Pergamon

Tetrahedron Letters 40 (1999) 177–180

TETRAHEDRON LETTERS

Stereoselective Sulfoxide Directed Reduction of 1,2-Diketo-Derivatives to Enantiomerically Pure *Syn* and *Anti* 1,2-Diols.

Correction of the Relative Configuration by X-Ray and Chemical Correlation to Goniobutenolides A and B.

Guy Solladié*, Gilles Hanquet and Catherine Rolland

Laboratoire de Stéréochimie associé au CNRS, ECPM, Université Louis Pasteur
1 rue Blaise Pascal, 67008-Strasbourg, France

Received 28 July 1998; accepted 26 October 1998

Abstract: In our recent report on the enantioselective synthesis of *syn* and *anti* 1,2-diols from oxalyl-di-(N-methyl-N-methoxyamide), an unfortunate sample inversion for ^{13}C NMR analysis led us to an incorrect attribution of their relative configurations. We report now the correction of the configurations of these diols by X-ray analysis and chemical correlation to two known natural products, goniobutenolides A and B.

We previously reported a straightforward synthesis of enantiomerically pure *syn* and *anti* 1,2-diols from an oxalic acid derivative.[1] Unfortunately a sample inversion for ^{13}C NMR analysis of the acetonides **8** and **9** (Scheme 1), derived from diols **6** led us to an incorrect attribution of their relative configurations. We report now the X-ray determination of the absolute configuration of diols **6** as well a chemical correlation to the known natural products goniobutenolides A and B.

The scheme 1 is the corrected version of the results already described.[1] The β-hydroxy-γ-ketosulfoxides **5** were obtained from the di-N-methyl-N-methoxyamide of oxalic acid in four steps *via* a high *S* diastereoselective DIBAL-H reduction of the β-keto sulfoxide **2** as a key step.[2] The β-hydroxysulfoxide (*R,S*)-**3** was easily transformed into **5** by a Grignard reaction. The absolute configuration of the hydroxy center in compound **5** was deduced from our previous results[2] and established by chemical correlation with the known product **7** where R' = Ph.

As shown in table I, which is the corrected version of the results already reported[1], DIBAL-H reduction of the β-silyloxy-γ-ketosulfoxide **5** afforded the corresponding *anti*-diol **6** with good to excellent yields and diastereoselectivity except for **5a** (R' = methyl) for which a Lewis acid catalysis [$Yb(OTf)_3$] was required. [1] In

* fax 33 3 88 61 65 31; e-mail: solladie@chimie.u-strasbg.fr

0040-4039/99/$ - see front matter
PII: S0040-4039(98)02308-9

sharp contrast the same reaction, in the presence of the chelating Lewis acid ZnI_2, afforded in high yield and high diastereoselectivity only the *syn*-diol **6** (Scheme 1, Table I). The error in the attribution of the relative configurations of carbons C-2 and C-3 in diols **6** was due to an inversion of the samples for the ^{13}C NMR analysis of the acetonides **8** and **9** (a smaller non-equivalence between the *gem*-dimethyl groups[3] for the *syn* diol , 0.8 ppm, than for the *anti* diol, 3 ppm). We report now a new assignment of the absolute and relative configurations, shown in scheme 1 and Table I, by X-ray analysis and chemical correlation.

Table I. Reduction of β-silyloxy γ-ketosulfoxide 5 to *syn* and/or *anti* β-silyloxy γ-hydroxysulfoxide 6.

[S(*R*),2(*S*)] **5**		Reduction Conditions			[S(*R*),2(*S*),3(*R*)]-*Syn* **6**,[S(*R*),2(*S*),3(*S*)]-*anti* **6**		
	R	Lewis Acid	reaction time	reaction temp.	isolated yield	de%	*Anti* -**6** / *Syn* -**6**
a	Me	$Yb(OTf)_3$	1h	-78°C	96%[a]	92%	96 / 4
a	Me	ZnI_2	3h	-78°C	96%[a]	94%	3 / 97
b	Ph		30 min	-78°C	95%[b]	92%	96 / 4
b	Ph	ZnI_2	30 min	-78°C	92%[b]	>95%	2 / 98
c	allyl		30 min	-78°C	93%[b,c]	>95%	98 / 2
c	allyl	ZnI_2	30 min	-78°C	90%[b]	94%	3 / 97
d	vinyl		30 min	-78°C	97%[a]	>95%	98 / 2
d	vinyl	ZnI_2	30 min	-78°C	91%[a]	>95%	2 / 98

a) isolated by crystallisation; b) isolated by chromatography; c) 2.5eq of DIBAL-H.

The erythro configuration of the *anti*-diol **6b** (R' = Ph) obtained by reduction with DIBAL-H was confirmed by-X ray analysis of the corresponding acetonide **8b** showing (figure 1) a S(*R*), 9(*S*), 10(*S*) configuration.

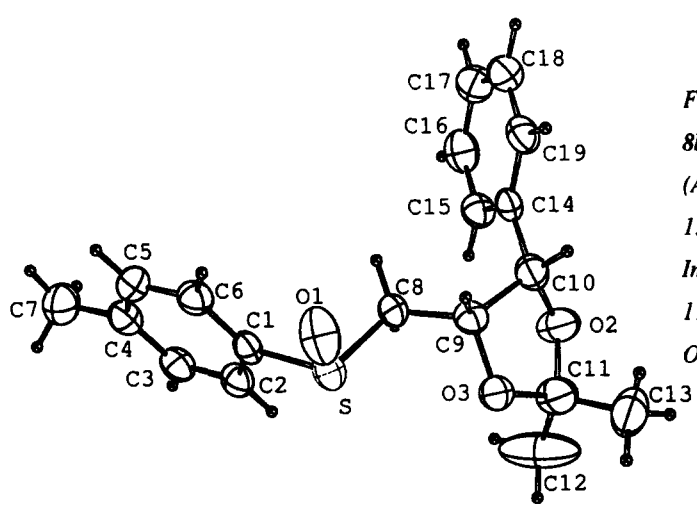
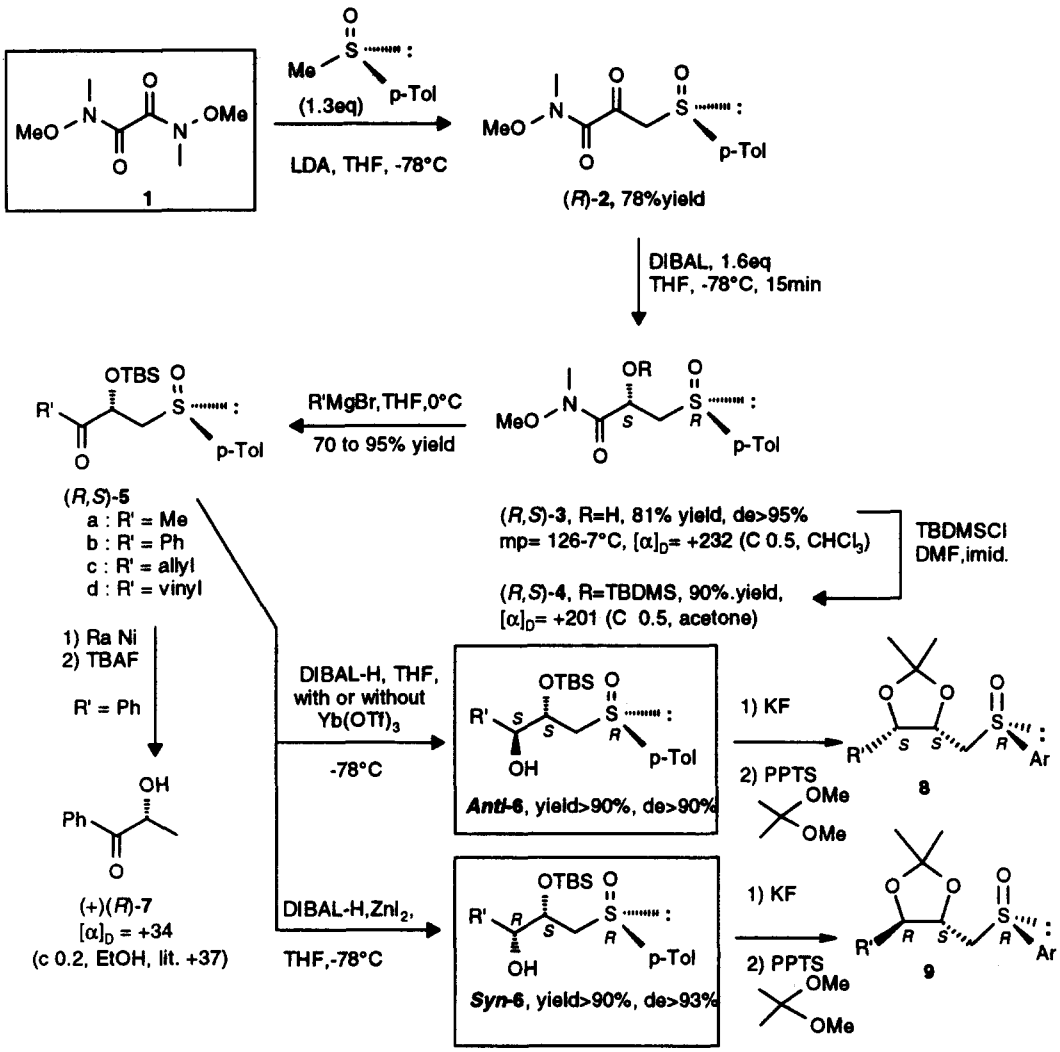


*Figure 1. ORTEP plot of the acetonide **8b**, R'=Ph. Selected mean bond lenghts (Å) : S-O1, 1.502; S-C8, 1.804; C8-C9, 1.511; C1-S, 1.795; C1-C2, 1.383. Important dihedral angles: C6-C1-S, 118.7; C1-S-C8, 97.6; C1-S-O1,107.5; O1-S-C8, 105.2; S-C8-C9, 108.9;*

The ^{13}C NMR spectra[4] of **8b** and **9b** respectively prepared from the *anti*-diol **6b** and the *syn*-diol **6b** are in agreement with the non-equivalence of the gem-dimethyl groups known for *syn* and *anti*-diol acetonides.[3]

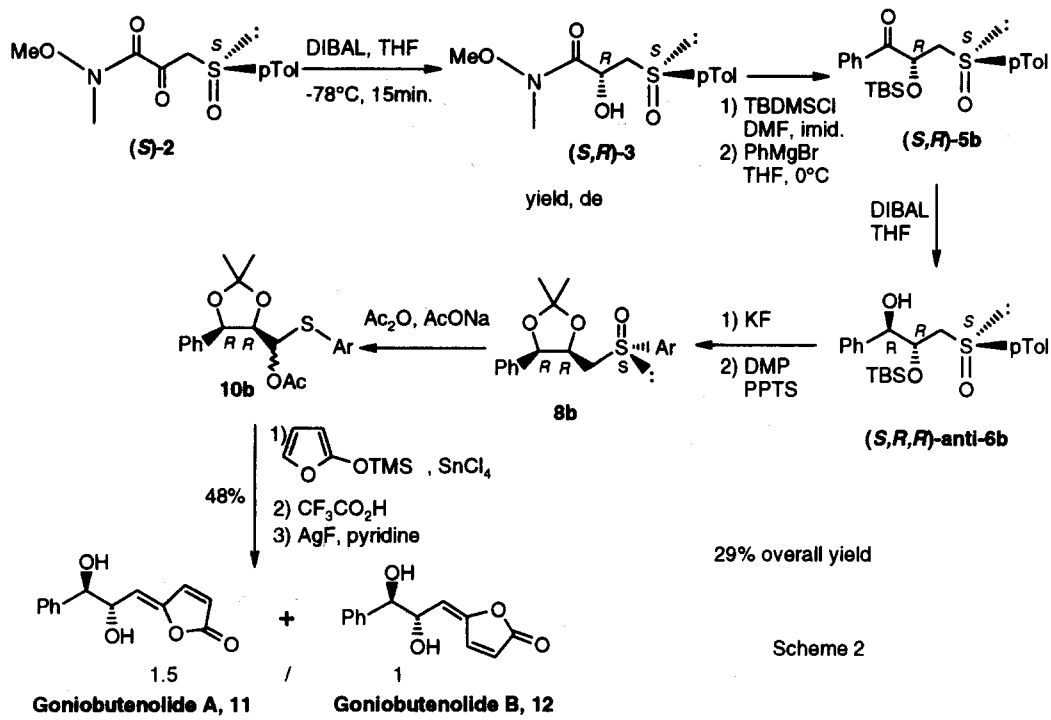


Scheme 1

Finally we made a chemical correlation with the known natural products[5] Goniobutenolides A, **11** and B, **12**, which are extracted from the stem bark of *Goniothalamus giganteous* Hook.f.& Thomas (Annonaceae).

The absolute configurations of the natural products **11** and **12** led us to prepare the *anti*-diol **6b** in the S(*S*), 2*R*,3*R*[6] configuration starting from (-)-(*S*)-methyl-p-tolylsulfoxide (Scheme 2). Then the corresponding S(*S*),2*R*,3*R*-acetonide **8b** was submitted to a Pummerer rearrangement to give the acetonide **10b,** which was finally transformed into a 1.5/1 mixture of goniobutenolides **A** and **B** following the procedure of Ko and

Lerpinière.[5] Compounds **11** and **12** were separated by flash chromatography. They both showed all the characteristics described in literature[5]: **11**: $[\alpha]_D$ +191 (c 0.1, $CHCl_3$); **12**: mp 142°, $[\alpha]_D$ -106 (c 0.1, $CHCl_3$).



In conclusion the relative configuration of the diols **6** obtained by stereoselective sulfoxide directed reduction of β-hydroxy-γ-ketosulfoxides of type **5** is corrected as erythro with DIBAL-H or DIBAL-H / $Yb(OTf)_3$ or threo with DIBAL-H/ZnI_2.

References and notes.

1) Solladié, G., Hanquet, G., Rolland, C. *Tetrahedron Lett.* **1997**, *38*, 5847-5850.
2) Solladié, G., Demailly, G., Greck, C., *J.Org.Chem.* **1985**, *50*, 1552-1554; Solladié, G., Almario, A., *Tetrahedron Lett.* **1994**, *35*, 1937-1940.Solladié, G., Huser, N., Fischer, J. Decian, A., *J. Org. Chem.* **1995**, *60*, 4988-4990.
3) Dana, G., Danechpajouh, H., *Bull.Soc.Chim. Fr.* **1980**, 395-399.
4) Acetonide **8b** [S(*R*),2(*S*),3(*S*)]: ^{13}C NMR: 21.35 ($\underline{C}H_3$,p-Tol), 25.05 ($\underline{C}H_3$, acetonide), 27.56 ($\underline{C}H_3$, acetonide), 61.31 ($\underline{C}H_2$), 72.94 ($\underline{C}$HO), 79.14 ($\underline{C}$HO), 109.48 ($\underline{C}Me_2$), 123.82 to 141.47 (arom. $\underline{C}$H and $\underline{C}$).
Acetonide **9b** [S(*R*), 2(*S*),3(*R*)] : ^{13}C NMR: 21.52 ($\underline{C}H_3$,p-Tol), 27.18($\underline{C}H_3$, acetonide), 27.39 ($\underline{C}H_3$, acetonide), 60.74 ($\underline{C}H_2$), 76.94 ($\underline{C}$HO), 83.08 ($\underline{C}$HO), 110.20 ($\underline{C}Me_2$), 123.95 to 141.82 (arom. $\underline{C}$H and $\underline{C}$).
5) Fang, X.P., Anderson, J.E., Chang, C.J., McLaughlin, J.L. *Tetrahedron* **1991**, *47*,; 9751-9758; Xu, D., Sharpless, B. *Tetrahedron Lett.* **1994**, *35*, 4685-4688; Shing, T.K.M., Tai, W.W.-F., Tsui, H.-C. *J. Chem. Soc., Chem. Commun.* **1994**, 1293-1294; Ko, S.Y., Lerpinière, J. *Tetrahedron Lett.* **1995**, *36*, 2101-2104.
6) *Anti*-**6b** [S(*S*),2(*R*),3(*R*)]: mp= 120°, $[\alpha]_D$ = -249 (c 0.5, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): 0.17 (s, 3H, MeSi), 0.3 (s, 3H, MeSi), 0.98 (s, 9H, tBuSi), , 2.38 (s, 3H, Me,pTol), 2.61 (AB part of ABX, 2H, J_{AB} = 8Hz, J_{AX} = 15Hz, Δν = 38Hz, CH_2SO). 2.81 (1H, OH), 4.48 (m, 1H, CHOTBS), 4.92 (d, 1H, J = 3.5 Hz, CHOH), 7.26 to 7.43 (m, 10H,arom.); 13C NMR (50mhz, CDCl3): -4.61 and -4.48 ($\underline{C}H_3Si$), 18.27 ($\underline{C}$tBuSi), 21.46 ($\underline{C}H_3$,pTol), 25.98 ($\underline{C}H_3$tBu), 60.61 ($\underline{C}H_2$), 71.44 ($\underline{C}$HOSi), 77.74 ($\underline{C}$HOH), 123.88 to 142.23 (arom. C and CH).