

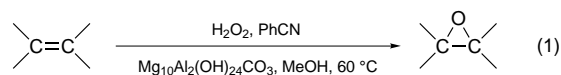
Hydrotalcite catalysis: heterogeneous epoxidation of olefins using hydrogen peroxide in the presence of nitriles

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The layered hydrotalcite, $\text{Mg}_{10}\text{Al}_2(\text{OH})_{24}\text{CO}_3$, acts as an efficient base catalyst for the epoxidation of various olefins using hydrogen peroxide in the presence of benzonitrile and with MeOH as solvent.

Hydrotalcites consist of Brucite-like layers having positive charge with anionic species in the interlayer, forming neutral materials.^{1,2} Combination of different elements, changing the element ratios in the Brucite-like layer and selection of different anionic species can tune up the basicity of the hydrotalcites and the interlayer distance.³ Recently, we found that hydrotalcites show high catalytic activities for the Baeyer–Villiger oxidation of various ketones using a combined oxidant of molecular oxygen and benzaldehyde or MCPBA; the surface hydroxy groups of the hydrotalcites acted as basic sites to promote the above oxidations.^{4–7} Here, in relation to our studies on the base catalysis of hydrotalcites, we report that the heterogeneous epoxidation of various olefins using hydrogen peroxide is catalysed by hydrotalcites to give the corresponding epoxides [eqn. (1)].



There are few reports concerning the oxidation of olefins by hydrotalcite catalysts using hydrogen peroxide.^{8–11} Shape selective epoxidation was observed in the case of poly-oxometalate-intercalated hydrotalcites. But diols and oxolanes were formed to some degree by successive cleavage of the epoxides. Notably, our oxidation system using hydrotalcites exclusively gives epoxides without other products.

Various hydrotalcites used in Table 1 were prepared by the literature procedures.^{1,12,13} Elemental analyses for the hydrotalcites are in good agreement with literature values. After

Table 1 The epoxidation of cyclohexene catalysed by various hydrotalcites and NaOH using H_2O_2 and benzonitrile^a

Catalyst	Conversion (%)	Yield (%) ^b	Heat of Adsorption ^c / J g^{-1}
$\text{Mg}_{10}\text{Al}_2(\text{OH})_{24}\text{CO}_3$	100	< 99	14.0
$\text{Mg}_5\text{Al}(\text{OH})_{11}\text{CO}_3$	80	79	8.1
$\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$	69	67	6.3
$\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{SO}_4$	58	54	5.1
NaOH ^d	95	53 ^e	—
Without catalyst	20	15	—

^a Reaction conditions: cyclohexene (3.9 mmol), benzonitrile (10.5 mmol), hydrotalcite (0.05 g), MeOH 10 (ml), 30% aq. H_2O_2 (2.4 ml), 60 °C, 24 h.

^b Yields of epoxides were determined by GC analysis using internal standards, based on the olefins. ^c The basicity of the hydrotalcites was estimated by calorimetric heats of benzoic acid adsorption. ^d NaOH was equivalent to the amount of hydroxy functions in hydrotalcites (1.5 mmol). ^e Ring opening products of the epoxide, *e.g.* cyclohexane-1,2-diol and 2-methoxycyclohexan-1-ol, were formed.

drying the hydrotalcites at 110 °C, they were stored in air and used without further pretreatment.[†]

In the presence of $\text{Mg}_{10}\text{Al}_2(\text{OH})_{24}\text{CO}_3$, oxidations of cyclohexene using hydrogen peroxide with benzonitrile were carried out in various solvents such as methanol, benzene, toluene and 1,2-dichloroethane.[‡] MeOH gave the highest yield of cyclohexene oxide. However, the oxidation hardly occurred in the absence of benzonitrile. Table 1 shows the catalytic effect of various hydrotalcites on the epoxidation of cyclohexene using benzonitrile in MeOH. Yields of cyclohexene oxide increased with increasing heat of benzoic acid adsorption on the hydrotalcites. The basicity of these hydrotalcites was estimated by a measurement of calorimetric heats of benzoic acid adsorption using microdifferential scanning calorimetry.⁷ It is likely that the basic hydroxy groups of the hydrotalcites play an important role in the epoxidation. Bases such as NaOH and KOH catalyse the epoxidation of olefins using hydrogen peroxide in the presence of nitriles.^{14,15} However, NaOH was not an effective base for our epoxidation.[§]

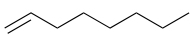
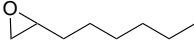
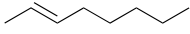
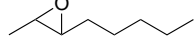
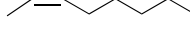
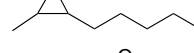












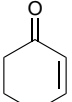

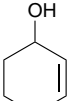

Table 2 shows results of the oxidation of olefins with benzonitrile in MeOH. Common linear and cyclic olefins such as oct-1-ene and cyclohexene gave the corresponding epoxides as sole products in excellent yield, respectively (entries 1–7). Norbornene gave only *exo*-norbornene oxide in quantitative yield (entry 8). Remarkably, styrene was oxidized to give styrene oxide in a high yield without formation of other oxidation products, *e.g.* acetophenone and benzaldehyde (entry 9). In the case of an α,β -unsaturated ketone, cyclohex-2-en-1-one, the epoxidation exclusively occurred without formation of the Baeyer–Villiger oxidation products (entry 10). This epoxidation proceeds stereospecifically with retention of configuration at the double bonds (entries 2 and 3).

Interestingly, we found that adding sodium dodecyl sulfate and sodium dodecylbenzene sulfate to the above oxidation system markedly increased the rates of the epoxidation; cyclooctene oxide was obtained quantitatively within 2 h.[¶] This epoxidation consists of two phases; the olefin and nitrile are in the organic phase, while the hydrogen peroxide and hydrotalcite are in the aqueous phase. The above additives might act as a surfactant to form reverse micelles (aqueous phase in organic medium), which helps to increase contact area of the interface between the two phases. The detailed role of the additives in this epoxidation system is under investigation in our laboratory.

This epoxidation involves the following two steps; (i) formation of peroxy-carboximidic acid by the reaction of a nitrile with hydrogen peroxide, and (ii) oxygen transfer from peroxy-carboximidic acid to olefin, in which step (i) is promoted by bases.¹⁴ It is likely that the hydrotalcite acts as a solid base and promotes the formation of peroxy-carboximidic acid, leading to high yields of the epoxides.

In conclusion, we have developed an efficient heterogeneous catalyst system utilising hydrotalcites for epoxidation and using a combined oxidant of aqueous hydrogen peroxide and benzonitrile. The solid hydrotalcites are easily separated from the reaction mixture *via* filtration, which makes the work-up procedure simple. The hydrotalcite can be reused without an

Table 2 The epoxidation of various olefins catalysed by Mg₁₀Al₂(OH)₂₄CO₃ using H₂O₂ and benzonitrile^a

Entry	Substrate	Product	Conversion (%)	Yield (%) ^b
1			95	95
2 ^c			100	96
3 ^c			94	93
4 ^d			100	95
5			100	>99
6			100	94
7			99	95
8			100	>99 (only exo)
9			97	92
10			84	84
11			90	89 (syn : anti = 80 : 20)

^a Reaction conditions: olefin (3.9 mmol), benzonitrile (10.5 mmol), Mg₁₀Al₂(OH)₂₄CO₃ (0.05 g), MeOH (10 ml), 30% aq. H₂O₂ (2.4 ml), 60 °C, 24 h.
^b Yields of epoxides were determined by GC analysis using internal standards, based on the olefins. ^c The relative epoxidation rate of *cis*- and *trans*-oct-2-ene was 1.5, which is similar to that of MCPBA. ^d 30 °C.

appreciable loss of catalytic activity. This system should prove useful for many base-catalysed selective oxidations.

Notes and References

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† A typical procedure for the epoxidation of cyclooctene: Into a reaction vessel with a reflux condenser were successively placed the hydrotalcite of Mg₁₀Al₂(OH)₂₄CO₃ (0.15 g), MeOH (40 ml), cyclooctene (14 mmol), benzonitrile (17 mmol) and 30% aq. H₂O₂ (7.5 ml). The resulting mixture was stirred at 60 °C for 24 h. The hydrotalcite was separated by filtration and the filtrate was treated with MnO₂ (0.03 g) to decompose the remaining H₂O₂. GC analysis of the filtrate showed a quantitative yield of cyclooctene oxide. The filtrate was diluted with deionized water (50 ml) and extracted with CHCl₃ (50 ml × 3). The extract was concentrated under reduced pressure and subjected to a silica gel chromatography using a mixture of *n*-hexane–Et₂O (40:1, v/v) as an eluent to give cyclooctene oxide (1.5 g, 87% yield). The isolated hydrotalcite can be reused without losing its high catalytic activity.

‡ The order for yields of cyclohexene oxide using different nitrile compounds is as follows; benzonitrile > acetonitrile > propionitrile.

§ Under our reaction conditions, use of NaOH in place of the hydrotalcites resulted in a 53% yield of cyclohexene oxides, as shown in Table 1.

¶ Use of cationic surfactants, e.g. cetylpyridinium chloride monohydrate and tetra-*n*-propylammonium bromide, did not increase yields of cyclooctene oxide.

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Received in Cambridge, UK, 23rd October 1997; 7/07655J