

[c010] **Oxidation reactions using *tert*-butyl hydroperoxide/*d*-metal chlorides systems with aid of microwaves**

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Abstract

The aim of present work was to check the possibility of microwave irradiation application for benzylic oxidation of diphenylmethane. The investigations were carried out using *tert*-butyl hydroperoxide (TBHP) both under conventional and microwave conditions. The catalysts tested were chlorides of transition *d*-metals: FeCl₃·6H₂O, CoCl₂·6H₂O, NiCl₂·6H₂O, CrCl₃·6H₂O, CuCl₂·2H₂O, ZnCl₂ and iodine. From all studied metal catalysts, FeCl₃·6H₂O, CoCl₂·6H₂O, NiCl₂·6H₂O, CrCl₃·6H₂O showed the best catalytic activity.

Keywords: microwave irradiation, benzylic oxidation, *tert*-butyl hydroperoxide, *d*-metal chlorides

Introduction

Modern organic synthesis requires using oxidants which are highly selective, efficient and environmental friendly. For this purpose ecological, cheap and readily available oxygen donors, such as hydrogen peroxide and TBHP are frequently used [1-3]. Using dangerous oxidants and organic solvents become a big problem in organic chemistry. Environmentally friendly oxidizing agents allow to eliminate harmful compounds in manufacturing processes. Because of too low reactivity towards organic substrates it is required to use the suitable catalysts. In recent years there is a growing interest in the field of catalysts for oxidation reactions. The topic of exploration a new catalytic systems has gained in importance after receiving Nobel Prize by Sharpless in 2001 for research on novel chiral catalysts for oxidation reactions. His study concerned the oxidation of allyl alcohols using the TBHP as oxidant in the presence of catalytic systems consisting of diethyl tartrate and titanium-organic compounds. Sharpless reaction is now applied in the synthesis of drugs used to treat heart disease [4].

Benzylic oxidation is one of the important transformations in organic chemistry. Ketones obtained by this method can be used as a valuable raw material for plant protection products or in pharmaceutical industry. Improvement of selectivity and efficiency of the reaction is carried out by developing new and more efficient catalytic systems. This leads to continuous research in this direction [5]. Emerging publications described a metal catalyst based on: Cr, Mn, Co, Bi, Ru, Rh, Fe [6-13].

The oxidation reactions under influence of iodine as well as iron chlorides as catalyst systems are widely described in literature [5, 6, 11-13]. Many of these reactions were carried out in the configuration catalyst-pyridine. It was noted that pyridine has a varied impact on the rate of decomposition of hydrogen peroxide which depend on the applied metal [8]. It can significantly accelerate or inhibit this process. For example, the presence of pyridine in the reaction with iodine improves the yield up to 99 %. The mechanism of its functioning is not fully understood. It is said that this is an intricate radical-ion mechanism (Fig. 1) [5].

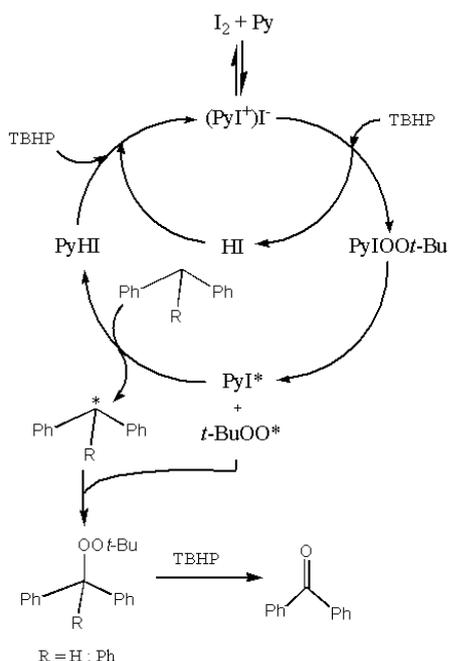


Fig. 1. Mechanism of benzylic oxidation catalysis with I_2 -Py-TBHP system [5]

Many researchers are interested in the application of TBHP for the oxidation reactions [5-15]. TBHP is a strong oxidant, often more effective than hydrogen peroxide or atmospheric oxygen [5]. Its combination with transition metals can selectively oxidize olefins and other organic compounds. Therefore, it was used in the agrochemical and pharmaceutical industries instead of other organic peroxides.

This article presents an alternative method for oxidation of benzylic compounds which proceeds under mild conditions in order to allow a better control of the reaction. The aim of the study was to determine the effect of various *d*-block metal chlorides on the model benzylic oxidation reaction under conventional and microwave conditions.

Experimental Procedure

The methodology of research was elaborate for diphenylmethane (DFM) oxidized by TBHP in the presence of some *d*-block metal chlorides (Fig. 2). The impact of various parameters e.g. type of catalyst, reaction time and source of heating on the model reactions was examined.

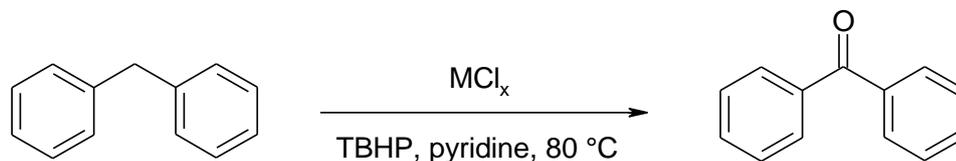


Fig. 2. Oxidation of diphenylmethane into benzophenone. $M = Fe^{III}, Co^{II}, Ni^{II}, Cr^{III}, Cu^{II}, Zn^{II}$

Materials

Pyridine and diphenylmethane (DFM) were purchased from Sigma-Aldrich. Other reagents: 70 % aqueous solution of tert-butyl hydroperoxide (TBHP), naphthalene, dichloromethane, concentrated hydrochloric acid, analytically pure crystalline iodine, iron(III)chloride hexahydrate $FeCl_3 \cdot 6H_2O$, cobalt(II)chloride hexahydrate $CoCl_2 \cdot 6H_2O$, nickel(II)chloride hexahydrate $NiCl_2 \cdot 6H_2O$, chromium(III)chloride hexahydrate $CrCl_3 \cdot 6H_2O$, copper(II)chloride dehydrate $CuCl_2 \cdot 2H_2O$, zinc chloride $ZnCl_2$ were supplied from POCH S.A.

Methods

Diphenylmethane (1.2 mmol) was added to the mixture of catalyst system which contained suitable metal chloride (0.2 mmol) and pyridine (1.2 mmol). The aqueous solution of TBHP (10 mmol) was used as an oxidizing agent. Mixture of all components was heated at 80 °C conventionally through 4 hours or 30 minutes and also under microwave irradiation for 30 minutes at 80 °C using a variable reactor power. Microwave experiments were carried out in Prolabo Synthewave[®] 402 (monomode microwave reactor, maximum power 300 W, frequency 2450 MHz). After assumed time samples were cooled to room temperature. Next 30 % solution of HCl (200 µl) was added in order to neutralize pyridine. Then mixture was diluted with H₂O (2 ml). At the end, whole composition was extracted with dichloromethane (2 ml). Agilent 6850 gas chromatograph with a flame ionization detector (FID) was used to identify the reaction products.

Results and Discussion

Many literature data are concerned with the study of new catalysts related to systems based on iodine and iron chlorides. An interesting problem was to confirm data which were presented in the literature and investigate other potential catalytic systems. The results of the experiments are shown in Table 1.

Table 1 Yields of benzylic oxidation of DFM for various metal catalysts

Catalyst	Conventional heating		Microwave heating
	4 h	30 min	30 min
iodine	94	74	89
FeCl ₃ ·6H ₂ O	85	10	80
CoCl ₂ ·6H ₂ O	93	83	12
NiCl ₂ ·6H ₂ O	83	27	41
CrCl ₃ ·6H ₂ O	96	88	83
CuCl ₂ ·2H ₂ O	58	53	63
ZnCl ₂	64	18	83
without catalyst	11	8	1

Obtained results confirmed the catalytic activity of iodine and FeCl₃·6H₂O. It led to an extended range of studies on *d*-block metal chlorides which could be potentially effective catalysts for oxidation reactions.

Examined chlorides exhibited diversified impact on the yield of the oxidation reaction. The least effective were CuCl₂·2H₂O and ZnCl₂. The highest catalytic activity was observed for chlorides: FeCl₃·6H₂O, CoCl₂·6H₂O, NiCl₂·6H₂O and CrCl₃·6H₂O. Addition of metallic catalyst significantly improved the reaction efficiency. In the system containing only pyridine the rate of conversion was only 11 % which confirmed the necessity of using the catalysts. In comparison to the literature data, presented results show that use of a smaller amount of pyridine with FeCl₃·6H₂O gives satisfactory 85 % yield after 4 hours [5]. For that reason, application of pyridine as a solvent medium is not justified.

In order to examine the rate of the oxidation reaction, yield of process was determined after 30 minutes. In this case, the most reactive systems contained chromium and cobalt salts. Obtained conversions are similar to these which were received after 4 hours. It can be found that mentioned systems are most effective. In their presence reactions proceeded with acceptable rate and efficiency.

The oxidation reactions of DFM both under microwave and conventional conditions were compared. Satisfactory conversion of DFM was observed using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{NiCl}_3 \cdot 6\text{H}_2\text{O}$ and ZnCl_2 under microwave irradiation, while lower values were noted for reactions catalyzed by $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CrCl}_2 \cdot 6\text{H}_2\text{O}$. Higher efficiency of the reactions carried out under microwave heating compare to conventional heating is probably connected with stronger absorption of microwave irradiation by the mentioned metal chlorides. In order to confirm above assumptions the analysis of the heating rate of ZnCl_2 and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was performed. Samples were heated to 80 °C both under conventional and microwave conditions. It was found that ZnCl_2 reached the expected value of the temperature during only 2 minutes. In the case of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, this time was more than three times longer.

Both the reactivity of the oxidant (TBHP) as well as catalyst affects on the value of conversion degree. It is due to different solubility of the chlorides in the reaction medium and probably precipitation of the catalyst-oxidant complexes. The mechanism of these reactions is intricate. Depending on the catalyst used, efficiency may differ significantly.

Conclusions

The mechanism of oxidation of benzylic compounds with TBHP in the presence of metal chloride catalysts is complicated and not yet well understood. Based on the conducted preliminary research it was stated that *d*-block transition metal chlorides have a chance to become an alternative source of catalyst in benzylic oxidation reactions. Further research will be focused on the optimization of benzylic oxidation conditions in the presence of various catalytic systems.

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