Heterogeneous Baeyer–Villiger Oxidation of Ketones using an Oxidant consisting of Molecular Oxygen and Aldehydes in the Presence of Hydrotalcite Catalysts

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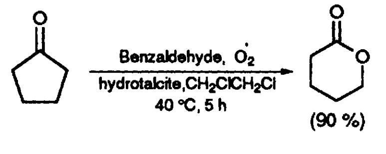
Hydrotalcites catalyse Baeyer–Villiger oxidation of ketones using a combination oxidant system of molecular oxygen and benzaldehyde to give high yields of lactones and esters at 40 °C.

Catalysis of clay minerals has attracted much interest, because they have potential abilities as shape recognition of guest materials and highly selective catalysts.[1] Such organic reactions directed by hydrotalcites of layered compounds, however, have not been explored extensively yet and there are few examples for oxidation.[2] In Baeyer–Villiger oxidation, various reagents and metal catalyst systems have been continuously developed.[3] Here, we wish to report heterogeneous Baeyer–Villiger oxidation of ketones catalysed by hydrotalcites using a combination oxidant of molecular oxygen and aldehydes.[4] Notably, the hydrotalcite catalyst sytem has not only an advantage on easy separation of a solid catalyst from the reaction mixture, but also has unique catalytic properties as a base; a higher activity for oxidation of five-membered ring ketones than for that of six-membered ones, whose phenomenon has not been observed in Baeyer–Villiger oxidation using organic peracids.[5,3c]

Various hydrotalcites of $Mg_2Al_2(OH)_8CO_3$,[6a] $Mg_6Al_2(OH)_{16}CO_3$,[6a] $Mg_{10}Al_2(OH)_{24}CO_3$,[6a] $Mg_{16}Al_2(OH)_{36}CO_3$,[6a] $Mg_5Al(OH)_{12}$(toluene-*p*-sulfonate)[6b] and $Mg_5Al(OH)_{12}Cl$[6c] were prepared according to literature procedures. A typical procedure of Baeyer–Villiger oxidation of ketones is as follows. Into a three-necked flask with a reflux condenser cooled at −15 °C were placed the hydrotalcite of $Mg_{10}Al_2(OH)_{24}CO_3$ (25 mg), benzaldehyde (12 mmol) and 1,2-dichloroethane (15 ml), and oxygen was bubbled into the stirred heterogeneous mixture at 40 °C for 30 min. A 1,2-dichloroethane solution (5 ml) of cyclopentanone (4 mmol) was added and the resulting mixture was stirred with bubbling of oxygen at 40 °C for 4.5 h. Hydrotalcite was separated by filtration, followed by successive treatment of the filtrate with Na_2SO_3 and $NaHCO_3$. Oxygenation products in the 1,2-dichloroethane solution were then analysed by GC and δ-valerolactone (0.328 g; 82%) was isolated by column chromatography on silica gel (hexane–ethyl acetate, 3 : 1).

We have already reported that the combination oxidant of aldehydes and molecular oxygen selectively epoxidized olefins even in the absence of metal catalysts.[7] Using ketones in place of olefins, Baeyer–Villiger oxidation of ketones occurred to give the corresponding lactones and ester. Bolm *et al.* have also found a similar phenomenon on the Baeyer–Villiger oxidation in the absence of metal catalysts.[4c] On the other hand, addition of the hydrotalcites to the above reaction system promoted to yield Baeyer–Villiger products. Catalytic effect of various hydrotalcites on oxidation of cyclopentanone using benzaldehyde is shown in Table 1, together with that of other base solid compounds. The hydrotalcites of $Mg_{10}Al_2(OH)_{24}CO_3$ and $Mg_5Al(OH)_{12}Cl$ have the highest activity for this Baeyer–Villiger oxidation. In series of hydrotalcites with carbonate anions (Mg : Al *ca.* 1 : 1–8 : 1), $Mg_{10}Al_2(OH)_{24}CO_3$ with Mg : Al = 5 : 1 is the best catalyst. Among the aldehydes used, benzaldehyde is the most effective, and aliphatic aldehydes, *e.g.* isobutyraldehyde and isovaleraldehyde, having high reactivity for the epoxidation of olefins,[7] showed low yield of the lactone. In all cases, the above aldehydes were oxidized to the corresponding carboxylic acids as coproducts. 1,2-Dichloroethane and tetrachloromethane are good solvents, respectively, while methanol did not yield the lactone.



(1)

Representative results of the oxidation of ketones with benzaldehyde in the presence and the absence of $Mg_{10}Al_2(OH)_{24}CO_3$ are shown in Table 2. Generally, the hydrotalcite system has high catalytic activities for five-membered ring ketones and *p*-methoxyacetophenone. It is interesting that oxidation of cyclopentanone is faster than that of cyclohexanone and reverse reactivity has been observed in the absence of the hydrotalcite and also in organic peracid sytems.[5] Both 2-methylcyclopentanone and 2-methylcyclohexanone gave the corresponding lactones in high yields, respectively, compared with those in the non-metal systems. Oxidation of substituted cyclic ketones, except norcamphor, gave exclusively one regioisomer of Baeyer–Villiger products.

It is said that inorganic bases, *e.g.* Na_2CO_3, $NaHCO_3$ and $NaHPO_4$, act as a buffer and catalyst in Baeyer–Villiger oxidation using organic peracids.[8] Under conditions similar to the above oxidation of cyclopentanone use of Na_2CO_3 and $NaHCO_3$ in place of hydrotalcites gave δ-valerolactone in 86 and 63% yields, respectively. Hydrotalcites composed of cationic Brucite layer and interlayer with anions have base character,[2a,9] which catalyse polymerization[10] and Aldol condensation.[11] We think that the basicity of the hydrotalcites plays an important role in this Baeyer–Villiger oxidation.[12] Basal spacing (Å) of the used hydrotalcites decreases as follows:[6] $Mg_5Al(OH)_{12}$(toluene-*p*-sulfonate), 17.7 > $Mg_5Al(OH)_{12}Cl$, 8.18 > $Mg_{10}Al_2(OH)_{24}CO_3$, 7.96 > $Mg_{10}Al_2(OH)_{24}CO_3$ and $Mg_5Al(OH)_{12}Cl$ with smaller basal spacing showed high catalytic activity for this Baeyer–Villiger oxidation, while $Mg_5Al(OH)_{12}$(toluene-*p*-sulfonate) gave a low yield of the lactone similar to the non-catalyst system. The above fact indicates that the oxidation might not occur mainly in the field of the interlayer gallery.

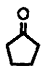
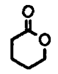
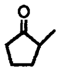
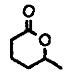
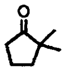
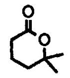
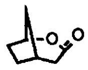
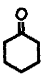
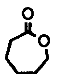
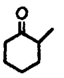
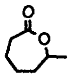
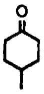
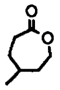
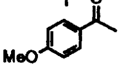
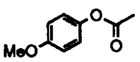
Application of this Baeyer–Villiger oxidation to other ketone substrates using various types of hydrotalcites and a detailed study of the catalytic properties of the hydrotalcites in

Table 1 Effect of various hydrotalcites, $Mg(OH)_2$ and $Al(OH)_3$, on cyclopentanone oxidation[a]

Run	Catalyst	Conv. (%)	Yield (%)
1	$Mg_2Al_2(OH)_8CO_3$	57	45
2	$Mg_6Al_2(OH)_{16}CO_3$	56	46
3	$Mg_{10}Al_2(OH)_{24}CO_3$	94	90
4	$Mg_{16}Al_2(OH)_{36}CO_3$	77	60
5	$Mg_5Al(OH)_{12}Cl$	93	83
6	$Mg_5Al(OH)_{12}$(toluene-*p*-sulfonate)	49	38
7	$Mg(OH)_2$	68	50
8	$Al(OH)_3$	52	30
9	No catalyst	45	40

[a] Reaction conditions: cyclopentanone (4 mmol) benzaldehyde (12 mmol), 1,2-dichloroethane (20 ml), catalyst (0.025 g), O_2 bubbling, 40 °C. 5 h.

Table 2 Baeyer–Villiger oxidation of ketones in the presence and the absence of $Mg_{10}Al_2(OH)_{24}CO_3$[a]

Substrate	Product	Reaction time/h	Conversion, yield (%)	
			$Mg_{10}Al_2(OH)_{24}CO_3$	No catalyst
		5 5 5 5	94, 90(82) 39, 17[b] 95, 83[c] 45, 35[d]	45, 40
		5	96, 95	10, 8
		24	65, 61	trace
		3	100, 91(83)[e]	26, 24
		5	72, 62	83, 80
		3	100, 93	77, 74
		3	63, 53	50, 49
		24	100, quantitative[f] (94)	15, 15

[a] *Reaction conditions*: substrate (4 mmol), benzaldehyde (12 mmol), 1,2-dichloroethane (20 ml), catalyst (0.025 g), 40 °C [b] Room temp. [c] *p*-Tolualdehyde was employed instead of benzaldehyde. [d] Isovaleraldehyde was used. [e] 3-Oxabicyclo[3.2.1]octa-2-one as a regioisomer (6%) was detected by NMR. [f] *Reaction conditions*: substrate (2 mmol), benzaldehyde (6 mmol), 1,2-dichloroethane (20 ml), catalyst (0.05 g), 40 °C.

relation to their basicity and structural character are currently being investigated in our laboratory.

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