

The influence of the solvent on the epoxidation of *cis,trans,trans*-1,5,9-cyclododecatriene to *trans*-1,2-epoxy-*cis,trans*-5,9-cyclododecadiene by catalytic system *tert*-butyl hydroperoxide/ $\text{Mo}(\text{CO})_6$

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Received 13 October 2004; received in revised form 30 December 2004; accepted 30 December 2004

Abstract

The epoxidation of *cis,trans,trans*-1,5,9-cyclododecatriene to *trans*-1,2-epoxy-*cis,trans*-5,9-cyclododecadiene with the use of commercial solution of *tert*-butyl hydroperoxide in various organic solvents: *tert*-butyl peroxide, isooctane, decane, and nonane was investigated. The process was investigated in different experimental conditions. The best results were achieved with the application of *tert*-butyl hydroperoxide in isooctane. A significant influence of the nature of the solvent on the results of *trans*-1,2-epoxy-*cis,trans*-5,9-cyclododecadiene synthesis was found.

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Keywords: Epoxidation; *cis,trans,trans*-1,5,9-Cyclododecatriene; *trans*-1,2-Epoxy-*cis,trans*-5,9-cyclododecadiene; *tert*-Butyl hydroperoxide

1. Introduction

The epoxides are an interesting class of chemical intermediates used in the laboratory and industrial synthesis of a wide spectrum of chemical compounds such as epoxide resins, paints, adhesives, diluents, and the surface active agents, moreover, for a series bioactive substances [1–3]. Specifically, the 1-epoxides are particularly important in a large-tonnage chemical production, whereas more substituted epoxides are usefulness in the synthesis of structurally more complex fine chemicals.

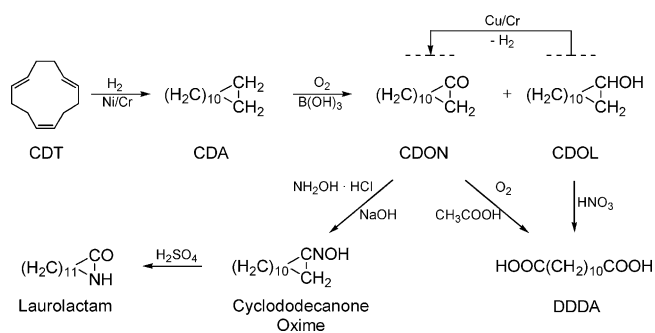
A universal method of epoxide production relies on the dehydrochlorinations of chlorohydrines by aqueous solution of alkalies [2,3]. In this method an equimolar quantity of waste aqueous solution of alkali metal chlorides is formed. Besides, considerable amounts of waste organic chloroderivatives which are the products of chlorine addition

to the double bond and the etherification of chlorohydrine are produced.

A more beneficial method is obviously a direct epoxidation of olefins. With regard to a need of effective “atom economy”, which is included in the Principles of Green Chemistry [3,4], a procedure of olefin epoxidation must be highly efficient and highly selective without any by-products. Both in the laboratory and industrial epoxidations, various oxidants are currently used, however their application is often limited due to the formation of difficult to dispose waste and a complex and expensive synthesis. The nature of the catalyst also plays an important role. A commercial success of catalytic epoxidation of propylene by means of *tert*-butyl or ethylbenzene hydroperoxide with the application of a relatively inexpensive and readily available, molybdenum catalysts make that the investigations of the epoxidation of other olefins by the hydroperoxides are still ongoing [4,5].

This paper presents the experimental results of the preliminary studies on the epoxidation of *cis,trans,trans*-1,5,9-cyclododecatriene (CDT) by *tert*-butyl hydroperoxide

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Scheme 1.

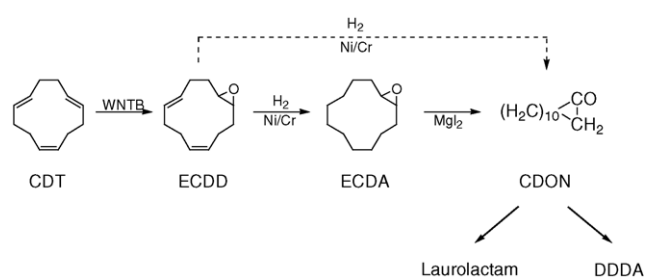
(TBHP) to *trans*-1,2-epoxy-*cis,trans*-5,9-cyclododecadiene (ECDD). This compound having the active epoxide group and two double bonds carbon–carbon is a valuable intermediate used in the synthesis of the polymeric components of paint and adhesives. The recent reports of the UBE and Degusa firms belonging besides Atofina and Ems-Grivory to the leading manufactures of Nylon 12 [6,7] (UBE—9000 t/y [8], Degusa—12000 t/y [9]) demonstrate that ECDD can be utilized as a semiproduct in the synthesis of 1,12-dodecanedioic acid (DDDA) and laulolactam [10–13].

DDDA finds the application as a raw material for the manufacture of polyesters and polyamides and a substitute of sebacic acid (1,10-decanedioic acid) in the preparation of plasticizers and high performance lubricating oils and lubricants. Whereas laulolactam is used for the manufacture of polyamide 12 (Nylon 12, Vestamid, Daiamid, Grilamid) which is characterized with a large hydrophobicity and flexibility in comparison with polyamide 6 or 6,6. These features cause that the products from polyamide 12 are a good dielectrics and demonstrate the stability dimensions in the environment with variable humidity.

DDDA and laulolactam are most often manufactured on a commercial scale by the Huels method (Scheme 1) [14].

In the first stage CDT is hydrogenated to cyclododecane (CDA) on the commercial catalyst Ni/Cr. The oxidation of CDA by oxygen from air in the presence of boric acid leads to cyclododecanol (CDOL) and cyclododecanone (CDON). CDON after the separation from the post-reaction mixture is subjected to the condensation with hydroxylamine hydrochloride to cyclododecanone oxime which as a result of the Beckmann rearrangement gives laulolactam. The oxidation of CDOL leads to DDDA. Although, the selectivity of CDA oxidation to useful products (CDON, CDOL) is high (92%) only a small degree of CDA conversion can be achieved (7%). This requires a continuous recycling of the large quantities of the CDA feedstock with a previous separation by the hydrolysis and the regeneration of the boric acid catalyst.

An interesting alternative to the Huels method is the route via the epoxidation of CDT to ECDD previously described by Wilke [15]. ECDD is then hydrogenated to epoxycyclododecane (ECDA) [16–18] (Scheme 2). The isomerization of ECDA [19] leads to CDON under the catalytic influence of



Scheme 2.

magnesium iodide. To convert the CDON to laulolactam, an oximation and Beckmann rearrangement are used, as described in the Huels method [20].

Hydrogenation of ECDD [13,21], over the nickel catalyst (Ni-Raney, Ni/ Al_2O_3 , Ni/ CrO_3) proceeds quantitatively giving CDOL with a small amount (10–15%) of CDON. The hydrogenation of CDOL to CDON also proceeds over the same catalyst. Hence, the process of CDON synthesis from CDT can be realized in the two stages.

2. Materials and methods

2.1. Chemicals

All experiments were performed with the following reagents: commercially available solutions of the TBHP in the organic solvents (3 M in isooctane, 5.5 M in decane, 5.5 M in nonane and 80 wt.% in *tert*-butyl peroxide (TBP)) were purchased from Aldrich, *cis,trans,trans*-1,5,9-cyclododecatriene (CDT) 98 wt.% was obtained from Fluka; molybdenum hexacarbonyl Mo(CO)_6 , pure was obtained from Merck–Schuchardt.

2.2. Experimental apparatus and procedure

The epoxidation of CDT with TBHP was carried out under pressure-less conditions in the apparatus shown in Fig. 1.

The three-neck flask (1) with 25 cm³ capacity, equipped with a reflux condenser (2), a dropping funnel (3), a thermometer (4), and a mechanical stirrer (5) was charged with weighed amount of CDT and catalyst (Mo(CO)_6). Weighed amount of TBHP was placed in the dropping funnel. The flask was immersed in ultrathermostat (6) with a determined temperature. After reaching a desired temperature, TBHP was added dropwise. The rate of TBHP dropping was adjusted in such a way that the temperature variations were not too large (maximum $\pm 3^\circ\text{C}$). After completing reaction, the mixture was rapidly cooled to ambient temperature in order to stop the reaction. The product was analyzed, and a mass balance was performed. The concentration of TBHP, CDT, and ECDD in the product was determined chromatographically. The TBHP concentration was additionally determined by an iodometric method [22]. For each experiment the following magnitudes

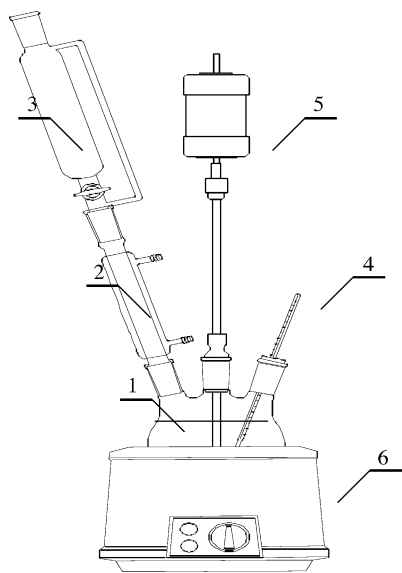


Fig. 1. Apparatus for epoxidation of CDT: (1) three-neck flask, 50 cm³ capacity; (2) reflux condenser; (3) dropping funnel 20 cm³ capacity; (4) thermometer; (5) mechanical stirrer; (6) ultrathermostate.

were calculated: the degree of conversion of TBHP and CDT, the selectivity of transformation to ECDD in relation to consumed TBHP and CDT, the ECDD yield in relation to TBHP and CDT introduced into reactor.

2.3. Analytical method

The chromatographic analyses were carried out on a Trace GC 2000 apparatus (Thermo-Finigan) with a flame-ionization detector (FID), equipped with a computer system sample collection and data handling Chrom-Card for Trace GC. The following conditions of determinations were used: a capillary column of J&W Scientific firm, 30 m × 0.25 mm × 0.25 μm; a detector temperature 250 °C, a sample chamber temperature of 200 °C. The analysis were performed using a programmed temperature gradient: 2.5 min isothermally, at temperature of 50 °C, temperature increase to 250 °C at the rate of 20 °C/min; 2.5 min isothermally at temperature 250 °C. The most favourable conditions of separation of determined compounds were achieved with a simultaneous application of a programmed increase of carrier gas (helium) pressure: 75 kPa (start); increase of pressure to 140 kPa at the rate of 5 kPa/min, 140 kPa isobaric for 2 min. The flow rates of gases were the following: air 350 cm³/min, hydrogen 35 cm³/min.

The assignment of peaks of particular components was confirmed by comparison with standard compounds.

The quantitative determinations of the post-reaction mixtures were performed by an internal standard method using dodecane. A percentage content of determined component was calculated from equation:

$$\% \text{mas}_i = f_i \frac{A_i}{A_w} \frac{m_w}{m_{pr}} \times 100$$

where f_i is the correction coefficient of determined component, A_i peak area of determined component, A_w the peak area of standard added to a sample, m_w the mass of standard added to a sample, and m_{pr} is the mass of analyzed sample.

3. Results and discussion

The investigation of CDT epoxidation with the use of commercially available solutions of TBHP were carried out at temperature of 70, 90 and 110 °C, at the molar ratio of CDT to TBHP of 3:1, catalyst concentration (Mo(CO)₆ of 0.5 mmol/dm³ for 120 min.

During the epoxidation with a TBHP solution in TBP (Table 1) with an increase of the temperature from 70 to 90 °C causes an increase in the ECDD yield both in relation to introduced CDT as well as TBHP, respectively, from 7.1 to 23.8 mol% and from 24.2 to 73.8 mol%. A further increase of temperature to 110 °C does not cause a significant change of ECDD yield. An increase in the conversion degree of both CDT and TBHP is accompanied by a non-effective decomposition of TBHP to *tert*-butyl alcohol (TBA) and oxygen and probably by the oligomerization or polymerization of CDT. This is confirmed by a significant decrease of the selectivity of transformation to ECDD both in relation to consumed CDT (from 94.1 to 69.6 mol%) and TBHP (from 85.2 to 77.4 mol%) at a change of temperature from 90 to 110 °C.

Due to the possibility of an explosive decomposition of TBP, especially during the separation of ECDD by a distillation method its decomposition is necessary. The decomposition of TBP is associated with the use of chemical reduction agents. For this reason a TBHP solution in TBP is only used on a small scale epoxidation process.

A similar tendency of the variations of the magnitudes describing the CDT epoxidation is observed during the application of TBHP solution in isoctane (Table 2). However, the process proceeds considerably intensive.

At a lowest studied temperature 70 °C the ECDD yield both in relation to TBHP and CDT introduced is about three-fold higher than in the TBP medium. The higher values of reactants conversions, selectivities, and as a result the yields were also achieved at higher temperatures. The process pro-

Table 1
Results of CDT epoxidation by 3 M solution of TBHP in TBP

	Temperature (°C)		
	70	90	110
Molar ratio CDT/TBHP (mol/mol)	3:1	3:1	3:1
Catalyst Mo(CO) ₆ concentration (mmol/dm ³)	0.5	0.5	0.5
Reaction time (h)	2	2	2
TBHP conversion (mol%)	37.2	86.7	96.3
ECDD selectivity/TBHP (mol%)	64.9	85.2	77.4
ECDD yield/TBHP (mol%)	24.1	73.9	74.5
CDT conversion (mol%)	23.5	25.3	34.6
ECDD selectivity/CDT (mol%)	30.4	94.1	69.6
ECDD yield/CDT (mol%)	7.1	23.8	24.1

Table 2
Results of CDT epoxidation by 3 M solution of TBHP in isooctane

	Temperature (°C)		
	70	90	110
Molar ratio CDT/TBHP (mol/mol)	3:1	3:1	3:1
Catalyst Mo(CO) ₆ concentration (mmol/dm ³)	0.5	0.5	0.5
Reaction time (h)	2	2	2
TBHP conversion (mol%)	95.7	99.8	99.8
ECDD selectivity/TBHP (mol%)	87.0	95.5	92.5
ECDD yield/TBHP (mol%)	83.3	95.3	93.3
CDT conversion (mol%)	44.8	31.1	30.8
ECDD selectivity/CDT (mol%)	50.7	99.6	99.1
ECDD yield/CDT (mol%)	22.7	31.0	30.5

ceeds the most effectively in the direction of ECDD at a temperature range of 90–110 °C.

The conversions of CDT and TBHP amount on an average 31.0 and 99.8 mol%, respectively. The selectivity of transformation to ECDD in relation to CDT in practice amounts to 100 mol%, and in relation to TBHP about 95 mol%. This indicates that the by-products associated with consumed CDT are not formed in the process. The only by-product is TBA. It is formed first of all as a co-product of the epoxidation reaction by means of TBHP. TBA is also formed in a minor amount as a result of thermal and catalytic decomposition of TBHP.

The application of this epoxidizing agent (TBHP solution in isooctane) creates the possibilities of achievement of almost 100% conversion of TBHP at temperature of 90 °C. This fact significantly simplifies the separation of ECDD without the necessity to decompose TBHP. The process is also a relatively safe (without the application of additional protections).

The epoxidation of CDT by 3 M solutions of TBHP in decane (Table 3) and in nonane (Table 4) proceed less effectively. In both cases the highest conversions of raw materials occur at temperature of 110 °C and they are shaping on a level of 66 mol% in the case of TBHP and 22 mol% for CDT. At temperatures below 110 °C they are achieve respectively lower values, with the maintenance of similarities in both solvents. The similarities in the courses of the process in nonane and decane also concern the selectivities of transformation to ECDD in relation to TBHP and CDT. At each temperature in the presence of these solvents, the differences

Table 3
Results of CDT epoxidation by 5.5 M solution of TBHP in decane

	Temperature (°C)		
	70	90	110
Molar ratio CDT/TBHP (mol/mol)	3:1	3:1	3:1
Catalyst Mo(CO) ₆ concentration (mmol/dm ³)	0.5	0.5	0.5
Reaction time (h)	2	2	2
TBHP conversion (mol%)	31.7	44.4	64.4
ECDD selectivity/TBHP (mol%)	18.1	39.1	58.0
ECDD yield/TBHP (mol%)	5.7	17.4	37.3
CDT conversion (mol%)	12.2	17.7	20.4
ECDD selectivity/CDT (mol%)	14.9	32.6	61.8
ECDD yield/CDT (mol%)	1.8	5.8	12.6

Table 4
Results of CDT epoxidation by 5.5 M solution of TBHP in nonane

	Temperature (°C)		
	70	90	110
Molar ratio CDT/TBHP (mol/mol)	3:1	3:1	3:1
Catalyst Mo(CO) ₆ concentration (mmol/dm ³)	0.5	0.5	0.5
Reaction time (h)	2	2	2
TBHP conversion (mol%)	16.9	35.7	68.3
ECDD selectivity/TBHP (mol%)	25.4	42.4	70.4
ECDD yield/TBHP (mol%)	4.3	15.1	48.1
CDT conversion (mol%)	16.3	17.5	22.6
ECDD selectivity/CDT (mol%)	11.7	31.4	71.4
ECDD yield/CDT (mol%)	1.9	5.5	16.1

in the selectivities related respectively to TBHP and CDT are small.

The studies demonstrate a considerable influence of the solvent on the CDT epoxidation (Figs. 2 and 3). At each temperature the highest degree of TBHP conversion and selectivities of transformations to ECDD in relation to TBHP were achieved in isooctane. Considerable poorer results were obtained in the case of application of decane and nonane.

Above a temperature of 90 °C the differences in the courses of the process decrease in the group of solvents: decane and nonane and isooctane and TBP. The degrees of conversions and the selectivities of transformation achieve the similar values. At the temperature of 110 °C in the presence

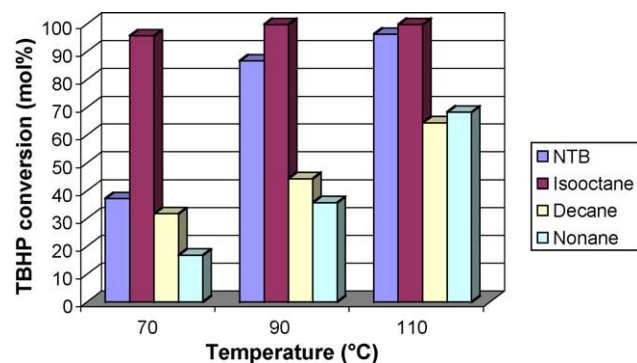


Fig. 2. The influence of temperature and the nature of the solvent on the TBHP conversion.

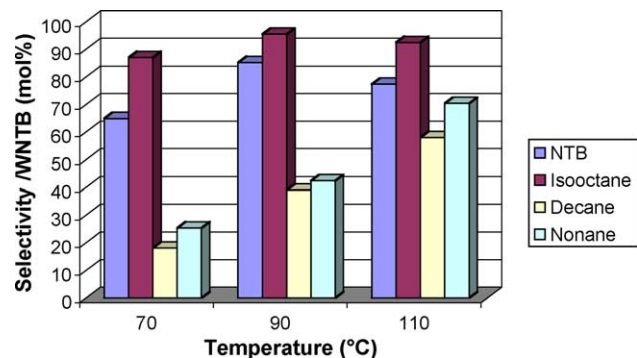


Fig. 3. The influence of temperature and the nature of the solvent on the selectivity of transformation to ECDD in relation to TBHP.

of TBP a significant increase of the degree of TBHP conversion takes place to a level comparable to that for isooctane. However, the selectivity of transformation both in relation to TBHP and CDT decreases simultaneously.

All the mechanisms of the epoxidation by hydroperoxides [23,24] in the presence of homogeneous molybdenum catalyst assume the formation of complexes of molybdenum with different ligands. The original and those occurring during the reaction as well as the nature of the original catalyst were decisive as far as the course of the process is concerned. Molybdenum hexacarbonyl $\text{Mo}(\text{CO})_6$ is in this situation a particular catalyst in which the CO groups can be exchanged by the molecules of hydroperoxide, alcohol or other ligand. However, none of the mechanisms of the epoxidation in the presence of $\text{Mo}(\text{CO})_6$ take into consideration the influence of the solvent. Whereas the elaborations [25] allowing the possibility of the formation of triple complex: $\text{Mo}(\text{CO})_{6-(n+1)}/\text{olefin}_n/\text{ROOH}$, where $n = 1, 2$ or a double complex: $\text{Mo}(\text{CO})_6/\text{ROOH}$, $\text{Mo}(\text{CO})_6/\text{olefine}$ are known [26,27].

The structure of such a type of complexes was confirmed by independent spectroscopic studies for separately obtained $\text{Mo}(\text{CO})_{6-n}\text{L}_n$ (L—ligands: pyridine, benzene, toluene, phenylphosphine) and the products of their reactions with TBHP and simple olefin [28].

Hence, the formation of complexes by $\text{Mo}(\text{CO})_6$ with the solvents (isooctane, TBP, nonane, and decane) used in this work is also probable. The observed differences in reactivity of TBHP result most probably from a different stability of the catalyst–solvent complexes, as well as those with the contribution of olefine and TBHP. In the case of structurally extended molecules of solvents (isooctane, TBP), these complexes are less stable than those formed with linear hydrocarbons (decane, nonane).

This reasoning finds the confirmation in the obtained experimental results. In the medium of decane and nonane with an increase of epoxidation temperature, especially from 90 to 110 °C, a significant increase of the conversion and selectivity take place. This may reveal to a gradual decomposition of nonactive catalyst–solvent complexes and the formation of catalytically active complexes of the type catalyst/olefin/TBHP or similar to them.

The effect of catalyst concentration (Table 5) for the solutions: TBHP in isooctane and nonane was also investigated. The studies were carried out at the temperature of 90 °C, at the molar ratio of CDT:TBHP = 3:1 for the reaction time 120 min. In the environment of isooctane, an increase in catalyst concentration from 0.1 to 0.5 mmol/dm³ causes a significant increase of all the indicators of epoxidation. The conversions of TBHP and CDT and the selectivity of transformation in relation to TBHP and CDT achieve a maximum values or values close to them. Therefore, a further increase of the catalyst concentration to 1 mmol/dm³ is not purposeful since it does not influence on the result of ECDD synthesis.

In the environment of nonane such beneficial results were not obtained. The conversions of TBHP and CDT are the same

Table 5
The influence of catalyst concentration (mmol/dm³) on the results of ECDD synthesis

	Solvent					
	Isooctane			Nonane		
	0.1	0.5	1.0	0.1	0.5	1.0
Temperature (°C)	90	90	90	90	90	90
Molar ratio CDT/TBHP (mol/mol)	3:1	3:1	3:1	3:1	3:1	3:1
Reaction time (h)	2	2	2	2	2	2
TBHP conversion (mol%)	66.0	99.8	99.8	31.0	35.7	36.5
ECDD selectivity/TBHP (mol%)	82.1	95.5	97.7	46.9	42.4	69.1
ECDD yield/TBHP (mol%)	54.2	95.3	97.5	14.6	15.1	25.2
CDT conversion (mol%)	19.9	31.1	31.2	10.7	17.5	11.3
ECDD selectivity/CDT (mol%)	91.6	99.6	100.0	45.5	31.4	74.8
ECDD yield/CDT (mol%)	18.3	31.0	31.2	4.9	5.5	8.4

level independently on the catalyst concentration. However, an increase of catalyst concentration to 1 mmol/dm³ enhances the selectivity of transformation to ECDD both in relation to TBHP and CDT. Consequences of this are higher yields ECDD.

Prolongation of the reaction time over 120 min does not cause an increase of the process indicators in the presence of isooctane or TBP. For TBHP in decane and nonane, a prolongation of the reaction time causes a linear increase of the degree of TBHP conversion.

4. Conclusions

The epoxidation of *cis,trans,trans*-1,5,9-cyclododecatriene to *trans*-1,2-epoxy-*cis,trans*-5,9-cyclododecadiene with the use of commercial solution of *tert*-butyl hydroperoxide proceeds better using a 3 M solution of TBHP in isooctane. At 90–110 °C, with a molar ratio of CDT:TBHP = 3:1, a catalyst concentration of 0.5 mmol/dm³, and after 2 h of the reaction time ECDD was obtained in the yield of 90–95 mol%. An increase of catalyst ($\text{Mo}(\text{CO})_6$) concentration to 1 mmol/dm³, as well as a prolongation of reaction time to 3 h have not a substantial influence on the course of the process.

Acknowledgement

This research project was financially supported by the State Committee for Scientific Research during a period of 2004–2007 as a grant no. 3T09B01126.

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