Oxidation of Furans with Dimethyldioxirane

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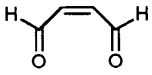
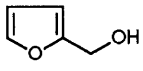
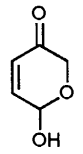
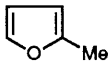
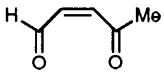
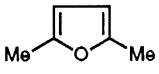
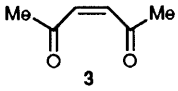
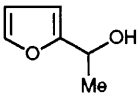
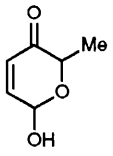
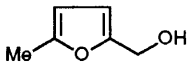
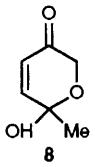
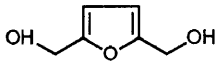
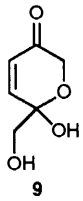
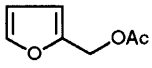
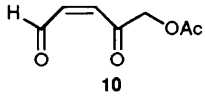
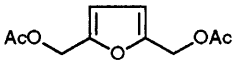
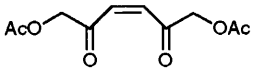
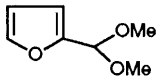
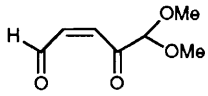
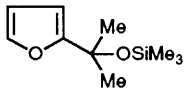
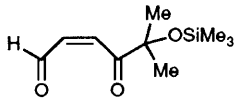
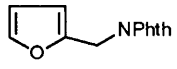
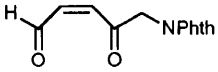
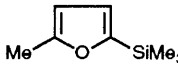
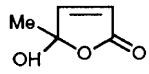
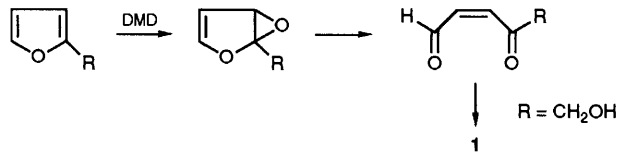
Dimethyldioxirane reacts rapidly at room temperature in acetone with a variety of furans, furnishing in high yield products of oxidative ring opening and, with 2-furanmethanol, 2*H*-pyran-3(6*H*)-one *via* subsequent ring closure.

Dimethyldioxirane (DMD) is an attractive reagent for oxidation of organic substrates.[1] It is easily generated and used as a solution in acetone, and oxidation products are recovered efficiently there being no by-product other than acetone. Although DMD has been applied to most oxidisable functional groups,[1] there are several unsaturated ring systems for which its efficacy in oxidation has yet to be explored. One such system is furan and its derivatives.[2] We now report that many furans are oxidised cleanly and rapidly at room temperature in acetone, furnishing two general product types depending on the substitution pattern of the substrate. The results summarised in Table 1 were obtained by adding DMD (1 equiv.) in acetone (*ca.* 0.05 mol dm^{-3} solution) to the substrate (1 equiv.) in acetone at room temperature. ^1H NMR analysis

Table 1

Entry	Furan	Product
1		
2		 **1**
3		 **2**
4		 **3**
5	 **4**	 **7**
6	 **5**	 **8**
7	 **6**	 **9**
8		 **10**
9		 **11**
10		 **12**
11		
12		 **13**
13		 **14**



Scheme 1

of the residue after removal of the solvent established that conversions and product purity were >95% in each case.†

Furan furnished the very unstable malealdehyde as the sole product (entry 1). Furfuryl alcohol (entry 2), in contrast, furnished 2*H*-pyran-3(6*H*)-one **1**,[3] a known product of oxidation with pyridinium chlorochromate, peroxyacid or *N*-bromosuccinimide, though the latter two processes have recently been described as unreliable.[4] The oxidation of furan and furfuryl alcohol by DMD can be accommodated mechanistically by a process initiated by formation of a transient epoxide (see Scheme 1) which ring opens, furan yielding the dialdehyde and furfuryl alcohol the enedione alcohol which promptly recyclises to **1** through the hydroxy group. The behaviour of several substituted furans on oxidation conforms to this general pattern. Notable examples include the formation of unstable *cis*-enedione **2** from 2-methylfuran (entry 3).[5] 2,5-Dimethylfuran (entry 4) furnished *cis*-hex-3-ene-2,5-dione **3**[6] in quantitative yield. Substituted furfuryl alcohols **4**, **5** and **6** (entries 5–7) were oxidised to pyranones **7**, **8**, **9**, compound **7** being obtained as a mixture of epimers. The acetate of furfuryl alcohol (entry 8) and the diacetate of 2,5-dihydroxymethylfuran (entry 9), on the other hand, yielded acyclic *cis*-ene-dicarbonyl products **10** and **11**, respectively; on standing these products slowly isomerised to the *trans* form. Furfural and 2-furoic acid were inert to DMD under the conditions employed here. The dimethylacetal of furfural, however (entry 10), was oxidised smoothly to the expected *cis*-enedicarbonyl product **12**, as was the trimethylsilyl ether of αα-dimethylfurfuryl alcohol (entry 11). Oxidation of furfuryl amine was complicated by what appeared to be oxidation of both the substituent and the ring, but the *N*-phthaloyl derivative was cleanly converted to the crystalline *cis*-enedione **13** (entry 12). The final entry illustrates the extension of oxidation with DMD to formation of lactones, 5-methyl-2-trimethylsilyfuran furnishing the hydroxybutenolide **14**.[7]

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References

1 For recent reviews of functional group oxidation with DMD see R. W. Murray, *Chem. Rev.*, 1989, **89**, 1184; W. Adam, R. Curci and J. O. Edwards, *Acc. Chem. Res.*, 1989, **22**, 205; R. Curci, in *Advances in Oxygenation Processes*, ed. A. L. Baumstark, JAI Press, Greenwich, CT, USA, vol. 2, ch. 1.
2 Aflatoxin B_1, which contains a dihydrofuran moiety, has been oxidised with DMD to give the very labile epoxide; see S. W. Baertschi, K. D. Raney, M. P. Stone and T. M. Harris, *J. Am. Chem. Soc.*, 1988, **110**, 7929.
3 O. Achmatowicz, Jr., P. Bukowski, B. Szechner, Z. Zwirtzchowska and A. Zamojski, *Tetrahedron*, 1971, **27**, 1973; M. P. Georgiadis and E. A. Couladouros, *J. Org. Chem.*, 1986, **51**, 2725.
4 M. Bennett, G. B. Gill, G. Pattenden, A. J. Shuker and A. Stapleton, *J. Chem. Soc., Perkin Trans. 1*, 1991, 929.
5 P. R. Hamann and A. Wissner, *Syn. Commun.*, 1989, **19**, 1509.
6 J. Levisalles, *Bull. Soc. Chim. Fr.*, 1957, **24**, 997.
7 R. Scheffold and P. Dubs, *Helv. Chim. Acta*, 1967, **79**, 798.

† All new compounds were fully characterised and the ^1H NMR data were consistent with the assigned structures.