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Catalytic Oxidation of α,β- and β,γ-Unsaturated Bicyclic Ketones by Hydrogen Peroxide

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Abstract

For the purpose of recycling the by-products formed during the obtaining of caprolactam, adipinic acid, *etc.* at the stage of liquid-phase cyclohexane oxidation by atmospheric oxygen, potentiality was studied for the oxidation of the compounds entering into the composition of so called X-oil light fraction such as α,β- and β,γ-unsaturated bicyclic ketones. The oxidation reaction was carried out using 30 % hydrogen peroxide solution at the temperature of 55–65 °C and atmospheric pressure in a two-phase system (aqueous phase–organic phase) in the presence of homogeneous bifunctional nanostructured catalysts on the base of tetra(oxodiperoxotungsteno) phosphate in combination with quaternary ammonium cations. The reaction products have been analyzed using GC-MS, TLC and GC assays.

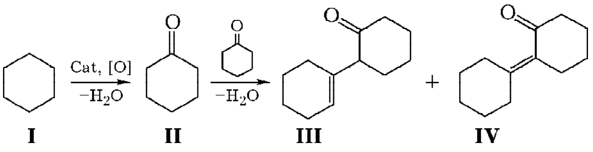
Key words: phase transfer catalysis, peroxopolyoxotungstates, unsaturated bicyclic ketones, epoxides, hydrogen peroxide

INTRODUCTION

In connection with toughening the ecostandards at the enterprises of chemical industry there is a necessity for solving the problem of using or recycling the waste products presented by so-called X-oils those are formed in the manufacture of adipinic acid and caprolactam. The present work deals with the studies on the potentiality of the oxidation of X-oil components such as unsaturated bicyclic ketones to produce epoxide compounds those represent valuable products for the general and fine organic synthesis. Being efficient modifiers, stabilizers, diluents of polymers, these compounds are used in order to obtain polymeric materials with prescribed properties. Many heterocyclic epoxides represent biologically active compounds or their precursors [1].

In realizing the process of liquid-phase catalytic oxidation of cyclohexane **I** by atmospheric oxygen the formation of a complex multicomponent mixture is observed. Alongside with the main product **II** as a result of cyclohaxanone dimerization reaction, α,β- and β,γ-unsaturated cyclic ketones are formed (1): 2-(1-cyclohexenyl)-1-cyclohexanone **III** and 2-cyclohexylidene-1-cyclohexanone **IV** are formed those are the components of a light fraction obtained by the distillation of X-oil in vacuum [2]. According to approximate evaluations carried out basing on the data of [2–4] the amount of such by-products ranges from 80 to 100 kg per 1 t of treated raw material **I**. Ketone **III** is thermodynamically unstable [5] undergoing isomerization at 150 °C to give **IV**. The reaction of isomerization is equilibrium one, therefore under usual conditions a mixture of isomers is formed in the ratio of 90 to 10 %, respectively (Scheme 1) [2].

An approximate composition of the multicomponent mixture of reaction products after



Scheme 1.

TABLE 1

Composition of stilling liquid from the cyclohexane separation column

Components	Amount, kg/t of raw material	Composition, mass % [3]
Cyclohexanol	400	35–40
Cyclohexanone	350	30–35
X-oil	240	15–25
Volatile species	10	1

the stage of unreacted cyclohexane isolation is presented in Table 1 [3].

A high-boiling fraction of X-oils is removed from the still of a vacuum rectification column. With the use of a subsequent vacuum rectification of X-oils one can isolate a head, first running “light fraction” that composes up to 50 % of its amount [3, 6]. The “light fraction” mainly consists of the compounds **III** and **IV**.

Nowadays in order to realize the reactions for various organic substrata oxidation a method is applied based, for example, on phase-transfer catalysis with the use of bifunctional homogeneous nanostructured catalysts on the basis of peroxopolyoxo tungstates [7–16]. With the help of various physicochemical methods (NMR, IR, Raman, UV spectroscopy, *etc.*) it was demonstrated that peroxo complexes formed in the H_2O_2–H_3PO_4–Na_2WO_4 and $H_3PW_{12}O_{40}$–H_2O_2 systems are stable enough; at the same time the most reactive anion with respect to oxidation reaction is $\{PO_4[WO(O_2)_2]_4\}^{3-}$ anion (Fig. 1) [9, 10, 12, 13]. The application of interphase-transfer catalysts such as quaternary ammonium cations (Q^+) in combination with an oxidation catalyst such as peroxopolyoxo tungstate allows one to perform oxidation reactions in two-phase systems within a single reactor (so-called one pot processes).

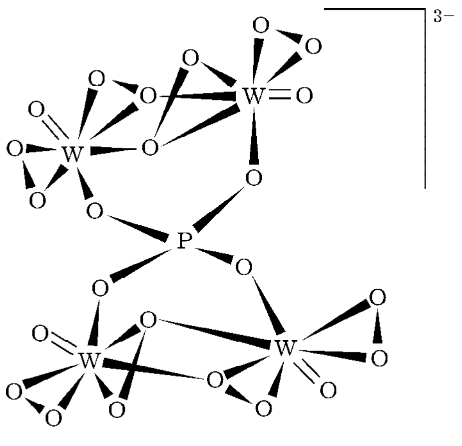


Fig. 1. Structure of peroxo anion $\{PO_4[WO(O_2)_2]_4\}^{3-}$.

The present work is devoted to realizing the method of phase-transfer catalysis in two-phase systems for the studies on the potentialities of obtaining epoxides from α,β- and β,γ-unsaturated cyclic ketones contained in so called light fraction of X-oils.

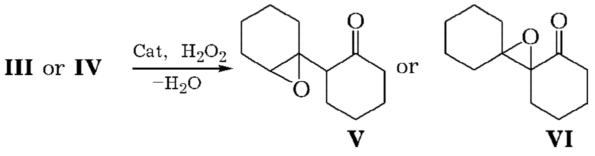
The approach offered for catalytic oxidation of cyclic ketones **III**, **IV** containing unsaturated C=C bonds by hydrogen peroxide could allow one to obtain such epoxides as 2-(7-oxabicyclo[4.1.0]hept-1-yl)-cyclohexanone **V** and 13-oxadispiro[5.0.5.1]tridecane-1-one **VI** (Scheme 2) [17].

EXPERIMENTAL

Reaction of oxidation was carried out in a shaken reactor such as a “catalytic duck” (300–400 double swinging/min), supplied with a backflow condenser and a jacket for thermostating. The reaction temperaturepe (55–65 °C) was maintained with the help of water thermostat with an accuracy of ±1.0 °C.

As a substrate we used a mixture isolated by means of vacuum distillation from the “light fraction” of X-oils of cyclohexanone manufacture (Azot JSC, Kemerovo, Russia). The mixture obtained represented a light yellow oily liquid of 1.1 g/cm^3 in density.

As a catalyst we used a quaternary ammonium salt of tetra(oxodiperoxotungsteno) phos-



Scheme 2.

phate $Q_3\{PO_4[WO(O_2)_2]_4\}$, where Q is tetra-*n*-butylammonium chloride $[(C_4H_9)_4N]Cl$ (95 %) or N-hexadecylpyridinium chloride $[\pi\text{-}C_5H_5N\text{-}(CH_2)_{15}CH_3]Cl$ (Acros). The synthesis of catalytic systems was carried according to the technique described in [13].

The analysis of the substrate and reaction mixture was carried out with the help of a Saturn 2000 GS-MS (Varian Inc.) supplied with an ion trap. The products were chromatographed using a CP-Sil 24 CB SLP quartz capillary column (30 m × 0.25 mm i. d.), the temperature programming being performed from 50 to 250 °C at a heating rate of 7 °C/min, the temperature of evaporator amounting to 300 °C. Data processing was carried out applying a normalization method [18].

The conversion level of bicyclic ketones depending on time was determined using a gas chromatography (GC) technique with the help of a Tsvet-570 chromatograph, supplied with a flame ionization detector (FID), at 180 °C. A stainless steel column (3 m × 2 mm) from was packed with graphitized thermal black modified with 0.4 mass % of OV-225. Nitrogen was used as the carrier gas, with the flow rate of 30 mL/min, H_2 flow rate being at 30 mL/min, air flow rate amounting to 300 mL/min. For performing the quantitative calculations of chromatographic data we used a standard addition technique [18]. In some experiments the analysis the reaction mixture was carried out using a Tsvet-500 chromatograph supplied with a glass capillary column (40 m × 0.25 mm) and a flame ionization detector, methylsilicon rubber or elastomer SE-30 being used as a stationary phase. Helium was used as the carrier gas. The analysis was carried out with a programmed column heating: 5 min hold at 60 °C, then heating with a rate of 20 °C/min up to 230 °C and 5 min hold at this temperature. The registration and analysis of chromatographic profiles was carried out using a Multichrom computer system [19].

The current monitoring of the conversion level of byciclic ketones was carried out with the help of a TLC technique using Sorbfil plates and a hexane-diethyl ether mixture (10 : 3) as the eluent.

For the separation of the mixture used as the substrate we applied a column chromatography technique. The adsorbent was a L 100/160 silica gel (Merck), a hexane–diethyl ether mixture (10 : 3) was used as the eluent.

RESULTS AND DISCUSSION

The analysis of the substrate (light fraction of X-oils), carried out in order to establish its composition has demonstrated (Table 2) that there are residual amounts of compound **II**, as well as ketones **III** and **IV** in the mixture. There are 1,2,3,4,6,7,8,9-octahydrodiben-zo[b,d]-furan VII found out in the substrate, as well as the compounds with the molecular ion mass *m*/*z* 258, corresponding the molecular mass value for tricyclic ketones such as 2,6-dicyclohexylidene-1-cyclohexanone **VIII** and 2,6-di(1-cyclohexenyl)-1-cyclohexanone **IX** those represent the products of cyclohexanone trimerization.

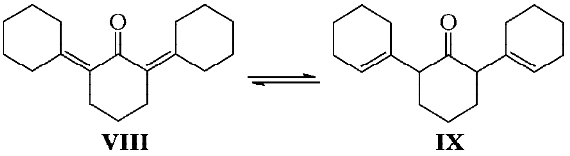
The results of the GC-MS analysis (see Table 2) have, as a whole, confirmed the correspondence between the composition of the substrate used and the composition of the light fraction of X-oils presented in [3].

TABLE 2

Results of the GC-MS analysis for X-oil light fraction used as the substrate

No.	Compound	Retention time, min	Molecular ion, *m*/*z*	Relative content (S_i), %
1	Cyclohexanone **II**	5.3	98	0.1
2	Octahydrobenzofuran **VII**	16.1	176	1.0
3	Cyclohexenylcyclohexanone **III**	16.8	178	78.5
4	Cyclohexylidenecyclohexanone **IV**	17.0	178	7.8
5	Tricyclic ketones **VIII**, **IX**	24.8–25.0	258	8.8
6	Non-identified	3.8		

Note. Here and in Table 3: S_i is the *i*-th peak area; $\Sigma S_i = 100$ %.



Scheme 3.

It should be noted that tricyclic ketones, the condensation products of three cyclohexanone molecules, can form isomeric species (Scheme 3) like bicyclic ketones.

According to the results of the GC-MS analysis, there were epoxide (13-oxadispiro[5.0.5.1]-tridecane-1-one) **VI**, cyclopentanecarbonic acid as well as the compounds contained in the initial mixture such as **II**, **III**, **IV**, **VIII**, **IX** found out in the reaction mixture after 3 h proceeding the catalytic oxidation of the substratum containing the mixture of ketones **III**, **IV** (Table 3). Moreover, an increase in the content of 1,2,3,4,6,7,8,9-octahydrodibenzo[b,d]furan **VII** is observed.

To reveal other components of the reaction mixture is difficult due to overlapping the peaks of minor analytes, which results in the distortion of mass spectra and thus does not allow one to identify the substances. In the course of the further studies aimed at establishing the composition of reaction products we are planning to perform the mixture separation with use of the techniques of fractional distillation and column chromatography.

Taking into account the fact that epoxide **V** has not been found out in the reaction mixture, whereas the conversion level for ketone **III** registered basing on GC method amounts to 90 % (Fig. 2), one can hypothesize the two scripts as it follows:

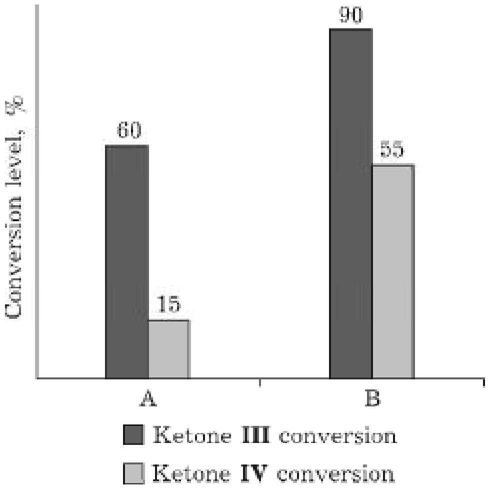


Fig. 2. Catalyst type influence upon the conversion of initial substances. $[H_2O_2]/[Substrate] = 3$, $[Substrate]/[Cat] = 200$, dichloroethane as solvent, $T = 65$ °C, the reaction time 3 h; A, B – catalytic complexes $[(C_4H_9)_4N]_3\{PO_4[W(O)(O_2)_2]_4\}$ and $[C_5H_5N(CH_2)_{15}CH_3]_3\{PO_4[W(O)(O_2)_2]_4\}$, respectively.

1. Epoxide **V** formed undergoes the destruction as a result, for example, of oxidation cleavage with respect to double C=C bond with the formation of carbonic acids.

2. A series of ketone **III** consecutive transformations, including catalytic ones takes place, with the formation of the compounds containing the furan cycle.

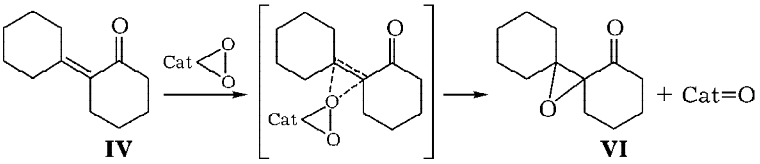
An argument in support of the first script is presented by the fact that carbonic acids are detected in the reaction mixture. However, the presence of carbonic acids in the reaction products gives rise to an increase in the acidity of the reaction mixture, which could, in turn, result in the reaction of the oxyrane ring decom-

TABLE 3

Results of the GC-MS analysis for the organic phase of the reaction mixture

No.	Compound	Retention time, min	Molecular ion, *m/z*	Relative content (S_i), %
1	Cyclohexanone **II**	5.3	98	1.8
2	Cyclopentanecarbonic acid	9.0	114	11.6
3	Octahydrodibenzofuran **VII**	16.1	176	5.5
4	Cyclohexenylcyclohexanone **III**	16.4	178	3.6
5	Cyclohexylidenecyclohexanone **IV**	16.7	178	3.0
6	13-Oxadispiro [5.0.5.1]tridecane-1-one **VI**	18.2	194	4.4
7	Tricyclic ketones **VIII**, **IX**	24.7–24.8	258	1.5
8	Non-identified			68.6

Note. For designations see Table 2.



Scheme 4.

position. Ultimately this could cause the formation of dibenzofuran derivatives.

The formation of compounds containing the furan cycle is described in [20] wherein 2-cyclohexylidene-1-cyclohexanone **IV** in very acidic medium was converted into **VII**. The authors of [21] presented a mechanism for the reaction of cyclic dehydration of the epoxide such as 2-(1-cyclohehenyl)-1-cyclohexanone **V** resulting in the formation of 1,2,3,4,6,7,8,9-octahydrodibenzo[b,d]furan **VII** [22, 23].

The formation of epoxide **VI** from ketone **IV** with the participation of the oxygen of the catalyst's peroxo groups proceeds in the organic phase according to Scheme 4.

The regeneration of the catalyst is realized by means of hydrogen peroxide at the interface (between the organic phase and the aqueous phase).

Among the two catalytic systems tested N-hexadecylpyridinium tetra(oxodiperoxotungsteno)phosphate is the most active (see Fig. 2, B). In the presence of this system one could succeed in obtaining 90 and 55 % conversion level with respect to initial ketones **III** and **IV**, respectively. The high activity observed indicates a higher lipophily of N-hexadecylpyridinium cation as compared to tetrabutylammonium cation (see Fig. 2, A) as a phase-transfer catalyst.

Decreasing the temperature of the catalytic oxidation process from 65 to 55 °C with the use of complex B (see Fig. 2) as a catalyst, all other factors being the same, does not influence the yield of epoxide **VI** to any considerable extent, but results in approximately two-fold reducing the yield of octahydrodibenzo-[b,d]furan **VII**. Moreover, an increase in the concentration of cyclopentanecarbonic acid from 8 up to 12 % has been observed in the mixture of products which is uncharacteristic under these conditions.

CONCLUSION

Using the method of phase transfer catalysis in two-phase systems a potentiality has been demonstrated for obtaining of useful and demanded products such as epoxides, dibenzofurane derivatives and carbonic acids from the waste products of caprolactam manufacture, so called light fraction of X-oils. The reactions of oxidation by hydrogen peroxide proceed within one technological stage under soft conditions: atmospheric pressure, the temperature of 55–65 °C, low catalyst concentration (ratio [substrate]/[catalyst] = 200).

It has been established that the oxidation of 2-cyclohehylidene-1-cyclohexanone by hydrogen peroxide int the presence of a homogeneous bifunctional catalyst such as N-hexadecylpyridinium tetra(oxodiperoxotungsteno)phosphate occurs with the formation of epoxide such as 13-oxadispiro[5.0.5.1]tridecane-1-one.

The oxidation of 2-(1-cyclohexenyl)-1-cyclohexanone by hydrogen peroxide in the presence of N-hexadecylpyridinium tetra(oxodiperoxotungsteno)phosphate should predominantly proceed with the formation of 1,2,3,4,6,7,8,9-octahydrodibenzo[b,d]furan and cyclopentanecarbonic acid.

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