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6-Bromo-8-thia-1,4-epoxybicyclo[4.3.0]non-2-ene

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Key indicators

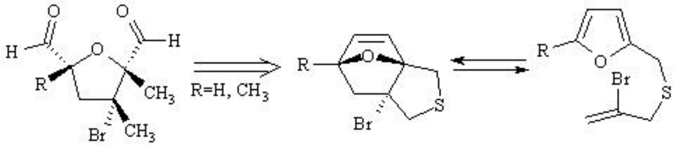
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.006 Å
R factor = 0.039
wR factor = 0.093
Data-to-parameter ratio = 17.0

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

In the title compound, C_8H_9BrOS, the molecules are linked only by weak van der Waals interactions.

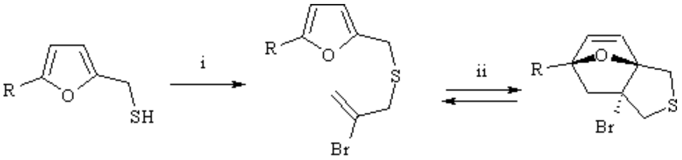
Comment

The intramolecular Diels–Alder (IMDA) reaction has been a valuable tool for the construction of polycyclic ring systems, which are a common structural element in various natural products (Kappe *et al.*, 1997; Padwa *et al.*, 1997; Rydberg & Meinwald, 1996). When a furan ring is tethered to a dienophile, the triene undergoes an IMDA reaction with excellent stereocontrol to provide a tricyclic ring system (Lipshutz, 1986). We have been interested in utilizing the tricyclic cycloadducts for the preparation of highly substituted tetrahydrofuran natural products such as (1).



(1) (2) (3)

This paper reports the crystal structure analysis of a new bromo Diels–Alder cycloaddition product. The tricyclic heterocyclic system (2**a**) may be synthetically useful for future work on furan-based IMDA reactions. We synthesized the rigid tricyclic compound (2**a**) so that one can use furfurylbromoalkene sulfides as a precursor for tetrahydrofurfuryl rings.



(4) (3) (2)

R=H		**a**	82%	**a**	35%
R=CH3		**b**	85%	**b**	32%

The ease with which these cycloadducts undergo a retro-cycloaddition has so far limited their use in synthesis. This problem can be avoided by the placement of bulky substituents in the side chain (Sammes & Weller, 1995). As a result, conformations that allow for the proper approach of diene and dienophile (Demircan & Parsons, 2002) are obtained.

The molecular structure of (2**a**) is shown in Fig. 1. Selected bond lengths and angles are listed in Table 1.

Experimental

Simple furanyl sulfides have been prepared *via* alkylation of furfuryl mercaptan; a sodium hydride suspension (1.2 mmol) dehydrogenated the mercaptanol (4) (0.8 mmol); dropwise addition of 2,3-dibromopropene (0.8 mmol) in tetrahydrofuran (10 ml) at 273 K afforded the precursors (3) quantitatively at 273 K (see second scheme above). Compound (3) was then refluxed in toluene (383 K) for 24 h. The reaction was monitored by thin layer chromatography and halted when no further change of (3) to cycloadduct (2) was noted. The ratio of furan starting material and cycloaddition product was obtained by flash column chromatography. The yield of cycloadditions can rise up to 75% when the IMDA reaction is repeated several times with recovered starting material. In general, the reactions were devoid of any side products, allowing for approximately 90% yield after purification. The relative stereochemistry of the cycloadducts is expected to be that of the previous examples, *i.e.* arising from '*exo*' conformation of the dienophile side chain (Parker & Adamchuk, 1978). Since the electronic effect cannot wholly explain these results, steric effects have to be taken into account during the cycloaddition process.

Crystal data

C_8H_9BrOS
$M_r = 233.12$
Triclinic, $P\bar{1}$
$a = 6.6508$ (10) Å
$b = 7.9576$ (12) Å
$c = 8.4012$ (12) Å
$\alpha = 81.030$ (12)°
$\beta = 88.572$ (12)°
$\gamma = 81.179$ (12)°
$V = 434.00$ (11) Å^3

$Z = 2$
$D_x = 1.784$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4150 reflections
$\theta = 2.5$–28.0°
$\mu = 4.91$ mm^{-1}
$T = 296$ (2) K
Prism, colourless
0.26 × 0.20 × 0.16 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: integration *X-RED* (Stoe & Cie, 2002)
$T_{min} = 0.371$, $T_{max} = 0.631$
5151 measured reflections
1704 independent reflections

1436 reflections with $I > 2\sigma(I)$
$R_{int} = 0.078$
$\theta_{max} = 26.0°$
$h = -8 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.093$
$S = 1.09$
1704 reflections
100 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.038P)^2 + 0.022P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.79$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—S1	1.813 (4)	C5—C6	1.314 (7)
C2—Br1	1.965 (3)	C7—O1	1.444 (4)
C4—O1	1.436 (5)	C8—S1	1.829 (4)
C1—C2—Br1	109.1 (3)	C4—O1—C7	95.7 (3)
C3—C2—Br1	113.0 (3)	C1—S1—C8	94.58 (18)
C7—C2—Br1	109.9 (2)		

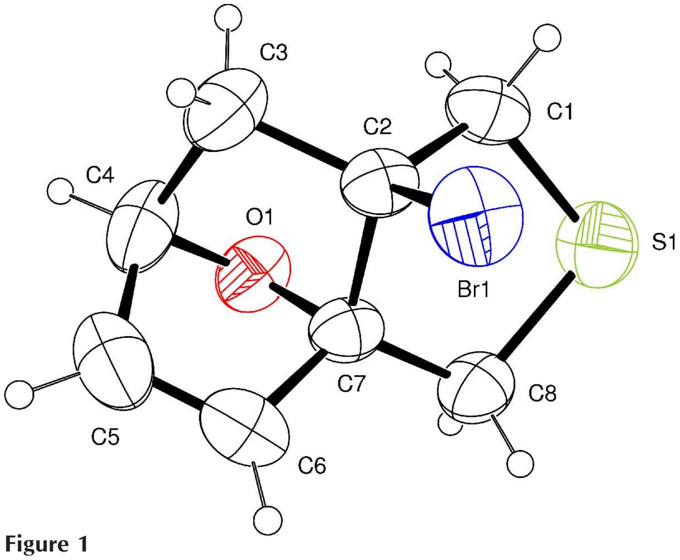


Figure 1
An *ORTEP-3* (Farrugia, 1997) view of the title compound, with the atom-numbering scheme and 50% probability displacement ellipsoids.

All H atoms were treated using a riding model, with C—H = 0.93, 0.97 and 0.98 Å for aromatic CH, CH_2 and CH groups, respectively. The isotropic displacement parameters were set to 1.2 times U_{eq} of the parent atom.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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