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Novel Polyaniline Supported Cobalt Catalyzed Aerobic Oxidation of Unsaturated Organic Compounds

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*The oxidation of organic compounds with carbon-carbon double bond with molecular oxygen under atmospheric pressure in the presence of new polyaniline supported catalyst **1** has been studied. This catalyst turned out to be efficient and selective for oxidation of some unsaturated organic compounds. Oxidation of alkenes, cycloalkenes and terpenes give corresponding epoxy derivatives, whereas organic compounds with carbon carbon double bond in benzylic position give ketones as a main product.*

Keywords Alkenes; epoxidations; polyaniline; polymer supported catalysis

Introduction

The selective oxidation of alkenes to epoxides is one of the most important and fundamental reaction in organic chemistry both at the laboratory and industrial scale. Numerous catalysts have been developed using a variety of reagents to achieve this purpose [1–8]. However, most of these reagents are required in stoichiometric quantities. Moreover those reagents are sometimes expensive and toxic. From an environmental as well as economic point of view, catalytic oxidation processes, especially those, in which molecular oxygen is used as primary oxidant, are particularly attractive. The use of polymer-supported catalysts offers several additional benefits in preparative procedures. The main advantage of this type of catalysts lies in the much simpler products purification, the possibility of isolation of a catalyst as well as reuse of catalyst and enhanced stability [9,10]. A new family of materials is in development to contribute important aspects to solving many different technical and ecological problems – the conducting organic polymers known as the organic metals. Due to their unique electronic properties, electrically conductive polymers are used in heterogeneous catalysis. For example, polyaniline was employed as a catalyst support used in oxidation of organic compounds [11,12]. Pielichowski and Iqbal [13–18] who used conductive polymer supported catalytic systems based on cobalt(II) salts

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and its complexes, have achieved remarkable results. They obtained some efficient catalytic systems, useful in oxidation of aromatic hydrocarbons and alcohols, characterized with high efficiency at relatively low temperatures.

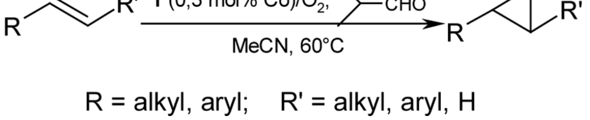
Results and Discussion

Interesting results in homogeneous catalysis have been achieved by using catalytic systems based on cobalt(II) salts or cobalt(II) complexes for selected oxidation processes. [19,20] Our purpose was to combine the advantages of supported catalysts and inexpensive oxidant – molecular oxygen. We have recently reported that cobalt(II) chloride immobilized in polyaniline(PANI) matrix catalyze the ooxidation of alkenes to the corresponding oxirane in mild conditions (Scheme 1). Reactions were carried out in the presence of molecular oxygen under atmospheric pressure at 60°C. During the course of our investigation on the oxidation of organic compounds, [21–23] we have found that polyaniline supported with cobalt(II) acetate and cobalt(II)Salen complexes are recyclable and catalyze efficiently the oxidation of alkenes to corresponding epoxides with molecular oxygen with high yields and selectivity.

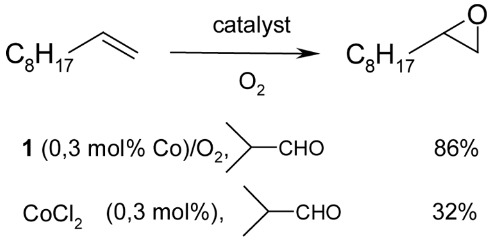
Catalysts **1** were prepared be a two-step method: (i) the preparation of the polymers by chemical oxidative polymerization of monomers in HCl solution at −5°C by ammonium persulfate and then deprotonation in aqueous ammonia solution [24] and (ii) supporting of cobalt based catalyst on polymer by stirring a 1:1 (w/w) mixture of polyaniline and $CoCl_2$ in CH_3CN/CH_3COOH mixture for 72 h at ambient temperature.

Oxidation reactions of alkenes were carried out in acetonitrile under mild conditions. We used molecular oxygen at atmospheric pressure as an oxidizing agent, which was bubbled through the reaction medium. 2-Methylpropanal present in the reaction medium plays the role both reductant of the catalytic center and co-catalyst of epoxidation reaction. Whole reaction mixture was stirred until completion of the reaction. Then the solvent was evaporated to yield a residue, which was dissolved in ethyl acetate. After that mixture was extracted with aqueous $NaHCO_3$ and then with water. To obtain final product organic layer should be dried and the solvent should be evaporated to give the desired product. The oxidation of dodec-1-ene was then examined in the presence of catalytic amount of **1** in acetonitrile under molecular oxygen atmosphere at room temperature. As it was expected, the oxidation took place affording 2-decyloxirane in 86% yield and 100% selectivity, when the reaction mixture was allowed to stir at 60°C for 24 h, whereas the corresponding homogeneous process using $CoCl_2$ was less effective and provided the same product in 32% yield (Scheme 2). Such behavior indicates on specific and beneficial interaction of catalyst and polymer support (polyaniline).

To study the scope of this procedure, the oxidation of broad group of organic compounds with carbon-carbon double bonds was next studied (Table 1,



Scheme 1. Alkenes oxidation with $CoCl_2$ immobilized in polyaniline matrix.



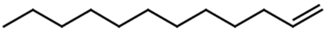
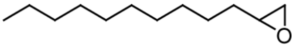
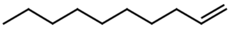
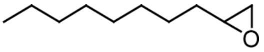
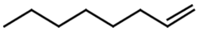
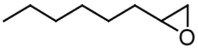
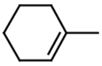
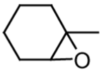
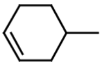
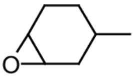
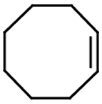
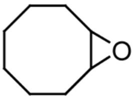
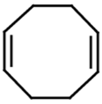
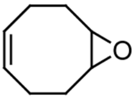
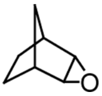
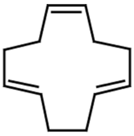
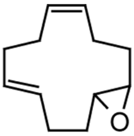
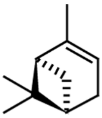
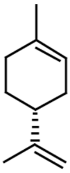
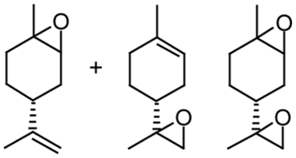
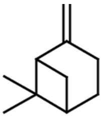
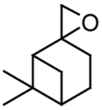
Scheme 2. Dodec-1-ene oxidation-homogeneous vs. heterogeneous condition.

entries 1–19). Oxidation of alkenes with terminal carbon-carbon double bond (Table 1, entries 1–3) occurs with high yield and selectivity. Corresponding epoxides are formed as an only product. It was also observed that in case of alkenes with single terminal carbon-carbon double bond, increasing of aliphatic chain length cause decreasing in yield of oxidation reaction. Much higher reactivity was observed with cyclic unsaturated hydrocarbons with one or more double bonds in their structure, which were oxidized to corresponding epoxides after 1–8 h, depending on substrate. Oxidation of 4-methyl-1-cyclohexane provides to corresponding monoepoxide with 100% yield, after 4 hours of reaction. Its isomer 1-methyl-1-cyclohexane, reacts so rapidly that substrate is consumed completely after 30 minutes of reaction. It was managed to find by gas chromatography that initially epoxy derivative is formed as intermediate product and then in reaction conditions degradation occurs to products of epoxide decomposition. 1-Cyclooctene required a slightly longer reaction time compared to methylcyclohexenes to afford corresponding epoxide as sole product in 92% yields. Oxidation of cyclic hydrocarbons which contains two (Table 1, entry 7) or three (Table 1, entry 9) carbon-carbon double bonds is not as selective, nevertheless corresponding monoepoxides are formed as a main products in 52% and 53% yields respectively. As it was pointed out in Table 1 *cis,cis*-1,5-cyclooctadiene forms corresponding diepoxide as a by product, whereas in case of *trans,trans, trans*-1,5,9-cyclododecatriene di- or triepoxide derivatives were not observed in reaction products.

Oxidation of terpenes in such conditions occurs also very easy, as a result corresponding epoxides are formed as main products. However, on account of peculiarity of this group of compounds and proceeded consecutive reactions, selectivity is lower than for alkenes and cycloalkenes. As it was pointed out oxidation of terpenes in reaction conditions occurs very easy, therefore it is important to carry out reaction very carefully. Because too long reaction time cause consecutive reactions of epoxy derivatives to undesired products.

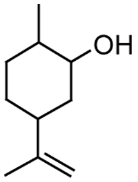
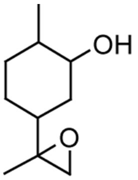
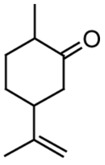
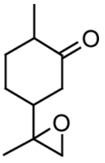
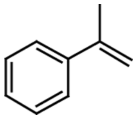
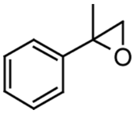
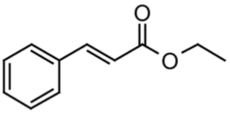
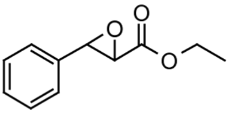
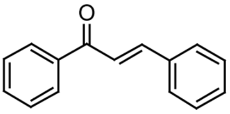
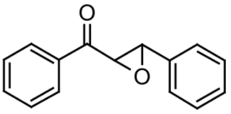
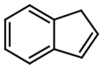
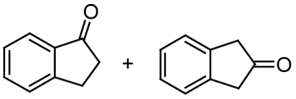
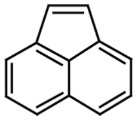
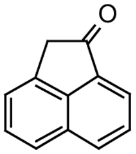
Oxidation of organic compounds with carbon-carbon double bond in benzyl position occurs much easier in comparison to alkenes. Such behavior is due to the fact that generated free radicals are stabilized by presence of benzene ring, therefore oxidation reaction occurs easier and time needed to complete conversion of substrates is shorter. Isopropylbenzene, ethyl cinnamate and 1,3-diphenylprop-1-en-2-one were oxidized to the corresponding epoxides with 18–39% yields and moderate selectivity. Due to high reactivity of derivatives with double bond in benzyl position, in the oxidation reaction significant amount of by-products are formed. It was managed to find by GC that some corresponding aldehydes and/or ketones are generated depending on substrate. However, oxidation of indene and acenaphthylene

Table 1. Aerobic oxidation of unsaturated organic compounds using polyaniline supported $CoCl_2$ – catalyst **1**.[a]

Entry	Substrate	Time [h]	Yield [%]	Product
1		24	86	
2		24	89	
3		18	99	
4		0,5	-[b]	
5		4	100	
6		8	92	
7		4	52[e]	
8		1	91[d]	
9		4	53	
10		3	47[f]	
11		1	52 21	
12		2	61	

(*Continued*)

Table 1. Continued

Entry	Substrate	Time [h]	Yield [%]	Product
13		2	30	
14		4	60	
15		8	18	
16		4	35	
17		2	39	
18		2	90[c]	
19		3	98	

[a] Substrate (5 mmol) and catalyst **1** (30 mg, 0,3 mol% equiv. Co) were stirred at 60°C under oxygen atmosphere for the appropriate time.

[b] Complete conversion of substrates; decomposition of products in reaction conditions.

[c] Yield calculated as a sum of both isomers.

[d] As a product 9% of bicyclo[2.2.1]heptan-2-ol and bicyclo[2.2.1]heptan-2-one is formed.

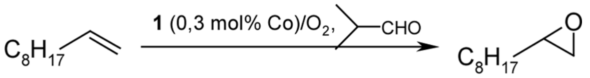
[e] Additionally 8% of 5,10-dioksatricyclo[7.1.0.04,6]decane is formed.

[f] As a by-product 15% 2,6,6-trimethylbicyclo[3.1.1]heptan-3-one and 6% of (1α,2α,5α)-2,6,6-trimethylobicyclo[3.1.1]hepten-3-one were formed.

afford corresponding ketones in high yield and selectivity. Oxidation of indene affords mixture of isomeric ketones, in case of acenaphthylene only acenaphenone is formed with only traces (<2%) of by-products.

We also studied possibility of catalyst reusing. Summarized results presented in Table 2 show that only insignificant loss of polymer catalyst is observed during

Table 2. Recycling of the catalyst **1**



Run	Product yield [%]	Recovery [%]
1	89	95
2	87	93
3	86	92

oxidation process. The main advantage of our catalyst is easiness of its reusing by filtering. For example, the oxidation of dec-1-ene was performed up to three runs with small loss of activity. Taking into consideration that Co(II) is supported on insoluble polymeric support, it could be supposed that only part of cobalt species are active catalytic centers. It was also observed that during doping reaction only small part of initial amount of catalyst is deposited into the polyaniline matrix.

In conclusion, the oxidation of organic compounds with carbon-carbon double bond with molecular oxygen in the presence of new polyaniline supported catalyst **1** has been studied. Specific and beneficial interactions of catalyst and polymer support were observed. Catalyst **1** turned out to be efficient and selective for oxidation of some group of unsaturated organic compounds. Cobalt(II) chloride supported on polyaniline turned out to be particularly effective in oxidation of alkenes with terminal carbon-carbon double-bond and cycloalkenes. As a result of oxidation alkenes, cycloalkenes and terpenes corresponding epoxy derivatives were obtained, whereas organic compounds with carbon-carbon double bond in benzylic position give ketones as a main product.

Experimental

IR spectra were recorded on a FT-IR Bio-Rad 165 spectrophotometer using KBr disks. 1H NMR spectra were recorded on Tesla BS-487 C (80 MHz) spectrometer in $CDCl_3$ using TMS as the internal standard. Gas chromatographic analyses were carried out on a Hawlett-Packard HP-5890 Series II gas chromatograph with MS detector and on Agilent 6850 with flame ionization detector. Both fitted with an Ultra 1 column type (30 m × 0.25 mm × 0.25 mm).

Preparation of Polyaniline Supported Cobalt(II) Chloride Catalyst. A suspension of polyaniline (500 mg) and cobalt(II) chloride (500 mg) was stirred in MeCN (25 mL) and AcOH (25 mL) mixture at room temperature for 72 h. After that, the reaction mixture was filtered and the solid catalyst was washed with acetonitrile (5 × 5 mL). The catalyst was dried at 110°C for 24 h.

Oxidation of Dodec-1-ene is Representative of the General Procedure Employed for Oxidation of Alkenes: The mixture of 2-methylpropanal (0.72 g, 10 mmol) and polymer-supported catalyst (30 mg, 0.3 mol% of Co) was dissolved in 30 mL of acetonitrile. The mixture was bubbled through with oxygen for 15 minutes at 60°C. Subsequently dodec-1-ene (0.84 g, 5 mmol) was added. The reaction was carried out for time period indicated in Table 1. After completion of the reaction the catalyst was filtered and the solvent was evaporated to yield a residue, which was dissolved in ethyl acetate, washed with sodium bicarbonate solution and water. The organic phase was dried over $MgSO_4$ and the evaporation of solvent yielded the desired product, which was purified by Kugelrohr distillation.

Acknowledgments

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