

Epoxidation of 1,4-bis(allyloxy)butane by hydrogen peroxide using phase transfer catalysis

E. Kaczmarczyk*, E. Janus, E. Milchert

Institute of Organic Chemical Technology, Szczecin University of Technology, Pulaskiego 10, 70-322 Szczecin, Poland

Received 29 June 2005; received in revised form 30 June 2005; accepted 12 September 2005

Available online 13 October 2005

Abstract

Epoxidation of 1,4-bis(allyloxy)butane by hydrogen peroxide under phase transfer catalysis and transition metal salts was investigated. The most advantageous conditions for the epoxidation were determined (temperature, reaction time, the type and amount of phase transfer catalyst, molar ratio of hydrogen peroxide to 1,4-bis(allyloxy)butane, the amount and molar ratio of $\text{H}_3\text{PO}_4:\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$). The process was evaluated in terms of the conversion of 1,4-bis(allyloxy)butane, hydrogen peroxide and the yields of monoepoxide and diepoxide.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Epoxidation; Hydrogen peroxide; Phase transfer catalysis; Epoxy-ethers

1. Introduction

The application of phase transfer catalysis (PTC) enables the preparation of a number of epoxy compounds impossible to obtain by other methods, or considerable improvement of the yields of those currently prepared. This concerns particularly the compounds containing the electron withdrawing substituents in the neighbourhood of the double bond such as: $-\text{Cl}$, $-\text{Br}$, $-\text{CN}$, $-\text{OH}$, $-\text{NO}_2$, or with the ethylene bond at the end of aliphatic chain [1].

In the epoxidation with PTC technique, an unsaturated compound is present in a non-polar organic solvent, whereas hydrogen peroxide in the aqueous phase. The phase transfer catalyst in the form of quaternary onium salt $[\text{Q}^+\text{X}^-]$ transfer the HO_2^- anion to an organic layer in the form of ionic couple OH^- and HO_2^- . In this phase, a rapid reaction proceeds and the catalyst cation returns to the interphase with the OH_2^- anion. Here, the ion-exchange of OH^- to HO_2^- takes place [2]. This process is modified by the epoxidation catalyst in the form of complexes of the transition metals (W, V, Mo and Ti) [3].

The epoxidation of 1,4-bis(allyloxy)butane by hydrogen peroxide in the presence of onium salt as the phase transfer catalyst as well as 40 wt% orthophosphoric acid and sodium tungstate

dihydrate creates the possibility of development of new useful compounds. In this process, the transition metal under the influence of hydrogen peroxide passes on a higher oxidation state. The most often used metallic catalysts of the oxidation in the presence of hydrogen peroxide and the phase transfer catalyst are Mo(VI) and W(VI) compounds.

The epoxy compounds on the basis of allylic ethers create the possibility of preparation of highly reactive connections also of an industrial importance. Beside the glycidyl group bounded with etheric oxygen, the epoxy compounds may contain second glycidyl group.

The application of allylic ethers as the monomers is well known [4], especially in the production of varnishes with a high hardness and the resistance on the action of solvents.

They are used for the modification of properties of other polymers, e.g. in the production the drying in the open air polyester resins and protective coatings, and also the fibers which are characterized by a good dyeability. The compounds with the glycidyl etherically bounded are used as flame retardant [5] and they are the raw material for production of valuable intermediates such as, e.g. Polyhedral Oligomeric Silsequioxane (POSS), utilized in the production of reinforcing plastics compounds [6]. Shell firm applies 1,4-bis(glycidylloxy)butane under the trade name Heloxy 67 in the synthesis of agent reinforcing the glass fiber [7]. The same compound under the trade name Araldit DY [8] is used in the production of polymeric composites.

* Corresponding author. Tel.: +48 91 449 4584; fax: +48 91 449 4365.
E-mail address: Elzbieta.Kaczmarczyk@ps.pl (E. Kaczmarczyk).

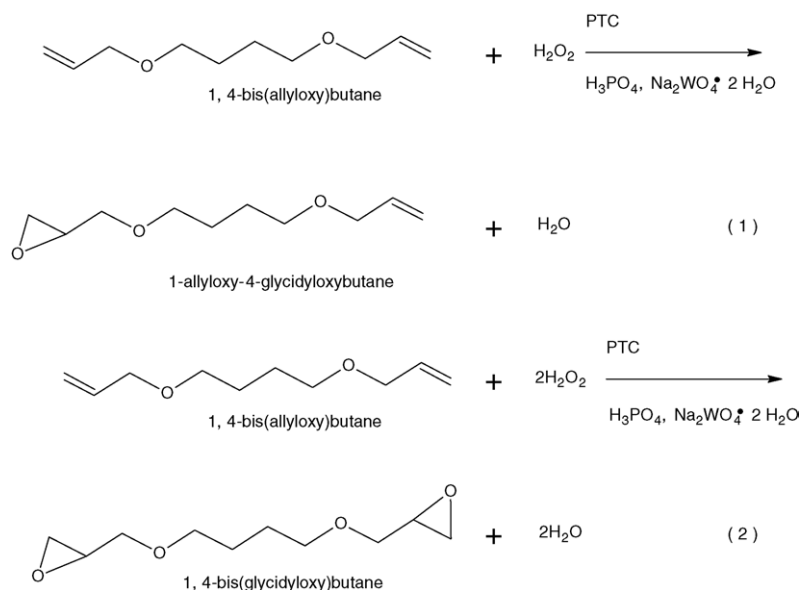


Fig. 1. Reactions proceeding in the process.

The objective of these studies was to determine the technological parameters of epoxidation of 1,4-bis(allyloxy)butane by hydrogen peroxide in the presence of 40 wt% orthophosphoric acid and sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) under the conditions of phase transfer catalysis.

The influence of the molar ratio of hydrogen peroxide to 1,4-bis(allyloxy)butane (DiAB) and orthophosphoric acid to sodium tungstate dihydrate, temperature, the nature of solvent and phase transfer catalyst on the epoxidation of 1,4-bis(allyloxy)butane to 1-allyloxy-4-glycidyloxybutane (monoxide) and 1,4-bis(glycidyloxy)butane (diepoxide) was determined in the performed studies. The results of previous investigations of epoxidation of compounds with a similar structure and the chemical and physical properties were taken as a basis in the selection of the reaction parameters.

The reactions proceeding in the process can be described by the equations in Fig. 1.

The hydrogen peroxide is becoming increasingly common used in the oxidation processes because it is a cheap raw material, readily available and is ecological. The only by-product of its transformations is water. The use of hydrogen peroxide in the oxidation processes by the method of phase transfer catalysis creates the possibility of development of new technological processes or syntheses of new compounds. The advantage of this method is versatility because it can be used for preparation of various epoxides including epoxy-ethers. Its advantage is competitiveness in relation to the processes carried out under the homogeneous conditions, first of all with regards on:

- elimination of expensive and anhydrous, polar, aprotic solvents, often required in a such type of the reactions. These solvents can be replaced with considerably cheaper, non-polar solvents;
- milder conditions of process operation;
- easier methodology of work.

Moreover, hydrogen peroxide can be used instead of the aggressive oxidants, thereby this method is very economical and ecological thus becoming an example of “green chemistry”.

It results from the previous studies of epoxidation of selected olefines and allylic compounds by hydrogen peroxide under PTC [9–12] conditions that the process depends on the following parameters: amount of 30% hydrogen peroxide, concentration and the type of the PT catalyst, process temperature and time of reaction, intensity of mixing, molar ratio of transition metal salts to orthophosphoric acid(V).

2. Experimental

2.1. Materials

The hydrogen peroxide with a concentration of 30% from POCh Gliwice, methyltrioctylammonium chloride ($\text{CH}_3\text{N}[(\text{CH}_2)_7\text{CH}_3]_3\text{Cl}$) under the trade name Aliquat[®]336 from Aldrich. Tetrabutylammonium bromide (Bu_4NBr), *n*-dodecyltrimethylammonium bromide ($\text{Me}_3\text{NC}_{12}\text{H}_{25}\text{Br}$), hexadecyltrimethylammonium bromide ($\text{Me}_3\text{NC}_{16}\text{H}_{33}\text{Br}$) and sodium tungstate dihydrate(VI) $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ pure 99% were purchased from Merck. Orthophosphoric acid(V) concentration 85 wt% from Lachema. DiAB was prepared according to the method described in the literature [13,14]. Chloroform, toluene, benzene, *n*-hexane, cyclohexane and dichloromethane with analytical grade were purchased from POCh Gliwice. The solvents were used without a further purification.

2.2. Analytical methods

A gas chromatograph Carlo Erba GC 8000, equipped with capillary column DB 17 (50% phenylmethylpolysiloxane), J&W (30 m × 0.25 mm × 0.25 μm) and the FID detector was used. The temperature of thermostate was programmed in

the following way: 3 min at the initial temperature 40 °C, an increase with a rate of 10° min⁻¹ to 120 °C and 5 min at this temperature, subsequent to an increase with a rate of 10° min⁻¹ to 200 °C and 20 min at this temperature. The total analysis time amounted to 44 min. The concentration of DiAB, 1-allyloxy-4-glycidyoxybutane (monoepoxide) and 1,4-bis(glycidyoxy)butane (diepoxide) was determined by this method.

The concentration of hydrogen peroxide in the water phase was determined by means of iodometric titration.

Monoepoxide identification was presented earlier [15]. The results identification of diepoxide by nuclear magnetic resonance ¹H NMR and ¹³C NMR are as follows:

¹H NMR (CDCl₃; ppm): δ = 3.74–3.71 (dd, ³J = 11.5 Hz, ²J = 3 Hz, 2H_a, oxirane group—CH₂—O—), 3.56–3.48 (m, 4H, —O—CH₂—CH₂—), 3.39–3.34 (dd, ³J = 11.4 Hz, ²J = 6 Hz, 2H_b,

oxirane group—CH₂—O—), 3.16–3.12 (m, 2H,

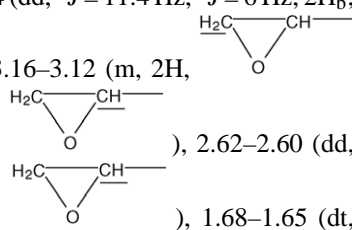
), 2.79 (t, ³J = 4.8 Hz, 2H_E,

³J = 5 Hz, ²J = 2.7 Hz, 2H_Z,

¹³C NMR (CDCl₃; ppm): δ = 71.4 (O—CH₂—oxirane group),

7.2 (—CH₂—O—CH₂—oxirane group), 50.9 (

44.2 (



2.3. Mode of synthesis

Syntheses were carried out in a glass reactor, with capacity of 25 ml immersed in the oil bath, at temperature of 30, 40, 50 or 60 °C, equipped with magnetic stirrer, thermometer and a reflux condenser. The reactor was charged with 0.875 mmol of sodium tungstate dihydrate(VI) and a such amount of 40 wt% orthophosphoric acid so that the appropriate molar

ratio of H₃PO₄ to Na₂WO₄·2H₂O (0.5:1, 1:1, 2:1, 3:1, 4:1 and 5:1) was maintained. Subsequently, a 30 wt% hydrogen peroxide was gradually added at the appropriate molar ratio resulting from the studies in relation to DiAB. In the case of processes performed in the presence of auxiliary solvent it was added in a volume of 5 cm³. The solvent facilitated the separation of organic and water layer. In all experiments, the same amount 18 mmol of 1,4-bis(allyloxy)butane as well as 0.35 mmol PT catalyst Aliquat[®]336 were applied. All experiments were carried for 2 h with vigorous stirring. After completing the reaction, the water and organic phase, were separated.

3. Results and discussion

The advancement of reaction was determined on the basis of GC analysis of the post-reaction mixture. The conversions of DiAB and the yields of 1-allyloxy-4-glycidyoxybutane (monoepoxide) and 1,4-bis(glycidyoxy)butane (diepoxide) were calculated. The conversions were calculated from the amount of raw material H₂O₂ or DiAB in the post-reaction mixture in relation to the amount introduced into the reactor, expressed in grams. The yield of monoepoxide or diepoxide was calculated from the amount determined for each one in relation to DiAB introduced to the reactor.

3.1. The influence of the molar ratio of H₃PO₄ to Na₂WO₄·2H₂O

In the first order the influence of molar ratio H₃PO₄ to Na₂WO₄·2H₂O was determined, carrying out the epoxidation of DiAB by 30% hydrogen peroxide without the addition of solvent, in the presence of Aliquat[®]336, as the phase transfer catalyst at 60 °C (Table 1).

When the molar ratio of orthophosphoric acid to sodium tungstate was increased from 0.5:1 to 3:1 a continuous increase of hydrogen peroxide conversion from 40 to 91% and DiAB conversion from 66 to 99% took place. A further increase of the amount of acid did not cause any changes of H₂O₂ conversion. However at the three-, four- and five-fold larger amount of

Table 1

Influence of the molar ratio of H₃PO₄ to Na₂WO₄·2H₂O on the epoxidation of 1,4-bis(allyloxy)butane by 30 wt% hydrogen peroxide in the presence of Aliquat[®]336 as PT catalyst^a

Experiment no.	Molar ratio		Conversion (wt%)		Yield of products (wt%)	
	H ₃ PO ₄ :Na ₂ WO ₄ ·2H ₂ O	H ₂ O ₂ :DiAB	H ₂ O ₂	DiAB	Monoepoxide	Diepoxide
1	0.5:1	2:1	40	56	17	2
2	1:1	2:1	57	78	18	2
3	2:1	2:1	82	88	27	6
4	3:1	2:1	91	94	14	10
5	4:1	2:1	90	98	<1	11
6	5:1	2:1	91	97	<1	30
7	2:1	3:1	53	99	5	2
8	2:1	4:1	42	91	14	4

^a The reactions were carried out by using 18 mmol of DiAB, 0.35 mmol of PT catalyst, 0.87 mmol of Na₂WO₄·2H₂O, temperature 60 °C, monoepoxide-(1-allyloxy-4-glycidyoxybutane), diepoxide-(1,4-bis(glycidyoxy)butane).

the moles of phosphoric acid than that of tungstate, the analyses exhibited a small amount of monoepoxide and an increase of the amount of diepoxide 1,4-bis(allyloxy)butane. Moreover, the post-reactions mixtures were monophased in these cases. The addition of 5 cm³ of chloroform to such a mixture enables the separation into the two phases. This testifies about a partial hydration of formed epoxy compounds to polyhydric alcohols and their transferring to the water layer. The presence of this type of connections was confirmed by the determination of glycols by the periodic method [14]. The molar ratio of H₃PO₄ to Na₂WO₄·2H₂O = 2:1 was determined as the optimum in the epoxidation of 1,4-bis(allyloxy)butane. This ratio ensures a high conversion of both substrates as well as the highest yield of products.

The studies were also performed at the molar ratio of H₃PO₄ to Na₂WO₄·2H₂O = 2:1 while the ratio of H₂O₂ to DiAB was increased to, respectively, 3:1 and 4:1 (experiments 7 and 8, Table 1). In these experiments were found that an increase of the quantity of H₂O₂ in relation to DiAB did not cause a significant increase of the yield of epoxidation products. Despite almost a quantitative conversion of the organic substrate it is difficult to separate the organic phase from the post-reaction mixture. This separation was possible after the addition of 4 ml of benzene to each of post-reaction mixture and cooling to 0 °C. The yields of obtained products were small.

3.2. The influence of the nature of solvent

The epoxidation with the molar ratio of H₃PO₄ to Na₂WO₄·2H₂O = 2:1 creates the possibility of a favourable realization of process. A high conversion of H₂O₂ and DiAB as well as satisfactory yields of monoepoxide and diepoxide was then achieved. In relation to these results the influence of the nature of aprotic solvents on the course of process was investigated. The same volume of the solvent (5 cm³) was applied in all experiments. Each of the solvents ensured the two-phase reaction system. The influence of the presence of the following solvents: dichloromethane, chloroform, *n*-hexane, cyclohexane, benzene and toluene in the reaction medium were investigated. The results are shown in Figs. 2 and 3.

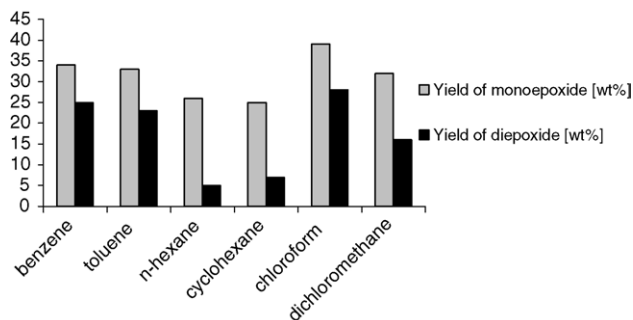


Fig. 2. Yields of 1-allyloxy-4-glycidyoxybutane (monoepoxide) and 1,4-bis(glycidyoxy)butane (diepoxide) in different kinds of solvent (18 mmol DiAB, 36 mmol H₂O₂, 0.35 mmol of PT catalyst, 0.87 mmol of Na₂WO₄·2H₂O and 5 cm³ of solvent).

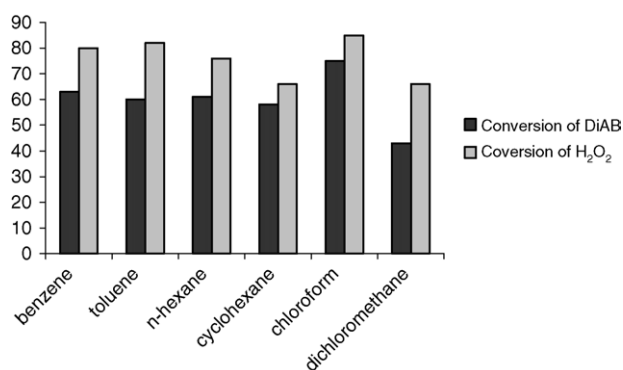


Fig. 3. The influence of kind of solvent on the conversions (wt%) of H₂O₂ and DiAB (18 mmol DiAB, 36 mmol H₂O₂, 0.35 mmol of PT catalyst, 0.87 mmol of Na₂WO₄·2H₂O and 5 cm³ of solvent were used).

As results from this comparison the highest conversion of DiAB and the yields of monoepoxide and diepoxide was achieved in the presence of chloroform. Other solvents (benzene, toluene, cyclohexane and *n*-hexane) ensure the similar values of the conversion of H₂O₂ and DiAB, a slightly lower yield of monoepoxide and a considerably lower yield of diepoxide. This is caused by their considerably lower polarity (Fig. 3).

3.3. The influence of the molar ratio H₂O₂:DiAB

In the subsequent experiments, the effect of increasing the molar ratio of H₂O₂ to DiAB and the amount of introduced Na₂WO₄·2H₂O on the process performed in the presence of chloroform was determined. In these studies, the molar ratio of H₃PO₄ to Na₂WO₄·2H₂O = 2:1 was maintained. Increasing the molar ratio of H₂O₂:DiAB from 2:1 to 4:1 (experiments 1–3, Table 3) an improvement in the conversion of DiAB and diepoxide yields was observed. The epoxidation was also carried out at two- and four-fold larger amount of H₃PO₄ to Na₂WO₄·2H₂O in relation to that used in previously described investigations. These experiments were performed at the molar ratios of H₂O₂ to DiAB of both 2:1 and 4:1 (Table 3). A significant improvement in the selectivity of transformation of DiAB in the direction of diepoxide occurred of the molar ratio of H₂O₂:DiAB = 1:4 simultaneously with the molar ratio of H₃PO₄:Na₂WO₄·2H₂O = 8:4. In order to achieve high yields of monoepoxide and diepoxide it is necessary to maintain at least a two-fold molar excess of H₂O₂ to DiAB and H₃PO₄ to Na₂WO₄·2H₂O, so that the molar ratio of H₂O₂:DiAB:H₃PO₄:Na₂WO₄·2H₂O should amount to at least 2:1:4:2. A larger excess of H₂O₂, H₃PO₄ and Na₂WO₄·2H₂O, thus, the molar ratio of H₂O₂:DiAB:H₃PO₄:Na₂WO₄·2H₂O = 4:1:8:4 enhances the diepoxide yield, but monoepoxide yield is small (Table 2, experiments 3 and 7).

3.4. The influence of the temperature

In the subsequent stage of the studies the influence of temperature on the course of process was examined. The Aliquat[®]336 as PT catalyst and 5 cm³ of chloroform

Table 2

The influence of the molar ratio of H₂O₂ to DiAB and H₃PO₄ to Na₂WO₄·2H₂O on the epoxidation of 1,4-bis(allyloxy)butane in the presence of chloroform and Aliquat[®]336, temperature 60 °C^a

Experiment no.	Molar ratio		Conversion (wt%)		Yield of products (wt%)	
	H ₂ O ₂ :DiAB	H ₃ PO ₄ :Na ₂ WO ₄ ·2H ₂ O	H ₂ O ₂	DiAB	Monoepoxide	Diepoxide
1	2:1	2:1	75	85	39	28
2	3:1	2:1	58	87	30	31
3	4:1	2:1	42	92	33	34
4	2:1	4:2 ^b	82	94	28	46
5	4:1	4:2 ^b	55	91	33	34
6	2:1	8:4 ^c	88	91	29	27
7	4:1	8:4 ^c	86	95	9	54

^a The reactions were carried out by using 18 mmol of DiAB, 0.35 mmol of PT catalyst, 0.87 mmol of Na₂WO₄·2H₂O and 5 cm³ of solvent.

^b 1.74 mmol Na₂WO₄·2H₂O.

^c 3.48 mmol Na₂WO₄·2H₂O, monoepoxide-(1-allyloxy-4-glycidioxybutane) and diepoxide-(1,4-bis(glycidioxy)butane).

Table 3

Influence of temperature on the epoxidation of 1,4-bis(allyloxy)butane in the presence of chloroform as solvent and Aliquat[®]336 as PT catalyst^a

Experiment no.	Temperature (°C)	Molar ratio		Conversion (wt%)		Yield of products (wt%)	
		H ₂ O ₂ :DiAB	H ₃ PO ₄ :Na ₂ WO ₄ ·2H ₂ O	H ₂ O ₂	DiAB	Monoepoxide	Diepoxide
1	60	2:1	2:1	75	85	39	28
2	60	4:1	8:4 ^b	86	95	9	54
3	50	2:1	2:1	67	90	33	57
4	50	4:1	8:4 ^b	61	98	19	79
5	40	2:1	2:1	45	72	43	29
6	40	4:1	8:4 ^b	40	87	41	46
7	30	2:1	2:1	40	87	43	29
8	30	4:1	8:4 ^b	12	50	29	6

^a The reactions were carried out by using 18 mmol of DiAB, 0.35 mmol of PT catalyst and 0.87 mmol of Na₂WO₄·2H₂O.

^b 3.48 mmol Na₂WO₄·2H₂O, monoepoxide-(1-allyloxy-4-glycidioxybutane) and diepoxide-(1,4-bis(glycidioxy)butane).

as an auxiliary solvent were used in all experiments. As shown in Table 3, the highest conversion of DiAB and the highest yields of products (monoepoxide and diepoxide) were achieved at temperature of 50 °C at the molar ratios of H₂O₂:DiAB = 4:1 and H₃PO₄:Na₂WO₄·2H₂O = 8:4. The highest yields of monoepoxide (43 wt%) was achieved at the temperatures of 30 and 40 °C and the molar ratio of H₂O₂:DiAB:H₃PO₄:Na₂WO₄·2H₂O = 2:1:2:1. Whereas the highest yield of diepoxide was achieved at temperature of 50 °C. This yield amounts 79 wt% at the molar ratio of H₂O₂:DiAB:H₃PO₄:Na₂WO₄·2H₂O = 4:1:8:4. An increase of the H₂O₂ conversion during elevation of temperature was partly caused by thermal decomposition. A simultaneous increase of DiAB conversion and the yields of products (monoepox-

ide and diepoxide) testify about the progress of desirable reactions.

3.5. The influence of the type of PT catalyst

The influence of the type of phase transfer catalyst on the epoxidation of DiAB by this method was also compared (Table 4). Each of used ammonium salts demonstrates the activity in the studied process of epoxidation. The formation of epoxidation products was not found without the ammonium salt. The best results were achieved in the presence of Aliquat[®]336, the ammonium salt containing three octyl and one methyl substitutes at the nitrogen. The remaining catalysts were found to be less active in the studied process. They caused a much smaller

Table 4

Influence of type of PT catalyst on the epoxidation of 1,4-bis(allyloxy)butane^a, the molar ratio H₃PO₄:Na₂WO₄·2H₂O = 2:1 and H₂O₂:DiAB = 2:1, temperature 60 °C

Experiment no.	PT catalyst	Conversion (wt%)		Yield of product (wt%)	
		H ₂ O ₂	DiAB	Monoepoxide	Diepoxide
1	Bu ₄ NBr	77	42	10	1
2	Me ₃ NC ₁₂ H ₂₅ Br	33	49	23	5
3	Me ₃ NC ₁₆ H ₃₃ Br	38	57	28	6
4	CH ₃ N[(CH ₂) ₇ CH ₃] ₃ Cl, Aliquat [®] 336	75	85	39	28

^a The reactions were carried out by using 18 mmol of DiAB, 0.87 mmol of Na₂WO₄·2H₂O, 5 cm³ of chloroform and PT catalyst 0.35 mmol, monoepoxide-(1-allyloxy-4-glycidioxybutane) and diepoxide-(1,4-bis(glycidioxy)butane).

conversion both DiAB and hydrogen peroxide. Such a type of behavior results from different surface activity of used PT catalysts. The surface tension was the most reduced by Aliquat[®] 336, thus results its highest activity.

4. Conclusion

In the epoxidation of DiAB by means of 30% H₂O₂ in presence of methyltrioctylammonium chloride as the phase transfer catalyst and the epoxidation catalyst Na₂WO₄·2H₂O, in the presence of orthophosphoric acid and an auxiliary solvent-chloroform 1-allyloxy-4-glycidyoxybutane (monoepoxide) and 1,4-bis(glycidyoxy)butane (diepoxide) are obtained with high yields.

The most advantageous conditions of epoxidation to monoepoxide are the following: temperature 40 °C, molar ratio of H₂O₂:DiAB:H₃PO₄:Na₂WO₄·2H₂O = 2:1:2:1, the PT catalyst in the amount of 2 mol% in relation to DiAB, chloroform in the amount of 240 wt% in relation to DiAB, reaction time 2 h. Under these conditions, the yield of monoepoxide amounts is 43 wt%, whereas diepoxide is 29 wt%. Simultaneously, the H₂O₂ conversion amounts 45 wt% and DiAB 72 wt%. An increase of the molar ratio of H₂O₂:DiAB to 4:1 and H₃PO₄:Na₂WO₄·2H₂O to 8:4 gives higher yield of diepoxide 46 wt%. The remaining magnitudes (conversion, monoepoxide yield) are close to the previously ones.

However, the highest yields of diepoxide equal to 79 wt% is achieved at temperature 50 °C, at the molar ratio of H₂O₂:DiAB:H₃PO₄:Na₂WO₄·2H₂O = 4:1:8:4. The remaining conditions of process operation are identical. Monoepoxide is formed with the yield of 19 wt%.

References

- [1] Z. Xi, N. Zhou, Y. Sun, K. Li, *Science* 292 (2001) 1139.
- [2] Y. Ishii, K. Yamawaki, T. Ura, H. Yamada, T. Yoshida, M. Ogawa, *J. Org. Chem.* 53 (1988) 3587.
- [3] I.W.C.E. Arens, R.A. Sheldon, *Top. Catal.* 19 (2002) 133.
- [4] M. Antoszczyszyn, E. Janus, D. Martysz, *Ekoplast* 17 (2000) 25.
- [5] J.V. Crivello, R. Malik, *J. Polym. Sci. Chem.* 35 (1997) 407.
- [6] S.-Y. Lu, I. Kamerton, *Prog. Polym. Sci.* 27 (2002) 1661.
- [7] A. Lee, J.D. Lichtenhan, *Macromolecules* 3 (1998) 49701.
- [8] M.H. Lamm, T. Chen, S.C. Glotzer, *Nano Lett.* 3 (2003) 8.
- [9] C. Venturello, R. D'Aloisio, *J. Org. Chem.* 53 (1998) 1553.
- [10] J. Prandi, H.B. Kagan, H. Mimosoun, *Tetrahedron Lett.* 27 (1988) 2617.
- [11] C. Venturello, E. Alneri, M. Ricci, *J. Org. Chem.* 48 (1983) 3831.
- [12] N. Rieber, R. Fischer, H.-M. Wertz, EP 0151289 (1984) to BASF AG.
- [13] M. Antoszczyszyn, E. Janus, M. Urbala, *Pol. J. Appl. Chem.* XLIII (1) (1999) 77.
- [14] M. Antoszczyszyn, M. Urbala, E. Janus, *Comptes Rendus de l'Académie Bulgare des Sciences*, 7–8 (39) (1999) 52.
- [15] E. Kaczmarczyk, E. Janus, E. Milchert, *J. Mol. Catal. A* 235 (2005) 52.