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Effective Oxidation of Alcohols under Heterogeneous Conditions with a New Reagent: Manganese Dioxide Supported on Graphite

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A new reagent, manganese dioxide supported on graphite, under heterogeneous conditions at reflux is described for the oxidation of benzylic and allylic alcohols into the corresponding aldehydes and ketones, respectively. The main advantage of the present oxidation is that the insoluble solid support, graphite, provides a particular reaction environment capable of enhancing the reaction selectivity and reactivity. Moreover, it turns out to be very profitable in the workup, which becomes reduced to a mere filtration. The mechanism for this oxidation is also discussed.

Keywords benzylic and allylic alcohols, graphite, manganese dioxide, oxidation, supported reagent

INTRODUCTION

Oxidation of alcohols to the corresponding carbonyl compounds is a fundamental transformation in organic synthesis. Because of its significant role, the development of newer methods or reagents is attracting much current interest in spite of the availability of numerous procedures reported in the literature. However, a drawback of most oxidants in the oxidation is their lack of selectivity, for instance, overoxidation of aldehydes to carboxylic acids and degradation of unsaturated substrates are often unavoidable side reactions. In addition to their lack of selectivity, oxidants like chromium-based reagents are corrosive, irritants, toxic, etc.

It has been found that reagents supported on insoluble solid supports, such as inorganic and polymeric supports, are particularly convenient for solving many problems in organic synthesis.^[1–3] One important aspect of reactions with solid supported reagents is that in many cases both the reagent and the product into which it is converted during reaction are strongly adsorbed on the surface of the solid support or remain intercalated in it; therefore, there is very little or probably no contamination

of organic products or solvents by solid materials. Other advantages of solid-supported reagents in organic synthesis are mainly that the reactions are normally carried out in common organic solvents, and the isolation of the organic products simply involves decantation or filtration to remove the spent solid support system, followed by evaporation of the solvent. Furthermore, it should be possible in many cases involving solid-supported reagents to regenerate the active reagent directly from the spent support system by standard inorganic reactions. It is well known that many reactions can be carried out cleanly, rapidly, and in high yield under mild conditions using solid-supported reagents, whereas attempts to carry out the same reactions with unsupported reagents frequently either fail or result in the formation of mixtures of products. In most cases, solid-supported reagents have been found superior to the nonsupported reagents.

EXPERIMENTAL

Preparation of Active Manganese Dioxide Supported on Graphite Reagent

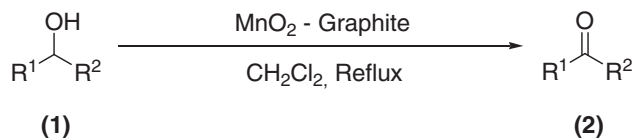
Active manganese dioxide is prepared according to the previous references.^[4–6] Potassium permanganate (1.9 g) was dissolved in water (50 mL) at room temperature, graphite (30 g) was added with stirring, and the water is evaporated at 60°C. The residue was ground to fine powder and then added to a solution of manganese sulfate monohydrate (4.7 g) in water (50 mL) with vigorous stirring. After the resulting precipitate was filtered and dried at 100°C for 4 h, 32.1 g of manganese dioxide supported on graphite reagent is obtained. Each gram of this supported reagent contains around 0.78 mmol manganese dioxide.

Oxidation of Benzyl Alcohol to Benzaldehyde, Typical Procedure

The preceding manganese dioxide supported on graphite reagent (2.4 g) is placed in a flask together with dichloromethane (25 mL) and the mixture is magnetically stirred. A solution of benzyl alcohol (108 mg, 1 mmol) in dichloromethane (5 mL) is added and after 10 h at reflux the solid is filtered and washed with dichloromethane (3 × 5 mL). The combined filtrates are

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SCH. 1.

evaporated to give crude product, which is purified by preparative thin-layer chromatography (TLC) with hexane:ethyl acetate (8:2) to afford 98 mg (92%) benzaldehyde.

RESULTS AND DISCUSSION

Manganese dioxide,^[4] a relatively environmentally friendly reagent, as a heterogeneous stoichiometric oxidizing agent has been extensively used for the oxidation of a variety of functional groups. However, to the best of our knowledge, only few manganese dioxide-based reagents have been employed in the selective oxidation of benzylic or allylic alcohols into the corresponding aldehydes and ketones, respectively: for example, solid manganese dioxide under heterogeneous conditions at reflux,^[7,8] manganese dioxide under solvent-free conditions,^[9,10] supported manganese dioxide reagent with or without microwave irradiation,^[11–15] etc.

In connection with our previous investigation on oxidizing agents supported on graphite for the selective oxidation of alcohols into carbonyl compounds, for instance, potassium permanganate adsorbed on graphite,^[16,17] ferric nitrate supported on graphite,^[18,19] and Jones reagent supported on graphite,^[20] we now report here that manganese dioxide supported on graphite is a new reagent suitable for the selective oxidation of benzylic and allylic alcohols (1) into the corresponding aldehydes and ketones (2), respectively, at reflux under heterogeneous conditions (Scheme 1). Meanwhile, some typical aliphatic alcohols are also investigated under the same reaction conditions.

The manganese dioxide supported on graphite reagent is easily prepared by mixing of potassium permanganate, manganese

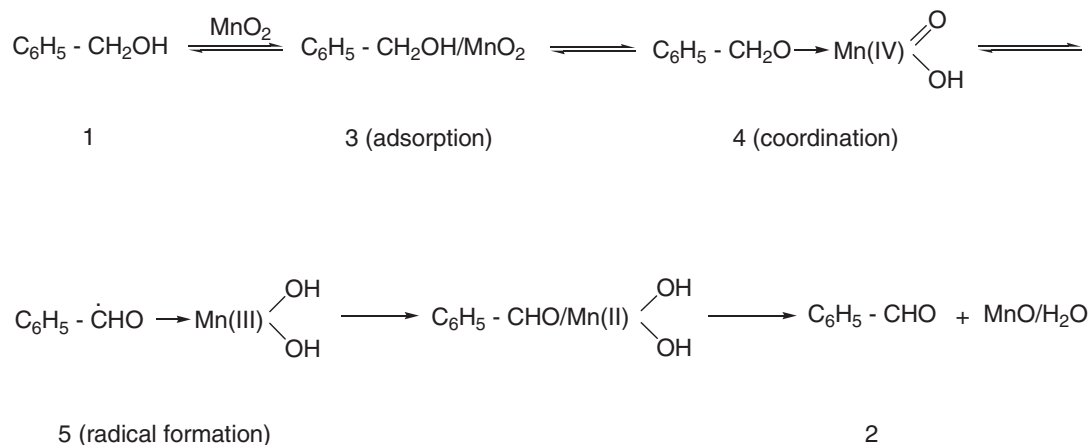
sulfate monohydrate, and graphite at 60°C. In our cases, the commercial potassium permanganate, manganese sulfate monohydrate, and graphite can be used without further purification.

In order to determine the role of graphite in this oxidation reaction, a blank test using benzyl alcohol as a representative with graphite in dichloromethane at reflux for 96 h has been performed, and we do not observe any conversion of benzyl alcohol under such conditions. However, when benzyl alcohol mixed with manganese dioxide supported on graphite reagent in dichloromethane at reflux for 30 min, benzaldehyde can be detected with thin-layer chromatography (TLC). Therefore, we conclude that graphite is as a support only in the present reaction.

The oxidation is very simple. After contact of alcohols with obtained reagent under heterogeneous and reflux conditions, the expected products are obtained. Under our investigations, a 1 to 2 molar ratio of the substrate to the oxidant is employed, and all reactions for benzylic and allylic alcohols are completed within 10 h with high yields. The product is purified by preparative TLC. The obtained products are all known compounds and identified by spectroscopic comparison with authentic samples.

The results, which are described in Table 1, show that the present reagent is generally applicable to a range of benzylic and allylic alcohols, and gives the corresponding aldehydes or ketones in good yields. What we can see from Table 1 is that benzylic alcohols, phenyl allylic alcohols, and benzoin (entries 1–6) are oxidized more readily than aliphatic alcohols (entries 7 and 8), which would indicate that the π -electrons of the double bond have some effects; phenyl allylic alcohols (entry 1) is oxidized more readily than benzyl alcohol (entries 2–4), which would be due to the steric effects.

The oxidation of aliphatic alcohols, 2-hexanol and 1-hexanol, is also investigated under this reaction conditions: After 12 h of oxidation of 2-hexanol and 1-hexanol (entries 7 and 8) the corresponding 2-hexanone in 25% yield and 1-hexanal in 16% yield are obtained, respectively. The longer reaction periods of 72 h are carried out as well; in this case the corresponding 2-hexanone is obtained in 30% yield and 1-hexanal is obtained in



SCH. 2.

TABLE 1
Oxidation of alcohols with manganese dioxide supported on graphite reagent

Entry	Substrate ^a	Product ^b	Reaction time (h)	Yield ^c (%)	m.p. (°C)	
					Found	Reported ^[22,23]
1			9	96	255–256 ^d	255 ^d
2			10	92	235–237 ^d	237 ^d
3			10	90	254–256 ^d	254 ^d
4			9	97	46–48	48–49
5			6	96	93–95	95
6			6	92	103–104	104–105
7			72	30	103–105 ^d	106 ^d
8			72	22	100–101 ^d	101–103 ^d

^aAll the substrates are commercially available.

^bAll the aldehydes and ketones have been described previously in the literature and were identified by their ¹H-NMR and IR spectra and melting points.

^cYield of isolated pure product.

^dMelting point of 2,4-dinitrophenylhydrazones.

22% yield, which may indicate that it is failed to increase the conversion with longer reaction periods, and they remain almost intact by this method.

We consider that the present oxidation is a free radical mechanism, which is the same as that proposed earlier by Goldman,^[21] for the oxidation of alcohol **1** by manganese dioxide supported on graphite reagent, which includes adsorption to give **3**, formation of a coordinated complex **4**, transfer of a hydrogen atom to give the stable radical **5**, and finally intramolecular electron transfer to afford the products **2**. Here oxidation of benzyl alcohol is as an example (Scheme 2).

The main advantages of this oxidation are that the insoluble solid support, graphite, provides a particular reaction environment capable of enhancing the reaction selectivity and reactivity. Compared to previous heterogeneous MnO₂ oxidation of alcohols, the amount of manganese dioxide used is quite reduced,^[7] the yields of the products are higher,^[8] and there is no need for using microwave equipment.^[11,12] Moreover, it is well known that for the reaction with manganese dioxide in the absence of support, the isolation of products from the ensuing residues is rendered more difficult and the oxidation is also accompanied by the formation of minor contaminants; however, in the current procedure it turns out to be very profitable in the workup, which becomes reduced to a mere filtration.

CONCLUSION

In conclusion, the present manganese dioxide supported on graphite reagent under heterogeneous conditions is a new and efficient reagent for the oxidation of benzylic and allylic alcohols to the corresponding aldehydes and ketones, respectively. The main advantage of this oxidation is that the insoluble solid support, graphite, provides a particular reaction environment capable of enhancing the reaction selectivity and reactivity. Moreover, it turns out to be very profitable in the workup, which becomes reduced to a mere filtration.

REFERENCES

- Fieser, L.F.; Fieser, M. *Reagents for Organic Synthesis*; John Wiley & Sons: New York, **1967**, Vol. 1, and subsequent volumes in the series.
- Mckillop, A.; Young, D.W. *Organic synthesis using supported reagents. Synthesis* **1979**, 401–422 (Part 1), 481–500 (Part 2).
- Laszlo, P. *Preparative Chemistry Using Supported Reagents*; Academic Press: San Diego, CA, **1987**.
- Fatiadi, A.J. Active manganese dioxide oxidation in organic chemistry. *Synthesis* **1976**, 65–104 (Part 1), 133–167 (Part 2).
- Giovanoli, R.; Bernhard, K.; Feitknecht, W. Über ein- und zweiphasige Reduktion von γ -MnO₂ durch Zimtalkohol. *Helv. Chim. Acta* **1968**, *51*, 355–366.
- Giovanoli, R.; Stahli, E.; Feitknecht, W. Über Oxidhydroxide des vierwertigen Mangans mit Schichtengitter 2. Mitteilung: Mangan (III)-manganat (IV). *Helv. Chim. Acta* **1970**, *53*, 453–464.

7. Gritter, R.J.; Wallace, T.J. The manganese dioxide oxidation of allylic alcohols. *J. Org. Chem.* **1959**, *24*, 1051–1056.
8. Pratt, E.F.; Van de Castle, J.F. Oxidation by solids. I. Oxidation of selected alcohols by manganese dioxide. *J. Org. Chem.* **1961**, *26*, 2973–2975.
9. Firouzabadi, H.; Karimi, B.; Abbassi, M. Efficient solvent-free oxidation of benzylic and aromatic allylic alcohols and biaryl acyloins by manganese dioxide and barium manganate. *J. Chem. Res. (S)* **1999**, 236–237.
10. Lou, J.D.; Xu, Z.N. Solvent free oxidation of alcohols with manganese dioxide. *Tetrahedron Lett.* **2002**, *43*, 6149–6150.
11. Varma, R.S.; Saini, R.K.; Dahiya, R. Active manganese dioxide on silica: Oxidation of alcohols under solvent-free conditions using microwaves. *Tetrahedron Lett.* **1997**, *38*, 7823–7824.
12. Khadilkar, B.M.; Gadre, S.A.; Makwana, V.D.; Madyar, V.R. An efficient and easy preparation of manganese dioxide–silica supported oxidant. *Indian J. Chem.* **1998**, *37A*, 189–190.
13. Khandekar, A.C.; Paul, A.M.; Khadilkar, B.M. Silica supported manganese dioxide: An efficient reagent for oxidation of benzoin. *Synth. Commun.* **2002**, *32*, 2931–2936.
14. Huang, L.H.; Wang, Q.; Ma, Y.C.; Lou, J.D.; Zhang, C. New reagent, manganese dioxide supported on kieselguhr, for effective oxidation of benzoin. *Synth. Commun.* **2011**, *41*, 1682–1687.
15. Huang, L.H.; Ma, Y.C.; Zhang, C.; Wang, Q.; Zou, X.; Lou, J.D. Manganese dioxide supported on aluminum silicate: A new reagent for oxidation of alcohols under heterogeneous conditions. *Synth. Commun.* **2011**, *41*, in press.
16. Lou, J.D.; Wang, G.Q.; Li, L.; Zhu, L.Y. Oxidation of alcohols catalyzed by a new potassium permanganate adsorbed on graphite reagent. *Synth. React. Inorg. Metal Org. Nano-Metal Chem.* **2005**, *35*, 281–283.
17. Lou, J.D.; Ma, Y.C.; Zhang, Y.J.; Gao, C. Solvent-free selective oxidation of alcohols with potassium permanganate adsorbed on graphite by shaking. *Synth. React. Inorg. Metal Org. Nano-Metal Chem.* **2006**, *36*, 317–319.
18. Lou, J.D.; Cai, X.X.; Li, F.; Li, L.; Gao, C. A new reagent, ferric(III) nitrate supported on graphite, for selective oxidation of alcohols under heterogeneous conditions. *Synth. React. Inorg. Metal Org. Nano-Metal Chem.* **2006**, *36*, 599–601.
19. Lou, J.D.; Piao, M.H.; Li, F.; Li, L. Selective oxidation of benzoin to benzil with ferric(III) nitrate supported on graphite reagent. *Synth. React. Inorg. Metal Org. Nano-Metal Chem.* **2007**, *37*, 553–555.
20. Lou, J.D.; Chen, Y.; Li, L.; Li, F. Selective oxidation of alcohols with Jones reagent supported on graphite. *Synth. React. Inorg. Metal Org. Nano-Metal Chem.* **2007**, *37*, 297–299.
21. Goldman, I.M. Large isotope effect in the manganese dioxide oxidation of benzyl alcohol. *J. Org. Chem.* **1969**, *34*, 3289–3295.
22. Buckingham, J. *Dictionary of Organic Compounds*, 6th ed.; Chapman & Hall: Cambridge, **1996**.
23. Okimoto, M.; Takahashi, Y.; Nagata, Y.; Sasaki, G.; Numata, K. Electrochemical oxidation of benzoin to benzil in the presence of a catalytic amount of KI in basic media. *Synthesis* **2005**, 705–707.