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OXIDATION OF R-(+)- LIMONENE WITH HYDROGEN PEROXIDE CATALYZED BY POLYOXOMETALATE COMPLEXES

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ABSTRACT. The oxidation of R-(+)-limonene (***1***) by d-electron-transition-metal-substituted polyoxometalate complexes (TMSP) with hydrogen peroxide as oxidant in acetone at 50^0C has been studied. In all cases, 1-methyl-4-(1-methylethenyl)-1,2-cyclohexanediol (***2a***, only one diastereoisomer) was the major oxidation product (around 30% yield).

INTRODUCTION

The development of new catalytic systems for selective oxidation of olefins by simple and stable peroxides (t-butyl hydroperoxide, hydrogen peroxide), continues to be the focus of many researches to develop new technologies for future industrial applications.

The oxidation of organic substrates with aqueous hydrogen peroxide is very atractive from the viewpoint of industrial technology anf synthetic organic chemistry since aqueous hydrogen peroxide is cheap and easy to handle. For instance, extensive attention has been devoted for a long time to the direct epoxidation of olefins by aqueous hydrogen peroxide. The transition metals are widely useful in many organic reactions, especially in oxidation of organic substrates. For the activation of hydrogen peroxide, catalytically active intermediates may be classified by the mechanism of their reaction. Thus, heterolytic cleavage is common for electron-poor d^0 complexes of Ti, V, Mo, W and Re. In the intermediate peroxo complex, the O-O bond is polarized, leading to transfer of an electrophilic oxigen to a nucleophilic substrate as in epoxidation of alkenes.

In recent years, it has been reported that olefins can be epoxidized by molybdenum and tungsten derivatives as catalysts with dilute hydrogen peroxide under phase-transfer conditions [1,2]. Heteropoly acids (HPA) such as 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$) or 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$) are often used not only for the acid-catalyzed reactions, but also for many oxidation of organic substrates [3].

Other transition metal oxygen anion clusters (polyoxometalates) are widely useful in many organic reactions, especially in oxidation of organic substrates [4-9].

R-(+)-limonene one of the most inexpensive natural product was the purpose of many researches concerned the oxidation of it to carvone. With low reggae and

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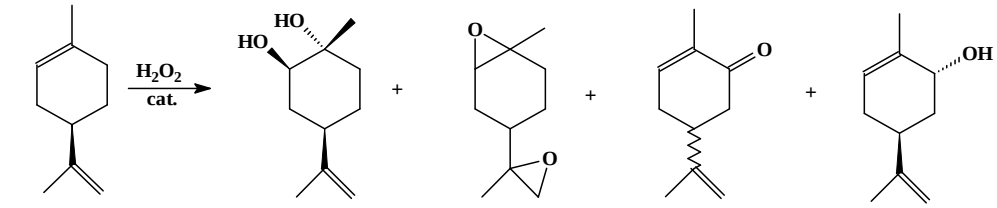
stereoselectivity, oxidation of limonene leads to a mixture of many products, both epoxides (1,2-epoxide, 8,9-epoxide and dioxide), diols and allylic oxidation products (cis and trans carveol, carvone, cis and trans dihydrocarvone, isopiperitenone etc).

In most cases, chromium (VI) reagents (t-butyl chromate [10], chromium trioxide in pyridine [11] have the best results in allylic oxidation of limonene to carvone (20-30% yield), but a large molar excess of complex to substrate 15:1 is required.

More recently, the TMSP complexes [11] and metalloporphirin catalysts [13] were used in epoxidation of limonene. Thus, epoxidation of (+)-limonene with the Mn(III) Wells-Dawson TMSP gave a 53% yield of 1,2-epoxide and a 22% yield of 8,9-epoxide [12]. Zeolites have also been successfully employed in allylic oxidation of limonene to carvone [14,15].

RESULTS AND DISCUSSION

In this paper we report on the use of transition metal substituted Keggin type polyoxometalates (TMSP) with the general formula, $Me^{n+}[PMo_xV_yO_{40}]$, as catalysts, in the oxidation of (+)-limonene. The reaction was performed in liquid homogeneous phase, by dissolving the catalyst in a small amount of hydrogen peroxide (35%), then added to the acetone solution of substrate. The aqueous hydrogen peroxide (35%), was then dropwise added, and the reaction mixture stirred for an extended period of time (10h) at 50^0C. The reaction was monitored by GC-MS analysis using a 20m methylsilicone capillary column. In all cases, the limonene was predominantly epoxidized to the endocyclic double bond to give 1,2-epoxide, which further transforms into *trans*-glycol (***2a***, see Scheme 1). This compound is obtained by cleavage reaction involving ring opening of epoxide in acid-catalysis.



1 — R-(+)-limonene

2a

2b — limonene-dioxide (mixture of stereoisomers)

2c — carvone

2d — trans-carveol

Scheme 1

Thus 1-methyl-4-(1-methylethenyl)-1,2-cyclohexanediol (***2a***, only one diastereo-isomer, [10,11] was obtained as a major oxidation product (yield around 30%) and the corresponding limonene dioxide (***2b***) in about 12% yield. The allylic oxidation products trans carveol and carvone were obtained as minor products (yield around 10% for ***2c***, and 5% for ***2d***). The other oxidation products: limonene 1,2-epoxide,

limonene 8,9-epoxide, isopiperitenone, piperitenone, trans-dihydrocarvone, were identified and quantified by GC-MS in very small amounts (around 15% combined yield).

The best results were obtained with $(NH_4)_5H_4[PMo_6V_6O_{40}]$ which led to a mixture consisting of glycol ***2a*** (37.2), limonen-dioxide (12%) and carvone (11,5%) as major products. (see Table 1). Probably, the NH_4 salt of heteropoly acid increases the stability and solubility of the catalyst in acidic solution. Decreasing the catalytic amount of polyoxo-metalate decreased the percentage of all oxidation products (run 5). Increasing two times the proportion of oxidizing agents increased slowly, only the yield af allylic oxidation products (carvone from 10% to 12% and trans-carveol from 5% to 8%, run 6).

The main oxidation products ***2a***, ***2b***, ***2c*** and ***2d*** were optically inactive. Most probably the abstraction of hydrogen from C-4 in allylic oxidation takes place with racemization. This study of (+)-limonene oxidation indicates attack primarly at the 1,2 double bond rather than allylic oxidation at C-6 to form these oxidation products (carveol and carvone).

Table 1.

Oxidation of (+)-limonene with H_2O_2 35% catalyzed by polyoxometalates

Run	Catalyst	GLC peak area %				Conversion
		2a	**2b**	**2c**	**2d**	
1	$Pd_{4,5}[PMo_6V_6O_{40}]$	28.8	11.5	7.6	3.2	71[a]
2	$Mn_{4,5}[PMo_6V_6O_{40}]$	32.6	13.4	9.9	4.3	72[a]
3	$Cu_{4,5}[PMo_6V_6O_{40}]$	24.7	10.5	7.6	3.2	69[a]
4	$(NH_4)_5H_4[PMo_6V_6O_{40}]$	37.2	12	11.5	4.7	80[a]
5	$(NH_4)_5H_4[PMo_6V_6O_{40}]$	21.3	7.4	4.3	2.1	67[b]
6	$(NH_4)_5H_4[PMo_6V_6O_{40}]$	38.4	12.7	12	8.1	80.5[c]

Reaction conditions: [a]0.10 mol substrate, 0.15 mmol catalyst, 0.20 mol H_2O_2
[b]0.10 mol substrate, 0.10 mmol catalyst, 0.2 mol H_2O_2
[c]0.30 mmol catalyst, 0.20 mol H_2O_2

EXPERIMENTAL

Gas chromatography-mass spectroscopy (GC-MS) coupling analyses were performed on a Hewlett-Packard 5890 (GCL)-5972 (MSD) using a HP-5MS 20m x 0.25 x 0.25μm capillary.

Polyoxometalates catalyst were prepared according to the literature procedure [16,17]. (+)-Limonene, (+)-carvone and trans-carveol were purchased from Aldrich.

Typical oxidation procedure. To the stirred solution of limonene (13.6 g, 0.1 mol) in 80 ml acetone, polyoxometalate catalyst 0.15 mmol (run 4) dissolved in 1 ml of 35% H_2O_2 was then added. After 10 min. 20 ml (0.2 mol) H_2O_2 35% was dropwise added for 2 h, and the solution was stirred at 50^0C for 10 hours. The solution was treated with a solution of 10% sodium hydrogen sulfite to decompose unreacted H_2O_2, them the solvent removed by distillation. The residual liquid was extracted wirh chloroform, dried on $MgSO_4$, filtered and final reaction product was analyzed by GC-MS (see Table 1). The material, after removal of unreacted

limonene by distillation, was subjected to separation by column chromatography (basic alumina grade III, eluent hexane-ether) which gave pure ***2a*** (2g, 15% yield, m.p. 68^0C [11], 67^0C).

The compounds ***2a***, ***2b***, ***2c*** and ***2d*** were analyzed by means of MS database. MS (m/e, rel. intensity); for ***2a***: 170(5,M^+), 152(34), 137(21), 71(85), 43(100); for ***2b***: 168(2,M^+), 107(26), 67(30), 43(100); for ***2c***: 150(12,M^+), 108(31), 82(100), 54(63), 39(53); for ***2d***: 152(M^+), 137(23), 109(100), 84(78), 55(64), 43(51).

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