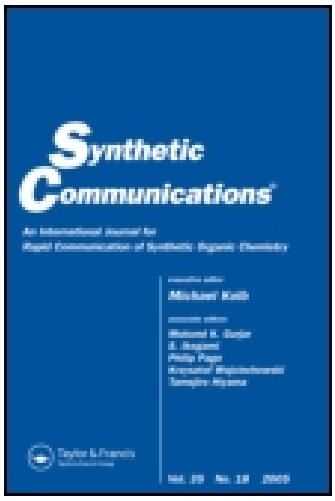

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SURFACE-MEDIATED HIGHLY EFFICIENT OXIDATION OF ALCOHOLS BY BISMUTH NITRATE

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SURFACE-MEDIATED HIGHLY EFFICIENT OXIDATION OF ALCOHOLS BY BISMUTH NITRATE

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ABSTRACT

Montmorillonite impregnated with bismuth nitrate was found to be an excellent reagent for the oxidation of a variety of alcohols in excellent yield.

Oxidation of organic compounds is one of the fundamental chemical transformations. Therefore, oxidation chemistry in organic or in aqueous solution continues to attract considerable attention. New versatile and selective reagents to achieve the oxidation of alcohols are constantly being sought and as a result, many oxidizing agents have been developed.[1] Some of the methods described for these reactions have significant limitations, such as, long reaction times, secondary reactions, low yield, the requirement for a number of solvents and strong acid medias, relative unavailability of the reagents, anhydrous conditions and in some cases stringent reaction conditions. To overcome these shortcomings, oxidation of

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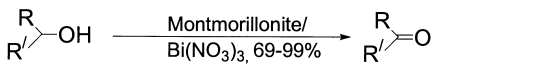
alcohols under solid phase[2a] and by catalytic reactions[2b] are very promising. We have been engaged in the synthesis and biological evaluation of several polyaromatic compounds and in a preliminary study have shown the anticancer activity of several of these derivatives.[3] Recently, we also develop a simple oxidation method[4] of benzylic methylenes to the ketones mediated by sodium bismuthate in acid media. The versatility of this method has been exploited through the facile oxidation of allylic and benzylic alcohols to the corresponding aldehydes.[4b]

Disposal of solvent and acid-base waste is a significant problem for chemical research and therefore, we also were interested in surface-mediated oxidation chemistry of alcohols and report here a highly efficient oxidation method of a wide variety of alcohols by montmorillonite impregnated with bismuth nitrate.[5] Montmorillonite has been used previously for the oxidation of secondary benzylic alcohols in the presence of "clayfen"[6] (montmorillonite-ferric nitrate) under the influence of microwave irradiation.[7] The notable advantages of our method include a general procedure for the oxidation of benzylic alcohol, allylic alcohol and aliphatic alcohol without any microwave irradiation or pre-treatment[6i] for the preparation of the solid support.

The montmorillonite-induced oxidation of the alcohols is shown in the Table 1. Saturated alcohols (entries 1–3), benzylic alcohols (entries 4–6) and allylic alcohols (entry 7 and 8) underwent facile oxidation in excellent yield[8] (69–99%) (Scheme 1).

Similar oxidation of 2-phenylethanol (entry 4) with silica gel or acidic alumina gave a complex mixture of products. However, oxidation of 2-phenylethanol (entry 4) with montmorillonite induced condition afforded acetophenone in 89% yield. Thus, we believe that the nature of the support, not the acidity is an important factor for the successful oxidation described in this present investigation. Although, oxidation of benzylic alcohols was reported by clayfen under microwave irradiation method, we found a facile oxidation of the same substrates by bismuth nitrate at room temperature within a few minutes without using microwave. The solid support being the same, this strongly suggests that bismuth nitrate is a superior oxidizing agent compared to ferric nitrate. Also this reagent in combination with montmorillonite was shown to be effective for the oxidation of allylic alcohol and saturated alcohol. No lactones acids or epoxides could be detected



R = R/ = aliphatic R = R/ = aromatic
R = unsaturated, R/ = aliphatic R = aliphatic, R/ = aromatic

Scheme 1.

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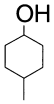
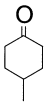
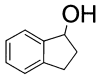
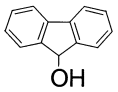
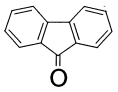
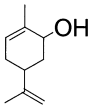
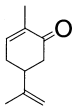
Table 1. $Bi(NO_3)_3$ Mediated Oxidation of Alcohols

Entry	Substrate	Product	Time (min)	Yield (%)	BP/MP (°C) Observed	Lit.[a]
1			5	91	150	149
2			5	81	168	169-171
3			5	69	163	162-163
4			2	89	202	202
5			3	73	242	243-245
6			4	99	81	82-85
7			5	91	167	168
8			7	73	228	227-230

a: Aldrich chemical company

in the reaction mixture. However, all attempts to oxidize the primary alcoholic substrates to generate the corresponding aldehydes failed.

In conclusion, we have demonstrated a facile synthetic method for the oxidation of several alcohols to the ketones by bismuth nitrate supported on montmorillonite.

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5. For the use of bismuth reagents in organic synthesis, see Suzuki, H.; Ikegami, T.; Matano, Y. Synthesis **1997**, 249.
6. Laszlo et al. studied reactions with montmorillonite in the presence of clayfen/claycop, for example, see: (a) Gigantee, B.; Prazeres, A.O.; Marcelo-Curto, M.J.; Cornelis, A.; Laszlo, P. J. Org. Chem. **1995**, *60*, 3445. (b) Cornelis, A.; Delaude, L.; Gertmans, A.; Laszlo, P. Tetrahedron Lett. **1988**, *29*, 5657. (c) Laszlo, P.; Cornelis, A. Aldrichim. Acta. **1988**, *21*, 97. (d) Laszlo, P.; Vandormael. J. Chem. Lett. **1988**, 1843. (e) Laszlo, P.; Cornelis, A.; Gerstmans, A.; Laszlo, P. Chem. Lett. **1988**, 1839. (f) Cornelis, A.; Laszlo, P. *Chemical Reactions in Organic and Constrained Systems*; Setton, Ed., 1986, p. 213. (g) Cornelis, A.; Laszlo, P. Synthesis **1985**, 909. (h) Cornelis, A.; Laszlo, P.; Pennetreau, P. Bull. Soc. Chim. Belg. **1984**, *93*, 961. (i) Cornelis, A.; Laszlo, P. Synthesis **1980**, 849.

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7. Varma, R.S.; Dahuya, R. Tetrahedron Lett. **1997**, *38*, 2043.
8. A representative procedure is as follows: The alcohol (1 mmol) and montmorillonite KSF (500 mg, Aldrich) was added to a suspension of bismuth nitrate (1 mmol) in THF (5 mL). The solvent was then evaporated under reduced pressure and dried in the vacuum pump for ~5 min. The mixture was then repeatedly washed with dichloromethane (~25 mL) and it was concentrated to afford the crude product. Pure product was isolated after column chromatography and by crystallization.
All compounds described in this paper gave satisfactory physico-chemical data.

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