

Note

Dielectric activation of MnO₂: Part 1 — Oxidation of conjugated unsaturated alcohols

Tapan K Lai, Julie Banerji*, Asima Chatterjee &
Bidyut Basak

Department of Chemistry, University College of Science and
Technology, 92, A. P. C. Road, Kolkata 700 009, India.

E-mail: julie@cucc.ernet.in

Received 29 September 2003; accepted (revised) 8 July 2004

The activation of 'wet' precipitated manganese dioxide through an environmentally benign and expeditious pathway involving the use of a specially manoeuvred domestic microwave oven and its applicability in several organic solvents for near quantitative conversion of a range of conjugated unsaturated alcohols is demonstrated. The protocol effectively replaces procedures that are strenuous, hazardous and prohibitively time consuming. Again compatibility in almost all common organic solvents offers additional advantages e.g. control over precise activation and remarkable flexibility in the choice of substrates and conditions.

IPC: Int.Cl.⁷ C 07 C 9/00

Among the widely used selective oxidizing agents for various types of transformations in organic syntheses, activated manganese dioxide (AMD) enjoys prominence undoubtedly owing to the advantages it offers e.g. remarkable selectivity of its reactions, inexpensive starting material, ease of handling the reagent and applicability in mild, neutral and anhydrous conditions. While oxidations with AMD are relatively simpler in operation, the reproducible preparation of the suitably activated reagent is experimentally so difficult. Traditional routes to activate precipitated manganese dioxide include successive drying and pulverizing sequences,¹ azeotroping with benzene², and exposure to ultrasound³. The time-consuming and strenuous pathway and handling of a carcinogen in bulk quantities do provide limitations to these processes. Two recent efforts in this direction involving the use of newer irradiation techniques in 'dry' conditions e.g. microwave on silica-gel⁴, and microwave or ultrasound on bentonite⁵ are confined to simplification of the oxidation step only, while starting from the active reagent. The preparation and properties of precipitated manganese dioxide activated by an expeditious and reproducible procedure are reported herein.

Precipitated manganese dioxide has a locked, water-associated chain structure⁶ (**Figure 1**) that houses oxidatively active sites of low electron density on the surface of the solid oxidant. On the assumption that activation of the wet cakes of the reagent involves the removal of the occluded water plus adsorbed water occupying the potentially active sites on the surface^{2,7}, and keeping in view that water has a very large dielectric constant value compared to most of the organic solvents, it was reasoned that activation might be effected by the simple expedient of discriminative elimination of water through dielectric heating using a suitably designed apparatus⁸.

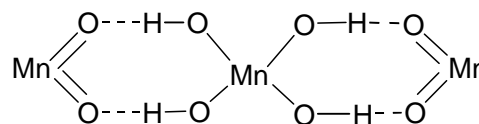


Figure 1 — Structure of hydrated manganese dioxide

Experimental Section

¹H and ¹³C NMR spectra were recorded on a BRUKER AM 300L (300 MHz) instrument using CDCl₃ as solvent and TMS as internal standard. The melting points were taken in an electrical melting point apparatus and are uncorrected. The silica-gel employed for column chromatography was from SRL (60-120 mesh). The chemicals employed were of A.R. grade and all the liquids were distilled before use. All the solvents were distilled and dried (where necessary) before use.

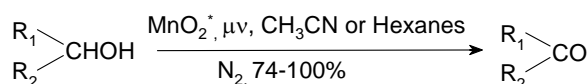
Representative procedure for activation and use of manganese dioxide

The wet reagent along with the solvent taken in a R. B. flask, a Dean and Stark water trap was set through a cavity at the roof of a domestic microwave oven and then irradiated for the specified time period and power level or till the desired amount of distillate was collected. The alcohol was then introduced into the flask under nitrogen atmosphere and irradiated for another 1 min or stirred magnetically for half an hour. The reaction mixture was filtered through a celite pad, solvent removed under vacuum and the products crystallized out or purified through chromatography.

Results and Discussion

Such a process has now been demonstrated successfully for the activation of precipitated manganese dioxide and its subsequent use in the oxidation of the following unsaturated alcohols (the unsaturation being ethylenic, acetylenic or part of an aromatic system) which were converted to the corresponding carbonyl compounds in excellent yields (**Scheme I**, **Table I**).

The reagent was prepared by a modified Attenburrow's method^{2,4} and after the final wash, the wet cakes containing about 40-60% water was stored in a closed bottle. Portions of the wet material were activated conveniently as needed and used up for carrying out the oxidations. The advantages are apparent. With adequate stirring (to break-up lumps) and exposure to microwave irradiation the activation



Scheme I — Oxidation of conjugated unsaturated alcohols using dielectrically activated manganese dioxide

Table I — Scope of dielectrically activated manganese dioxide in the oxidation of conjugated unsaturated alcohols^a (substrate-wet reagent; 1:7, hexanes, N₂ atmos.)

| R ¹ | R ² | Time period ^b | m.p. ^c °C | Yield ^d (%) |
|---|----------------|--------------------------|-------------------------|---------------------------|
| C ₆ H ₅ | H | 3.5 | 218-20 | 97 |
| C ₆ H ₅ CH=CH | H | 3 | 232 | 100 |
| H ₂ C=CH | H | 3 | 165 | 74 ^e |
| C ₆ H ₅ CH ₂ | H | 3.5 | — | — |
| 4-NO ₂ C ₆ H ₄ | H | 3.5 | 318(d) | 97 |
| 2-OHC ₆ H ₄ | H | 4.5 | 240 | 88 |
| 2-OMeC ₆ H ₄ | H | 3 | 248-50 | 99 |
| Hydroquinone | | 3 | 112 ^f | 98 ^f |
| 3,4-di-OMeC ₆ H ₃ | H | 3 | 238-40 | 99 |
| 4-MeC ₆ H ₄ | H | 3 | 226-28 | 98 |
| C ₆ H ₅ | C≡CH | 3.5 | — | 84 ^g |
| 4-OH-3-OMeC ₆ H ₃ | H | 4.5 | 258(d) | 90 |
| HC≡C | H | 3 | 200(d) | 94 ^e |

^a Best results were obtained when the reaction mixture was irradiated for a further 1-1.5 min at 80% power level after activation. ^b Time for activation, in min at 80% power level of the M.W. oven. ^c Of 2,4-DNP dvt. ^d As 2,4-DNP dvt. ^e Highly volatile product, hexanes (40-60°) employed and necessary precaution was taken during work-up. ^f Of the pure product. ^g The product was characterized by spectral analysis, supplied as a supporting information.

is complete in 2-6 min. The wet material can be employed directly. Substrate to reagent ratio is reduced. The most important of all a wide variety of solvents can be employed with comparable efficiency (**Table II**). The reagent once activated, however, has been stored under some solvent for more than six months. The danger of 'over drying' past the critical point⁵ can be obviated just by choosing a low boiling solvent and/ or control of microwave exposure (**Table III**). In order to study the effect of solvents, the activation was carried out using a variety of solvents keeping the amount of 'azeotropic' distillate¹⁰ fixed, and the active reagent so obtained was graded for the activity scale using the conventional oxidation of cinnamyl alcohol method. The observations are given in **Table II**.

Again, in an effort to simplify this methodology, the activation was studied with acetonitrile and hexanes for

Table II — Characterization of dielectrically activated manganese dioxide in different solvents [substrate (80 mg), wet reagent (560 mg), solvent (30 mL), 'distillate' collected (14 mL), N₂ atmos.]

| Solvent | Time in min (power level) | Yield (%) ^a |
|---------------------------------|------------------------------|---------------------------|
| CH ₃ CN | 1.50 (80) | 100 |
| Hexanes | 2.30 (80) | 100 |
| CHCl ₃ | 2.00 (80) | 90 |
| CH ₂ Cl ₂ | 1.40 (80) | 90 |
| Benzene | 1.50 (90) | 86 |
| THF | 3.57 (80) | 40 |
| CCl ₄ | 6.06 (80) | 80 |
| Acetic acid | 4.12 (100) | 65 |
| Et ₂ O | 1.35 (80) | 70 |

^a As 2,4-DNP dvt.

Table III — Effect of microwave exposure on the efficiency of dielectrically activated manganese dioxide in two solvents [substrate (80 mg), wet reagent (560 mg), solvent (30 mL), N₂ atmos.]

| Solvent | Time in sec. (power level) | 'Distillate' Vol.(mL.) | Conversion (%) ^a |
|--------------------|-------------------------------|---------------------------|--------------------------------|
| CH ₃ CN | 40 (90%) | 6 | 60 |
| | 80 (90%) | 16 | 100 |
| | 120 (90%) | 24 | 100 |
| Hexanes | 66 (80%) | 6.5 | 80 |
| | 76 (80%) | 10.5 | 100 |
| | 144 (80%) | 26 | 100 |

^a As 2,4-DNP dvt.

different extents of microwave exposure under the same external conditions and the active reagent so obtained was graded for the activity scale using the same method. The observations are given in **Table III**. With the reagent from two different batches, the activation time period varied slightly owing to the different extents of occluded water present in the wet material. Attempts to activate the wet cakes by direct microwave exposure in 'dry' condition afforded inconsistent results, though activation to some extent did take place in each attempt.

In conclusion we have developed an environment friendly, cost-effective, simple, yet efficient method for preparing active manganese dioxide, the versatile reagent for organic syntheses, directly from the wet precipitated reagent. Compatibility of the protocol in a wide range of solvents earns the all important element of environmental friendliness. Activation in presence of a solvent of choice ensures that the precise control over the extent of selective desorption of water from the oxidatively active sites on the surface of MnO_2 is achieved even with a coarse heating technique like dielectric irradiation. Although the most appropriate conditions for activating a particular batch of reagent and solvent combination must be determined empirically, the simplicity, rapidity and efficiency of the process justify necessary exploration. Studies directed toward the control of selectivity in this reaction as well as the use of manganese dioxide such activated, in other transformations are currently underway. Extension works of this protocol have great applicability in interesting organic conversions.

Acknowledgements

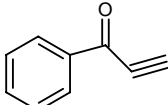
The work was supported by the U.G.C., New Delhi, India under the Scheme 'Center of Advanced

Studies on Natural Products including Organic Synthesis.'

References and Notes

- (a) Attenburrow J, Cameron A F B, Chapman J M, Evans R M, Hems B A, Jansen A B A, Walker T, *J Chem Soc*, **1954**, 1094.
(b) Pratt E F, Van de Castle J F, *J Org Chem*, 26, **1961**, 2973.
(c) Carpino L A, *J Org Chem*, 35, **1970**, 3971.
- Goldman I M, *J Org Chem*, 34, **1969**, 1979.
- Kimura Takahide, Fujita Mitsue & Ando Takashi, *Chem Lett*, 8, **1988**, 1387.
- Rajender S Varma, Saini Rajesh K & Dahiya Rajender, *Tetrahedron Lett*, 38, **1997**, 7823.
- Martinez Luis A, Garcia Olivia, Delgado Francisco, Alvarez Cecillo & Patinio Rocio, *Tetrahedron Lett*, 34, **1993**, 5293.
- Fatiadi Alexander J, *Synthesis*, **1976**, 65, 133.
- (a) Henbest H B, Jones E R H & Owen T C, *J Chem Soc*, **1957**, 4909.
(b) Henbest H B & Thomas A, *J Chem Soc*, **1957**, 3032.
- The design involves piercing the roof of a domestic microwave oven and as such, proper sealing must be done in order to avoid the hazards of direct microwave exposure to the investigator.
- Part of this work was presented at the *National Symposium on Organic Chemistry-II (Recent trends and prospects)*, Jadavpur, Calcutta, India, December 17, **2003**.
- Azeotroping under dielectric conditions yielded different distillate composition to that under traditional thermal conditions as confirmed in some preliminary experiments in our laboratory.

Supporting information

The spectral data of  Table I, footnote (g)

| ^1H NMR (δ , ppm) | ^{13}C NMR (δ , ppm) |
|------------------------------------|---|
| 2.65 (1H,s), 7.4-7.84 (5H,m) | 83.1 (CH), 81.6(C), 128.8(2, CH), 129.6(2, CH), 134.1(CH), 136.4(C), 168(C) |
