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Selective epoxidation of 1,4-bis(allyloxy)butane to 1-allyloxy-glycidoloxybutane in the presence of ionic liquids

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Abstract

The course of epoxidation of 1,4-bis(allyloxy)butane with hydrogen peroxide in the presence of $H_3PO_4/Na_2WO_4 \cdot 2H_2O$ or heteropolyacids: $H_3PW_{12}O_{40}$ and $H_3PM_{012}O_{40}$ as the catalysts and the ionic liquids as the phase transfer catalysts (cocatalysts) has been investigated. Imidazolium lactates and salicylates with *N*-alkyl or alkoxy substitute with different length were used as the cocatalysts. The influence of the kind and amount of catalyst on the yield of 1-allyloxy-4-glycidoloxybutane has been determined.

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1. Introduction

The application of hydrogen peroxide for the oxidation of organic compounds can be very beneficial from a point of view of both technology and the chemical synthesis. Hydrogen peroxide is relatively inexpensive, environmentally friendly and safe. The epoxidation of unsaturated compounds with the ethylene bond using a 30 wt% solution of H₂O₂ can be carried out in the presence of molybdenum and tungsten compounds as the catalysts and under the conditions of phase transfer catalyst (PTC). The quaternary onium salts (ammonium, phosphonium), including ionic liquids containing in the molecule a quaternary nitrogen atom can be used as the phase transfer catalysts (cocatalysts).

In accordance with the studies performed by Venturello and Ishii [1–5], the epoxidation catalyst with the Keggin structure is formed in the presence of hydrogen peroxide from the mixture of phosphoric acid (H_3PO_4) and sodium tungstate or in the presence of heteropolyacids ($H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$). A phase transfer cocatalyst performs a role of agent transporting the epoxidation species from the aqueous phase to the organic phase, where the organic reagent is present. The most frequently used cocatalysts include the quaternary onium salts—mainly methyl-trioctylammonium chloride (trade name Aliquat[®] 336) [6–8].

In the presented studies was used an active catalytic system composed of $H_3PO_4/Na_2WO_4 \cdot 2H_2O$ or the heteropolyacids (HPA) together with the ionic liquids. There has been no information concerning the application of ionic liquids as the cocatalysts in the epoxidation process using a 30 wt% aqueous solution of hydrogen peroxide.

The objective of the performed studies was to determine the influence of the kind and amount of PT cocatalyst on the epoxidation of 1,4-bis(allyloxy)butane (DiAB). It results from previous work [9] that the epoxidation of DiAB in the presence of Aliquat[®]336 leads to a mixture of 1-allyloxy-4-glycidoloxybutane (monoepoxide) and 1,4bis(glycidoloxy)butane (diepoxide). The application of ionic liquids instead of Aliquat[®]336 improves the selectivity of transformation. The only product is 1-allyloxy-4-glycidoloxybutane (Fig. 1).

2. Experimental

2.1. Materials and reagents

Hydrogen peroxide with concentration of 30 wt% was purchased from POCh Gliwice, whereas methyltrioctylammonium chloride (CH₃N[(CH₂)₇CH₃]₃Cl) under the trade name Aliquat[®]336 was from Aldrich. Sodium tungstate(VI) dihydrate Na₂WO₄·2H₂O pure 99% from Merck. Phosphorous(V)

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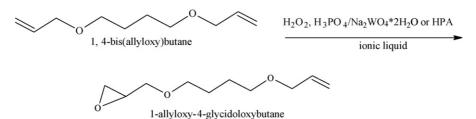


Fig. 1. The course of reaction in the studied process.

acid with concentration of 85 wt% was from Lachema. The heteropolyacids: $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ were purchased from Fluka. Chloroform from POCh Gliwice was used without further purification. 1,4-Bis(allyloxy)butane (DiAB) was obtained according to the method described in the literature [10,11]. The ionic liquids—lactates 3-alkil-1H-imidazolium and lactates and salicylates of 3-alkoxymethyl-1H-imidazolium were obtained according to the method described in the literature [12].

2.2. Analytical methods

The concentrations of organic compounds were determined by gas chromatography method. The analyses were performed using a SRI 8610 gas chromatograph equipped with a DB-5 column (5%-(phenyl)methylpolysiloxane) J&W ($30 \text{ m} \times 0.53 \text{ mm} \times 1.5 \mu \text{m}$) and the FID detector. The thermostat temperature was programmed in the following way: 1 min at temperature 50 °C, ramping the temperature at 10 °C/min to 200 °C, 2 min isothermally, subsequently ramping the temperature at 20 °C/min to 250 °C, consecutive ramping at 25 °C/min to 280 °C and isothermally at 10 min. The total time of analysis amounted to 31.7 min.

2.3. Epoxidation reaction

The syntheses were carried out in a glass reactor of 100 cm^3 capacity, equipped with a magnetic stirrer and a reflux condenser. The reactor was immersed in the oil bath at the temperature $50 \,^{\circ}$ C. The reactor was charged with an appropriate amount of sodium tungstate(VI) dihydrate and a 40 wt% *o*-phosphorous(V) acid in such amount, that the molar ratio of Na₂WO₄·2H₂O to H₃PO₄ amounted to 1:2. In the case of the process carried out in the presence of HPAs, they were used in the amount of 0.6 mol% in relation to the organic reagent. Subsequently, a 30 wt% hydrogen peroxide and DiAB were added, so that the molar ratio of H₂O₂ to DiAB was maintained at 4:1. The ionic liquids were used in the amount of: 2, 4, 6, 8 and 10 mol% in relation to DiAB. The reactions were carried out in the presence of an auxiliary solvent—chloroform.

Samples for chromatographic analysis (GC) were collected after mixing the reagents, then every hour. The quantity determinations were carried out by a method of internal standard. The quantitative determinations of 1,4-bis(allyloxy)butane were utilized for the calculations of its conversion. The conversion was calculated from the amount of consumed DiAB in relation to 1,4-bi(allyloxy)butane introduced into the reaction. The yield of monoepoxide was calculated on the basis of its determined amount in relation to 1,4-bis(allyloxy)butane introduces into the reaction.

3. Results and discussion

3.1. Epoxidation of 1,4-bis(allyloxy)butane in the presence of $H_3PO_4/Na_2WO_4 \cdot 2H_2O$ and the ionic liquids as catalyst

The epoxidation of 1,4-bis(allyloxy)butane was initially carried out in the presence of the catalytic system composed of $H_3PO_4/Na_2WO_4.2H_2O$ and the ionic liquid performing a role of cocatalyst.

The active epoxidation catalyst in this system is formed in situ under the action of H_2O_2 . In the previous studies with Aliquat[®]336 as the cocatalyst (phase transfer catalyst) [13] it has been established that the discussed reaction proceeds the most advantageously in the presence of a small amount of chloroform as an auxiliary solvent. The following technological parameters have been established: temperature, molar ratio of reagents, reaction time which leads to the highest yield of products. In the presence of Aliquat®336, a mixture of 1-allyloxy-4glycidoloxybutane and 1,4-bis(glycidoloxy)butane was always obtained. Depending on the conditions of process operation, the amount of one of the epoxides predominated in the mixture. In this work the ionic liquids from a group of imidazolium salts (Fig. 2) were used instead of Aliquat[®] 336. The imidazolium lactates and salicylates with alkyl or alkoxyalkyl substitute (with different length) at one nitrogen of the imidazolium ring.

These salts were used in the amount of 2 mol% in relation to DiAB. A comparison of the ionic liquid activities with the different chemical structure used in the epoxidation process studied was presented in Table 1.

Among used imidazolium salts, only those that contained the alkyl or alkoxy substitutes with at least nine carbon atoms in the chain were found to catalyse the epoxidation of 1,4bis(allyloxy)butane. In the presence of 3-decyloxymethyl-1H-

$ \begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & $		
$R_1=H; R_2=C_4H_9-, C_7H_{17}-, C_{10}H_{21}-;$	X ⁻ =lactate	
R ₁ =H; R ₂ =C ₄ H ₉ OCH ₂ -, C ₄ H ₉ OCH ₂ -;	X ⁻ =lactate	
R ₁ =H; R ₂ = C ₄ H ₉ OCH ₂ -, C ₆ H ₁₃ OCH ₂ -, C ₉ H ₁₉ OCH ₂ -;	X ⁻ =salicylate	

Fig. 2. Imidazolium salts used in these studies.

Table 1	
Comparison of ionic liquid activities in the epoxidation of 1,4-bis(allyloxy)butane	

IL	Conversion of DiAB (wt%)	Conversion of H ₂ O ₂ (wt%)	Yield of monoepoxide (wt%)	
[C ₄ H ₉ OCH ₂ HIm][lactate]	<1	22	_	
$[C_6H_{13}OCH_2HIm][lactate]$	<1	34	_	
[C ₁₀ H ₂₁ OCH ₂ HIm][lactate]	39 (45) ^a	31	$27(32)^{a}$	
$[C_4H_9HIm][lactate]$	<1	29	_	
[C ₇ H ₁₅ HIm][lactate]	<1	41	-	
[C ₁₀ H ₂₁ HIm][lactate]	9 (21) ^a	24	$5(18)^{a}$	
[C ₄ H ₉ OCH ₂ HIm][salicylate]	_	32	_	
[C ₆ H ₁₃ OCH ₂ HIm][salicylate]	<1	32	_	
[C ₉ H ₁₉ OCH ₂ HIm][salicylate]	37 (39) ^a	37	29 (35) ^a	
Without ionic liquid	_	17	-	
Aliquat [®] 336	91 (93) ^a	42	56 ^b	

Reaction conditions: 18 mmol of DiAB; molar ratio of Na_2WO_4 ·2H₂O:DiAB 1:21; Na_2WO_4 ·2H₂O:H₃PO₄ 1:2; DiAB:H₂O₂ 1:4; ionic liquid in the amount of 2 mol% in relation to DiAB; temperature 50 °C, reaction time 4 h. HIm: 1H-imidazolium, IL: ionic liquid.

^a Values given in parentheses were determined after reaction time of 24 h.

^b Yield of 1,4-bis(glycidoloxy)butane amounted to 14 wt%.

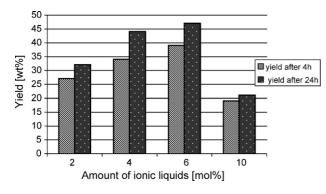


Fig. 3. The influence of the amount of ionic liquid $[CH_2OC_{10}H_{21}HIm][lactate]$ on the yield of 1-allyloxy-4-glycidoloxybutane (*Reaction conditions*: 18 mmol of DiAB; molar ratio of Na₂WO₄·2H₂O:DiAB 1:21; Na₂WO₄·2H₂O:H₃PO₄ 1:2; DiAB:H₂O₂ 1:4; temperature 50 °C, reaction time 4 h).

imidazolium lactate and 1H-3-nonyloxymethylimidazolium salicylates the yield of monoepoxide was close to 30 wt% after 4 h of the reaction time and practically did not change after the prolongation of the reaction time up to 24 h.

A lower monoepoxide yield (5 wt%) and DiAB conversion (9 wt%) was achieved in the presence of 3-decyl-1Himidazolium lactate. In this case, a prolongation of the reaction time up to 24 h caused almost four-fold increase in the yield (to 18 wt%) and over a two-fold increase in the DiAB conversion (to 21 wt%). However, in the presence of imidazolium salts containing shorter substitutes, a conversion of hydrogen peroxide was observed exclusively. Hydro-

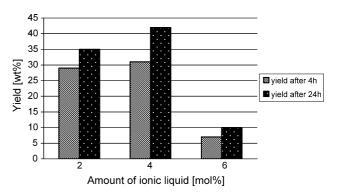


Fig. 4. The influence of the amount of ionic liquid $[CH_2OC_9H_{19}HIm][salicylate]$ on the yield of 1-allyloxy-4-glycidoloxybutane (*Reaction conditions*: 18 mmol of DiAB; molar ratio of Na₂WO₄·2H₂O:DiAB 1:21; Na₂WO₄·2H₂O:H₃PO₄ 1:2; DiAB:H₂O₂ 1:4; temperature 50 °C, reaction time 4 h).

gen peroxide decomposed into water and oxygen. Hence, in further studies was used $[CH_2OC_{10}H_{21}HIm][lactate]$ and $[CH_2OC_9H_{19}HIm][salicylate]$. In the processes carried out by the PTC technique, the rate of process is significantly affected by the amount of phase transfer catalyst. Therefore, the experiments were also carried out in which the amount of the catalyst was 4%, 6% and 10 mol% in relation to DiAB (Figs. 3 and 4; Tables 2 and 3).

In the case of using 3-decyloxymethyl-1H-imidazolium as the cocatalyst (Fig. 3), an increase of its amount from 2 to 4 mol%, and subsequently to 6 mol% caused an increase of

Table 2

Conversion of DiAB and hydrogen peroxide as a function of the amount of [CH₂OC₁₀H₂₁HIm][lactate]

Amount of [C ₁₀ H ₂₁ OCH ₂ HIm][lactate] (mol%)	Conversion of DiAB (wt%)		Conversion of H ₂ O ₂ (wt%)	
	4 h	24 h	24 h	
2	38	45	31	
4	39	51	31	
6	42	53	27	
10	20	23	27	

Reaction conditions: 18 mmol of DiAB; molar ratio of Na₂WO₄·2H₂O:DiAB 1:21; Na₂WO₄·2H₂O:H₃PO₄ 1:2; DiAB:H₂O₂ 1:4; temperature 50 °C, reaction time 4 h.

Amount of [C ₁₀ H ₂₁ OCH ₂ HIm] [salicylate] (mol%)	Conversion of DiAB (wt%)		Conversion of H ₂ O ₂ (wt%)	
	4 h	24 h		
2	37	39	37	
4	33	45	38	
6	9	12	25	

Conversion of DiAB and hydrogen peroxide as a function of the amount of [CH₂OC₉H₁₉HIm][salicylate]

Reaction conditions: 18 mmol of DiAB; molar ratio of Na₂WO₄·2H₂O:DiAB 1:21; Na₂WO₄·2H₂O:H₃PO₄ 1:2; DiAB:H₂O₂ 1:4; temperature 50 °C, reaction time 4 h.

the monoepoxide yield. This yield also increased along with a prolongation of the reaction time. As a result, the yield of 1allyloxy-4-glycidoloxybutane in the presence of 6 mol% of lactate was 50 wt% after 24 h of the reaction time. The conversion of DiAB amounted to 53 wt%, whereas that of hydrogen peroxide 27 wt% (Table 2). An increase of the amount of ionic liquid up to 10 mol% caused a significant decrease of the monoepoxide yield and the DiAB conversion to ca 20 wt% (Fig. 3; Table 2). A reason of reaction inhibition was a higher pH of the reaction medium. It is known, that the epoxidation in the catalytic system Na₂WO₄·2H₂O/H₃PO₄/H₂O₂ requires an adequately low pH, hence, it decreases the activity of epoxidation catalyst. As a consequence, both the DiAB conversion and monoepoxide yield were decreased.

The similar dependences as for lactate were obtained for 1H-3-nonyloxymethylimidazolium salicylate (Fig. 4; Table 3). In this case, an increase of the amount of ionic liquid from 2 to 4 mol% caused an increase of the monoepoxide yield to 42 wt% after the time of 24 h (Fig. 4). However, a significant decrease of both the monoepoxide yield to 10 wt%, and the DiAB conversion to 12 wt% was observed in the presence of 6 mol% of salicylate.

The obtained results indicate, that during the epoxidation in the system $Na_2WO_4 \cdot 2H_2O/H_3PO_4/H_2O_2/imidazolium salt, the latter should be used in the amount of 4–6 mol% in relation to DiAB. Such amount of imidazolium salt allows to achieve a relatively high conversion of DiAB (45–53 wt% after 24 h) and the yield of 1-allyloxy-4-glycidoloxybutane at a level of 42–47 wt%.$

3.2. Epoxidation of DiAB in the presence of heteropolyacids $(H_3PW_{12}O_{40}, H_3PMo_{12}O_{40})$ and ionic liquids as cocatalyst

In the epoxidation of olefins with an aqueous solution of hydrogen peroxide as the catalyst besides the system Na₂WO₄·2H₂O/H₃PO₄ are also used the heteropolyacids It result from previous studies [9] that the epoxidation of 1,4bis(allyloxy)butane in the presence of Aliquat[®]336 as a cocatalyst proceeds when a phosphotungstic heteropolyacid (H₃PW₁₂O₄₀) will be used. However, an increase of the pH of the reaction mixture to a value of 0.26–0.28 becomes necessary. This was performed with 10 wt% aqueous solution of NaOH. The products were not obtained in the presence of phosphomolybdic heteropolyacid (H₃PMo₁₂O₄₀) irrespective on the pH of the reaction medium.

In these studies the course of epoxidation in the presence of phosphotungstic or phosphomolybdic heteropolyacids and the ionic liquid as cocatalyst has been determined. The ionic liquid exhibiting the largest activity in the catalytic system Na₂WO₄·2H₂O/H₃PO₄/H₂O₂ such as [CH₂OC₉H₁₉HIm][salicylate] and [CH₂OC₁₀H₂₁HIm][lactate] were used in the investigations. Contrary to Aliquat[®]336, both imidazolium salts catalysed the epoxidation in the presence of phosphotungstic and phosphomolybdic acids, whereas 1-allyloxy-4-glycidoloxybutane was formed exclusively.

A control of process over time allowed observing that an increase in the monoepoxide yield and the DiAB conversion takes place during the first 4 h in the case of phosphotungstic acid (Table 4). The application of lactate or salicylate as a cocatalyst resulted in the monoepoxide after 4 h with yields of 37 and 34 wt%, respectively. A prolongation of time to 24 h caused an increase of the DiAB conversion, however, the yield of monoepoxide decreased. As a result, after 24 h in the presence of $H_3PW_{12}O_{40}$ the DiAB conversion amounted to 59 and 87 wt%, respectively for lactate and salicylate, whereas the yield of monoepoxide decreased to about 15 wt% for both ionic liquids.

A high conversion of DiAB simultaneously with a low yield of monoepoxide is caused by the hydrolysis of oxirane ring with the formation of diol.

Table 4

Table 3

Comparison of the activity of ionic liquids and Aliquat® 336 in the epoxidation process of 1,4-bis(allyloxy)butane in the presence of heteropolyacids

HPA	Yield of epoxid	Yield of epoxide (DiAB conversion) (wt%)					
	[CH ₂ OC ₁₀ H ₂₁ H	[CH ₂ OC ₁₀ H ₂₁ HIm][lactate]		[CH ₂ OC ₉ H ₁₉ HIm][salicylate]		Aliquat [®] 336 ^a	
	4 h	24 h	4 h	24 h	4 h	24 h	
H ₃ PW ₁₂ O ₄₀ H ₃ PMo ₁₂ O ₄₀	37 (38) 17 (25)	15 (59) 19 (29)	34 (67) 27 (31)	14(87) 31(39)	17 (67) 0 (0)	0(0) 0(0)	

Reaction conditions: 18 mmol of DiAB; molar ratio of Na₂WO₄·2H₂O:DiAB 1:21; Na₂WO₄·2H₂O:H₃PO₄ 1:2; DiAB:H₂O₂ 1:4; temperature 50 °C, reaction time 4 h, 4 mol% of ionic liquid in relation to DiAB was used.

^a 2 mol% in relation to DiAB.

On the other hand, an increase of the monoepoxide yield and the DiAB conversion took place as a result of prolongation of the reaction time within a range to 24 h in the presence of phosphomolybdic heteropolyacid and the imidazolium salts [CH2OC9H19HIm][salicylate] and [CH₂OC₁₀H₂₁HIm][lactate]. In this case, 1H-3-nonyloxymethylimidazolium salicylate has turned out to be a better cocatalyst. In the presence of this salt after 24 h, the monoepoxide yield of 31 wt% at the DiAB conversion of 39 wt% was achieved. The similar values of the monoepoxide yield and DiAB conversion after both 4 h and 24 h indicate, that the hydrolysis of monoepoxide proceeds only to a slight degree in the presence of H₃PMo₁₂O₄₀ and [CH₂OC₁₀H₂₁HIm][lactate]. In the case of phosphomolybdic acid the epoxidation proceeds slower than in the presence of phosphotungstic acid. However, the selectivity of transformation to 1-allyloxy-4-glycidoloxybutane was lower.

4. Conclusion

The obtained results indicate that the imidazolium salts from a group of lactates or salicylates containing at least one *N*-alkyl or *N*-alkoxyalkyl with at least 10 atoms of carbon are efficient cocatalysts in the epoxidation process of 1,4-bis(allyloxy)butane both in the catalytic system $Na_2WO_4 \cdot 2H_2O/H_3PO_4/H_2O_2$ and in HPA/H₂O₂. In the presence of ionic liquids and the mentioned system the only product of epoxidation is 1allyloxy-4-glycidoloxybutane. A selective transformation of 1,4-bis(allyloxy)butane to 1-allyloxy-4-glycidoloxybutane significantly facilitates its separation and the purification by distillation method under a reduced pressure.

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