

A mild and clean Baeyer–Villiger oxidation of ketones using sodium peroxydisulfate as oxidant catalyzed by silica-supported aluminum chloride

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Abstract Sodium peroxydisulfate was used as the oxidant for Baeyer–Villiger oxidation of a variety of cyclic and acyclic ketones at room temperature in the presence of silica-supported aluminum chloride (silica- AlCl_3) as catalyst. The catalyst was prepared by a simple procedure, which exhibited high catalytic activity for the Baeyer–Villiger oxidation of ketones using environmental friendly sodium peroxydisulfate as oxidizing agent.

Keywords Baeyer–Villiger oxidation · Silica-supported aluminum chloride · Sodium peroxydisulfate · Silica- AlCl_3

Introduction

The Baeyer–Villiger oxidation is one of the major reactions in organic chemistry, particularly, in conversion of cyclic and acyclic ketones into lactones or esters by regioselective oxygen insertion into C–C bond [1]. Baeyer–Villiger oxidations traditionally have conducted using organic peracids such as trifluoroperacetic acid, perbenzoic acid and *m*-chloroperbenzoic acid. Excess utilization of these oxidants potentially produces large amounts of harmful wastes that lead to serious environmental problems [2–5]. In addition, the preparation of these reagents requires hazardous concentration levels of hydrogen peroxide (H_2O_2). Recently, there have been many researches trying to find chemically green reagents, oxidants and catalysts, which can overcome to abovementioned disadvantages [6, 7].

In this regard, a number of different catalytic systems have been developed to accomplish Baeyer–Villiger oxidation. The catalysts based on polymer-anchored metal complexes [8–10], solid acids [11, 12], zeolites [13], titanium silicalite [14], Sn-MCM-41 [15], sulfonated resins [16], Sn-synthesized hydrotalcites [17], Sn- β zeolite [18], hydrotalcite-supported Sb catalyst [19], Pt [20], Zr [21], Re [22], Se [23], As [24] and Mo [25] are examples of some of the heterogeneous and homogeneous catalysts used to perform the Baeyer–Villiger oxidation. These catalysts activate H_2O_2 as a clean oxidant by increasing its nucleophilicity and facilitate attack by the oxidizing species on the carbonyl carbon atom [26]. Most of these processes, however, suffer from some disadvantages like low activity or selectivity and expensive catalyst or the need for high concentration of H_2O_2 .

In order to overcome the above problems, the new effective heterogeneous catalysts based on cellulose-supported dendritic Sn complex [27] montmorillonite (MMT) supported tin (II) chloride [28], Sn-palygorskite [29] and aminomethyl polystyrene resin-supported tin complex [30] were reported for the chemoselective Baeyer–Villiger oxidation of a variety of cyclic and acyclic that can selectively activate the ketone instead of the H_2O_2 . This way readily leads to increase of the positive charge on the carbon atom of the carbonyl group and facilitates the nucleophilic attack on this group by H_2O_2 . Therefore, high yields and excellent selectivities can obtain in low concentration of H_2O_2 using these catalytic systems.

As another potential catalyst for this reaction, Lei et al. [31] have recently used a silica-supported aluminum chloride heterogeneous catalyst containing 2.65% Al with H_2O_2 as oxidant, for the chemoselective Baeyer–Villiger oxidation of a variety of cyclic and acyclic ketones at 70 °C. The utilization of hydrogen peroxide as oxidizing

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agent produces water (byproduct) which may decrease the activity of the catalyst and even hydrolyze reaction product in reaction media. In order to solve these problems, we employed sodium peroxydisulfate as good alternative to H_2O_2 for selective oxidation of a wide variety of cyclic and acyclic ketones into the corresponding lactones and esters in the presence of silica-supported aluminum chloride as catalyst. Since peroxydisulfate ion is one of the strongest oxidizing agents and is even stronger than H_2O_2 (Standard redox potential in aqueous solution is estimated to be 2.01 compared to 1.77 for H_2O_2) [32], we expected to obtain higher yields with sodium peroxydisulfate under mild conditions (room temperature) compared to H_2O_2 (at 70 °C). Hence, to show the ability of this new oxidation system we successfully prepared the silica-supported aluminum chloride and used it along with sodium peroxydisulfate for Baeyer–Villiger oxidation of cyclic and acyclic ketones under mild conditions (room temperature). In continuation of work, some of the results of our experiments are compared with some of those reported for the current heterogeneous catalysts with respect to their yield, selectivity and the reaction temperature.

Experimental

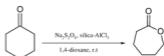
Aluminum chloride, peroxydisulfate salts, silica gel (chromatographic-grade, 70–230 mesh), and all the ketones used in the experiments were purchased from Merck Company and used without further purification. All solvents obtained from commercial sources were used as received.

Methods and instrumentations

The progress of the reactions were monitored by thin-layer chromatography (TLC) carried out on Sigma-Aldrich silica gel 60 F254 plates. The products were washed twice with 1,4-dioxane and then dried in the vacuo. The obtained products were detected via retention times as measured by GC/MS analysis on a Hewlett-Packard 6890 GC instrument (Helium as carrier gas) furnished with an HP-5MS (30 m \times 0.25 mm \times 0.25 μ m) column and Hewlett-Packard 5973N MSD instrument. The loading of $AlCl_3$ in the catalyst was determined by the Mohr titration. IR spectra were recorded on a Shimadzu 470-IR spectrophotometer as neat films on KBr pellets.

Catalyst preparation

Catalyst was prepared according to the literature method [31]. Chromatographic-grade Silica gel (1 g, 70–230 mesh) was leached with 1 M HCl (40 mL) at room temperature



Scheme 1 Baeyer–Villiger oxidation of cyclohexanone into ϵ -caprolactone

for 1 h. Aluminum chloride (2 g) was then added to the mixture and resultant slurry was stirred at room temperature for 2 days. The precipitates were collected by filtration under reduced pressure, washed with excess amounts of ethanol, and dried at 100 °C under vacuum for 3 h. In order to determine the amount of $AlCl_3$ on the silica surface, 0.5 g of solid catalyst was fused with Na metal, extracted with 5 ml of water and filtered. The aluminum and chloride content of the filtrate was determined by the Mohr titration method [33].

Ketone oxidation

A typical procedure for the Baeyer–Villiger oxidation is as the following: silica-supported aluminum chloride (0.97 g) was added to a stirred mixture of cyclohexanone (0.25 mL, 2.5 mmol) and sodium peroxydisulfate (1.19 g, 5 mmol) in 5 mL of 1,4-dioxane. The suspension was stirred at room temperature for 24 h (Scheme 1). The progress of the reaction was monitored by thin-layer chromatography (TLC) (eluent: diethyl ether/ethyl acetate: 3/1). After the completion of reaction, the catalyst was removed by filtration, and washed twice with 1,4-dioxane. The combined filtrates were evaporated to remove the solvent in vacuo and then the resulting residue was identified by GC/MS analysis procedure. Other cyclic and acyclic ketones were also oxidized in this oxidation system to give the corresponding lactones or esters. All of the products were known, and their structures determined by comparing mass spectra and fragmentation patterns with a GC/MS instrument library search (Wiley 275) and those of the authentic compounds [34].

Results and discussion

Catalyst preparation and characterization

Aluminum chloride is very active catalyst in oxidation of cyclic and acyclic ketones that is soluble in many organic solvents and produces unwanted side reactions. Using silica-supported aluminum chloride, the high reactivity of this active Lewis acid is under control that leads to quantitative and selective yields [35].

Silica-supported aluminum chloride that is a Brønsted acid with a strength intermediate between zeolites and magic acid was prepared by reacting of aluminum chloride with silica under carefully controlled conditions [36]. At the first, the silica was conditioned via leaching with 1 M HCl to form a specified range of surface silanols. The silica is then reacted with aluminum chloride by stirring at room temperature (Scheme 2).

Figure 1 displays IR spectra of natural silica and silica-supported aluminum chloride. Comparison of two IR spectra reveals that the peak positions and shapes of the main specific bands in the spectra are quite similar to each other. For example, the bands corresponding to the symmetric and asymmetric vibrations of Si–O–Si are situated at 829 and 1,110 cm^{-1} , respectively, and are similar in the two spectra. The main differences between the two spectra is due to the two additional bands at 600 and 660 cm^{-1} corresponding to backbone vibrations of Al–O groups,

while there is not any peak at these positions in the spectrum of the natural silica. The loading of AlCl_3 in the catalyst based on its chloride determination was 1.6 mmol AlCl_3/g . The result confirms that silica-supported aluminum chloride catalyst was successfully prepared in this work.

Oxidation mechanism

A possible reaction mechanism using silica-supported aluminum chloride as catalyst for the Baeyer–Villiger oxidation of cyclopentanone is shown in Scheme 3.

First, the ketone is coordinated to the Lewis acid Al^{3+} center, and thereby, the carbonyl group is activated. Sodium peroxydisulfate subsequently attacks the electrophilic carbonyl carbon atom of coordinated ketone that leads to Criegee adduct intermediate. After the intramolecular rearrangement, the lactone product is replaced by a

Scheme 2 Reaction of AlCl_3 with silica gel

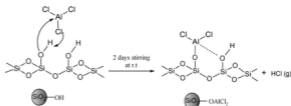
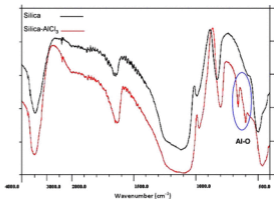
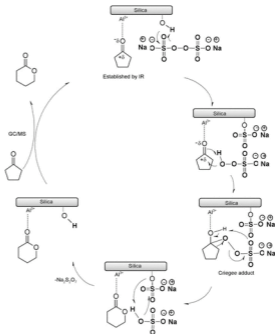


Fig. 1 The IR spectra of natural silica and silica- AlCl_3



Scheme 3 Catalytic mechanism for the oxidation of cyclopentanone with $\text{Na}_2\text{S}_2\text{O}_8/\text{silica-AlCl}_3$



new substrate molecule. This mechanism is analogous to that for peracids, which Coema et al. [6] have confirmed by means of an ^{18}O labeling experiment, infrared spectroscopy and gas chromatography–mass spectrometry.

Reaction optimization

Amount of catalyst is very important for a reaction, so we investigated the effect of amount of silica-supported aluminum chloride catalyst on the Baeyer–Villiger oxidation of cyclohexanone. Generally, the reaction yield was increased over the amount of catalyst. It was found that 0.97 g of catalyst was appropriate amount for reaction. The less amounts gave a low yield, and more amounts could not cause the obvious increase for yield of product. Hence, the optimum ratio of catalyst to substrates was chosen 0.97 g: 5 mmol, and cyclohexanone was converted

into corresponding lactone quantitatively when the reaction was carried out using 1,4-dioxane as the solvent at room temperature for 24 h.

Subsequently, as Table 1 shows, the effect of the molar of substrate to oxidant under reaction conditions has been investigated. The results show the molar ratio of cyclohexanone to sodium peroxydisulfate had significant effect on the oxidation reaction. When the molar ratio of cyclohexanone to sodium peroxydisulfate was 2.5:2.5, the corresponding lactone was obtained in 74% yield (Entry 1). The yield of reaction with 2.5 mmol of cyclohexanone increased slowly with increasing the amount of sodium peroxydisulfate up to 5 mmol, giving 84%. When the ratio was increased to 2.5:6, the yield was 84% that was not increased (Entry 5). Hence, the optimum molar ratio of cyclohexanone to sodium peroxydisulfate was chosen 2.5:5.

Table 1 The effect of cyclohexanone/Sodium peroxydisulfate molar ratio on Baeyer–Villiger oxidation of the cyclohexanone by silica- AlCl_3 

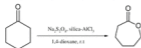
Entry	Substrate/oxidant	Conversion ^a (%)
1	2.5:2.5	74
2	2.5:3	77
3	2.5:4	81
4	2.5:5	84
5	2.5:6	84

Reaction condition: Substrate 2.5 mmol, reagent 2.5–6 mmol, Catalyst 0.97 g, 1,4-dioxane 5 ml, r.t., 24 h

^a Conversion percentage was determined by GC/MS analysis

Baeyer–Villiger oxidations of cyclohexanone with different peroxydisulfate salts

Actually, commercially available compounds containing peroxydisulfate ion are sodium peroxydisulfate, potassium peroxydisulfate and di-ammonium peroxydisulfate. For comparison of the effect of different peroxydisulfate salts as oxidant on yield of cyclohexanone under established optimum conditions, cyclohexanone has been used as the substrate with different peroxydisulfate salts in the presence of silica-supported aluminum chloride. The mixture of reaction was also stirred at room temperature for 24 h. The results are summarized in Table 2.

Table 2 Oxidation of cyclohexanone with different peroxydisulfate salts

Entry	Reagent	Conversion ^a (%)
1	$\text{Na}_2\text{S}_2\text{O}_8$	84
2	$\text{K}_2\text{S}_2\text{O}_8$	77
3	$(\text{NH}_4)_2\text{S}_2\text{O}_8$	70

Reaction condition: substrate 2.5 mmol, reagent 5 mmol, catalyst 0.97 g, 1,4-dioxane 5 ml, r.t., 24 h

^a Conversion percentage was determined by GC/MS analysis

From Table 2, it can be observed the fact that using sodium peroxydisulfate as oxidant exhibits the higher conversion of cyclohexanone into corresponding lactone, indicating that sodium peroxydisulfate is the best reagent among all peroxydisulfate salts used in Baeyer–Villiger oxidation of cyclohexanone. For this reason, sodium peroxydisulfate oxidation of other cyclic and acyclic ketones in the presence of silica-supported aluminum chloride as catalyst at room temperature has been developed.

Oxidation of other cyclic and acyclic ketones

A series of cyclic and acyclic ketones were oxidized with sodium peroxydisulfate catalyzed by silica- AlCl_3 affording the corresponding lactones or esters. Table 3 summarizes the related results.



























It can be seen from Table 3 that the yields of reactions were good-to-excellent which shows sodium peroxydisulfate is an active and efficient oxidant in the Baeyer–Villiger oxidation of cyclic and acyclic ketones in the presence of silica-supported aluminum chloride as catalyst.

The conversion after 24 h of reaction for Entry 2 was equal to 84%. With substituted methylcyclohexanone (Entry 4 in Table 3), the catalytic activity for the desired product decreased to 74%. Actually, this result is consistent with the proposed mechanism. In fact, the presence of two methyl substitutes in methylcyclohexanone must hinder the adsorption of the catalyst and hence the formation of the Criegee adduct. This could be the reason why the catalyst activity is lower for substituted methylcyclohexanone compared to cyclohexanone. In case of unsymmetrical ketones (Entries 10–13 in Table 3), the expected esters were obtained in ratios depending on the migratory aptitude of the group adjacent to the carbonyl moiety. In fact, less than 100% selectivity can be ascribed to their asymmetry allowing the formation of two different esters. The outstanding of this catalytic system was that the catalyst is active for the oxidation of cyclic and acyclic ketones under mild reaction conditions, and it may facilitate the development of its industrial applications. Furthermore, the silica-supported aluminum chloride could be easily separated from the reaction mixture only by filtration.

Catalyst reuse

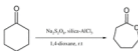
In order to investigate the recycling properties of silica-supported aluminum chloride as the catalyst, three batches of the experiments (Table 4) were carried out for 24 h at room temperature in 1,4-dioxane. Then, cyclohexanone was chosen as the test substrate for the oxidation with sodium peroxydisulfate. The catalyst is repeatedly filtered out and washed with excess 1,4-dioxane, afterward it was submitted to a new reaction batch. At this step, it could be

Table 3 Baeyer–Villiger oxidation of the ketones by $\text{Na}_2\text{S}_2\text{O}_8/\text{silica-AlCl}_3$

Entry	Substrate (a)	Selectivity ^a (%)	Conversion ^a (%)	Product (b)
1		100	100	
2		100	84	
3		100	73	
4		100	72	
5		100	90	
6		100	85	
7		100	82	
8		100	65	
9		100	78	
10		83	72	
11		73	71	
12		72	78	
13		75	82	

Reaction condition: substrate 2.5 mmol, reagent 5 mmol, catalyst 0.97 g, 1,4-dioxane 5 ml, r.t., 24 h

^a Conversion percentage was determined by GC/MS analysis


Table 4 The recycling of silica-supported aluminum chloride


Recycling time	1	2	3
Conversion ^a (%)	84	76	63

Reaction condition: substrate 2.5 mmol, reagent 5 mmol, catalyst 0.97 g, 1,4-dioxane 5 ml, r.t., 24 h

^a Conversion percentage was determined by GC/MS analysis

obtained that the activity is 76 and 63% after two and three cycles, respectively. As shown in Table 4, silica-supported aluminum chloride could be recycled as the heterogeneous catalyst, even although the catalytic conversion is lowered to about 63% from the original 84% after three batches of the recycling experiment. Actually, the reason of decreasing the catalytic activity is unclear. It could be due to happening the continuous catalyst leaching at each cycle or blocking of the active sites in the catalyst by either products or intermediates involved in the reaction.

Table 5 Comparison of some of the results obtained from $\text{Na}_2\text{S}_2\text{O}_8/\text{Silica-AlCl}_3$ and some of those reported with $\text{H}_2\text{O}_2/\text{Sn-MMT}$, $\text{H}_2\text{O}_2/\text{Sn-palygorskite}$, $\text{H}_2\text{O}_2/\text{Sn-PS}$ and $\text{H}_2\text{O}_2/\text{Silica-AlCl}_3$


Entry	Oxidation system	Conversion ^a (%)	Selectivity (%)	Temp (°C)	Ref.
1	$\text{Na}_2\text{S}_2\text{O}_8/\text{Silica-AlCl}_3$	100	100	r.t.	–
2	$\text{H}_2\text{O}_2/\text{Sn-MMT}$	45	100	90	[28]
3	$\text{H}_2\text{O}_2/\text{Sn-palygorskite}$	81	100	70	[29]
4	$\text{H}_2\text{O}_2/\text{Sn-PS}$	22	100	70	[30]
5	$\text{H}_2\text{O}_2/\text{Silica-AlCl}_3$	37	75	70	[31]

^a Reaction condition: substrate 2.5 mmol, $\text{Na}_2\text{S}_2\text{O}_8$ 5 mmol, catalyst 0.97 g, 1,4-dioxane 5 ml, r.t., 24 h

^b Conversion percentage was determined by GC/MS analysis

Comparison with other oxidation systems

In Table 5, some of the results of the experiments are compared with those reported by other methods. The results show that when the oxidative activities of H_2O_2 and sodium peroxydisulfate for the Baeyer–Villiger oxidation of cyclopentanone in the presence of silica-supported aluminum chloride as catalyst were compared (Entries 1 and 5), using sodium peroxydisulfate as oxidant led to higher yield and selectivity than using H_2O_2 . The utilization of hydrogen peroxide as oxidant produces water (byproduct) which could decrease the activity of the catalyst and even hydrolyze reaction product in Baeyer–Villiger oxidation. In contrast, the usage of sodium peroxydisulfate as oxidizing agent avoids the hydrolysis of products, since no water is formed in reaction media. These could be the reasons why the H_2O_2 shows low yield and selectivity compared to sodium peroxydisulfate in the presence of same catalyst. The oxidation under mild conditions (room temperature) and high yield could be the obvious advantages for Baeyer–Villiger oxidation of cyclopentanone with sodium peroxydisulfate in the presence of silica-supported aluminum chloride compared to those reported with H_2O_2 oxidant in the presence of other catalysts (Entries 1–4).

Conclusion

At this work, an efficient and mild method has been described for the Baeyer–Villiger oxidation of cyclic and acyclic ketones to the relevant lactones or esters at room temperature using sodium peroxydisulfate in the presence of silica- AlCl_3 as catalyst. This procedure leads to high product yields together with the complete absence of byproduct problems. However, the proposed method could strongly be considered as a procedure for the future works due to mild reaction conditions, reasonable results, ease of workup and reusability of the catalyst as well.

Mass spectroscopic data

Compound 1b: GC–MS (EI^+ , 70 eV): m/z 100 (M^+), 70, 56, 42, 41 (100%), 28, 27.

Compound 2b: GC–MS (EI^+ , 70 eV): m/z 114(M^+), 84, 70, 55 (100%), 56, 42, 41, 28, 27.

Compound 3b: GC–MS (EI^+ , 70 eV): m/z 128(M^+), 98, 84, 70, 69, 55 (100%), 41, 31, 29, 27.

Compound 4b: GC–MS (EI^+ , 70 eV): m/z 142(M^+) (100%), 127, 114, 98, 84, 70, 56, 42, 28, 15.

Compound 5b: GC–MS (EI^+ , 70 eV): m/z 170(M^+), 155, 137, 125, 114 (100%), 97, 86, 68, 57.

Compound 6b: GC–MS (EI^+ , 70 eV): m/z 210 (M^+), 127, 111, 99, 83 (100%), 71, 55, 43.

Compound 7b: GC–MS (EI⁺, 70 eV): *m/z* 166 (M⁺, 5), 122, 107, 93, 80 (100), 67, 53, 41.

Compound 8b: GC–MS (EI⁺, 70 eV): *m/z* 102 (M⁺), 87, 75, 57 (100%), 45, 43, 29, 27, 15

Compound 9b: GC–MS (EI⁺, 70 eV): *m/z* 130 (M⁺), 101, 89, 71 (100%), 60, 43, 27, 15.

Compound 10b: GC–MS (EI⁺, 70 eV): *m/z* 88 (M⁺), 73, 70, 61, 43 (100%), 29.

Compound 11b: GC–MS (EI⁺, 70 eV): *m/z* 115 (M⁺ – 1), 101, 86, 73, 61, 56, 43 (100%), 29.

Compound 12b: GC–MS (EI⁺, 70 eV): *m/z* 102 (M⁺), 87, 61, 43 (100%), 31, 27, 15.

Compound 13b: GC–MS (EI⁺, 70 eV): *m/z* 116 (M⁺), 101, 57, 43 (100%), 29, 15.

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