

# Efficiency of selected phase transfer catalysts for the synthesis of 1,2-epoxy-5,9-cyclododecadiene in the presence of $\text{H}_2\text{O}_2/\text{H}_3\text{PW}_{12}\text{O}_{40}$ as catalytic system

Grzegorz Lewandowski

West Pomeranian University of Technology, Szczecin, Institute of Chemical Organic Technology, ul. Pułaskiego 10, 70-322 Szczecin, Poland, e-mail: grzegorz.lewandowski@zut.edu.pl

The results of the studies on the influence of the phase transfer catalyst on the epoxidation of (Z,E,E)-1,5,9-cyclododecatriene (CDT) to 1,2-epoxy-5,9-cyclododecadiene (ECDD) in the  $\text{H}_2\text{O}_2/\text{H}_3\text{PW}_{12}\text{O}_{40}$  system by a method of phase transfer catalysis (PTC) were presented. The following quaternary ammonium salts were used as phase transfer catalysts: methyltributylammonium chloride, (cetyl)pyridinium bromide, methyltrioctylammonium chloride, (cetyl)pyridinium chloride, dimethyl[diocetyl(76%) + dihexadecyl(24%)] ammonium chloride, tetrabutylammonium hydrogensulfate, didodecyldimethylammonium bromide and methyltrioctylammonium bromide. Their catalytic activity was evaluated on the basis of the degree of CDT and hydrogen peroxide conversion and the selectivities of transformation to ECDD in relation to consumed CDT and hydrogen peroxide. The most effective PT catalysts were selected based on the obtained results. Among the onium salts under study, the epoxidation of CDT with hydrogen peroxide proceeds the most effectively in the presence of methyltrioctylammonium chloride (Aliquat® 336) and (cetyl)pyridinium chloride (CPC). The relatively good results of CDT epoxidation were also achieved in the presence of Arquad® 2HT and (cetyl)pyridinium bromide.

**Keywords:** epoxidation, (Z,E,E)-1,5,9-cyclododecatriene, 1,2-epoxy-5,9-cyclododecadiene,  $\text{H}_2\text{O}_2/\text{H}_3\text{PW}_{12}\text{O}_{40}$  catalytic system, phase transfer catalysis.

## INTRODUCTION

A search of economically effective and environmentally friendly methods of production is one of the fundamental objectives of modern organic synthesis<sup>1</sup>. This particularly relates to the processes for the preparation of epoxides. Epoxides are one of the most important intermediates used in the synthesis of numerous of fine and special chemicals (surface-active agents, flavour and fragrance agents, pharmaceuticals). Unfortunately, the major method for the synthesis of epoxides is the dehydrochlorination of chlorohydrins by aqueous alkali solutions despite its unfavourable impact on the environment. Although the process is characterized by remarkable selectivity and epoxide yield, an equimolar amount of alkali metal chloride is formed as a by-product along with the contamination of the aqueous phase by chloroorganic compounds. As a result of this the epoxide products also contain impurities such as chloroorganic derivatives and inorganic chlorides. Hydroperoxide-mediated epoxidation is widely used in industry, as is it both effective and efficient, however, its application requires anhydrous condition. Moreover, as with the application of organic peracids as the oxidant, it is associated with a relative large hazard resulting from the explosive properties of these compounds. For these reasons, new methods for the preparation of epoxides that could limit or eliminate toxic and/or dangerous oxidants are required<sup>1</sup>. In this context, hydrogen peroxide deserves particular attention. It possesses a high content of potentially active oxygen and the methods of its production ensure its high purity and moderate price.

Interesting results have been obtained for the epoxidation of various olefins with hydrogen peroxide under phase transfer catalysis (PTC) conditions involving a system of two immiscible liquid phases, most often aqueous and organic. During the 1980s, Venturello et al.<sup>2,3</sup> discovered that less reactive terminal olefins

can be effective in the epoxidations with the use of 8% hydrogen peroxide in the presence of catalytic amounts of sodium tungstate, phosphoric acid, and quaternary ammonium chloride as the phase transfer catalyst (PT catalyst) (Venturello system), in a mixture of 1,2-dichloroethane-water. However, the Venturello procedure requires an excess of olefin substrate. The epoxidation of olefins by 30%  $\text{H}_2\text{O}_2$  proceeds with a high yield in the presence of catalytic system composed of sodium tungstate ( $\alpha$ -aminomethyl)phosphonic acid and methyltrioctylammonium hydrogensulfate as the PT catalyst (Sato system)<sup>1</sup>. The reaction with  $\text{H}_2\text{O}_2$  proceeds without the solvents or with the addition of toluene, under the chlorine-free conditions. The high selectivity of the process is determined by lipophilic ammonium hydrogensulfate and ( $\alpha$ -aminomethyl)phosphonic acid. The epoxidation of olefins with 35% aqueous solution of hydrogen peroxide under the conditions of PTC proceeds also effectively in the presence of the system composed of the tungsten or molybdenum heteropolyacids (HPA) and *N*-hexadecylpyridinium chloride (CPC) as the PT catalyst (Ishii system)<sup>4,5</sup>.

The factor enabling the combination of reagents which are initially located in the different phases is the PT catalyst. In general, the PT catalysts are quaternary onium salts, crown ethers or cryptands<sup>6-8</sup>. Amongst the mentioned types of the PT catalyst, the most common are the quaternary ammonium salts. They are characterized by a high activity and stability at temperatures up to 100°C in neutral or acidic media (in a basic environment they are significantly less durable). The catalytic activity of these salts depends on the length of alkyl chain of quaternary ammonium cation. The nature of their action relies on lipophilic ionic couples or complexes composed of the anion of hydrophilic reagent and the PT catalyst being continuously formed in the aqueous phase followed by the extraction of formed species into

the organic (nonpolar) phase where the reaction with the lipophilic reagent proceeds.

The objective of this work was to investigate the catalytic activity of selected ammonium salts in the epoxidation of (*Z,E,E*)-1,5,9-cyclododecatriene (CDT) to 1,2-epoxy-5,9-cyclododecadiene (sum of *trans*- and *cis*-isomers) (ECDD) in the  $\text{H}_2\text{O}_2/\text{H}_3\text{PW}_{12}\text{O}_{40}$  system by the PTC method. ECDD<sup>9</sup> is a valuable raw material in the preparation of epoxyresins, surfactants, and numerous other compounds of a significant importance in the production of fine chemicals<sup>10</sup>. It may also constitute an intermediate in the synthesis of polyamide 12<sup>11</sup>.

## EXPERIMENTAL

### Reagents

In the epoxidation of CDT with hydrogen peroxide by the method of PTC were used the following reagents: (*Z,E,E*)-1,5,9-cyclododecatriene 98%, dodecane, methyltrioctylammonium chloride (Aliquat 336<sup>®</sup>), methyltrioctylammonium bromide ( $\text{CH}_3(\text{C}_8\text{H}_{17})_3\text{NBr}$ ), (cetyl)pyridinium chloride (CPC), and tetrabutylammonium hydrogensulfate (TBAHS), all of them from Aldrich, hydrogen peroxide, 30% POCh Gliwice, Poland, hydrate of dodecatungstenphosphoric acid, methyltributylammonium chloride (Aliquat 175<sup>®</sup>), (cetyl)pyridinium bromide (CPB), dimethyl[diocetadecyl(76%) + dihexadecyl(24%)] ammonium chloride (Arquad 2TH<sup>®</sup>), and didodecyl-dimethylammonium bromide (DDMAB), all of them from Fluka.

### Procedure of CDT epoxidation

The epoxidation process of CDT with 30% hydrogen peroxide under the PTC conditions was carried out according to the following procedure: a 25 cm<sup>3</sup>, three necked flask (1) fitted with a thermometer (2) and mechanical stirrer (3) was charged with a determined amount of solid  $\text{H}_3\text{O}_{40}\text{PW}_{12}\cdot x\text{H}_2\text{O}$  and then with a 30% aqueous solution of hydrogen peroxide. Subsequently, the mixture was vigorously stirred at room temperature (22–30°C) for 30 min. After that time the reactor was charged with determined amount of phase transfer catalyst. Vigorous stirring of the mixture at room temperature was continued for the next 30 min. After that time a solution of CDT along with an internal standard was introduced. The moment of CDT introduction was assumed to be the beginning of reaction. The mixture was heated in a water bath or was cooled with water with ice (0°C) in order to ensure the constant reaction temperature of 50°C throughout the course of the process. At the time 10, 20, 30, and 60 min samples were taken for the analyses: chromatographic and iodometric. In order to inhibit the course of reaction, the samples were immediately mixed with chloroform (in order to increase organic phase) and then cooled to 0°C. A quantitative determination of composition of collected samples of the reaction mixtures was performed on the basis of calibration an internal standard (dodecane). The determination of hydrogen peroxide concentration in both phases was carried out by iodometric method. On that basis the CDT conversion, the selectivity of transformation to ECDD in relation

to consumed CDT and the yield of ECDD in relation to introduced CDT were calculated.

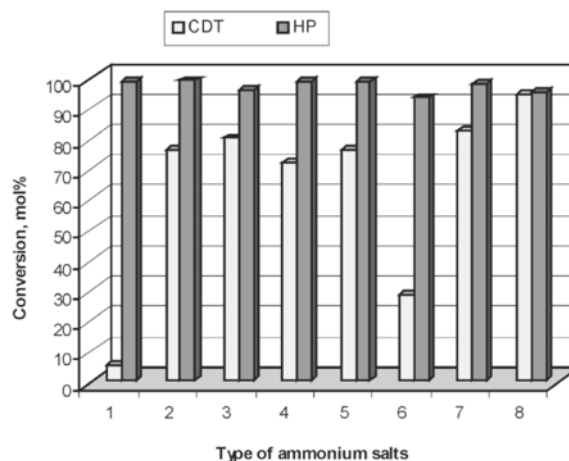
### Analytical procedures

The quantitative determination of the composition of the post reaction mixtures was performed by the method of gas chromatography using Trace GC 2000 chromatograph (Thermo-Finnigan) equipped with computer system for data handling Chrom-Card for Trace GC. A DB-5 capillary column J&W Scientific, 30 m x 0.25 mm x 0.25 μm was used. The detector temperature was 250°C, whereas of sample chamber was 200°C. The column temperature was programmed as follows: isothermally at 50°C for 2.5 min, then increase to 250°C at the rate 20°C/min and isothermally at 250°C for 2.5 min. The flow gas was as follows: air 250 cm<sup>3</sup>/min, hydrogen 35 cm<sup>3</sup>/min, carrier gas (helium) 0.7 cm<sup>3</sup>/min (initial). The percentage content of the component of the given mixture was determined by the internal standard method using dodecane as the reference.

The determination of the concentration of unreacted hydrogen peroxide both in the organic layer and water layer was performed by the iodometric method.

## RESULT AND DISCUSSION

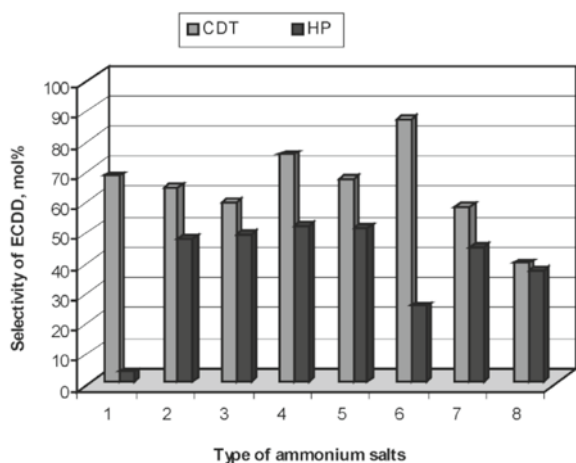
The studies of the catalytic activity of selected ammonium salts as a PT catalysts in the epoxidation of CDT with a 30% hydrogen peroxide to ECDD by the PTC method were carried out at a constant temperature of 50°C, the molar ratio of  $\text{H}_2\text{O}_2/\text{CDT} = 1$ , the molar ratio of PT catalysts/ $\text{H}_3\text{PW}_{12}\text{O}_{40}$  amounted to about 3, and the concentration of  $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$  1.5%. Samples were taken at specified intervals: 10, 20, 30, and 60 min for chromatographic and iodometric analyses. The type of PT catalyst has a relatively small influence on the conversion of hydrogen peroxide (Fig. 1). The lowest degree of  $\text{H}_2\text{O}_2$  conversion was about 93 mol% was obtained with the application of TBAHS (6) and  $\text{CH}_3(\text{C}_8\text{H}_{17})_3\text{NBr}$  (8). In the presence of remaining ammonium salts under study, the conversion of hydrogen peroxide is higher and exceeds 98 mol%. This shows that in the epoxidation process, hydrogen peroxide almost completely undergoes conver-



**Figure 1.** The effect of type of ammonium salts on substrate and hydrogen peroxide conversion 1 – Aliquat<sup>®</sup> 175, 2 – CPB, 3 – Aliquat<sup>®</sup> 336, 4 – CPC, 5 – Arquad<sup>®</sup> 2HT, 6 – TBAHS, 7 – DDMAB, 8 –  $\text{CH}_3(\text{C}_8\text{H}_{17})_3\text{NBr}$

sion, although not always to the desired products. This is confirmed by the degree of CDT conversion, which is significantly lower in a comparison to the degree of hydrogen peroxide consumption (Fig. 1). The highest degree of CDT conversion equal to 94.3 mol% was achieved with the application of  $\text{CH}_3(\text{C}_8\text{H}_{17})_3\text{NBr}$  (8). Moreover, the CDT conversion was a relatively high in the cases of using the following PT catalysts: Aliquat<sup>®</sup> 336, Arquad<sup>®</sup> 2HT, CPC, CPB, and DDMAB. Despite of a relatively high conversion of hydrogen peroxide, Aliquat 175 and TBAHS were found to be inactive in the CDT consumption (conversion was 5.1 and 28.2 mol%, respectively).

The most selective reagents for the transformation to ECDD in relation to the CDT consumed were TBAHS, CPC or Aliquat<sup>®</sup> 175. Their values amounted to 86.6, 74.9 and 68.0 mol%, respectively (Fig. 2). When the epoxidation is carried out in the presence of, CPB, Aliquat<sup>®</sup> 336, CPC, and Arquad<sup>®</sup> 2HT, the lower selectivities of transformation to ECDD in relation to consumed CDT (59.3–67.1 %mol) were obtained. The lowest selectivities of transformation to ECDD were achieved in the presence of  $\text{CH}_3(\text{C}_8\text{H}_{17})_3\text{NBr}$  and DDMAB, respectively 39.1 and 57.7 mol%.



**Figure 2.** The effect of ammonium salt on the selectivities of transformation to ECDD in relation to CDT and  $\text{H}_2\text{O}_2$ . Notation of salts the same as in Figure 1

In relation to consumed hydrogen peroxide, the selectivities of transformation to ECDD are lower than those in relation to consumed CDT (Fig. 2). The lowest selectivities of the transformation to ECDD in relation to the consumed hydrogen peroxide were achieved in the presence of Aliquat<sup>®</sup> 175, TBAHS, and  $\text{CH}_3(\text{C}_8\text{H}_{17})_3\text{NBr}$ , respectively 3.4, 25.1, and 36.4 mol%. In the presence of the remaining ammonium salts under study, the selectivities of the transformation to ECDD in relation to the consumed hydrogen peroxide exceed 45 mol%.

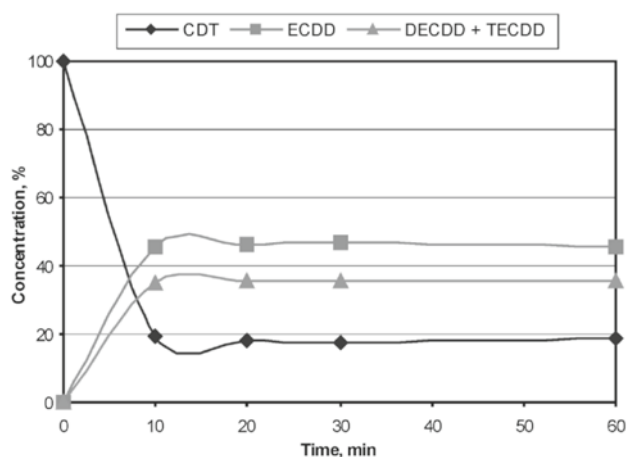
Summarizing the results obtained for the epoxidation of CDT to ECDD in the presence of different ammonium salts, it can be concluded, that the catalytic activity of PT catalysts depends distinctly on the chemical constitution of ammonium salts. The result of CDT epoxidation is affected by both the total number of carbon atoms joined to a nitrogen atom as well as the structure itself of joined groups. The anion joined to the quaternary ammonium group seems to be of less importance, especially in the case of halide anions.

The maximum selectivity of transformation to ECDD both in relation to consumed hydrogen peroxide as well as CDT respectively, exhibit the ammonium salts having an asymmetrical chemical constitution such as Arquad<sup>®</sup> 2HT, CPC, Aliquat<sup>®</sup> 336, and CPB. The symmetrical ammonium salts with low molecular weight alkyl substituents (Aliquat<sup>®</sup> 175, TBAHS) were found to be largely less active as the phase transfer catalysts in the epoxidation of CDT. Test experiments (not presented in this work) with the use of  $\text{Pr}_4\text{NBr}$ ,  $\text{Et}_4\text{NBr}$ , and  $\text{Et}_4\text{NCl}$ , demonstrate that these salts are completely inactive for the epoxidation in the  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{H}_2\text{O}_2$  system.

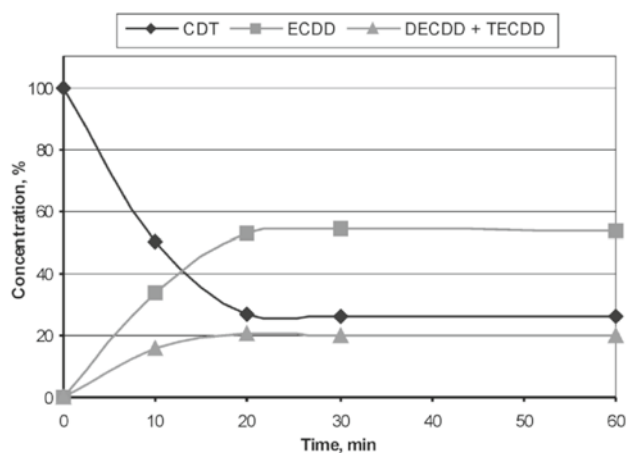
The anion also influences the catalytic activity of ammonium salts, although its influence is not so unequivocal as the influence is not pronounced as that of the cation. The exchange of chloride anion with bromide anion makes little difference to the degree of hydrogen peroxide conversion for both of ammonium salts or the pyridinium salts. Moreover, only in the case of ammonium salts, after an application of the bromide derivative ( $\text{CH}_3(\text{C}_8\text{H}_{17})_3\text{NBr}$ ) instead of the chloride derivative (Aliquat<sup>®</sup> 336) as the PT catalyst an increase in the CDT conversion was found. In the case of pyridinium salts for both chloride (CPC) as well as bromide (CPB), almost identical values of all indicators of CDT epoxidation were achieved. On the other hand, the exchange of chloride anion (Aliquat<sup>®</sup> 175) with hydrogensulfate anion (TBAHS) causes a significant increase in the catalytic activity of the PT system.

It should be also mentioned that the maximal selectivities of transformation to ECDD in relation to the consumed CDT are fairly high and they are located in the range 64–75 mol%. This testifies that about 25–36 mol% of the consumed CDT undergoes the conversion to other products. Because CDT is the olefin containing the three double bonds, hence, as a result of its epoxidation, simultaneous or consecutive preparation of both the monoepoxide ECDD as well as diepoxides (DECDD) and triepoxides (TECDA) is possible. This confirms the charts presenting the changes of the concentrations of CDT, ECDD and DECDD+TECDA as a function of time for the  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{H}_2\text{O}_2/\text{Aliquat}^{\text{®}} 336$  system (Fig. 3) and the  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{H}_2\text{O}_2/\text{CPC}$  system (Fig. 4).

As can be noticed, the ECDD was formed at a high rate during the initial period of running the epoxidation process. DECDD and TECDA were rather formed as a result of the simultaneous epoxidation of the two or three double bonds in CDT than as a result of successive reaction. Moreover, the catalytic system seems to be exceptionally favourable for the epoxides being formed despite a relatively high acidity of the aqueous phase containing  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ . Under the reaction conditions no significant decrease of ECDD concentration was observed, even after a prolonged reaction time (between 60 and 120 min). On the other hand, after 10 min of running the reaction in the presence of Aliquat<sup>®</sup> 336 or for 20 min in the presence of CPC, inhibition of epoxides concentration growth was observed. Moreover, a further decrease in CDT concentration does not proceed after that time. This indicates that inhibition of the reaction course proceeds as a result of  $\text{H}_2\text{O}_2$  depletion in reaction mixture. This can also be a result of an inhibiting



**Figure 3.** Influence of reaction time on the composition of products of CDT epoxidation in the  $H_3PW_{12}O_{40}/H_2O_2$ /Aliquat® 336 system



**Figure 4.** Influence of reaction time on the composition of products of CDT epoxidation in the  $H_3PW_{12}O_{40}/H_2O_2$ /CPC system

influence of the epoxide products on the catalytic system. This will be the subject of further studies.

## CONCLUSIONS

The influence of different types of phase transfer catalysts on the epoxidation of (*Z,E,E*)-1,5,9-cyclododecatriene to 1,2-epoxy-5,9-cyclododecadiene (sum of *trans*- and *cis*-isomers) in the  $H_3PW_{12}O_{40}/H_2O_2$  system has been investigated. Despite the high Lewis acidity of  $H_3PW_{12}O_{40}$ , a significant decomposition of formed epoxide was not found, even at a prolonged time of the process operation. This is caused by a limited miscibility of acidic aqueous phase with the organic phase containing epoxide product. The obtained results suggest that both the stage of the transport of an oxidized form of the catalyst from the aqueous phase to the organic phase and in particular, a transport of the reduced form of the catalyst from the organic phase to the aqueous phase is relatively fast. In the opposite case, a longer contact of acidic catalyst with the organic phase containing ECDD would cause a significant decrease in the selectivity of transformation of CDT to ECDD. Among the onium salts under study, the epoxidation of CDT with hydrogen peroxide in the presence of methyltrioctylammonium chloride (Aliquat® 336) and (cetyl)pyridinium chloride

(CPC) proceeds the most effectively. The relatively good results of CDT epoxidation were also achieved in the presence of Arquad® 2HT and (cetyl)pyridinium bromide. However, it should be pointed out that in the CDT epoxidation process not only monoepoxide ECDD is formed, but also DECDD and TECDA, as a result of the simultaneous epoxidation of the second or third double bonds in CDT.

## ACKNOWLEDGMENT

This research was carried out with the financial support of the Ministry of Science and Higher Education in Poland in the years 2010–2013, project number N N209 373439.

## LITERATURE CITED

- Sato, K., Aoki, M., Ogawa, M., Hashimoto, T., Panyella, D. & Noyori, R. (1997). A halide-free method for olefin epoxidation with 30 % hydrogen peroxide. *Bull. Chem. Soc. Jpn.* 70, 905–915. Retrieved March 15, 2013, from [http://www.csj.jp/journals/bcsj/J-STAGE/7004/pdf/70\\_905.pdf](http://www.csj.jp/journals/bcsj/J-STAGE/7004/pdf/70_905.pdf). DOI: 10.1246/bcsj.70.905.
- Venturello, C. & D'Aloisio, R. (1988). Quaternary ammonium tetrakis(diperoxotungsto)phosphates(3-) as a new class of catalysts for efficient alkene epoxidation with hydrogen peroxide. *J. Org. Chem.* 53, 1553–1557. Retrieved March 15, 2013, from <http://pubs.acs.org>. DOI: 10.1021/jo00242a041.
- Venturello, C., D'Aloisio, R., Bart, J.C.J. & Ricci, M. (1985). A new peroxotungsten heteropoly anion with special oxidizing properties: synthesis and structure of tetrahexylammonium tetra (diperoxotungsto) phosphate (3-). *J. Mol. Catal.*, 32, 107–110.
- Ishii, Y., Yamawaki, K., Ura, T., Yamada, H., Yoshida, T. & Ogawa, M. (1988). Hydrogen peroxide oxidation catalyzed by heteropoly acids combined with cetylpyridinium chloride. Epoxidation of olefins and allylic alcohols, ketonization of alcohols and diols, and oxidative cleavage of 1,2-diols and olefins. *J. Org. Chem.*, 53, 3587–3593. Retrieved March 15, 2013, from <http://pubs.acs.org>. DOI: 10.1021/jo00250a032.
- Sakaguchi, S., Nishiyama, Y. & Ishii, Y. (1996). Selective oxidation of monoterpenes with hydrogen peroxide catalyzed by peroxotungstophosphate (PCWP). *J. Org. Chem.* 61, 5307–5311. Retrieved March 15, 2013, from <http://pubs.acs.org>. DOI: 10.1021/jo960275q.
- Młochowski, J. (1994). *Chemistry of heterocyclic compounds*, Warszawa, Wydawnictwo Naukowe PWN (in Polish).
- Zhao, W., Ding, Y., Zhang, Zh., Ma, B., Qiu, W. (2011).  $[(C_{18}H_{37})_2(CH_3)_2N]_7[PW_{11}O_{39}]$ : a temperature-controlled phase transfer catalyst for olefin epoxidation. *Reac. Kinet. Mech. Cat.* 102, 93–102. DOI: 10.1007/s11144-010-0242-7.
- Mahha, Y., Salles, L., Piquemal, J.M., Briot, E., Atlamsani, A., Brégeault, J.M. (2007). Environmentally friendly epoxidation of olefins under phase-transfer catalysis conditions with hydrogen peroxide. *J. Catal.*, 249, 338–348. DOI: 10.1016/j.jcat.2007.05.001.
- Lewandowski, G. (2001). Cyclotrimerization of 1,3-butadiene to 1,5,9-cyclododecatriene. Synthesis of cyclododecane and cyclooctadiene. *Przem. Chem.*, 80 (11), 507–513 (in Polish).
- Lewandowski, G. & Rytwińska, E. (2006). Reactions and applications of *trans*-1,2-epoxy-(*Z,E*)-cyclododeca-5,9-diene. *Chem. Pap.* 60 (2), 160–168. DOI: 10.2478/s11696-006-0029-5.
- Gruszkowska, E. & Lewandowski, G. (2004). Epoxidation of 1,5,9-cyclododecatriene (CDT) to 1,2-epoxy-5,9-cyclododecadiene (ECDD). *Przem. Chem.* 83 (11), 559–563 (in Polish).