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Heterogeneous Baeyer-Villiger Oxidation of Ketones Using *m*-Chloroperbenzoic Acid Catalyzed by Hydrotalcites

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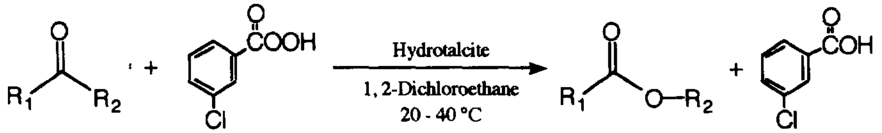
Abstract: Hydrotalcites promote the Baeyer-Villiger oxidation of various ketones using *m*-chloroperbenzoic acid to give high yields of lactones and esters.

m-Chloroperbenzoic acid (*m*-CPBA) is a useful oxidizing reagent for epoxidation of olefins, the Baeyer-Villiger oxidation of ketones, and oxidation of amines, sulfides, and selenides.[1] Since *m*-CPBA by itself generally can be used for the above oxidations without the aid of promotors or catalysts, there are few studies on oxidation with a combined system of *m*-CPBA and such activators.[2] Hydrotalcites consist of the Brucite-like layer with a positive charge and anionic compounds in the interlayer to form neutral materials.[3] The combination of several elements in the Brucite-like layer and the selection of anionic compounds can tune the basicity of the hydrotalcites and their interlayer distance. Here, we wish to report the Baeyer-Villiger oxidation with *m*-CPBA in the presence of hydrotalcites as base catalysts.[4] The hydrotalcites act as heterogeneous catalysts for the Baeyer-Villiger oxidation of various ketones to give high yields of lactones and esters (Eq. 1). After the oxidation, the hydrotalcites can be easily removed from the reaction mixture by filtration and they are further usable as catalysts for the oxidation.



(1)

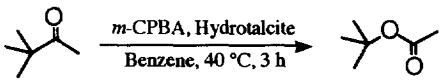
Hydrotalcites without transition metals were prepared by the procedure of Reichle *et al.*[5] Multi-metallic types of Mg-Al-Ni-CO_3 and Mg-Al-Cu-CO_3 hydrotalcites were prepared according to our previous paper.[4b, 6] All the prepared hydrotalcites were dried at 110°C overnight before use in the oxidation. A typical procedure of the Baeyer-Villiger oxidation of ketones is as follows. Into a three-necked flask with a reflux condenser cooled at -15 °C were placed cyclopentanone (0.555 g, 6.6 mmol), the hydrotalcite (75 mg), *m*-CPBA (8.9 mmol), and 1, 2-dichloroethane (45 ml). The resulting mixture was stirred at 40 °C for 2 h. The hydrotalcite was separated by filtration. GC analysis of the filtrate showed a quantitative yield of δ-valerolactone. The filtrate was successively treated with aqueous Na_2SO_3 and $NaHCO_3$ solution. δ-Valerolactone (0.534 g, 81 %) was isolated by column chromatography on silica gel (hexane / ethyl acetate, 10 : 1). In addition, the spent hydrotalcite after the oxidation was treated with aqueous Na_2CO_3. The oxidation of cyclopentanone with the washed hydrotalcites under the same conditions as those with fresh hydrotalcites gave a quantitative yield of δ-valerolactone.

We prepared various kinds of hydrotalcites, changing the Mg / Al ratios in the Brucite-like layer and the selection of the anionic compounds in the interlayer. Oxidation of cyclopentanone with *m*-CPBA was carried out using the above hydrotalcites. The ratios of Al to Mg (Mg / Al = 1 - 8) did not strongly affect catalytic activity for the Baeyer-Villiger oxidation under our reaction conditions. As regards the anionic compounds in the interlayer, the catalytic activity of the hydrotalcites decreased as follows:

CO_3^{2-} > terephthalate, Cl^- > *p*-toluenesulfonate.[7]

Representative results of the Baeyer-Villiger oxidation using *m*-CPBA in the presence of the hydrotalcite having a CO_3 anion (Mg / Al = 5) are shown in Table 1 together with those in the absence of the hydrotalcite catalyst. Oxidation of cyclopentanone with the hydrotalcite gave a quantitative yield of δ-valerolactone in a short time (Run 1). Similarly, the hydrotalcite catalyzed the Baeyer-Villiger oxidation of 2-methylcyclopentanone regioselectively to afford 5-methylvalerolactone as the sole product, while norcamphor was converted into 2-oxabicyclo[3.2.1]octan-3-one, accompanied with 6 % of 3-oxabicyclo[3.2.1]octan-2-one as a regioisomer. The catalytic effect of the hydrotalcite was not significant in the cases of six-membered ketones (Runs 5 and 6). Furthermore, the hydrotalcite had the catalytic activity for the Baeyer-Villiger oxidation of acyclic ketones. Pinacolone was converted into *t*-butyl acetate in an almost quantitative yield after 5 h (Run 7). Oxidations of benzyl methyl ketone and benzyl phenyl ketone occurred regioselectively *via* migration of the benzyl group to give the corresponding esters, respectively.

A possible reaction mechanism of the Baeyer-Villiger oxidation can be considered to be as follows.[8] Reaction of a hydroxyl group on the hydrotalcite surface with perbenzoic acid gives a metal perbenzoate and H_2O. The perbenzoate attacks ketone to form a metal alkoxide intermediate which undergoes rearrangement to give lactone or ester, and benzoic acid. Transition metals, *e.g.*, Ni, Fe, and Cu, were found to be effective catalysts for the Baeyer-Villiger oxidation using a combination oxidant of molecular oxygen and aldehydes.[9]

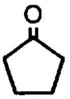
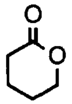
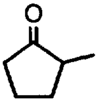
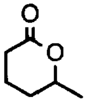
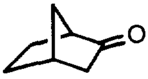
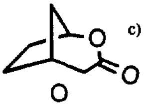
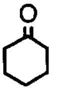
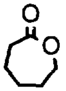
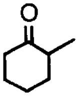
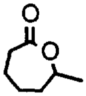
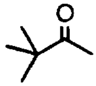
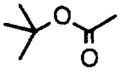
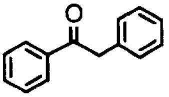
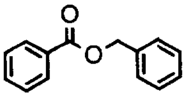
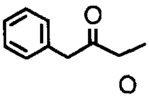
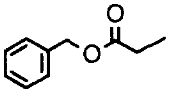
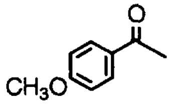
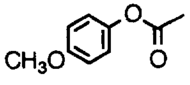
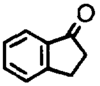
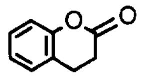


(2)

Hydrotalcite:	yield
$Mg_6Al_2(OH)_{16}CO_3$	72 %
$Mg_6Al_2Ni_{0.6}(OH)_{17.2}CO_3$	89 %
$Mg_6Al_2Cu_{0.6}(OH)_{17.2}CO_3$	99 %

Eq. 2 shows typical results of oxidation in the presence of $Mg_6Al_2Ni_{0.6}(OH)_{17.2}CO_3$ and $Mg_6Al_2Cu_{0.6}(OH)_{17.2}CO_3$ together with those of the corresponding hydrotalcite without transition metals. Introduction of such transition metals into the Brucite layer could increase the catalytic activity of hydrotalcites for the Baeyer-Villiger oxidation. A similar phenomenon has been also observed in the case of a combination oxidant of molecular oxygen and benzaldehyde.[4b]

Table 1. The Baeyer-Villiger Oxidation of Various Ketones Using *m*-CPBA Catalyzed by Hydrotalcite[a)]

Run	Substrate	Product	Time (h)	Temp.	Yield[b)] (%)	
					$Mg_{10}Al_2(OH)_{24}CO_3$	no cat.
1			1	40°C	76	30
2			2	40°C	96 (81)	
3			5	40°C	99	33
4		 c)	3	r.t.	94 (81)	24
5			5	r.t.	100 (89)	98
6			3	r.t.	99	81
7			5	40°C	92	45
8			5	40°C	57	29
9			5	40°C	66	43
10			5	r.t.	99 (86)	22
11			31	40°C	84 (72)	84

[a)] Reaction conditions: substrate (2.3 mmol), m-CPBA (3 mmol), 1, 2-dichloroethane (15 ml), $Mg_{10}Al_2(OH)_{24}CO_3$ (0.025 g) [b)] Yields were determined by GLC analysis. Values in parentheses are isolated yields. In the isolation of products, the reaction scale was three-fold. [c)] An isomer is 6 % of products.

In conclusion, hydrotalcites promote the Baeyer-Villiger oxidation using *m*-CPBA and can be recovered and reused. As basicity of the hydrotalcites and their interlayer distance can be controlled by the combination of several elements in the Brucite-like layer and by selection of the anionic compounds, the hydrotalcites might be promising catalyst materials having not only high activity but also the ability of shape molecular recognition.10)

References and Notes

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6. XRD spectra of the Mg-Al-Fe-CO_3 and Mg-Al-Cu-CO_3 type hydrotalcites showed 7.75 and 7.86 Å of d spacings, respectively, which are almost the same values to 7.66 Å of $Mg_6Al_2(OH)_{16}CO_3$. These results support that the Mg-Al-Fe-CO_3 and Mg-Al-Cu-CO_3 type hydrotalcites had layer structures with formulas of $Mg_6Al_2Fe_{0.6}(OH)_{17.2}(CO_3)_{1.3}$ and $Mg_6Al_2Cu_{0.6}(OH)_{17.2}CO_3$, respectively.
7. Yields of benzyl benzoate were 83 % for the hydrotalcite having CO_3^{2-}, 71 % for terephtalate, 70 % for Cl^-, and 46 % for *p*-toluenesulfonate, respectively.
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