Tetrahedron Letters,Vol.27,No.25,pp 2867-2870,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

STEREOSPECIFIC HYDROXYLATION OF CHIRAL ALLYLIC β-HYDROXYSULFOXIDES : APPLICATIONS TO THE ASYMMETRIC SYNTHESIS OF OPTICALLY ACTIVE VICINAL TRIOLS

Guy Solladié*, Catherine Fréchou and Gilles Demailly

Ecole Nationale Supérieure de Chimie (U.A. 466)
Université Louis Pasteur
67008 STRASBOURG (France)

ABSTRACT : Chiral allylic β-hydroxysulfoxides 2 have been hydroxylated by the osmium tetroxide catalyzed reaction. The reaction can be highly stereoselective depending on the nature of the substituant linked to the double bond and the configurations of the sulfoxide and hydroxylic groups. The diastereoselectivity can be as high as 90%.

We recently reported[1,2] that optically active allylic β-hydroxysulfoxides 2 are readily prepared in both diastereoisomeric forms by reduction of the corresponding β-ketosulfoxides 1 (scheme 1).

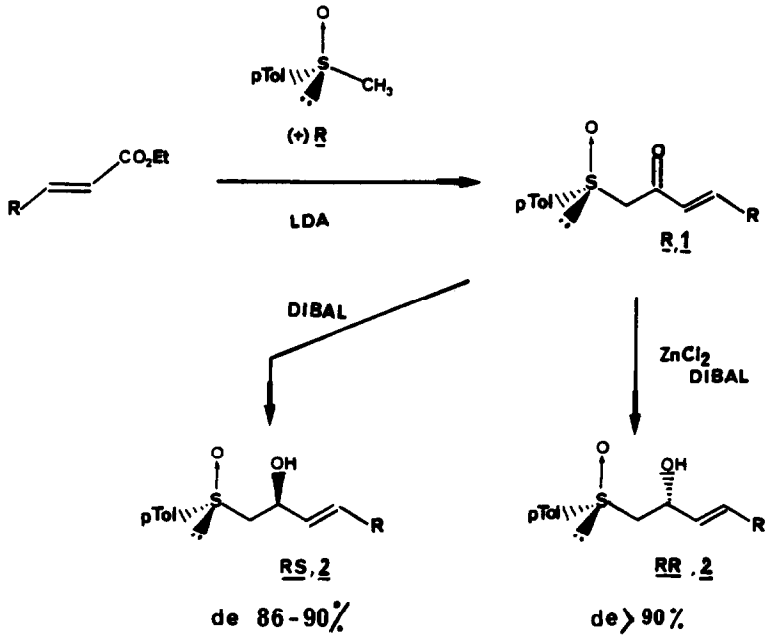
We report now in this paper results concerning osmium tetroxide catalyzed hydroxylation of the double bond of allylic β-hydroxysulfoxides 2.

Osmium tetroxide is probably one of the most powerful reagent to oxidize a double bond into a cis diol. Even more interesting is the reaction using a catalytic amount of Osmium tetroxide in presence of N-methylmorpholine N-oxide[3] or trimethylamine N-oxide[4] as a co-oxidant agent.

Allylic alcohols have already been oxidized by this method[5,8]. It was shown that the hydroxyl group could have a modérate but clear directive effect on the stereochemistry of the reaction : the erythro-threo diastereoisomer being the main diastereoisomer.

Hauser[9], has shown also that the hydroxylation of allylic γ-aminosulfoxides was completely controled by the chirality of the sulfoxide as well as the hydroxylation of cyclic allylic β-hydroxysulfoximines studied by Johnson[10].

In this study, the β-hydroxysulfoxides 2 (RR) and 2 (RS) were prepared according to scheme 1. The observed d.e. during the reduction of the corresponding β-ketosulfoxides 1 (R) are listed in Table I. The absolute configurations were deduced from the reaction mechanism[1]. Furthermore in every case, the RR diastereoisomer 2 presented in NMR a smaller non equivalence for the methylene protons α to the sulfoxide than the RS diastereoisomer[1].



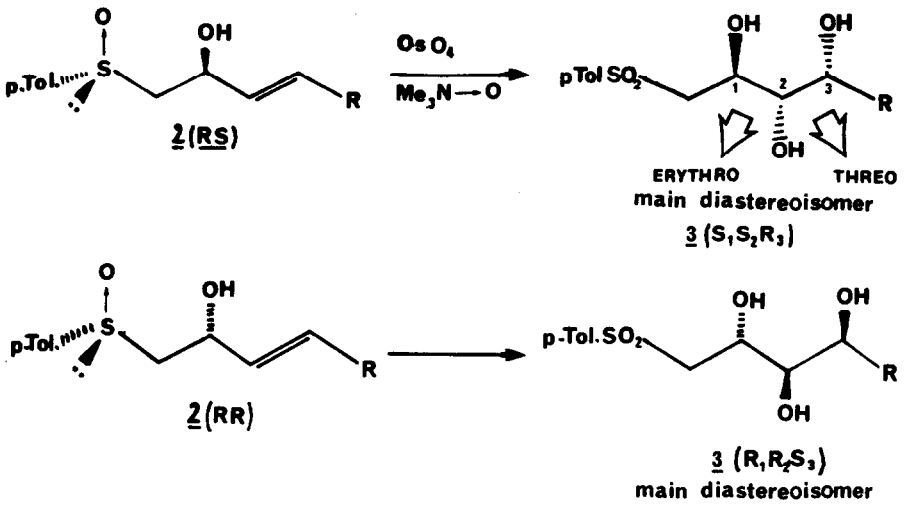
Scheme 1

TABLE I

Reduction of allylic β-ketosulfoxides

R	β-ketosulfoxide 1 R		β-hydroxysulfoxide 2			
	Yield%	$[\alpha]_D^{25}$ ($CHCl_3$, c=1)	DIBAL RS/RR	DIBAL Yield %	$ZnCl_2$-DIBAL RS/RR	$ZnCl_2$-DIBAL Yield %
a CH_3	65	+ 245°	94/6	91	> 5/95	90
b n-C_5H_{11}	61	+ 177°	93/7	96	> 5/95	97
c C_6H_5	70	+ 278°	> 95/5	95	> 5/95	95
d R-phytyl	70	+ 142°	95/5	96	> 5/95	97

Osmylation of optically pure hydroxysulfoxides 2 were performed in a mixture THF/H_2O at room temperature with 2 equivalents of trimethylamine N-oxide trihydrate and a catalytic amount of Osmium tetroxide (5%). The reaction was shown to be quantitative by TLC.



Scheme 2

Diastereoisomeric excess of the trihydroxysulfones 3 were determined by ^1H NMR from the signal of H_1 in the case of 3a, 3b and 3d and from the para-tolylmethyl group in the case of 3c. The absolute configurations were also deduced from NMR studies and calculated spectra : a small coupling constant of 2 Hz between H_1-H_2 is consistent with the main conformation of the diastereoisomer 3 threo-threo while a large coupling constant of 6 Hz between H_1-H_2 is consistent with the main conformation of 3 erythro-threo[11].

The diastereoselectivities of the Osmium tetroxide catalyzed reaction of β-hydroxysulfoxides 2 are listed in Table II.

TABLE II

Trihydroxysulfones 3

R	From 2 (RS)		From 2 (RR)	
	Yield %	Erythro/threo* (de %)	Yield %	Erythro/threo* (de %)
a CH_3	74	79/21 (58)	70	81/19 (62)
b n-C_5H_{11}	75	82/18 (64)	74	> 95/5 (90)
c Ph	90	72/28 (44)	90	72/28 (44)
d R-Phytyl	85	71/29 (42)	86	72/28 (44)

* *Relative configuration C_1-C_2.*

In every case, the main diastereoisomer obtained has the erythro-threo configuration. It can be noticed from Table II, that in each diastereoisomeric series, 2(RS) and 2(RR), the presence of a long unsubstituted chain such as n-pentyl increased significantly the d.e. This effect is much more important in the case of β-hydroxysulfoxide 2b(RR), indicating that both configurations at sulfur and at the hydroxylic center control the asymmetric induction. We obtained indeed from the compound 2b(RR) only one diastereoisomer 3b erythro-threo (the other diastereoisomer could not be detected by ^{1}H NMR). For comparison, the prior oxidation of the sulfoxide group into a sulfone in the case of compound 2a(RR), lowered the diastereoselectivity of the hydroxylation to 30% (26% d.e. was observed from the sulfone derived from 2b(RS). A similar result (34% d.e.) was obtained during the hydroxylation of the parent penten-3 ol.

Therefore, osmylation of allylic β-hydroxysulfoxides afforded a stereospecific synthesis of optically active triols as long as the two inducing centers have the same absolute configuration and a long unsubstituted chain substitutes the double bond.

BIBLIOGRAPHY

1) G. Solladié, G. Demailly, C. Greck, Tetrahedron Letters, 1985, 26, 435.
2) G. Solladié, G. Demailly, C. Greck, J. Org. Chem., 1985, 50, 1552 and for a related study : H. Kosugi, H. Konto, H. Uda, J. Chem. Soc. Chem. Comm., 1985, 211.
3) M. Schröder, Chem. Res., 1980, 80, 187.
4) R. Ray, D.S. Matteson, Tetrahedron Letters, 1980, 21, 449.
5) J.K. Cha, W.J. Christ, Y. Kishi, Tetrahedron, 1983, 24, 3943.
6) W.J. Christ, J.K. Cha, Y. Kishi, Tetrahedron, 1983, 24, 3947.
7) J.K. Cha, W.J. Christ, Y. Kishi, Tetrahedron Letters, 1983, 40 , 2247.
8) G. Stork, M. Kahn, Tetrahedron Letters, 1983, 24, 3951.
9) F.M. Hauser, S.R. Ellenberger, J.C. Clardy, L.S. Bass, J. Am. Chem. Soc., 1984, 106, 2458
10) C.R. Johnson, M.R. Barbachyn, J. Am. Chem. Soc., 1984, 106, 2459.
11) C. Fréchou, Thèse Strasbourg 1985.

(Received in France 25 April 1986)