

Ultrasound assisted oxidation of various alcohols to corresponding aldehydes by using KMnO_4 and catalytic amount of Al_2O_3

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Abstract

A convenient approach for oxidation of structurally diverse alcohols has been developed using KMnO_4 as an oxidant agent in the presence of a catalytic amount of Al_2O_3 in aqueous acetonitrile. In this method various alcohols generally afforded the corresponding carbonyl compounds directly in good to high yield under ultrasound irradiation conditions. It shows that this kind of catalysis system is very active, selective and suitable for oxidation of benzylic alcohols. Furthermore, all products were obtained through a simple filtration and washed with solvent, and there was no need for column chromatography. All products have been characterized by IR and ¹HNMR spectral data.

Keywords: Oxidation; alcohols; potassium permanganate; ultrasound.

Introduction

The selective oxidation of primary and secondary alcohols to the corresponding carbonyl compounds is a key transformation in modern organic synthesis. Selective oxidation of alcohols to their corresponding carbonyl compounds is one of the most important organic transformations. The carbonyl compounds are widely used in food, beverages, pharmaceutical and chemical industries [1]. Recently, some of catalytic oxidation methods, which employ a variety of metal-containing catalysts such as Cu(I), [2,3] Ni(II), [4,5] Co(II), [6,7] Pd(II) and manganese oxides [8-11] developed quickly. However, these procedures

suffer from one or more drawbacks, such as the use of expensive metal catalysts like ruthenium and palladium, the need for a sacrificial aldehyde, and severe reaction conditions, for example, high temperature or pressure, leaving scope for further improvements in the catalytic oxidation of alcohols to corresponding carbonyl compounds. Potassium permanganate (KMnO_4) has long been used as oxidant for a variety of organic functional groups [12, 13]. Ultrasonic assisted organic synthesis as a green synthetic approach is a powerful technique that is being used more and more to accelerate organic reactions. A large number of organic reactions can be carried out in higher

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yields, shorter reaction times, or milder conditions under ultrasound irradiation [14].

In recent years oxidation of hydroxy groups with KMnO_4 has also been supplemented by the new method involving solid supports, such as molecular sieve, [15] copper sulfate pentahydrate, [16] bentonite, [17] Kieselguhr, [18] zeolite, [19] and zirconyl chloride octahydrate, [20] whose supported reagents are, in general, performed under heterogenous conditions, simpler processing, and often higher selectivity.

Experimental

General

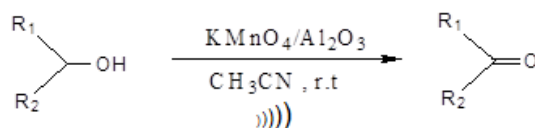
Chemicals were purchased from Fluka, Merck and Aldrich Chemical Companies. The authenticity of the products was established by comparing

their melting point with the data in the literature and spectral data (IR; $^1\text{H NMR}$). All yields refer to the isolated products.

General procedure for oxidation of various alcohols by using Al_2O_3

KMnO_4 (0.1 gr = 1 mmol), aryl alcohol (1 mmol), and Al_2O_3 (0.3 gr = 2 mmol) was dissolved in 3 ml of acetonitrile. The reaction mixture was irradiated in water bath of the ultrasonic cleaner at room temperature for a period as indicated in Table 1.

The progress of the reaction is monitored by TLC using hexane: ethyl acetate (9:1) as eluent. After completion, the mixture was filtered and the solvent was evaporated to afford the pure product.



($R_1 = \text{Aryl}$, $R_2 = \text{H, Alkyl}$)

Scheme 1. Oxidation of alcohols using KMnO_4 as oxidant catalyzed by Al_2O_3 under ultrasound irradiation

Results and discussion

Primary and secondary benzylic alcohols are oxidized cleanly and easily to their corresponding aldehyds and ketones in good to high yields (Table 2). Notably the oxidation of aldehyds to their corresponding carboxylic acid was not observed.

As a part of our ongoing research program to develop new synthetic methods for oxidation of various functional groups, [21-24] we wish to describe a new procedure for oxidation of aryl alcohols to corresponding aldehydes and ketons using the combination of supported reagents ($\text{KMnO}_4/\text{Al}_2\text{O}_3$) and ultrasound

irradiation in almost quantitative yields (Scheme 1). Our initial efforts focused on identifying the optimum conditions for the oxidation of 4-methoxybenzyl alcohol as model substrate in the presence of various solvents under ultrasound irradiation. These results are summarized in Table 1. Among the used solvents, acetonitrile delivered the best results (Table 1, Entry 1) and was then used for all other substrates.

In this study, a 1: 2: 1 molar ratio of KMnO_4 : Al_2O_3 : substrate is employed and the reagent can be reused at least twice. As can be seen in Table 2, this method is generally applicable to a range of alcohols, and gives the

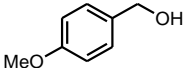
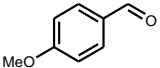
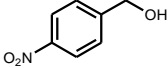
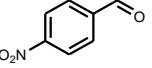
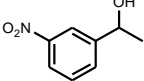
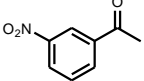
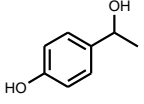
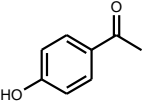
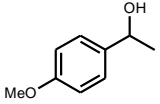
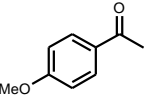
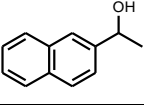
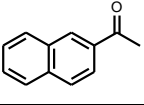
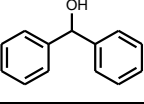
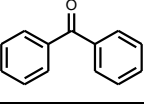
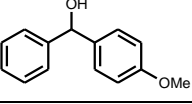
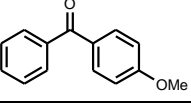
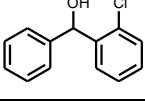
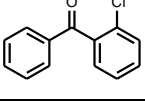
corresponding aldehydes and ketones in high yields.

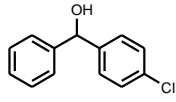
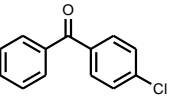
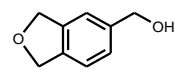
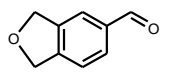


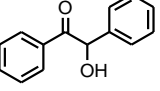
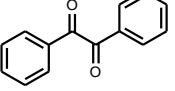
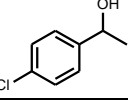
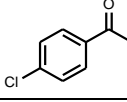
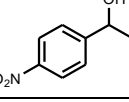
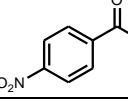
Table 1. Oxidation of 4-methoxy benzyl alcohol (1 mmol) with KMnO_4 (1 mmol) as oxidant catalyzed by Al_2O_3 (2 mmol) in the presence of various solvents under ultrasound irradiation.

Entry	Solvents	Time (min)	*Yield %
1	CH_3CN	15	87
2	CH_2Cl_2	60	-
3	CHCl_3	60	-
4	n-Hexane	60	20
5	Acetone	15	10
6	Toluene	60	20
7	Xylene	60	20

*(Conversion)%

Table 2. Oxidation of alcohols using KMnO_4 (1mmol) in the presence of catalytic amount of Al_2O_3 under ultrasound irradiation

Entry	Substrate	product	Time (min)	Yield (isolated)/%
1			15	87
2			20	83
3			20	65
4			10	41
5			10	55
6			5	55
7			5	90
8			5	85
9			10	75

10			10	86
11			15	90
12			15	60
13			5	84
14			15	82
15			20	61

All products were characterized by comparison of their spectral data (^1H NMR; IR) with those of authentic samples

Conclusion

The procedure reported here is simple and allows for the oxidation of alcohols to carbonyl compounds under very mild and neutral conditions. The method seems to be as convenient for selective oxidation of both primary and secondary alcohols to carbonyl compounds without over-oxidation to carboxylic acids and can be used as a valid alternative oxidation method by avoiding the use of toxic reagents.

Acknowledgments

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