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Clean Baeyer–Villiger Oxidation Using Hydrogen Peroxide as Oxidant Catalyzed by Aluminium Trichloride in Ethanol

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Abstract Baeyer–Villiger oxidation of ketones was carried out using $AlCl_3$ as catalyst, H_2O_2 (30%) as oxidant in innocuity and environmentally friendly ethanol conditions. Cyclic ketones and acyclic ketones were transformed into the corresponding lactones or esters in 5–24 h at 40–70 °C with very high conversion and selectivity. A possible reaction mechanism was also given.

Keywords Baeyer–Villiger oxidation · Ketones · Aluminium trichloride · Ethanol

1 Introduction

The Baeyer–Villiger oxidation, discovered as early as 1899 [1], is one of the major reactions in organic chemistry and plays an important role in practice. Earlier Baeyer–Villiger oxidation was generally carried out by the utilization of peroxy compounds such as *m*-chloroperbenzoic acid, trifluoroperacetic acid, and peroxybenzoic acid [2]. Excess utilization of these oxidants gives rise to large amount of harmful wastes which lead to serious environmental problems. For economic and environmental reasons a variety of researches have been made to develop new catalytic methods. Low concentration of hydrogen peroxide (<30%) is a highly attractive oxidant for a number of reasons: it is a cheap, mild and an environmentally benign reagent with a high content of active oxygen, and water is formed as only by-product. However, expensive catalysts are normally required to affect oxygen transfer from hydrogen peroxide to the substrate. Recently much effort has been devoted to finding new chemical methods which use low concentration hydrogen peroxide as oxidant and recyclable catalysts [3–9]. Among many metal catalysts, Sn based catalysts which assist the utilization of hydrogen peroxide were studied extensively [10–15]. Strukul, one of the pioneer researchers in the field of Baeyer–Villiger oxidation, remarked [16] that the best system was the catalytic system for the Baeyer–Villiger reaction reported by Corma and his colleagues. Corma et al. [10] found that Sn-Zeolite beta was a very active and selective catalyst for the Baeyer–Villiger oxidation of cycloketones with environmentally benign hydrogen peroxide as an alternative to organic peroxy acids. The Sn-zeolite beta was synthesized using dealuminated nanocrystalline (20 nm) zeolite as seeds and a crystallization procedure was performed in Teflon-lined stainless steel autoclaves, which were heated to 140 °C and rotated over a period of 20 days.

We have found that $AlCl_3$ is active in the oxidation of cyclic and acyclic ketones using H_2O_2 as oxidant, and developed a clean and simple protocol for the oxidation of ketones by using environmentally friendly reagents. The nontoxic catalyst $AlCl_3$, for example, is commercially available and very cheap. The mild reaction conditions, environmentally friendly oxidant, halogen free reaction medium, short reaction time and high to excellent yields for a series of ketones are the obvious advantages of the present method. The procedure can be carried out smoothly without the utilization of any expensive or harmful substance.

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2 Experimental

2.1 Materials and Instrumentation

$AlCl_3$, ethanol, 2-andamantanone, cyclopentanone, cyclohexanone, 2-methylcyclohexanone, 4-methylcyclohexanone, 2-*tert*-butylcyclohexanone, 4-*tert*-butylcyclohexanone, cyclooctanone, carvone, DL-menthone, 4-methyl-2-pentanone and 2,6-dimethyl-4-heptanone were obtained from commercial sources and used as received without further purification. GC analysis was carried out on a GC (SHIMADZU, GC-2010); GC-MS measurement was performed on a GC/MS (HP GC 6890/MS 5973) instrument. The NMR spectra were recorded on FT-NMR 400 MHz (Brucker) in $CDCl_3$ using TMS as an internal standard.

2.2 Oxidation Procedure

Oxidation of ketones was carried out in a 10 mL glass reactor. A typical procedure for the Baeyer–Villiger oxidation was as follows: 2-Adamantanone (15 mg, 0.1 mmol) were dissolved in 3 mL ethanol, 3 mg (2.2×10^{-2}) of $AlCl_3$ were added in the solution, and 10 min later 30% hydrogen peroxide (2.0 eq. to the ketone) was added. The mixture was stirred for 5–24 h at 40–70 °C. A series of the experiments have been done in order to investigate the effect of catalyst amount, reaction temperature and time on 2-Adamantanone conversion and product selectivity. The results are summarized in Figs. 1–3.

2.3 Oxidation Procedure for Getting Isolated Product

To a 25 mL glass reactor, 30 mg (0.2 mmol) of 2-adamantanone, 5 mL of ethanol and 6 mg (4.5×10^{-2}) of $AlCl_3$ were added and stirred, and then 30% hydrogen peroxide (0.4 mmol) was added. The mixture was stirred for 8 h at 40 °C. Pure product was obtained through column chromatography (silica gel) using petroleum ether and ethyl acetate (10:1, v/v) as eluent. The yield is 96%.

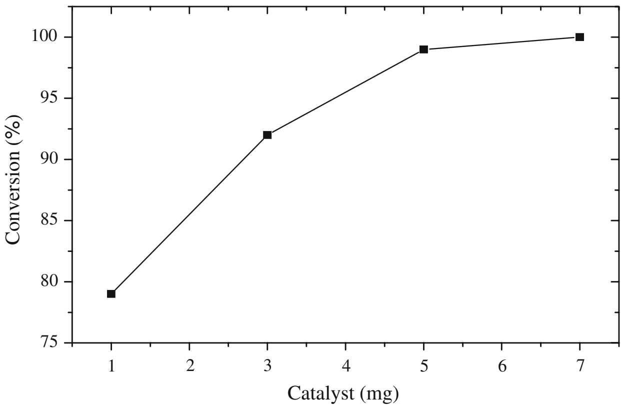


Fig. 1 Oxidation of 2-andamantanone with different amount of catalyst. Reaction condition: substrate 0.1 mmol, 30% H_2O_2 2.0 eq, 6 h at 50 °C

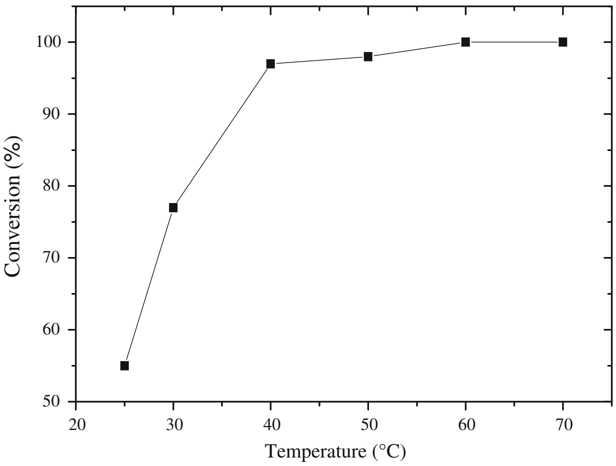


Fig. 2 Oxidation of 2-andanamtanone at different temperature. Reaction condition: substrate 0.1 mmol, 30% H_2O_2 2.0 eq, cat. 3 mg, 6 h

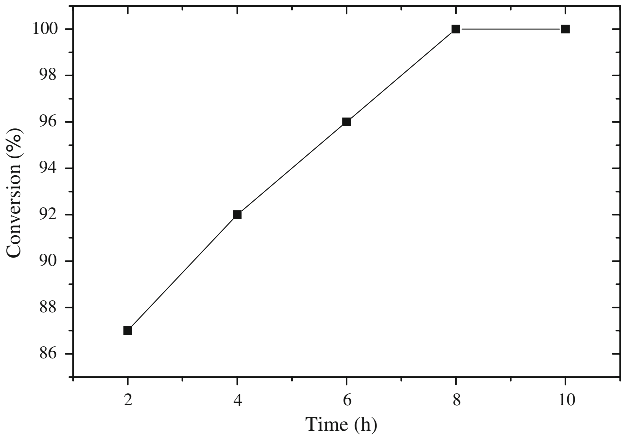


Fig. 3 Oxidation of 2-andanamtanone with different reaction period. Reaction condition: substrate 0.1 mmol, 30% H_2O_2 2.0 eq, cat. 3 mg, 40 °C

2-Adamantanlactone: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.489(CH–O), 3.09(CH), 3.076(CH), 3.061(CH), 2.099(CH_2), 2.011(CH_2), 1.943(CH_2), 1.840(CH_2), 1.722(CH_2): ^{13}C NMR ($CDCl_3$, 400 MHz): δ 178.960, 73.121, 41.174, 35.801, 35.710, 33.744 30.894, 25.826, 25.780.

3 Results and Discussion

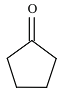
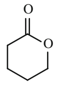
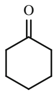
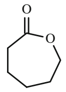
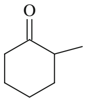
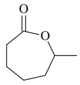
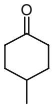
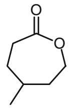
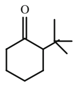
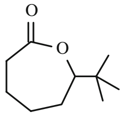
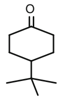
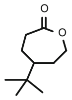
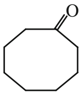
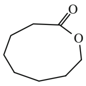
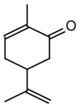
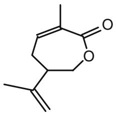
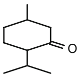
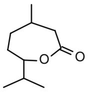
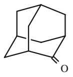
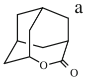
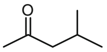
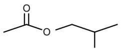
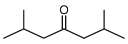
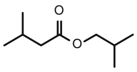
Experiments have been done to investigate effect of use of catalyst amount, reaction temperature and time on some ketones conversion and products selectivity. In order to study the effect of the ratio of catalyst to substrate the reaction was carried out for 6 h at 50 °C. 2-Adamantanone was chosen as test substrate for the oxidation with hydrogen peroxide. Different amount of catalyst was used to investigate the corresponding variations of oxidation results. If the amount of the substrate 2-adamantanone was stabilized, the oxidation results vary with the amount of the catalyst. The results were shown in Fig. 1. The conversion of the substrate reaches 79%, 92%, 99% and 100% when the corresponding amount of catalyst was used.

Temperature is another factor which influences the oxidation. The reactions were carried out for 6 h at different temperatures to investigate the influence of the reaction temperature on the Baeyer–Villiger oxidation reactions. 2-Adamantanone was also chosen to test oxidation with hydrogen peroxide as oxidant. The effect of the reaction temperature was summarized in Fig. 2. The oxidation occurs at a relatively low temperature, for instance, 2-adamantanone can be oxidized with 55% substrate conversion at room temperature. The result shows that the conversion increased from 55% to 100% as the reaction temperature increased from 25 to 60 °C. Although relatively higher conversion can be obtained at higher temperatures; the selectivity to the product was decreased with the temperature.

The reactions were also carried out to investigate the effect of the reaction time on the substrate conversion and product selectivity; the results were shown in Fig. 3. For the oxidation of 2-adamantanone, the reactions generally begin with relatively fast rates in the first 2–8 h. The results also indicated that the conversion increases with the reaction time in a period of 10 h.

Having established the optimum reaction condition, the procedure was successfully extended to a number of other ketones such as cyclohexanone, 2-methylcyclohexanone, 4-methylcyclohexanone, 2-*tert*-butylcyclohexanone, 4-*tert*-butylcyclohexanone, cyclopentanone, cyclooctanone, carvone, DL-menthone, 4-methyl-2-pentanone and 2,6-dimethyl 4-heptanone. An unsaturated ketone carvone was completely oxidized in ethanol using 3 mg of $AlCl_3$ in 8 h at 60 °C. The unsaturated bond tends to be stable in this oxidation system. As shown in Table 1, the substrate conversion obtained were generally encouraging for 2-andamantanone, 2-methylcyclohexanone, 4-methylcyclohexanone, 2-*tert*-butylcyclohexanone, 4-*tert*-butylcyclohexanone, cyclopentanone, cyclooctanone, carvone, DL-menthone, 4-methyl-2-pentanone and 2,6-dimethyl 4-heptanone. The selectivity to the product exceeds 99% for 2-andamantanone, 4-methylcyclohexanone, 4-*tert*-butylcyclohexanone, cyclopentanone, cyclooctanone, carvone, DL-menthone, 4-methyl-2-pentanone and 2,6-dimethyl

Table 1 Baeyer–Villiger oxidation of several ketones catalyzed by $AlCl_3$

Substrate	Temp. (°C)	Time (h)	Conv. (%)	Select. (%)	Product
	70	24	100	>99	
	70	24	80	>99	
	60	5	100	>72	
	60	7	100	>99	
	60	16	100	>67	
	60	9	100	>99	
	70	14	100	>99	
	60	8	100	>95	
	70	9	100	>99	
	40	8	100	>99	 [a]
	40	24	100	>99	
	70	24	100	>99	

Reaction condition: substrate 0.1 mmol, 30% H_2O_2 2.0 eq, Cat.3 mg. Percentage conversion and product selectivity were determined using GC analysis

[a] Getting isolated product

4-heptanone. The outstanding of this catalytic system was that besides cyclic ketones, the catalyst was also active for the oxidation of acyclic ketones. The results show that $AlCl_3$ was an active and efficient catalyst for oxidation of cyclic and acyclic ketones in mild reaction condition. The products we reported here were much cleaner than the traditional BV oxidation as it gave relatively higher conversion in a relatively shorter reaction period without the utilization of any toxic or expensive materials.

Some authors previously used high concentration hydrogen peroxide (60%) [17] or 2–6 equivalent of hydrogen peroxide [18]. High concentration hydrogen peroxide is very dangerous .More hydrogen peroxide would bring more water which could debase the activity of catalyst and even hydrolyze ester in Baeyer–Villiger oxidation. We used 2 equivalents of 30% H_2O_2 as oxidant. According to the mass balance the oxidant could be remain 0.1 mmol at least at the end of the reaction.

As used 2 equivalent H_2O_2 (30%) as oxidant, there was about 8–10% of the reaction medium. $AlCl_3$ was excellent Lewis acid catalysts in water under proper condition [19] and Lewis acid catalysts can activate carbonyl groups [20]. As a hard Lewis acid $AlCl_3$ could coordinates with hard basic centres. The ketones which would be oxidated have carbonyl group, and the oxygen atom of the carbonyl group is hard basic, therefore Al^{3+} would coordinate with the oxygen atom, activating the ketones for a nucleophilic attack. Water is another hard base, When we added H_2O_2 (30%) some $AlCl_3$ dissociates in water very quickly and hydration occurs immediately with the formation of the corresponding aquaion, such as $Al(H_2O)_6{}^{3+}$, at the same time, H_2O_2 that has alkalescent peroxide group could coordinate with $Al(H_2O)_6{}^{3+}$ as is the formation of $Al(H_2O)_5(H_2O_2)^{3+}$, or even $Al(H_2O)_5(OOH)^{2+}$ (i.e. a peracid) with H^+ release. Therefore $AlCl_3$ may be not the only active catalytic species in this catalytic system.

We confirmed that the oxidation reaction did not occur in the absence of the catalyst. Moreover $Al(OH)_3$ which is $AlCl_3$ completely hydrated product also could not catalyze the reaction.

The reaction mechanism using $AlCl_3$ as catalyst for the Baeyer–Villiger oxidation could be very complicated, for there was not one active catalytic species in this catalytic system. Further work exploring the utility of this novel catalyst is on-going in our laboratory.

4 Conclusions

In this study we have shown that $AlCl_3$ is an active and efficient catalyst for the B–V oxidation reactions using environmentally benign H_2O_2 as oxidant. The system provides excellent catalytic activity, good product selectivity for the oxidation of general cyclic and acyclic ketones. It is noteworthy that the system is very simple, mild and environmentally benign. The materials used in this oxidation process are cheap, nontoxic and commercially available.

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