

Oxidations Catalysed by Rhenium(V) Oxo Species 1. Conversion of Furans to Enediones using Methyltrioxorhenium and Urea Hydrogen Peroxide

James Finlay, M. Anthony McKervey* and H. Q. Nimal Gunaratne

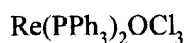
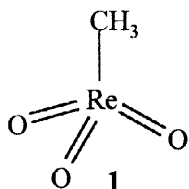
QUESTOR Centre and School of Chemistry, The Queen's University, Belfast, BT9 5AG, N. Ireland

Received 17 April 1998; accepted 26 May 1998

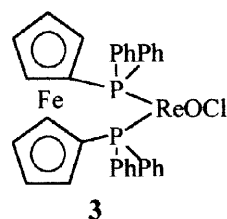
Abstract: Methyltrioxorhenium is an efficient catalyst for the oxidative ring opening of several substituted furans to enediones using urea hydrogen peroxide

© 1998 Elsevier Science Ltd. All rights reserved.

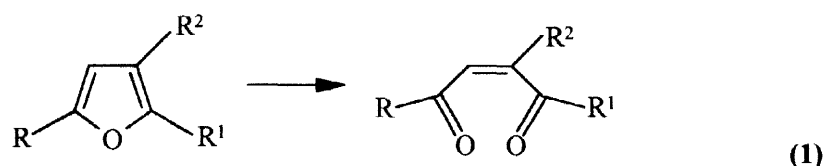
Over the past five years methyltrioxorhenium (MTO) **1** has emerged as an efficient catalyst in combination with hydrogen peroxide for epoxidation for alkenes¹, oxidation of amines², sulfides³, phosphines⁴, alkynes⁵ and arenes⁶, and oxygen insertion reactions of C-H bonds to form alcohols⁷. Hydrogen peroxide reacts with MTO to form peroxy species in situ and it is the latter which catalyse the oxygen transfer processes. A solid, conveniently handled, source of anhydrous hydrogen peroxide is now available in the form of its urea adduct (UHP). This adduct has been found to perform oxidation reactions in combination with acid anhydrides⁸ and several metal complexes⁹. It has also been used for epoxidation of alkenes catalysed by MTO^{10,11}. Unlike MTO, UHP is insoluble in non-polar solvents, but addition to dichloromethane containing a catalytic amount of MTO results in the rapid development of the yellow color characteristic of the peroxorhenium intermediate(s).



2



Recently we reported that distilled dimethyldioxirane (DMD) in acetone is capable of oxidising a wide range of furans to ring-opened enediones¹², the advantage of this oxidant over others being the clean environment associated with the process which allows particularly unstable products to be formed, eg. malealdehyde, and subsequently trapped in synthetically useful reactions. One disadvantage of the process is that it is not catalytic, except in acetone, and there is a yield inefficiency associated with the conversion of potassium peroxymonosulfate (oxone) in acetone into DMD which has yet to be improved. We now report that certain furans (equation 1) are oxidised rapidly under mild conditions in dichloromethane with UHP catalysed by MTO.



The results summarised in Table 1 were obtained by adding a catalytic amount of MTO (5 mol%) to a stirred suspension of UHP (1.2 equiv) in dichloromethane at room temperature.

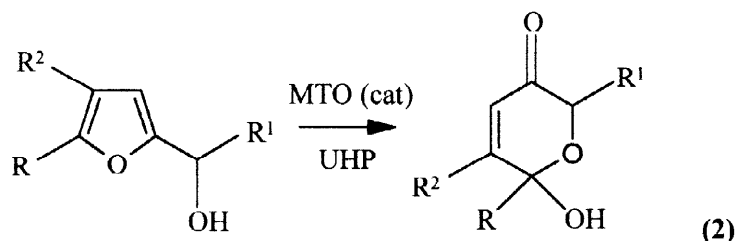
No.	R	R ¹	R ²	YIELD (%) ^a
1a	Me	Me	H	97
1b	Me	Et	H	87
1c	Ph	Ph	H	92
1d	Me	CH ₂ OAc	H	96
1e	Me	CH(Me)OAc	H	96
1f	CH ₂ OCO(CH ₂) ₁₂ CH ₃	CH ₂ OCO(CH ₂) ₁₂ CH ₃	H	90
1g	Me	CH(Et)OAc	H	89
1h	Me	Me	COCH ₃	73
1i	Et	Me	CO ₂ Et	75
1j	H	OMe	H	95
1k	H	t-Butyl	H	96
1l	Me	Br (OEt)*	H	67

^a Yield of pure product

Table 1

* Reaction carried out in dry ethanol to trap the intermediate acyl bromide; product (R¹ = OEt) was a mixture of *cis* and *trans* keto ethyl esters.

After 10 minutes the furan (1 equiv) was added and the mixture was stirred until oxidation was complete as revealed by tlc and NMR analysis. After removal of urea by filtration, the solution was concentrated to leave the reaction product of >95% purity. Where necessary further purification was accomplished by chromatography through a small plug of silica gel. The process is applicable to a range of mono-, di- and tri- substituted furans a selection which are summarised in Table 1. Two further rhenium complexes, **2** and **3**, have been found to oxidise sulfides to sulfoxides with UHP¹³. However these complexes were inert in furan oxidation. Furthermore, we also find that these furan oxidations with MTO exhibit striking solvent effects. Much faster rate of reaction was observed in acetonitrile compared to methylene chloride as a solvent, though the work up was much simpler in the case of methylene chloride¹⁴. Furans containing hydroxymethyl groups at the 2-position, e.g. methylfurfuryl alcohol (R=Me; R¹= H, R²= H) were also oxidised under the same conditions to afford substituted pyranones in high yields as shown in equation 2.



R= Me, Et; R¹= H, Me, Et, CH=CH₂; R²= H, Me. Yields 75-95%

Typical experimental procedure

To a suspension of urea hydrogen peroxide (0.051g, 0.55mmol) in methylene chloride (15ml), was added a catalytic amount of methyltrioxorhenium (6mg, 0.023mmol). After 10 minutes the furan **1f** (0.250g, 0.46mmol) was added to the mixture and stirring was continued until the reaction was complete. The reaction mixture was filtered and evaporated *in vacuo* to give tetradecanoic acid 2,5-dioxo-6-tetradecanoyloxyhex-3-enyl ester as a white crystalline solid (0.235g, 90%) m.p. 77-79°C (Found: C, 72.65; H, 10.84. C₃₄H₆₀O₆ requires: C, 72.34; H, 10.64%); ν_{\max} (KBr)/cm⁻¹, 1725 (CO), 1714 (CO); δ_{H} (300MHz, CDCl₃) 0.88 (6H, t, 2x CH₃), 1.26 (40H, s, 20x CH₂), 1.72 (4H, m, 2x CH₂), 2.41 (4H, t, 2x CH₂), 4.78 (4H, s, 2x CH₂), 6.44 (2H, s, CH=CH); m/z 564(<1%, M⁺), 110(100%).

ACKNOWLEDGMENTS

We acknowledge support from the EU European Regional Development Fund, Department of Education for Northern Ireland and Great Lakes (Europe) Ltd.

REFERENCES

1. Herrmann, W. A.; Fischer, R. W.; Marz, D. W. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1638-1641; Herrmann, W. A.; Fischer, R. W.; Scherer, W.; Rauch, M. U. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1157-1160; Herrmann, W. A.; Fischer, R. W.; Rauch, M. U., Scherer, W. *J. Mol. Catal.* **1994**, *86*, 243-266; Al-Ajlouni, A. M.; Espenson, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 9243-9250. Romao, C. C.; Khun, F. E.; Herrmann, W. A.; *Chem. Rev.* **1997**, *97*, 3197-3246.
2. Zhu, Z.; Espenson, J. H. *J. Org. Chem.* **1995**, *60*, 1326-1332.
3. Adam, W.; Mitchell, C. M.; Saha-Moller, C. R.; *Tetrahedron* **1994**, *50*, 13121-13124; Vasell, K. A.; Espenson, J. H. *Inorg. Chem.* **1994**, *33*, 5491-5498.
4. Abu-Omar, M. M.; Espenson, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 272-280.
5. Zhu, Z.; Espenson, J. H. *J. Org. Chem.* **1995**, *60*, 7728-7732.
6. Adam, W.; Herrmann, W. A.; Lin, J.; Saha-Moller, C. R.; Fischer, R. W.; Correia, J. D. G. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2475-2477.
7. Murray, R. W.; Iyanar, K.; Chen, J.; Wearing, J. T. *Tetrahedron Lett.* **1995**, *36*, 6415-6418.
8. a) Heaney, H. *Aldrichchimica Acta* **1993**, *26*, 35-45; b) Cooper, M. S.; Heaney, H.; Newbold, A. J.; Sanderson, W. R. *Syn Lett.* **1990**, 533-535; c) Ballini, R.; Marcantoni, E.; Petrini, M. *Tetrahedron Lett.* **1992**, *33*, 4835-4838.
9. Marcantoni, E.; Petrini, M.; Polimanti, O. *Tetrahedron Lett.* **1995**, *36*, 3561-3562.
10. Boehlow, T. R.; Spilling, C. D. *Tetrahedron Lett.* **1996**, *37*, 2717-2720.
11. Adam, W.; Mitchell, M. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 533-535.
12. Adger, B.; Barrett, C.; Brennan, J.; M^cKervey, M. A.; Murray, R. W. *J. Chem. Soc., Chem Comm.* **1991**, 1553-1554.
13. Adger, B.; Barrett, C.; Brennan, J.; M^cGuigan, P.; M^cKervey, M. A.; Tarbit, B. *J. Chem. Soc., Chem Comm.* **1993**, 1220-1222.