

Epoxidation of 1,4-diallyloxybutane to 1-allyloxy-4-glycidyoxybutane by the method of phase transfer catalysis

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Abstract

The epoxidation of 1,4-diallyloxybutane (DiAB) with 30 wt% hydrogen peroxide in the presence of phosphorotungstic acid (PTA) hydrate or phosphoric(V)-acid-sodium tungsten(VI) dihydrate system ($\text{PO}_4^{3-}/\text{WO}_4^{2-}$) as the catalysts and an onium salt as a phase transfer catalyst has been investigated. The influence of the type and amount of epoxidation catalyst, the molar ratio of 1,4-diallyloxybutane to H_2O_2 , the amount and nature of auxiliary solvent on the course of the epoxidation was studied.

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1. Introduction

The oxidation of organic compounds with an aqueous solution of hydrogen peroxide is very advantageous from the point of view of chemical technology and synthesis, since hydrogen peroxide is a relatively inexpensive, environmentally friendly and safe. In the recent years, the possibility of olefins epoxidation by a dilute solution of hydrogen peroxide in the presence of molybdenum and tungsten compounds as the catalysts under the conditions of phase transfer catalysis (PTC) has been found. The catalytic system ($\text{W}^{\text{IV}}/\text{P}^{\text{V}}/\text{PTC}/\text{H}_2\text{O}/\text{CHCl}_3$) developed by Venturello has appeared to be useful in the epoxidation of olefins with a small reactivity [1–3]. A considerable drawback this method is a need to use the toxic and carcinogenic chloride solvents. However, their presence is required to achieve high yields of the products. Ishii and co-workers [4–6] have demonstrated that the epoxidation of alkenes and other organic compounds with a 35 wt% hydrogen peroxide can be carried out in the two phase system in the presence of heteropolyacids catalyst of the type of phosphorotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$). A

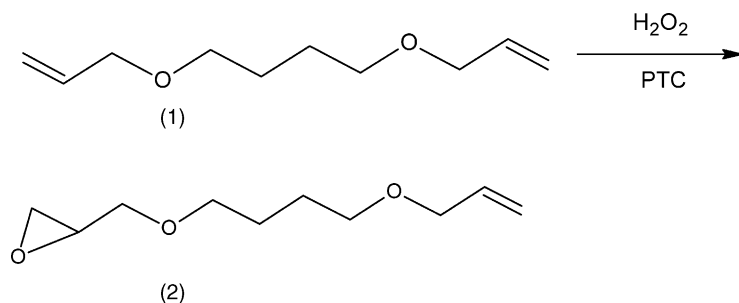
peroxy complex with the phase transfer catalyst Q^+ cation is transferred into the organic phase and is subsequently regenerated in the interphase via the interaction with H_2O_2 . Over the past few years, the investigations on the catalytic system, Venturello–Ishii, by many workers in relation to different compounds have been carried out [7–11]. They have demonstrated, that various catalyst precursors can be used in the epoxidation of olefins by the Venturello–Ishii method and the identical intermediate peroxy complexes are always formed [7,8].

Two-component associates containing the tungsten and phosphate ions under the acidic conditions were found to be a valuable catalytic system for olefins epoxidation by hydrogen peroxide with the utilization of the phase transfer catalysis. Such associates are in situ formed in the reaction mixture as a result of the introduction of both components, most frequently in the form of sodium tungstate and *o*-phosphoric acid.

The heteropolyacids such as phosphorotungstic acid (PTA) are not only used for the oxidation of organic compounds, but also in many reactions catalysed by acids. They have the catalytic properties both in the oxidation processes and in the reactions requiring a high acidity [12,13].

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The objective of these studies was the determination of the influence of both catalytic systems on the course of epoxidation of 1,4-diallyloxybutane (DiAB). The effect of solvent on the reactions carried out in the presence of PTA and the system of $\text{PO}_4^{3-}/\text{WO}_4^{2-}$ anions was also investigated. The influence of the molar ratio of DiAB to hydrogen peroxide was also studied. The effect of the catalytic system on the DiAB epoxidation in the direction of 1-allyloxy-4-glycidyloxybutane was investigated at the molar ratio of DiAB to H_2O_2 1:2 and 1:4 using methyltrioctylammonium chloride (Aliquat[®]336) as the phase transfer catalyst. The nature and amount of solvent was also investigated. The epoxidation of DiAB with 30 wt% H_2O_2 under the PTC conditions leads to mono- and dioxide. 1-Allyloxy-4-glycidyloxybutane (monoepoxide) is a compound that has not yet been described in the literature. However, 1,4-bis(glycidyloxy)butane is a commercially available compound and known under the trade name Araldite DY [14].



2. Experimental

2.1. Materials

Hydrogen peroxide 30 wt% aqueous solution was purchased from POCH Gliwice, whereas methyltrioctylammonium chloride ($\text{CH}_3\text{N}[(\text{CH}_2)_7\text{CH}_3]_7\text{Cl}$) under the trade name Aliquat[®]336 was from Aldrich. Sodium tungstate dihydrate $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, pure 99%, was purchased from Merck. Phosphorous acid with concentration of 85 wt% from Lachema. Phosphorotungstic acid hydrate $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was purchased from Fluka. The following solvents (analytical grade, POCh Gliwice) were used in the studies: chloroform, toluene, benzene and methylene chloride. The solvents were used without further purification. DiAB was prepared according to the method described in the literature [15,16].

2.2. Analytical methods

The concentrations of organic compounds were determined by gas chromatography method. The analyses were performed using a Carlo Erba GC 8000 gas chromatograph with a DB-17 column (50% (phenyl)-methylpolysiloxane) J&W (30 m \times 0.25 mm \times 0.25 μm) and the FID detector. The thermostat temperature was programmed in the following

way: 3 min at temperature 40 °C, ramping the temperature at 10 °C/min to 120 °C, 5 min at this temperature subsequently ramping the temperature at 10 °C/min to 200 °C and 20 min at this temperature. The total time of analysis amounted to 44 min.

The concentration of hydrogen peroxide was determined by iodometric titration method using 0.1N solution of sodium thiosulfate.

The ^1H NMR and ^{13}C NMR spectra were recorded using a Brücker DPX 400 MHz spectrometer. As a solvent of analysed samples was used CDCl_3 , whereas TMS as an internal standard.

2.3. Epoxidation of 1,4-diallyloxybutane

The syntheses were carried out in a glass reactor of 100 cm^3 capacity equipped with a magnetic stirrer, thermometer and a reflux condenser. The reactor was charged

with sodium tungstate(VI) dihydrate in the amount of 0.875 or 3.48 mmol and a 40 wt% *o*-phosphoric acid or if the reactions were carried out in the presence of heteropolyacid it was added in the amount of 1.08×10^{-4} mol. The reactor was then immersed in the oil bath at temperature 50 °C. In the case of the process carried out in the presence of *o*-phosphoric acid and sodium tungstate dihydrate, the molar ratio of *o*-phosphoric acid to sodium tungstate dihydrate amounted to 1 or 2. Subsequently, hydrogen peroxide was added in the amount of 36×10^{-3} or 72×10^{-3} mol, so that the molar ratio of DiAB to H_2O_2 was maintained at 1:2 or 1:4. At these amounts of the reagents, the aqueous phase has the pH value of 0.26–0.28. In the case of the processes carried out in the presence of heteropolyacids, the pH of the aqueous layer was initially below 1. In order to obtain the pH value of 0.26–0.28, a 10 wt% solution of sodium hydroxide was added in an appropriate amount. Subsequently, DiAB and the Aliquat[®]336 phase transfer catalyst were introduced in the amounts of 18×10^{-3} and 35×10^{-4} mol, respectively, and eventually a solvent was added. All the experiments were carried out under the vigorous stirring for 2 h. In the process carried out without an auxiliary solvent (in mass), chloroform was added to the post reaction mixture in order to separate the product. After the reaction was completed, the aqueous and organic phases were separated. When the hydrogen peroxide concentration in the aqueous phase was determined the conversion of H_2O_2

was calculated. After the chromatographic determination of the concentration of 1,4-diallyloxybutane, the conversion of organic raw material and the monoepoxide yield were calculated. The conversions were calculated from the amount of the respective raw materials consumed (H_2O_2 or DiAB) in relation to that introduced into the reaction. The yields were calculated from the quantity of obtained monoepoxide in relation to DiAB introduced into the reaction. The amounts of raw materials and the products were expressed in grams.

Identification of 1-allyloxy-4-glycidyoxybutane was performed by the method of nuclear magnetic resonance ^1H NMR and ^{13}C NMR. The boiling point of monoepoxide amounted to 91–94 °C (4 mmHg). The results of identification were as follows:

^1H NMR (CDCl_3 ; ppm): $\delta = 5.95\text{--}5.86$ (m, 1H, $\text{CH}_2=\text{CH}-$), $5.29\text{--}5.24$ (dd, $^3J = 17.2$ Hz, 1H_E, $\text{CH}_2=\text{CH}-$), $5.17\text{--}5.14$ (d, $^3J = 10.4$ Hz, 1H_Z, $\text{CH}_2=\text{CH}-$), $3.97\text{--}3.95$ (d, $^3J = 5.62$ Hz, 2H, $=\text{CH}-\text{CH}_2-\text{O}-$), $3.73\text{--}3.69$ (dd, $^3J = 11.5$ Hz, $^2J = 3$ Hz, 1H_a, oxirane group- $\text{CH}_2-\text{O}-$), $3.55\text{--}3.48$ (m, 2H, $-\text{CH}_2-\text{CH}_2-\text{O}-$), $3.46\text{--}3.43$ (t, $^3J = 3$ Hz, 2H, $\text{CH}_2-\text{O}-$), $3.39\text{--}3.35$ (dd, $^3J = 11.4$ Hz, $^2J = 6$ Hz, 1H_b, oxirane group- $\text{CH}_2-\text{O}-$), $3.15\text{--}3.11$ (m, 1H, $\text{CH}_2-\text{O}-$), $2.79\text{--}2.77$ (t, $^3J = 9.2$ Hz, 1H_E, $\text{CH}_2-\text{O}-$), $2.61\text{--}2.59$ (dd, $^3J = 5$ Hz, $^2J = 2.7$ Hz, 1H_Z, $\text{CH}_2-\text{O}-$), $1.68\text{--}1.63$ (dt, 4H, $-\text{CH}_2-$).

^{13}C NMR (CDCl_3 ; ppm): $\delta = 135.0$ ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-$), 116.6 ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-$), 71.7 ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-$), 71.4 ($-\text{O}-\text{CH}_2-\text{oxirane}$ group), 71.3 ($-\text{CH}_2-\text{O}-\text{CH}_2-\text{oxirane}$ group), 70.0 ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-\text{CH}_2-$), 50.9 ($\text{CH}_2-\text{O}-$), 44.2 ($\text{CH}_2-\text{O}-$), 26.3 ($-\text{O}-\text{CH}_2-\text{CH}_2-$).

3. Results and discussion

The influence of the nature of solvent on the course of reaction in the presence of $\text{PO}_4^{3-}/\text{WO}_4^{2-}$ associates or phosphotungstic acid was studied. The effect of enhancement of the molar ratio of DiAB to hydrogen peroxide from 1:2 to 1:4 was also determined.

Table 1

The influence of catalytic system on the epoxidation of 1,4-diallyloxybutane (18 mmol) with 30 wt% H_2O_2 (36 mmol) in presence of Aliquat[®]336 (0.35 mmol) as the PT catalyst at temperature 50 °C for 2 h

Solvent	Conversion ^a			Yield ^a of monoepoxide (wt%)	Conversion ^b			Yield ^b of monoepoxide (wt%)
	H_2O_2 (wt%)	DiAB (wt%)			H_2O_2 (wt%)	DiAB (wt%)		
1 Methylene chloride	54	88		33	42	33	17	
2 Chloroform	67	90		35	68	61	17	
3 Benzene	48	69		24	37	41	4	
4 Toluene	54	71		26	39	39	5	
5 –	44	52		16	60	63	15	

^a Reaction carried out in the presence of $\text{PO}_4^{3-}/\text{WO}_4^{2-}$ system (1.75/0.875 mmol).

^b Reaction carried out in the presence of PTA (1.08×10^{-4} mmol).

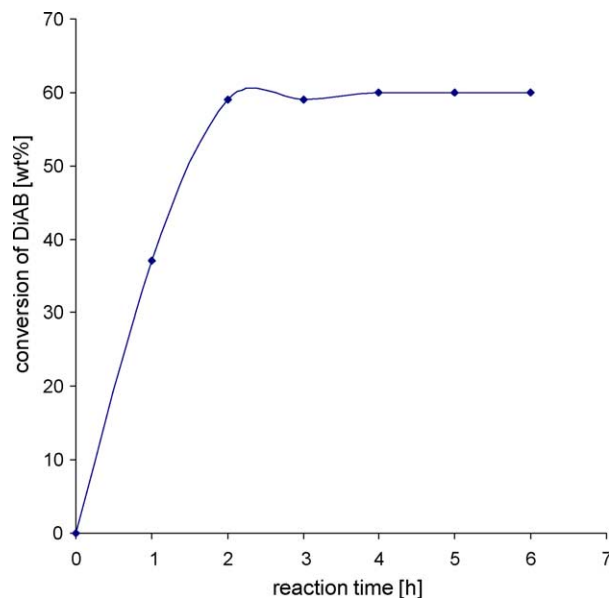


Fig. 1. The influence of time on the DiAB conversion in the presence of PTA (1.08×10^{-4} mol), temperature 50 °C, Aliquat[®]336 (0.35 mmol), molar ratio of DiAB to $\text{H}_2\text{O}_2 = 1:2$, solvent CHCl_3 .

Initially, the selection of the catalytic system has been performed. In one of the series the epoxidation of DiAB with a 30 wt% hydrogen peroxide was performed in the presence of phosphotungstic acid whereas in the second one the $\text{PO}_4^{3-}/\text{WO}_4^{2-}$ system was used. In both cases the experiments were carried out at the molar ratio of DiAB: $\text{H}_2\text{O}_2 = 1:2$, using the following solvents (5 cm³): methylene chloride, chloroform, benzene and toluene. Aliquat[®]336 was used as the phase transfer catalyst. The processes were operated at temperature of 50 °C for 2 h (Table 1). The reaction time and process temperature were recognized as the most advantageous based on the variations of DiAB conversion (Figs. 1 and 2). It results from Fig. 1 that a prolongation of the reaction time over 2 h does not increase the DiAB conversion. The same results were achieved in the presence of both $\text{PO}_4^{3-}/\text{WO}_4^{2-}$ system and PTA. The highest conversion of DiAB was achieved at temperature 50 °C, and the presence of chloroform as the solvent, while the remaining parameters were similar (Fig. 2). The conversions of hydrogen peroxide in both processes are close and they amounted

Table 2

The influence of catalytic system on the epoxidation of 1,4-diallyloxybutane (18 mmol) with 30 wt% H₂O₂ (72 mmol) in presence of Aliquat[®]336 (0.35 mmol) as the PT catalyst at temperature 50 °C for 2 h

	Solvent ^a	Conversion ^b		Yield ^b of monoepoxide (wt%)	Conversion ^c		Yield ^c of monoepoxide (wt%)
		H ₂ O ₂ (wt%)	DiAB (wt%)		H ₂ O ₂ (wt%)	DiAB (wt%)	
1	Methylene chloride	54	89	26	29	52	17
2	Chloroform	62	90	36	23	40	37
3	Benzene	46	82	21	22	63	16
4	Toluene	54	71	22	40	52	11
5	–	56	0	0	24	82	23

^a Five cubic centimeters of solvent was used.

^b Reaction carried out in the presence of PO₄³⁻/WO₄²⁻ systems (6.96/3.48 mmol).

^c Reaction carried out in the presence of PTA (1.08 × 10⁻⁴ mmol).

to about 68 wt%. The epoxidation process also proceeds in both catalytic systems without the addition of auxiliary solvent. However, the effect of solvent addition is higher in the presence of PO₄³⁻/WO₄²⁻ system. The addition of solvent independently on its nature causes an increase of both raw materials conversion and the yield of monoepoxide. In the presence of PTA the improvement of raw materials conversion and the yields was found only in the case of chloroform. A decrease of the monoepoxide yield was observed in the presence of benzene and toluene. This testifies to a considerably larger activity of the PO₄³⁻/WO₄²⁻ catalytic system and indicates that an enhancement of the yield and conversion can be achieved in the presence of the polar solvents. A higher yield and conversion is caused by an ionic character of the phenomena of oxygen transfer in the form of ionic couple during the phase transfer catalysis [17]. The highest yield of monoepoxide 35 wt% was achieved in the process carried out in the presence of PO₄³⁻/WO₄²⁻ system. In the presence of PTA the yield of monoepoxide was decreased by half.

The same investigations were carried out increasing both the molar ratio of DiAB to H₂O₂ to 1:4 and the amount of sodium tungstate dihydrate. However, the molar ratio of sodium tungstate to *o*-phosphorous acid was 1:2 (Table 2). An increase of the amount of hydrogen peroxide and the ratio these reagents (PO₄³⁻/WO₄²⁻ system) does not increase the

maximum yield of monoepoxide. The conversions of raw materials and the monoepoxide yield reach similar values in this process in the presence of methylene chloride, benzene and toluene. Significantly, higher values were reached in the presence of chloroform. However, monoepoxide is not formed despite of a considerable conversion of hydrogen peroxide without the presence of chloroform. These results confirm the beneficial influence of polar solvent on the monoepoxide yield. A high conversion of hydrogen peroxide in this case results from thermo-catalytic decomposition. When the process is carried out in the presence of PTA as the catalyst, a change of the molar ratio of DiAB: H₂O₂ from 1:2 to 1:4 causes a noticeable increase of the product yield. This increase of the yield is the largest in the presence of the following solvents: chloroform, benzene and toluene. The same tendency is observed in the process carried out without the auxiliary solvent. The yield of monoepoxide is almost identical in the presence of the PO₄³⁻/WO₄²⁻ system and PTA after increasing the molar ratio of DiAB to H₂O₂ to 1:4 and in the presence of chloroform. However, the DiAB conversion is reduced by half in the presence of PTA due to formation of a smaller amount of by-products associated with DiAB. An increase of the amount of hydrogen peroxide most probably enhances the activity of the catalytic system based on PTA. Owing to this the highest yields of monoepoxide were achieved. Since the use of chloroform allows to achieve the highest yield of 1-allyloxy-4-glycidyoxybutane, the effect of increasing its amount in the PO₄³⁻/WO₄²⁻ system, at the molar ratio of DiAB to H₂O₂ = 1:2 was investigated (Table 3).

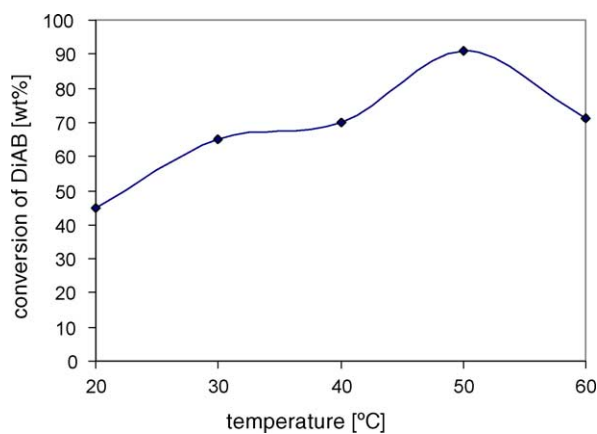


Fig. 2. The effect of temperature on the DiAB conversion in the presence of PO₄³⁻/WO₄²⁻ system (1.75/0.875 mmol), temperature 50 °C, Aliquat[®]336 (0.35 mmol), molar ratio of DiAB:H₂O₂ = 1:2, solvent CHCl₃.

Table 3

The influence of the amount of solvent on the epoxidation of 1,4-diallyloxybutane (18 mmol) with 30 wt% H₂O₂ (72 mmol) in presence of Aliquat[®]336 (0.35 mmol) as the PT catalyst at temperature 50 °C for 2 h

	Solvent Chloroform (cm ³)	Conversion ^a		Yield ^a of monoepoxide (wt%)
		H ₂ O ₂ (wt%)	DiAB (wt%)	
1	5	62	90	36
2	10	33	77	23
3	15	29	69	15

^a Reaction carried out in the presence of PO₄³⁻/WO₄²⁻ system (6.96/3.48 mmol).

From this compilation results that the highest yield of product can be achieved at 5 cm³ of chloroform. However, a dilution of the reaction medium by chloroform in the amount above 5 cm³ renders the separation of product in the form of organic layer more difficult.

4. Conclusion

The most advantageous conditions of epoxidation of 1,4-diallyloxybutane to 1-allyloxy-4-glycidyoxybutane by a 30 wt% hydrogen peroxide with the phase transfer catalysis method are the following: temperature 50 °C, molar ratio of 1,4-diallyloxybutane to H₂O₂ = 1:4, the amount of epoxidation catalyst in the form of phosphorotungstic acid (H₃PW₁₂O₄₀) 6 × 10⁻¹ mol% in relation to DiAB. The phase transfer catalyst used was methyltrioctylammonium chloride (Aliquat[®] 336) in the amount of 0.1 mol% in relation to H₂O₂, and auxiliary solvent was chloroform in the amount of 245 wt% in relation to DiAB. Under these conditions, the yield of monoepoxide amounted to 37 wt% and the conversions of H₂O₂ and 1,4-diallyloxybutane were 23 and 40 wt%, respectively.

In the case of application of WO₄²⁻/PO₄³⁻ catalytic system, the best results were achieved at the molar ratio of Na₂WO₄ of 3.5 mmol per 18 mmol DiAB. The molar ratio of WO₄²⁻/PO₄³⁻ amounted to 1:2. Under these conditions, the DiAB conversion was 90 wt%, whereas that of hydrogen peroxide was 62 wt% and the yield of monoepoxide 36 wt%. A beneficial amount of auxiliary solvent chloroform in

this process amounted to 245 wt% calculated in relation to DiAB.

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