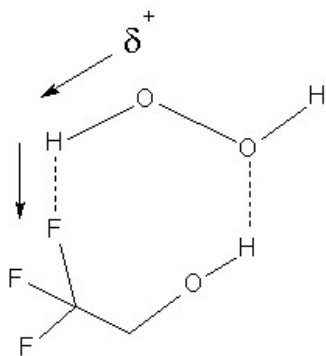


Fig. 1. A simplified structure of activated hydrogen peroxide molecule by TFE [2].

In other words, fluoro alcohols activate hydrogen peroxide for oxygen atom transfer through hydrogen bonding. The yield of the epoxidation is higher when electron-rich alkene is oxidized, concentration of H₂O₂ is higher or more fluorine substituted alcohol is used (e.g. HFIP rather than TFE). Microwave irradiation (2.45 GHz) is a non-conventional energy source, very popular and useful technology in organic chemistry. The acceleration of reactions in microwave field results from electromagnetic wave - material interaction leading to thermal and non-thermal (specific) effects [3]. Recently, it was postulated that acceleration of reaction in microwave field can be expected, when polarity of a system is enhanced from ground state to the transition state [4]. Keeping in mind a structure of fluoro alcohol activated hydrogen peroxide (Fig. 1), we reasoned that under microwave condition epoxidation of olefins with such system should be more effective. For preliminaries study we chose TFE rather than more effective HFIP because of TFE higher boiling point (74° C, HFIP 59°C) and reasonable price.

Experimental

Reactions in conventional condition were carried out in capped 7 ml vials by mixing the alkene (4 mmol), hydrogen peroxide (6,6 mmol as 30% water solution) and TFE (3ml) and heating at 60°C for appropriate time. In the case of cyclooctene epoxidation, reaction in boiled TFE was also carried out in a flask equipped with reflux condenser (12 mmol of the olefin, 20 mmol of hydrogen peroxide - as 30% water solution - and 10 ml TFE). Microwave assisted epoxidations were carried out in multimode microwave reactor (Plazmatronika, Poland) equipped with a flask connected to reflux condenser. A mixture of 12 mmol of the olefin, 20 mmol of hydrogen peroxide - as 30% water solution - and 10 ml TFE, was irradiated to keep at boiling point. The mixtures were analyzed by GC-FID and the yield was estimated based on peak's areas of the product and the substrate.

Results and discussion

Tab. 1. Yields of microwave assisted epoxidation (MW) with comparison to reactions carried out in conventional condition.

Entry	Substrate	Reaction condition	Yield, % (Time, h)	Remarks
1	Cyclooctene	60°C	23 (3.5)	
2	Cyclooctene	reflux	62 (3.5)	
3	Cyclooctene	MW, reflux	15 (1) 66 (2) 90 (3) 97 (3.5)	
4	1,5-Cyclooctadiene	60°C	6 (3)	
5	1,5-Cyclooctadiene	MW, reflux	8 (0.5) 19 (1) 30 (1.5)	
6	1-Methylcyclohexen-1	60°C	40 (3)	
7	1-Methylcyclohexen-1	MW, reflux	22 (0.25) 29 (1) 40 (1.5)	By-product detected

As can be seen (Tab. 1) application of microwave irradiation causes improving of epoxidation yield. The effect is most spectacular in the case of cyclooctene, where after 3.5h only traces of unreacted olefine was detected, whereas in conventional condition the yield was 62%. A presence of additional double bond in hydrocarbon ring, decrease reaction yield (entry 4 and 1), but under microwave condition the difference between cyclooctene and 1,5-cyclooctadiene activity is negligible (entry 5 and 3, both after 1h of epoxidation). It should be noted presence of significant amounts of by-product during microwave assisted 1-methylcyclohexen-1 epoxidation. In this case, conventional conditions are more useful in spite of not so high yield.

Conclusion

Application of microwave irradiation to cycloalkenes epoxidation by hydrogen peroxide/trifluoroethanol system seems very promising. However, more investigations are needed to find which cyclic olefins are most reactive under such conditions.

Acknowledgment

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