

## Johnson orthoester Claisen rearrangement products of some (1-oxa-4-thiaspiro[4.5]dec-6-en-6-yl)alkanols

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Received 17 July 2000

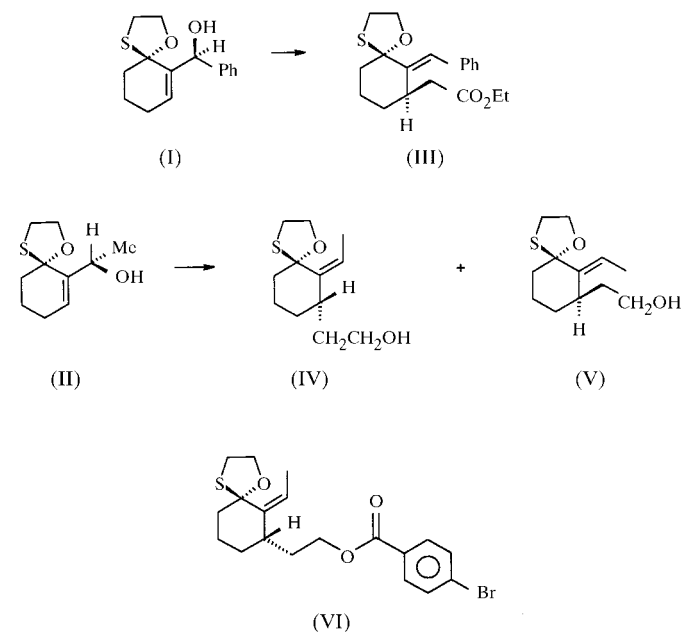
Accepted 29 September 2000

The crystal structures of two 1-oxa-4-thiaspiro[4.5]decane derivatives, ethyl 6-benzylidene-1-oxa-4-thiaspiro[4.5]decane-7-acetate, C<sub>19</sub>H<sub>24</sub>O<sub>3</sub>S, and (6-ethylidene-1-oxa-4-thiaspiro[4.5]decane-7-yl)ethyl 4-bromobenzoate, C<sub>19</sub>H<sub>23</sub>BrO<sub>3</sub>S, obtained under Johnson orthoester Claisen rearrangement conditions, exhibit different olefin geometry. Both structures are composed of independent molecules separated by normal van der Waals distances. The S—Csp<sup>3</sup> bond distances are significantly different from each other, as has been observed in similar structures; the remaining molecular dimensions are as expected.

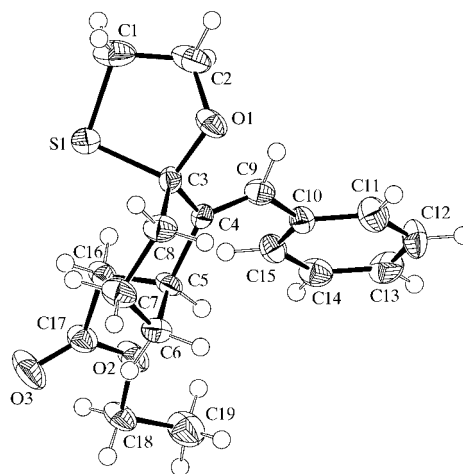
### Comment

In studies of 1,3-diastereoface selection under Johnson orthoester Claisen rearrangement conditions, we have reacted (1-oxa-4-thiaspiro[4.5]dec-6-en-6-yl)(phenyl)methanol, (I), and (1-oxa-4-thiaspiro[4.5]dec-6-en-6-yl)(methyl)methanol, (II), with triethyl orthoacetate. Whereas (I) furnished a single product identified as ethyl 6-benzylidene-1-oxa-4-thiaspiro[4.5]decane-7-acetate, (III), (II) furnished an almost 1:1 mixture of two products which were inseparable by routine chromatographic techniques. However, the corresponding alcohols, obtained on LiAlH<sub>4</sub> reduction in Et<sub>2</sub>O, separated well by radial chromatography. The more polar alcohol was identified, from its 4-bromobenzoate ester derivative, as (6-ethylidene-1-oxa-4-thiaspiro[4.5]decane-7-yl)ethanol, (IV). Since (IV) is a consequence of rearrangement *anti* to the acetal sulfur, the less polar alcohol must, therefore, be a product of rearrangement *syn* to the acetal sulfur and possess the stereostructure shown for (V). Compound (III) is also a consequence of rearrangement *syn* to the acetal sulfur. The difference in the olefin geometry of (IV) from that of (III) and (V) must be noted. In this paper, we describe the crystal structures of (III) and the 4-bromobenzoate ester of (IV), *i.e.* compound (VI).

The structures of (III) and (VI) are presented in Figs. 1 and 2, respectively, and are composed of independent molecules separated by normal van der Waals distances. One C atom of the heterocyclic ring in (III) is disordered over two sites, C1 and C1\*, with non-equivalent site-occupancy factors of 0.58 (2) and 0.42 (2), respectively, indicating the presence of two conformations of the five-membered ring. It is interesting



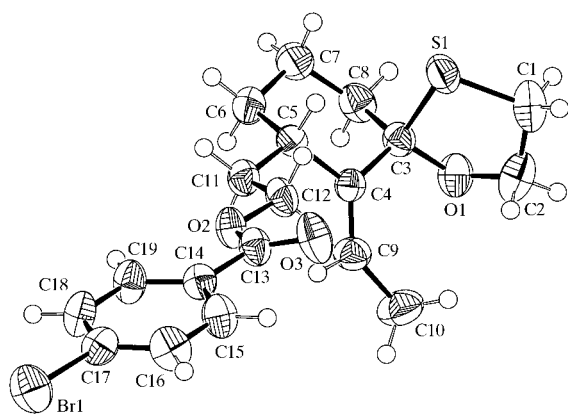
to note that in (III), as a result of the disorder, the rings S1/C1/C2/O1/C3 and S1/C1\*/C2/O1/C3 adopt C2- and S1-envelope conformations, with atoms S1 and C2 0.773 (19) and 0.554 (11) Å, respectively, out of the planes of the remaining ring atoms [maximum deviations 0.009 (5) and 0.014 (4) Å, respectively]. The corresponding heterocyclic ring in (VI) adopts a C2-envelope conformation, with C2 0.542 (9) Å out of the plane formed by the remaining ring atoms [maximum deviation 0.030 (3) Å for C3]. In both structures, the C3—C8



**Figure 1**  
ORTEPII (Johnson, 1976) drawing of (III) with 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as small spheres of arbitrary radii.

six-membered ring adopts a chair conformation, with puckering parameters (Cremer & Pople, 1975)  $Q = 0.539$  (6) and  $0.590$  (6) Å,  $\theta = 171.0$  (6) and  $5.1$  (6)°, and  $\varphi = 69$  (4) and  $83$  (6)°, in (III) and (VI), respectively. The phenyl rings in both structures are essentially planar.

The bond distances and angles in the two structures are normal and agree well with the corresponding values reported for similar compounds in the Cambridge Structural Database (Allen & Kennard, 1993). The S—Csp<sup>3</sup> bond distances, although significantly different from each other in (III) [1.880 (5) Å for S—C3, and a mean of 1.811 (5) Å for S—C1 and S—C1\*], are in excellent agreement with the corresponding bond distances in (VI) [1.878 (5) and 1.798 (6) Å]. Similar non-equivalent S—C bond distances have been reported in the crystal structures of cyclohexanespiro-2'-(1',3'-oxathiolan-5'-one 3'-oxide) (Frechina *et al.*, 1992), (+)-(3*S*,4*R*)-6-phenyl-1-oxa-4-thiaspiro[4.5]decan-8-one (Sonoda *et al.*, 1992), two derivatives of an oxathiaspirodecene (Parvez *et al.*, 1997) and 2-(7-ethylidene-6-methyl-1-oxa-4-thiaspiro[4.5]dec-7-yl)ethanol (Parvez *et al.*, 1998).



**Figure 2** ORTEP (Johnson, 1976) drawing of (VI) with 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as small spheres of arbitrary radii.

## Experimental

Compound (III) was prepared by the Johnson orthoester Claisen rearrangement of (I) on treatment with triethyl orthoacetate in toluene at reflux under nitrogen. A similar reaction using (II) furnished an ester, which was reduced with lithium aluminium hydride in diethyl ether at 253–273 K to generate the alcohol, (IV). Alcohol (IV) was then esterified with 4-bromobenzoyl chloride following standard methods to obtain (VI).

### Compound (III)

#### Crystal data

C<sub>19</sub>H<sub>24</sub>O<sub>3</sub>S  
*M<sub>r</sub>* = 332.44  
 Orthorhombic, *Pna*2<sub>1</sub>  
*a* = 10.369 (2) Å  
*b* = 20.791 (3) Å  
*c* = 8.071 (3) Å  
*V* = 1740.0 (8) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.269 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 25 reflections  
 $\theta = 10\text{--}15^\circ$   
 $\mu = 0.20$  mm<sup>-1</sup>  
*T* = 170 (2) K  
 Plate, colourless  
 0.52 × 0.48 × 0.14 mm

#### Data collection

Rigaku AFC-6S diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: empirical  
 via  $\psi$  scan (3 reflections; North *et al.*, 1968)  
 $T_{\min} = 0.90$ ,  $T_{\max} = 0.97$   
 2150 measured reflections  
 2150 independent reflections

1147 reflections with  $I > 2\sigma(I)$   
 $\theta_{\max} = 27.5^\circ$   
 $h = 0 \rightarrow 13$   
 $k = 0 \rightarrow 27$   
 $l = 0 \rightarrow 10$   
 3 standard reflections  
 every 200 reflections  
 intensity decay: <0.1%

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.044$   
 $wR(F^2) = 0.140$   
 $S = 1.01$   
 2150 reflections  
 219 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 0.82P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.01$   
 $\Delta\rho_{\max} = 0.33$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.28$  e Å<sup>-3</sup>  
 Absolute structure: (Flack, 1983)  
 Flack parameter = 0.05 (18)

**Table 1**

Selected geometric parameters (Å, °) for (III).

S1—C1*	1.806 (14)	O1—C2	1.442 (7)
S1—C1	1.816 (11)	O2—C17	1.335 (6)
S1—C3	1.880 (5)	O2—C18	1.462 (6)
O1—C3	1.421 (6)	O3—C17	1.191 (7)
C1*—S1—C3	86.8 (5)	C3—O1—C2	112.1 (4)
C1—S1—C3	93.1 (4)	C17—O2—C18	116.7 (4)

### Compound (VI)

#### Crystal data

C<sub>19</sub>H<sub>23</sub>BrO<sub>3</sub>S  
*M<sub>r</sub>* = 411.34  
 Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 7.243 (2) Å  
*b* = 11.5410 (10) Å  
*c* = 22.180 (5) Å  
 $\beta = 94.09$  (2)°  
*V* = 1849.3 (7) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.477 Mg m<sup>-3</sup>  
 Cu *K*α radiation  
 Cell parameters from 25 reflections  
 $\theta = 20\text{--}30^\circ$   
 $\mu = 4.20$  mm<sup>-1</sup>  
*T* = 293 (2) K  
 Needle, colourless  
 0.30 × 0.16 × 0.10 mm

#### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $R_{\text{int}} = 0.03$   
 $\theta_{\max} = 68^\circ$   
 $h = 0 \rightarrow 8$   
 $k = 0 \rightarrow 13$   
 $l = -26 \rightarrow 26$   
 3 standard reflections  
 every 200 reflections  
 intensity decay: <0.1%

2207 reflections with  $I > 2\sigma(I)$

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.054$   
 $wR(F^2) = 0.164$   
 $S = 1.04$   
 3372 reflections  
 217 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0736P)^2 + 2.357P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.01$   
 $\Delta\rho_{\max} = 0.43$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.83$  e Å<sup>-3</sup>

One C atom of the heterocyclic ring in (III) was disordered over two sites, C1 and C1\*, with non-equivalent site-occupancy factors of 0.58 (2) and 0.42 (2), respectively. For both compounds (III) and (VI), most of the H atoms were located from difference Fourier syntheses but these were included in the refinements at geometrically idealized positions, with C—H distances in the range 0.93–1.00 Å,

**Table 2**

Selected geometric parameters (Å, °) for (VI).

Br1—C17	1.878 (5)	O1—C3	1.423 (6)
S1—C1	1.798 (6)	O2—C13	1.325 (6)
S1—C3	1.876 (5)	O2—C12	1.434 (5)
O1—C2	1.418 (7)	O3—C13	1.201 (6)
C1—S1—C3	92.6 (3)	C13—O2—C12	116.3 (4)
C2—O1—C3	111.6 (4)		

utilizing a riding model and isotropic displacement parameters. No Friedel reflections were measured for (III).

For compound (III), data collection: *MSC/AFD Diffractometer Control Software* (Molecular Structure Corporation, 1988); for compound (VI), data collection: *CAD-4 Software* (Enraf-Nonius, 1989); for compound (III), cell refinement: *MSC/AFD Diffractometer Control Software*; for compound (VI), cell refinement: *CAD-4 Software*; for both compounds, data reduction: *TEXSAN* (Molecular Structure Corporation, 1994); program(s) used to solve structure: *SAPI91* (Fan, 1991); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *TEXSAN*; software used to prepare material for publication: *SHELXL97*.

The authors thank the Natural Sciences and Engineering Research Council of Canada for providing the Rigaku

AFD-6S diffractometer through an equipment grant to the University of Calgary.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1149). Services for accessing these data are described at the back of the journal.

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