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(4a*SR*,7*SR*,9a*RS*)-9a-Bromo-7-methyl-5,5-dioxo-1,2,4a,6,7,9a-hexahydro-8-oxa-5λ^6-thia-1,4-benzocyclohepten-9-one

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Key indicators

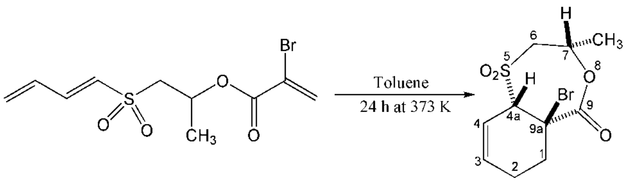
Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.004 Å
R factor = 0.040
wR factor = 0.107
Data-to-parameter ratio = 15.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{10}H_{13}BrO_4S$, crystallizes as a racemic mixture in space group $P\overline{1}$. The seven-membered ring exhibits a boat conformation; the methyl group points away from the bromine substituent.

Comment

The use of temporary tethers to control the regio- and stereoselectivity of Diels–Alder cycloaddition reactions has received considerable attention (Gauthier *et al.*, 1998; Bear *et al.*, 2001). For example, a variety of silicon-containing tethers (Gauthier *et al.*, 1998; Bear *et al.*, 2001; Coelho & Blanco, 2001; Brosius *et al.*, 1999), and a more limited range of boron- (Gauthier *et al.*, 1998; Bear *et al.*, 2001) and metal alkoxide-based (Ward & Abaee, 2000; Barriault *et al.*, 2003; Bertozzi *et al.*, 2000) tethers have been described. Interestingly, only two types of tethers based on sulfur-containing functional groups have been reported, involving the use of sulfonate esters (Gauthier *et al.*, 1998) or sulfonamides (Brosius *et al.*, 1999). Two of us (NC and PS) have begun to explore the potential utility of sulfone-based tethers for such cycloaddition reactions. We have found that β-acyloxysulfonyl tethers can facilitate highly regioselective and diastereoselective thermally mediated intramolecular Diels–Alder cycloaddition reactions between 1-sulfonylbutadienes and various acrylate ester dienophiles. These studies have resulted in the synthesis of a series of bicyclic β-acyloxysulfone cycloadducts. In several cases, we were able to crystallize the major and/or minor diastereomeric cycloadducts in a form suitable for analysis using single-crystal X-ray diffraction. Details of the synthesis of the cycloadducts will be reported elsewhere (Chumachenko *et al.*, 2004). In the present paper, the solid-state structure of the title cycloadduct, (I), as established by single-crystal X-ray diffraction methods, is described.



(I)
(minor diastereomer)

Compound (I) crystallizes as a racemic mixture of both enantiomers. The six-membered ring exhibits the half-chair conformation expected for cyclohexenes, and the angles at the unsaturated C atoms are 122.9 (2)° (for C4—C3—C2) and 124.4 (2)° (for C3—C4—C4*A*; Fig. 1). The seven-membered ring displays a boat-like conformation, with the carbonyl and SO_2 groups below the plane defined by the cyclohexene ring and the other groups pointing upwards. The methyl group on atom C7 is located in the equatorial position, pointing away from the bromine substituent on the bridgehead atom C9*A*.

Experimental

Compound (I) was isolated as the minor diastereomer from an intramolecular Diels–Alder cycloaddition reaction of 1-[(*E*)-buta-1,3-dienylsulfonyl]propan-2-yl 2-bromoacrylate in toluene at 373 K. Although it partially decomposed during silica column chromatography, we were able to obtain a mixed fraction containing cycloadduct (I) along with decomposition products. Crystals of (I) suitable for X-ray diffraction analysis were grown from this mixture *via* slow evaporation of a $CDCl_3$ solution.

Crystal data

$C_{10}H_{13}BrO_4S$
$M_r = 309.17$
Triclinic, $P\overline{1}$
$a = 6.2069\ (10)$ Å
$b = 9.2067\ (15)$ Å
$c = 10.4197\ (17)$ Å
$\alpha = 92.724\ (3)^\circ$
$\beta = 94.191\ (3)^\circ$
$\gamma = 101.615\ (3)^\circ$
$V = 580.50\ (16)$ Å^3

$Z = 2$
$D_x = 1.769$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 4693 reflections
$\theta = 2.3$–28.3°
$\mu = 3.72$ mm^{-1}
$T = 100\ (2)$ K
Block, colorless
0.60 × 0.18 × 0.18 mm

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: multi scan (*SADABS* in *SAINT-Plus*; Bruker, 1997–1999)
$T_{\min} = 0.186$, $T_{\max} = 0.510$
5489 measured reflections

2814 independent reflections
2627 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.038$
$\theta_{\max} = 28.3^\circ$
$h = -8 \rightarrow 8$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$

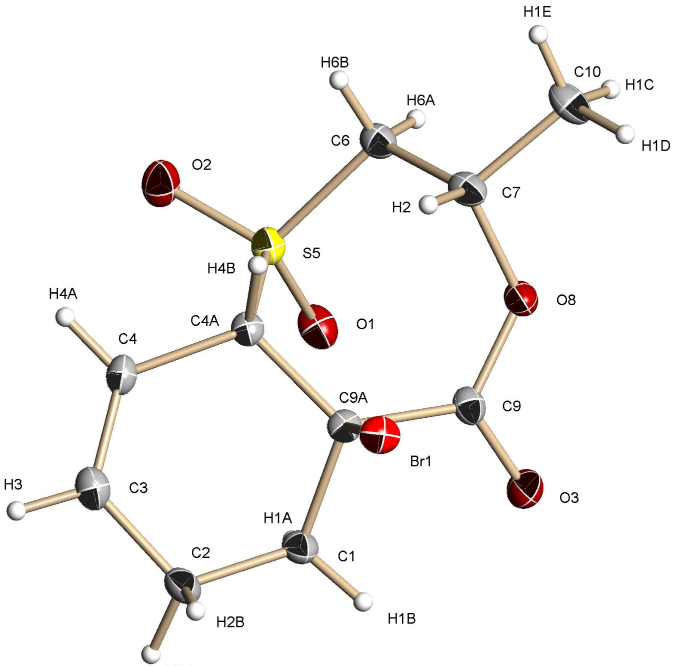


Figure 1
The molecular structure, showing 50% probability displacement ellipsoids.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.107$
$S = 1.04$
2814 reflections
184 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0552P)^2 + 0.2933P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.59$ e Å^{-3}
$\Delta\rho_{\min} = -1.25$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Br1—C9*A*	1.992 (2)	C4*A*—C9*A*	1.551 (3)
C1—C2	1.523 (3)	C4*A*—S5	1.810 (2)
C1—C9*A*	1.525 (3)	S5—C6	1.777 (3)
O1—S5	1.4428 (19)	C6—C7	1.522 (4)
C2—C3	1.492 (4)	C7—O8	1.458 (3)
O2—S5	1.4381 (19)	C7—C10	1.511 (4)
C3—C4	1.327 (4)	O8—C9	1.342 (3)
O3—C9	1.200 (3)	C9—C9A	1.554 (3)
C4—C4*A*	1.509 (3)		
C2—C1—C9*A*	114.24 (19)	O8—C7—C10	105.4 (2)
C3—C2—C1	111.1 (2)	O8—C7—C6	110.17 (19)
C4—C3—C2	122.9 (2)	C10—C7—C6	110.9 (2)
C3—C4—C4*A*	124.4 (2)	C9—O8—C7	124.22 (18)
C4—C4*A*—C9*A*	114.47 (19)	O3—C9—O8	117.0 (2)
C4—C4*A*—S5	109.29 (16)	O3—C9—C9*A*	119.9 (2)
C9*A*—C4*A*—S5	110.78 (15)	O8—C9—C9*A*	123.0 (2)
O2—S5—O1	118.32 (12)	C1—C9*A*—C4*A*	111.64 (19)
O2—S5—C6	108.81 (12)	C1—C9*A*—C9	107.40 (18)
O1—S5—C6	109.25 (11)	C4*A*—C9*A*—C9	119.39 (19)
O2—S5—C4*A*	109.93 (11)	C1—C9*A*—Br1	109.00 (16)
O1—S5—C4*A*	107.43 (11)	C4*A*—C9*A*—Br1	105.72 (15)
C6—S5—C4*A*	101.83 (12)	C9—C9*A*—Br1	103.00 (15)
C7—C6—S5	113.61 (17)		

All H atoms were positioned geometrically. Their coordinates were then refined freely, and their $U_{\rm iso}$ values were defined as 1.2 or $1.5U_{\rm eq}$ of the parent C atom. The s.u. values of the cell parameters are taken from the software, recognizing that the values are unreasonably small (Herbstein, 2000). The maximum and minimum electron-density peaks are located 0.85 and 0.96 Å, respectively, from atom Br1.

Data collection: *SMART* (Bruker, 1997–2000); cell refinement: *SAINT-Plus* (Bruker, 1997–1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXL*97.

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