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단 신

$KMnO_4$-Montmorillonite를 이용한 초음파적 알코올의 산화반응

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Oxidation of Alcohols under Sonication by $KMnO_4$ Supported on Montmorillonite

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Recent studies have demonstrated the application of montmorillonite clay(K-10)-based reagents such as aldol reaction[1], synthesis of enolthioether[2], Friedel-Crafts alkylation[3], acetal formation from alcohols and organic gem-dihalides[4], porphyrin synthesis by condensation of pyrrole with aldehydes[5], nitration of phenols[6], conversion of alcohols to nitrites[7], oxidation of alcohols to aldehyde or ketones[8] and benzoins to benzils[9]. The above examples are promoted by either clay supported metal salts[3], metal nitrates[1,4~9] or clay itself[2,10]. Some of these are phase transfer process with clay supported catalysts[4]. We recently reported the montmorillonite catalyzed reduction of nitroarenes with hydrazine[10] and ultrasound acceletrated permanganate oxidation of alcohols[11]. In this paper, we wish to present the oxidation reaction of alcohols under sonication in the presence of potassium permanganate supported on montmorillonite. Results are summarized in the *Table*. Excellent yields of products were obtained in relatively short reaction time when the alcohol, dissolved in 1,2-dichloroethane, was added to montmorillonite and $KMnO_4$. A reaction mixture was sonicated and the products were analyzed by G. C. *Table* also shows the results of the oxidation reaction of $KMnO_4$ that was powdered, dried, and used without nomtmorillonite. Astonishingly, the catalytic activity of $KMnO_4$ that is not supported was found to be very low (entry 1~4, 9). For example, the cyclohexanone was obtained in 100% yield in the presence of montmorillonite, while only 35% yield in the absence of the supporter (entry 1).

Overoxidation product was observed only in the case of cinnamyl alcohol (entry 5) like as previous results[11].

In an attempt to obtain additional information which might lead to a better understanding of these important oxidants supported on montmorillonite, we have undertaken a similar study of the oxidation of various alcohols by montmorillonite supported-MnO_2. As expected, the yields obtained after a comparable period time at same reaction condition were improved moderately (15% was improved with clay for cycloheptanol; 30% for benzyl alcohol and 40% 4-chlorobenzyl alcohol). But, oven dried (12 hr, 150℃) montmorillonite before use did not effect the yields.

Typical procedure for this oxidation is as follows. Alcohol (0.01 mol), 0.7 g of montmorillonite (K-10), 1.58 g (0.01 mol) of powdered and dried $KMnO_4$ and 6 m*l* of 1,2-dichloroethane were added to the ultrasonic reactor[11] under nitrogen and the mixture was sonicated. Reaction vessel temperature was maintained at 35℃ by using a running water bath. A strong atomization phenomena (fogginess) was occurred during sonication. The reaction was monitored by GC. Because of the

Table 1. Ultrasound accelerated oxidation of alcohols by $KMnO_4$ supported on montmorillonite

Entry	Alcohol	Product	$KMnO_4$-Clay-Ultrasound[a] % yield(time, hr)[c]	$KMnO_4$-Clay-Stirring[b] % yield(time, hr)[c]
1	Cyclohexanol	Cyclohexanone	100(1.5), 35[c]	33(3), 4.2(5)[g]
2	Cycloheptanol	Cycloheptanone	100(1), 45[d]	32(1.5), 4.5(5)[g]
3	$PhCH_2OH$	PhCHO	100(1), 40[d]	46(2)
4	4-$ClPhCH_2OH$	4-ClPhCHO	100(1), 40[d]	69(2), 16(5)[g]
5	$PhCH=CHCH_2OH$	PhCH=CHCHO	59(3)[e]	8(3), 4.5(3)[g]
6	2-$ClPhCH_2OH$	2-ClPhCHO	100(1.5)[f], 88[d]	76(2.5)[f]
7	1-Octanol	1-Otanal	100(1.5)[f]	
8	2-Octanol	2-Octanone	100(2)[f]	49(2.5)[f], 2.6(5)[g]
9	4-CH_3OPhCH_2OH	4-$CH_3OPhCHO$	100(1), 74[d]	45(2)

[a]10 : 10 mmol of alcohol : $KMnO_4$ and 0.7 g of montmorillonite were employed at 35℃ in 10 ml of 1,2-dichloroethane and sonicated. [b]Stirring at same reaction condition. [c]G.C.yield. [d]Sonication without montmorillonite. [e]21% of benzaldehyde and 8% of benzoic acid were also found by G.C. along with 12% of cinnamyl alcohol. [f]3 mmol of $KMnO_4$ was employed. [g]2 : 12.8 mmol of alcohol : $KMnO_4$ were employed in 6 ml of benzene.

experimental simplicity and high yield of the $KMnO_4$ supported on montmorillonite oxidation of alcohols, it is anticipated that the reaction by clay supported reagents will find wide application in syntheic organic chemistry. In conclusion, high yields and short reaction time are the obvious advantages to $KMnO_4$-montmorillonite clay (K-10) system.

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REFERENCES

1. M. Kawai, M. Onaka, and Y. Izumi, *Bull. Soc. Japan.* **61**, 1237 (1988).
2. B. Labiad and D. Vilemin, *Synthesis*, 143 (1989).
3. L. H. Clark, A. P. Kybett, D. J. Macquarrie, S. J. Barlow, and P. Landon, *J. Chem. Soc., Chem. Commun.*, 1353 (1989).
4. A. Cornelis and P. Laszlo, *Synthesis*, 162 (1982).
5. A. Cornelis, P. Laszlo and P. Pennetreau, *Clay Miner.*, 437 (1983).
6. A. Corelis, P. Pennetreau and P. Laszlo, *Bull. Soc. Chim. Belg.*, 961 (1984).
7. A. Corelis, P. Y. Herze, and P. Laszlo, *Tetrahedron Lett.*, **23**, 5035 (1982).
8. A. Corelis and P. Laszlo, *Synthesis*, 845 (1980).
9. M. Besemann, A. Corelis, and P. Laszlo, P. C. R. *Acad. Sci. Ser.* C. **299**, 427 (1984).
10. B. H. Han and D. G. Jang, *Tetrahedron Lett.*, **31** (8), 1181 (1990).
11. B. H. Han D. H. Shin, D. G. Jang and S. N. Kim, *Bull. Kor. Chem. Soc.*, **11**(2), 157 (1990).