Tetrahedron Letters, Vol.31, No.52, pp 7669-7670, 1990
Printed in Great Britain

0040-4039/90 $3.00 +.00
Pergamon Press plc

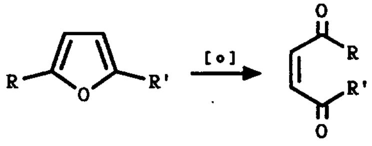
MAGNESIUM MONOPEROXYPHTALATE: A NEW REAGENT FOR THE OXIDATIVE RING OPENING OF FURANS TO CIS-ENEDIONES

Carmen Domínguez, Aurelio G. Csáky and Joaquín Plumet*
Universidad Complutense de Madrid. Facultad de Química. Departamento de Química Orgánica I. Ciudad Universitaria. E-28040 Madrid. Spain.

Abstract : Ring opening of furans can be accomplished with the title reagent to afford cis-enediones stereospecifically, with great advantages over the hazardous MCPBA.

Although ring opening of furans to afford enedione systems has been performed with a great variety of reagents[1], only m-chloroperbenzoic acid (MCPBA) has proven to be efficient in their stereospecific oxidation to give pure cis-enediones[2]. However, MCPBA is a shock-sensitive potentially explosive chemical which will probably soon not be available from commercial sources due to the hazards involved in its manufacture procedure. On the other hand, magnesium monoperoxyphtalate hexahydrate (MMPP) is a recently developed product which has already been successfully used in replacement of MCPBA in several classical oxidation reactions[3], even though its ability in the ring opening of furans has not yet been put to a test.

In the course of the synthesis of certain insect pheromones we felt in the need of turning several 2,5-disubstituted furan moieties into cis-enedione systems, and therefore, we have considered it interesting to try out the applicability of MMPP in this transformation in comparison with MCPBA.



1 2

a $R = R' = CH_3$
b $R = R' = (CH_2)_2CO_2CH_3$
c $R = R' = (CH_2)_2COCH_3$
d $R = (CH_2)_2COCH_3$
$R' = (CH_2)_2CO_2CH_3$
e $R = CH_3$
$R' = (CH_2)_2CO_2CH_3$
f $R = CH_3$
$R' = (CH_2)_2COCH_3$
g $R = R' = CHO$
h $R = R' = CH{=}CH{-}CO_2CH_3$
i $R = CHO$
$R' = CH_2OH$
j $R = CH_3$; $R' = CHO$
k $R = R' = CH_2OH$

Scheme 1

Although 2,5-dialkylfurans **1a-f** (Scheme 1) are readily converted into cis-enediones **2a-f** both with MMPP and MCPBA, the former shows a number of useful advantages: **i)** reaction times are considerably shorter (Table 1); **ii)** an $EtOH-H_2O$ mixture can be used as solvent; **iii)** reactions are carried out at room temperature; **iv)** work-up procedures are much simpler[4]; **v)** only 0.5 equivalents of reagent are required; **vi)** labile functional groups such as esther or ketone are not affected under the reaction conditions.

Table 1

Product	Oxidant agent	t_r (h)	Yield[*] (%)
2a	MMPP	0.25	99
	MCPBA	15	99
2b	MMPP	0.50	90
	MCPBA	17	80
2c	MMPP	0.50	90
	MCPBA	17	85
2d	MMPP	0.50	95
	MCPBA	17	85
2e	MMPP	0.45	90
	MCPBA	17	90
2f	MMPP	0.45	95
	MCPBA	17	85

[*] Pure, isolated yield

However, in the presence of electron withdrawing substituents **1g-j** or hydroxymethyl **1k**, a complete recover of starting materials is observed either with MCPBA or MMPP at room temperature or reflux, even increasing the molar rate of MMPP as well as the reaction time[5].

Notwithstanding, full isomerization of compounds **2** to the corresponding trans enediones is observed *in situ* after 2 h. reflux[6].

In conclusion, MMPP can be used in the oxidation of 2,5-dialkylfurans in the place of MCPBA, and can be foreseen as a practical alternative to the latter especially in large-scale preparations.

Acknowledgements: This investigation was supported by the CICYT, grant PB890099. Prof. A. Gaset (ENSCT-INP Toulouse) is gratefully acknowledged.

REFERENCES AND NOTES

1 P. Bosshard and C. H. Eugster, Adv.Het.Chem., 1966, 7, 377; M.V. Sargent and T.M. Cresp, Comprehensive Organic Chemistry, D.H.R. Barton and W. D. Ollis Ed., Pergamon Press, Oxford, 1979; F.M. Dean, Adv.Het.Chem., 1982, 30, 167.

2 See for example: P.D. Williams and E. Le Goff, Tetrahedron Lett., 1985, 1367; J. Jurzak and S. Pikul, Tetrahedron Lett., 1985, 3039; and references therein cited.

3 P.Brougham., M.S.Cooper, D.A.Cummerson, H.Heaney, and N.Thompson, Synthesis, 1987, 1015 and references within cited.

4 In a typical procedure, a solution of MMPP (247 mg, 0.5 mmol) in water (2 ml) was added to a stirred solution of the corresponding compound **1** (1 mmol) in EtOH (4 ml). When the reaction was complete (TLC monitoring), saturated aqueous solution of sodium bicarbonate was added, the mixture extracted with methylene chloride, and dried over anhydrous magnesium sulphate. Evaporation of the solvent gives the crude product **2**, which is percolated in a silica gel column (eluent: hexane/ethyl acetate - 1/1).

5 For compound **1g**, formation of the monodiethylacetal was complete after 24 h. reflux, but no trace of ring opening was found.

6 For isomerization of cis-enediones see reference **2** and B.P. Gunn, Tetrahedron Lett., 1985, 2869

(Received in UK 24 October 1990)