



New and efficient technique for the synthesis of ϵ -caprolactone using KHSO_5 as an oxidising agent in the presence of a phase transfer catalyst

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ABSTRACT

A new method for the synthesis of ϵ -caprolactone based on the Baeyer–Villiger oxidation of cyclohexanone was developed. In the proposed reaction, potassium peroxomonosulphate was used as an oxidising agent under phase transfer catalysis conditions. The effects of the reaction parameters, including the type of phase transfer catalyst, the concentration of the oxidising agent, the type of organic solvent and temperature, were investigated. When dichloromethane was used as an organic solvent and an adequate amount of water was added to the reaction mixture, the highest yield and selectivity for ϵ -caprolactone were achieved at 40 °C.

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1. Introduction

The Baeyer–Villiger (BV) reaction is one of the most important transformations in organic chemistry [1,2]. Nearly a century ago, just one year after potassium peroxomonosulphate (KHSO_5) was first described, the BV oxidation was reported by Baeyer and Villiger [3]. Although KHSO_5 has since been replaced by organic peracids, hydrogen peroxide and alkyl hydroperoxides [4,5], the use of KHSO_5 in the BV reaction has recently increased. KHSO_5 is a versatile oxidising agent and is commercially available as the stable triple salt ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$, e.g., oxone®), which is easy to handle, non-toxic and relatively inexpensive. As a result, the triple salt has been studied as a routine reagent for epoxidation reactions, the oxidation of aldehydes to carboxylic acids and other oxidation processes for the synthesis of fine chemicals [6,7].

Oxone® has also been used as an oxidising agent in the BV oxidation. However, to use oxone®, an aqueous reaction medium must be employed, which can cause the products of the reaction to hydrolyse. Alternatively, anhydrous potassium peroxomonosulphate on silica can also be used ($\text{SiO}_2 \cdot \text{KHSO}_5$) [8,9]. Moreover, in the synthesis of lactones, selected ionic liquids have been used as solvents for KHSO_5 [10].

In the present study, BV oxidation was achieved with KHSO_5 in the presence of a phase transfer catalyst (PTC). Until now, only one report on the use of PTC for the oxidation of ketones to lactones

has been presented. However, in the aforementioned study, borax and H_2O_2 was used as the oxidising agent [11]. Borax forms peroxy species with H_2O_2 , which can be transferred into the organic phase. Herein, we present the synthesis of ϵ -caprolactone from cyclohexanone using potassium peroxomonosulphate as an oxidising agent.

2. Experimental

2.1. Materials

All the phase transfer catalysts used in the present study were commercially available materials. Tetrabutylammonium bromide (TBAB) and tetrabutylphosphonium bromide hydrosulphate (TBPB) were obtained from Fluka Chemie AG. Benzyltributylammonium chloride (BTBAC) and tributylmethylammonium chloride (TBMAC) were purchased from Merck. 18-Crown-6, dibenzo-18-crown-6 and dicyclohexano-18-crown-6 were obtained from Fluka. $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$, n-decane and cyclohexanone (99% pure) were purchased from Acros Organics.

2.2. Experimental procedure

2.2.1. Analysis

^1H NMR and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz in CDCl_3 , respectively (Varian Unity Inova plus, TMS as the internal standard). GC analysis was performed on a PerkinElmer chromatography equipped with a PerkinElmer Elite-624 column (30 m, 0.53 mm ID, 3 μm df), and decane was used as an internal standard.

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2.2.2. Kinetics measurements

Cyclohexanone (10.2 mmol), decane (an internal standard, 0.5 g), $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ (10.2 mmol), H_2O (10 cm^3) and an organic solvent (30 cm^3) were introduced into a three-neck round bottom flask (150 cm^3) equipped with a mechanical stirrer and a condenser. The vessel was placed in a temperature-controlled oil bath with an accuracy of $\pm 1^\circ\text{C}$, and a phase transfer catalyst (1.02 mmol) was added to the flask. The reaction was stirred at 40°C for 6 h and was monitored by GC. Samples were taken from organic layer after 15, 30, 60, 90, 150, 240, 360 min and analyzed by GC. When the reaction was complete, phases were separated. When hexane or toluene was used as the organic solvent, dichloromethane (25 cm^3) was added to the post-reaction mixture to dissolve the product. The organic layer was washed with water (10 cm^3) and 5% aqueous NaOH ($3 \times 10\text{ cm}^3$) to remove all residual peroxy compounds and phase transfer catalyst. Next, the crude mixture was washed with water ($2 \times 10\text{ cm}^3$), dried over anhydrous MgSO_4 and the solvent was evaporated under vacuum. The crude, concentrated mixture was analysed by NMR.

2.2.3. Synthesis of ϵ -caprolactone

Cyclohexanone (0.102 mol), $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ (0.102 mol), H_2O (100 cm^3) and CH_2Cl_2 (300 cm^3) were introduced into a three-neck round bottom flask (750 cm^3) equipped with a mechanical stirrer and a condenser. The vessel was placed in a temperature-controlled oil bath with an accuracy of $\pm 1^\circ\text{C}$, and TBAB as a phase transfer catalyst (10.2 mmol) was added to the flask. The reaction was stirred at 40°C for 6 h. When the reaction was complete, phases were separated. The organic layer was washed with water (50 cm^3) and 5% aqueous NaOH ($3 \times 50\text{ cm}^3$) to remove all residual peroxy compounds and TBAB. Next, the crude mixture was washed with water ($2 \times 50\text{ cm}^3$), dried over anhydrous MgSO_4 and concentrated. The crude product was chromatographed with hexane/ethyl acetate (v/v 3/1) as the eluent. The solvent was evaporated under vacuum and ϵ -caprolactone was obtained with 77%. $^1\text{H-NMR}$ (300 MHz, CDCl_3 , TMS): $\delta = 4.23$ (m, 2H); 2.63 (m, 2H); 1.77 (m, 6H); $^{13}\text{C NMR}$ (CDCl_3): $\delta = 175.55$; 68.53; 33.75; 28.57; 28.07; 22.23; b.p. 235°C .

3. Results and discussion

The oxidation of the cyclohexanone to ϵ -caprolactone was selected as a model reaction. The synthesis of ϵ -caprolactone is of great importance in the chemical industry. Currently, ϵ -caprolactone is prepared through the oxidation of cyclohexanone using O_2 /acetaldehyde (BASF) or peroxyacetic acid (Perstorp).

Potassium peroxomonosulphate, the active compound in the triple salt ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$), was selected as an alternative oxidising agent to organic peroxyacids for the Baeyer-Villiger reaction. However, because potassium peroxomonosulphate is only soluble in water, it was essential to find a solvent system to carry out to the synthesis of ϵ -caprolactone.

In our preliminary studies (Table 1), it was found out that the oxidation process in a two-phase system consisting of organic phase (cyclohexanone dissolved in dichloromethane) and inorganic solid phase ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) conducted at 40°C did not proceed. ϵ -Caprolactone was not detected, and the conversion of cyclohexanone was not observed. Although high conversions were obtained after water was added to the reaction mixture, the synthesis of ϵ -caprolactone was not achieved. Rather, the product of lactone hydrolysis, 6-hydroxyhexanoic acid, was detected in the crude mixture. Thus, the results suggested that the BV lactone product was sensitive to hydrolysis.

Phase transfer catalysis is a powerful method that allows reactions to be conducted in a two phase system (liquid–liquid or liquid–solid). The role of the PT catalyst is to facilitate the transfer

Table 1

The effect of the addition of water (10 cm^3) and phase transfer catalyst (TBAB, 1.02 mmol) on the oxidation of cyclohexanone. Reaction conditions: cyclohexanone, 1.0 g, 10.2 mmol; $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$, 6.3 g, 10.2 mmol; dichloromethane, 30 cm^3 ; decane, 0.5 g, 3.5 mmol; temperature, 40°C ; 800 rpm.

Water (cm^3)	TBAB – PTC	Conversion of cyclohexanone after 6 h (%)	Yield of ϵ -caprolactone after 6 h (%)
–	–	0	0
+	–	98	0
–	+	0	0
+	+	82	82

of the reactant from one phase to another. This technique allows for acceleration of the reaction rate and easy separation of reaction mixtures. With phase transfer catalysis, good selectivity for hydrolytically unstable reagents can be obtained despite the presence of water in the reaction medium [12,13].

In the present study, TBAB, the most common PT catalyst, was added to the studied reaction systems, which consisted of an organic phase and inorganic phase (a solid triple salt or a triple salt and water). As a result, only in the system with water high yields of ϵ -caprolactone were obtained, and by-products were not detected (Table 1). Thus, to achieve BV oxidation with KHSO_5 , water and a phase transfer catalyst are necessary.

An interesting phenomenon was observed when toluene and hexane were used as the solvent. As shown in Fig. 1, the type of organic solvent had a significant effect on the oxidation of cyclohexanone. For instance, when hexane was used as the organic solvent, 100% conversion of cyclohexanone was obtained within 30 min. ϵ -Caprolactone is not soluble in hexane and is only partially soluble in toluene; thus, the reaction rate may have increased due to the formation of a separate layer based on the insoluble product. Unfortunately, in the aforementioned layer, the desired product was exposed to the effects of water, and ϵ -caprolactone was hydrolysed, and in hexane only 6-hydroxyhexanoic acid was

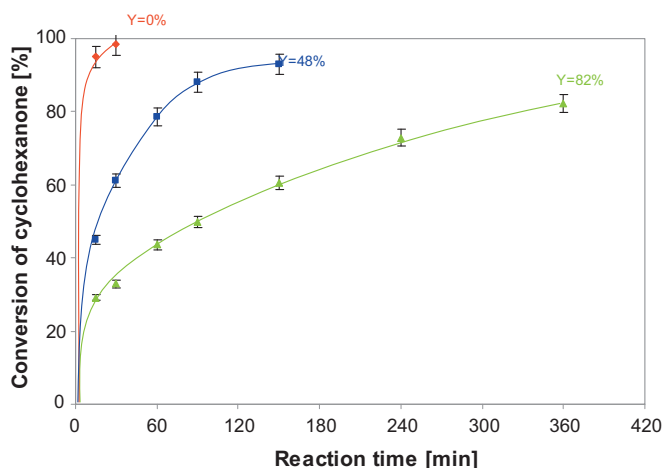


Fig. 1. Variation of the conversion of cyclohexanone with the time on stream during the reaction of cyclohexanone with $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ in the presence of different solvents (30 cm^3): (♦) hexane; (■) toluene; (▲) dichloromethane. Reaction conditions: cyclohexanone, 1.0 g, 10.2 mmol; $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$, 6.3 g, 10.2 mmol; TBAB, 1.02 mmol; H_2O , 10 cm^3 ; decane, 0.5 g, 3.5 mmol; temperature, 40°C ; 800 rpm. Y – yield of ϵ -caprolactone after 6 h.

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