Acta Cryst. (1997). C**53**, 1961–1963

Oxa-thia-spiro-decene Derivatives

Masood Parvez,[a] Duraiswamy A. Jeyaraj[b] and
Veejendra K. Yadav[b]

[a]*Department of Chemistry, The University of Calgary, 2500 University Drive NW, Calgary, Alberta, Canada T2N 1N4, and* [b]*Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India. E-mail: parvez@acs.ucalgary.ca*

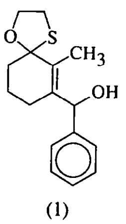
(*Received 17 March 1997; accepted 27 June 1997*)

Abstract

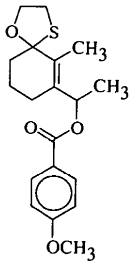
The crystal structures of (5*R*)-(10-methyl-1-oxa-4-thiaspiro[4.5]dec-9-en-9-yl)phenyl-(*S*)-methanol, $C_{16}H_{20}O_2S$, (1), and 1(*S*)-[(5*R*)-10-methyl-1-oxa-4-thiaspiro[4.5]dec-9-en-9-yl]ethyl 4-methoxybenzoate, $C_{19}H_{24}O_4S$, (2), are composed of independent molecules separated by normal van der Waals distances. The molecular dimensions in both structures are normal. The hydroxyl and heterocyclic ring O atoms exhibit a short intermolecular hydrogen bond of the order of 2.814 (4) Å in (1), forming a chain of molecules along the *c* axis.

Comment

The study of diastereoface selection due to an allylic stereogenic centre bearing heteroatoms has generated much interest recently. The O and N atoms in allylic positions to a π bond are well known to direct reactions *syn* to them. Macaulay & Fallis (1988, 1990) have studied the Diels–Alder reactions of 5-sulfur-substituted pentamethylcyclopentadienes and observed that the addition proceeds *anti* to the S atom. There are, however, very few studies on substrates with both S and O atoms on the same allylic C atom. Ginsburg (1983) reported *syn*-to-sulfur addition only from his study of the Diels–Alder cycloaddition of an oxygen- and sulfur-bridged [4.3.3]propellane. Paquette *et al.* (1995) studied a [4.4.4]propellane with both the S and O atoms present in the form of an acetal at a C atom adjacent to a dienic system, and observed a 20:1 mixture of Diels–Alder adducts in favour of *syn*-to-oxygen addition. The different heteroatom positioning in the two studies led us to investigate the ortho-ester Claissen rearrangement and we synthesized two alcohols, each as a mixture of two isomeric components. Both diastereomers in each case exhibited indistinguishable ^1H NMR spectra and hence a single-crystal X-ray structure analysis was performed to determine their relative stereochemistry. While the less polar compound, (1), was crystalline (m.p. 403 K, uncorrected), the more polar compound, (3), was transformed into its 4-methoxybenzoate derivative, (2), and recrystallized. Both compounds were in racemic form, but the crystal of (2) chosen for data collection belongs to a non-centrosymmetric space group indicating resolution of the racemic mixture during crystallization.



(1)



(2)

Figs. 1 and 2 show *ORTEP*II (Johnson, 1976) drawings of compounds (1) and (2), respectively. The absolute structure of (2) was established to be *R* and *S* at C3 and C10, respectively. The molecular dimensions in (1) and (2) are within expected values with identical corresponding bond distances and angles in the two structures. In both structures, S—C bond distances are inequivalent, with S1—C1 [1.803 (3) in (1) and 1.800 (9) Å in (2)] significantly shorter than S1—C3 [1.865 (2) in (1) and 1.883 (7) Å in (2)]. Similar inequivalent 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) and (+)-(3*S*,4*R*)-6-phenyl-1-oxa-4-thiaspiro[4.5]decan-8-one (Sonoda, Houchigai, Asaoka & Takei, 1992).

The five-membered heterocyclic rings in the two structures adopt a C2-envelope conformation with the

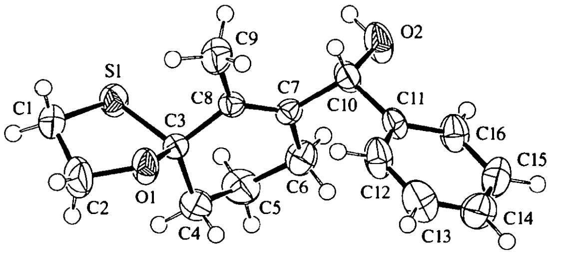


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (1) with the atomic numbering scheme. Displacement ellipsoids are plotted at the 50% probability level and H atoms have been assigned arbitrary radii.

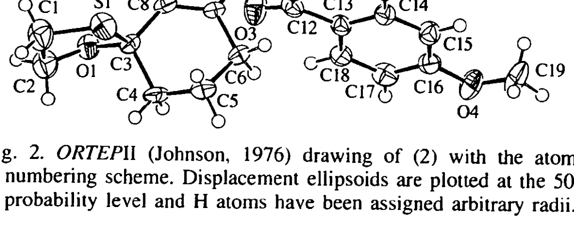


Fig. 2. *ORTEP*II (Johnson, 1976) drawing of (2) with the atomic numbering scheme. Displacement ellipsoids are plotted at the 50% probability level and H atoms have been assigned arbitrary radii.

C2 atoms 0.564 (5) and 0.538 (12) Å out of the planes of the remaining ring atoms in (1) and (2), respectively. The six-membered rings C3–C8 have half-chair conformations, with C4 0.641 (4) and 0.634 (12) Å out of the planes of the remaining ring atoms in (1) and (2), respectively. The mean planes (of the atoms in the planes) in these two rings are inclined at 72.63 (10) and 72.5 (3)° in (1) and (2), respectively. The methoxybenzoate moiety in (2) is non-planar, with O2 0.344 (11) Å below and O3 0.207 (11) Å above the planar phenyl ring which was constrained to be a regular hexagon during refinement.

There is a short intermolecular hydrogen bond involving the hydroxyl H and heterocyclic ring O atoms, with O1···H2 1.88 and O···O(x, y, $z - 1$) 2.814 (4) Å in (1), forming a chain of molecules along the *c* axis. No such interaction is observed in (2).

Experimental

Compounds (1) and (2) were prepared from the coupling of the acetal of 3-lithio-2-methyl-2-cyclohexenone with acetaldehyde and benzaldehyde, respectively. The lithio derivative was made available from the respective 3-bromo species on application of an Li–halogen exchange protocol effected with ^{n}BuLi at 193 K. In each case, two isomers formed, both displaying very similar spectral characteristics but distinctly different in their behaviour to TLC, making their separation easy by simple chromatographic techniques. From each pair, only one was used for X-ray structure determination.

Compound (1)

Crystal data

$C_{16}H_{20}O_2S$
$M_r = 276.38$
Triclinic
$P\bar{1}$
$a = 10.955$ (2) Å
$b = 11.186$ (2) Å
$c = 6.221$ (2) Å
$\alpha = 97.13$ (2)°
$\beta = 100.69$ (2)°
$\gamma = 79.52$ (2)°
$V = 733.4$ (3) Å^3
$Z = 2$
$D_x = 1.252$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 9.0$–$15.0°$
$\mu = 0.216$ mm^{-1}
$T = 170$ (1) K
Prismatic
0.52 × 0.40 × 0.30 mm
Colourless

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical ψ scans of 3 reflections (North, Phillips & Mathews, 1968)
$T_{\min} = 0.915$, $T_{\max} = 0.937$
2749 measured reflections
2599 independent reflections

1831 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.021$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = -7 \rightarrow 7$
3 standard reflections every 200 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.046$
$wR(F^2) = 0.122$
$S = 1.009$
2594 reflections
162 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0714P)^2 + 0.5376P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.312$ e Å^{-3}
$\Delta\rho_{\min} = -0.218$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (1)*

S1—C1	1.803 (3)	O1—C2	1.429 (3)
S1—C3	1.865 (2)	O2—C10	1.421 (3)
O1—C3	1.427 (3)		
C1—S1—C3	92.51 (13)	O1—C3—S1	104.6 (2)
C3—O1—C2	111.2 (2)	C8—C3—S1	111.1 (2)
C2—C1—S1	104.7 (2)	C4—C3—S1	111.2 (2)

Table 2. *Hydrogen-bonding geometry (Å, °) for (1)*

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O1$^{\text{i}}$	0.95	1.88	2.814 (4)	169

Symmetry code: (i) $x, y, z - 1$.

Compound (2)

Crystal data

$C_{19}H_{24}O_4S$
$M_r = 348.44$
Monoclinic
$P2_1$
$a = 6.620$ (3) Å
$b = 11.322$ (3) Å
$c = 12.297$ (3) Å
$\beta = 103.52$ (3)°
$V = 896.1$ (5) Å^3
$Z = 2$
$D_x = 1.291$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 24 reflections
$\theta = 8.0$–$12.0°$
$\mu = 0.200$ mm^{-1}
$T = 200$ (1) K
Prismatic
0.50 × 0.33 × 0.31 mm
Colourless

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical ψ scans of 3 reflections (North, Phillips & Mathews, 1968)
$T_{\min} = 0.747$, $T_{\max} = 0.940$
1668 measured reflections
1668 independent reflections

1038 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 13$
$l = -14 \rightarrow 14$
3 standard reflections every 200 reflections intensity decay: 0.17%

Refinement

Refinement on F^2
$R(F) = 0.054$
$wR(F^2) = 0.140$
$S = 1.192$
1660 reflections
203 parameters
H atoms riding

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.299$ e Å^{-3}
$\Delta\rho_{\min} = -0.549$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

$w = 1/[\sigma^2(F_o^2) + (0.0871P)^2$
$+ 0.3698P]$
where $P = (F_o^2 + 2F_c^2)/3$

Absolute configuration:
Flack (1983)
Flack parameter = −0.3 (2)

Table 3. *Selected geometric parameters (Å, °) for (2)*

S1—C1	1.800 (9)	O2—C10	1.477 (8)
S1—C3	1.883 (7)	O3—C12	1.185 (10)
O1—C3	1.413 (8)	O4—C16	1.360 (5)
O1—C2	1.429 (9)	O4—C19	1.416 (9)
O2—C12	1.337 (9)		
C1—S1—C3	92.3 (4)	C2—C1—S1	105.0 (6)
C3—O1—C2	111.5 (6)	O1—C3—S1	104.6 (4)
C12—O2—C10	116.5 (6)	C8—C3—S1	109.5 (5)
C16—O4—C19	118.2 (6)	C4—C3—S1	108.4 (5)

For (1), the space group $P\bar{1}$ was determined from the statistical analysis, intensity distribution and successful solution and refinement of the structure. Based on the systematic absences, statistical analysis, intensity distribution, successful solution and refinement of the structure, the space group $P2_1$ was assigned to (2). The phenyl rings in both structures were constrained to refine as regular hexagons.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1994); program(s) used to solve structures: *SAPI*91 (Fan, 1991); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*93.

The authors thank the Natural Sciences and Engineering Research Council, Canada, for providing the diffractometer through an equipment grant to the University of Calgary.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1317). Services for accessing these data are described at the back of the journal.

References

Fan, H.-F. (1991). *SAPI91. Structure Analysis Programs with Intelligent Control.* Rigaku Corporation, Tokyo, Japan.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Frechina, J. V., Sanz, V., Cervilla, A., Ramirez, J. A., Ghilardi, C. A. & Orlandini, A. (1992). *Acta Cryst.* C**48**, 1523–1525.
Ginsburg, D. (1983). *Tetrahedron*, **39**, 2095–2135.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Macaulay, J. B. & Fallis, A. G. (1988). *J. Am. Chem. Soc.* **110**, 4074–4076.
Macaulay, J. B. & Fallis, A. G. (1990). *J. Am. Chem. Soc.* **112**, 1136–1144.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1994). *TEXSAN. TEXRAY Structure Analysis Package.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Paquette, L. A., Branan, B. M., Rogers, R. D., Bond, A. H., Lange, H. & Gleiter, R. (1995). *J. Am. Chem. Soc.* **117**, 5992–6001.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Sonoda, S., Houchigai, H., Asaoka, M. & Takei, H. (1992). *Tetrahedron Lett.* **33**, 3145–3146.

Acta Cryst. (1997). C**53**, 1963–1966

cis-anti-cis-Tricyclo[6.4.0.0^{2,7}]dodecane-3,12-dione and *cis-anti-cis*-Tricyclo[6.4.0.0^{2,7}]dodecane-3,9-dione

Angela Taylor, Edmund J. Eisenbraun, Clinton E. Browne and Elizabeth M. Holt

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, USA. E-mail: chememh@mvs.okstate.edu

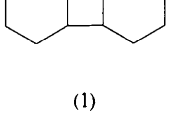
(Received 8 April 1997; accepted 1 September 1997)

Abstract

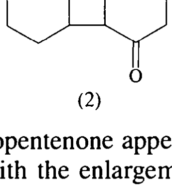
The single-crystal X-ray structures of two photochemical products of 2-cyclohexenone have identified them as the head-to-head and head-to-tail *cis-anti-cis* dimers ($C_{12}H_{16}O_2$) formed by 2+2 addition. The cyclobutane ring is twisted in the head-to-head isomer but flat in the head-to-tail compound.

Comment

The photochemical dimerization of 2-cyclopentenone or 2-cyclohexenone has been shown to proceed *via* an excited triplet state to give dimers of head-to-head (HH) and head-to-tail (HT) orientation along with photorearrangement, photoreduction and photocycloaddition products (Schuster, 1989; Schuster & Insogna, 1991). The relative positions of substituents at the adjacent junctures of the four-membered central ring and two different five- or six-membered rings are identified by *anti* or *syn* terminology (Fig. 1). The relative positions of substituents at the junction of one four- and one five- or six-membered ring are identified by *cis* or *trans*.



(1)



(2)

The dimerization of 2-cyclopentenone appears to lead exclusively to *cis* isomers. With the enlargement of the cyclo-enone ring to six members, there are reports of *trans* isomers (Eaton, 1962; Lem *et al.*, 1993).