

## Some Diels–Alder adducts of 6-vinyl-1-oxa-4-thiaspiro[4.5]dec-6-ene

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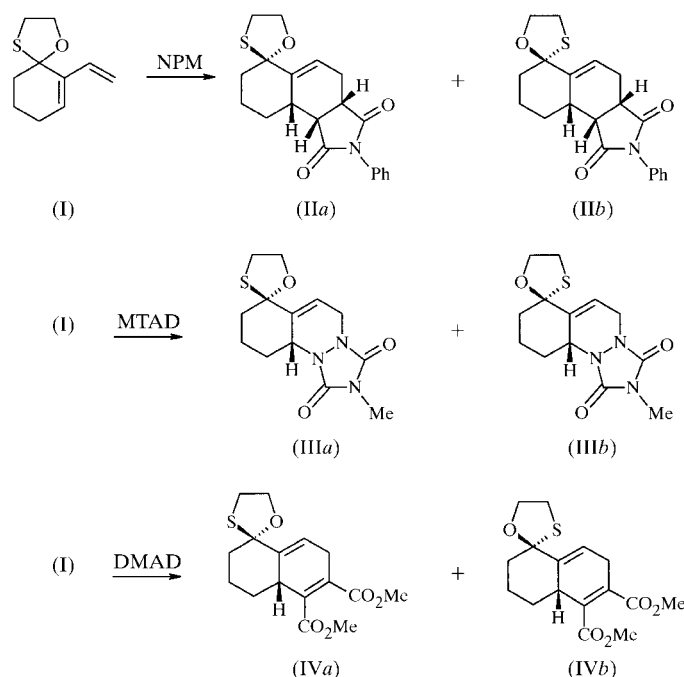
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6-Vinyl-1-oxa-4-thiaspiro[4.5]dec-6-ene has been reacted with dienophiles, such as *N*-phenylmaleimide (NPM), *N*-methyltriazoline-2,5-dione (MTAD) and dimethylacetylene dicarboxylate (DMAD), to assess the 1,3-diastereofacial selection caused by the acetal function. In each case, a mixture of two diastereoisomers was produced. The crystal structures of the products of the addition of NPM and MTAD *syn* to the acetal oxygen, 2-phenyl-2,3,3a,4,5,5a,6,7,8,9,9a,9b-dodecahydro-1*H*-benz[*e*]isoindole-6-spiro-2'-[1',3']oxathiolane-1,3-dione, C<sub>20</sub>H<sub>21</sub>NO<sub>3</sub>S, (IIa), and 2-methyl-5,7,8,9,10,10a-hexahydro-1*H*-1,2,4-triazolo[1,2-*a*]cinnoline-7-spiro-2'-[1',3']-oxathiolane-1,3-dione, C<sub>13</sub>H<sub>17</sub>N<sub>3</sub>O<sub>3</sub>S, (IIIa), respectively, and the product of the addition of DMAD *syn* to the acetal sulfur, dimethyl 1,2,3,4,4a,7-hexahydronaphthalene-1-spiro-2'-[1',3']-oxathiolane-5,6-dicarboxylate, C<sub>16</sub>H<sub>20</sub>O<sub>5</sub>S, (IVb), have been determined. All three structures are composed of independent molecules separated by normal van der Waals distances. The 1-oxa-4-thia heterocyclic ring has an envelope conformation in the three structures and the S—Csp<sup>3</sup> bond distances differ significantly from each other, as observed in comparable structures; the remaining molecular dimensions are as expected.

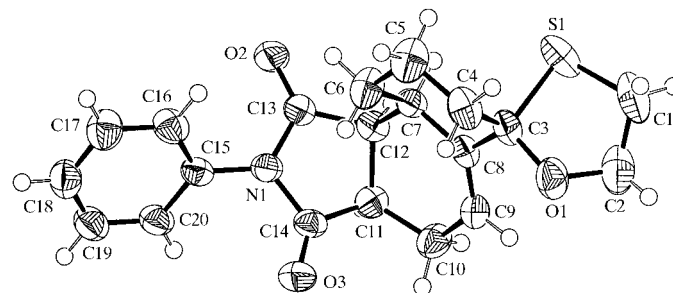
### Comment

We have reacted 6-vinyl-1-oxa-4-thiaspiro[4.5]dec-6-ene, (I), with dienophiles such as *N*-phenylmaleimide (NPM), *N*-methyltriazoline-2,5-dione (MTAD) and dimethylacetylene dicarboxylate (DMAD) to study the 1,3-diastereofacial selection caused by the acetyl function. In each case, a mixture of two adducts was obtained (see Scheme); the additions have been examined under a variety of conditions including the use of selected Lewis acids to achieve different product distributions, and the results of this study will be reported elsewhere (Yadav *et al.*, 2001).

The products (IIa)–(IVa) were formed from addition *syn* to the acetyl O atom. Compounds (IIa) and (IIb) were separated by radial chromatography and (IIa) was recrystallized from toluene to furnish a single diastereoisomer (m.p. 397 K). The products (IIIa) and (IIIb) were inseparable by routine chromatographic means; the major product (IIIa), however, recrystallized from methanol–dichloromethane as a diastereoisomeric mixture (m.p. 431 K). The products (IVa) and (IVb) were separated and the less polar, (IVb), was recrystallized from ethyl acetate–petroleum ether (m.p. 357 K). The ratios of the adducts formed were determined from the relative integrals of the vinylic H atoms. The diastereo-determination was achieved from single-crystal X-ray crystallography of one of the two adducts formed. In this paper, we describe the crystal structures of (IIa), (IIIa) and (IVb).

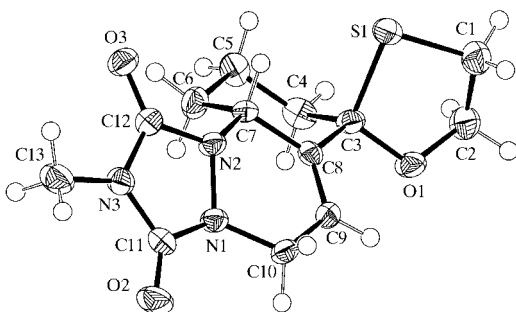


The structure of (IIa) (Fig. 1) is composed of independent molecules separated by normal van der Waals distances. The heterocyclic S1/C1/C2/O1/C3 ring adopts a C2-envelope conformation, with C2 0.598 (6) Å out of the plane formed by the rest of the atoms of the ring; the maximum deviation of any atom from this plane is 0.061 (2) Å. The heterocyclic N1/



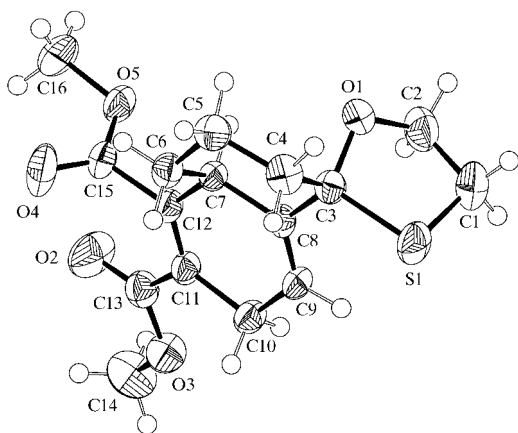
**Figure 1**  
An ORTEP (Johnson, 1976) drawing of (IIa) with 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as small spheres of arbitrary radii.

C13/C12/C11/C14 ring also adopts an envelope conformation, with C11 0.483 (4) Å out the plane of the rest of the ring atoms. The six-membered C3–C8 ring adopts a chair conformation, with puckering parameters (Cremer & Pople, 1975)  $Q = 0.561$  (4) Å, and  $\theta = 5.3$  (4) and  $\varphi = 195$  (4)°. The six-membered C7–C12 ring adopts a sofa conformation, with C11 0.402 (4) Å from the remaining atoms of the ring [maximum deviation 0.071 (2) Å] and the phenyl C15–C20 ring is essentially planar [maximum deviation 0.011 (3) Å].



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

The structure of (IIIa) (Fig. 2) is similarly composed of independent molecules separated by normal van der Waals distances. The heterocyclic S1/C1/C2/O1/C3 ring also adopts a C2-envelope conformation, with C2 0.566 (5) Å out of the plane formed by the rest of the atoms of the ring; the maximum deviation of any atom from this plane is 0.061 (2) Å. The heterocyclic N1/N2/C12/N3/C11 ring is planar to within 0.082 (2) Å. The six-membered C3–C8 ring adopts a chair conformation, with puckering parameters  $Q = 0.569$  (4) Å, and  $\theta = 179.5$  (4) and  $\varphi = 271$  (17)°. The six-membered N1/N2/C7/C8/C9/C10 ring adopts a sofa conformation, with N1 0.540 (4) Å from the remaining atoms of the ring [maximum deviation 0.071 (2) Å].



**Figure 3**  
An ORTEPII (Johnson, 1976) drawing of (IVb) with 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as small spheres of arbitrary radii.

Unlike the heterocyclic S1/C1/C2/O1/C3 rings in (IIa) and (IIIa), the corresponding ring in the structure of (IVb) (Fig. 3) adopts an O1-envelope conformation, with O1 0.564 (3) Å out of the plane formed by the rest of the atoms of the ring; the maximum deviation of any atom from this plane is 0.024 (2) Å. The six-membered C3–C8 ring adopts a chair conformation, with puckering parameters  $Q = 0.571$  (3) Å, and  $\theta = 6.4$  (3) and  $\varphi = 212$  (2)°. The six-membered C7–C12 ring is essentially planar [maximum deviation 0.055 (2) Å], with the carboxylate groups O2/C13/O3/C14 and O4/C15/O5/C16 inclined to this ring at angles of 10.7 (2) and 84.53 (11)°, respectively. The structure is composed of independent molecules which are separated by normal van der Waals distances.

The S–Csp<sup>3</sup> bond distances, although significantly different in all three structures [1.860 (3) and 1.802 (6) Å in (IIa), 1.872 (3) and 1.805 (4) Å in (IIIa), and 1.848 (3) and 1.793 (4) Å in (IVb)], are in excellent agreement with the corresponding bond distances 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). The remaining bond distances and angles in the three structures are normal and agree well with the corresponding values reported for similar compounds contained in the Cambridge Structural Database (Allen & Kennard, 1993).

## Experimental

Cyclohexanone was hydroxymethylated following the Baylis–Hillman reaction (Rezgui & Gaied, 1998) to furnish 2-hydroxymethyl-2-cyclohexenone, which produced an acetal when condensed with mercaptoethanol in the presence of 2 mol% pyridinium *p*-toluenesulfonate in benzene under azeotropic removal of water. Finally, Wittig olefination of the aldehyde that was formed from the oxidation of the alcohol with pyridinium dichromate generated the desired diene, namely 6-vinyl-1-oxa-4-thiaspiro[4.5]dec-6-ene, (I).

## Compound (IIa)

### Crystal data

C<sub>20</sub>H<sub>21</sub>NO<sub>3</sub>S  
*M<sub>r</sub>* = 355.44  
 Monoclinic, *P*<sub>2</sub><sub>1</sub>  
*a* = 12.047 (2) Å  
*b* = 7.808 (2) Å  
*c* = 9.7180 (10) Å  
 $\beta$  = 108.710 (10)°  
*V* = 865.8 (3) Å<sup>3</sup>  
*Z* = 2

*D<sub>x</sub>* = 1.363 Mg m<sup>-3</sup>  
 Cu *K*α radiation  
 Cell parameters from 25 reflections  
 $\theta$  = 12.5–20.0°  
 $\mu$  = 1.82 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Prismatic, colourless  
 0.6 × 0.4 × 0.2 mm

### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: empirical via  $\psi$  scan (3 reflections; North *et al.*, 1968)  
*T<sub>min</sub>* = 0.41, *T<sub>max</sub>* = 0.71  
 1788 measured reflections  
 1705 independent reflections

1653 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.014  
 $\theta_{\text{max}}$  = 68°  
*h* = 0 → 14  
*k* = 0 → 9  
*l* = -11 → 11  
 3 standard reflections every 200 reflections  
 intensity decay: <0.1%

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.049$   
 $wR(F^2) = 0.125$   
 $S = 1.15$   
 1705 reflections  
 226 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.092P)^2 + 0.087P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.01$   
 $\Delta\rho_{\max} = 0.64 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.29 \text{ e } \text{\AA}^{-3}$   
 Absolute structure: Flack (1983)  
 Flack parameter = 0.04 (3)

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (IIa).

S1—C1	1.802 (6)	O3—C14	1.203 (4)
S1—C3	1.860 (3)	N1—C13	1.392 (4)
O1—C2	1.403 (5)	N1—C14	1.409 (4)
O1—C3	1.427 (4)	N1—C15	1.427 (4)
O2—C13	1.218 (4)		
C1—S1—C3	90.60 (18)	C13—N1—C15	125.2 (3)
C2—O1—C3	113.5 (3)	C14—N1—C15	123.7 (2)
C13—N1—C14	111.2 (3)		

Compound (IIIa)

Crystal data

$\text{C}_{13}\text{H}_{17}\text{N}_3\text{O}_3\text{S}$   
 $M_r = 295.36$   
 Monoclinic,  $P2_1/c$   
 $a = 13.258 (2) \text{ \AA}$   
 $b = 7.3897 (17) \text{ \AA}$   
 $c = 14.2874 (13) \text{ \AA}$   
 $\beta = 105.944 (9)^\circ$   
 $V = 1345.9 (4) \text{ \AA}^3$   
 $Z = 4$

$D_x = 1.458 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 12 reflections  
 $\theta = 10\text{--}15^\circ$   
 $\mu = 0.25 \text{ mm}^{-1}$   
 $T = 170 (2) \text{ K}$   
 Block, colourless  
 $0.42 \times 0.35 \times 0.31 \text{ mm}$

Data collection

Rigaku AFC-6S diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: empirical via  $\psi$  scan (3 reflections; North *et al.*, 1968)  
 $T_{\min} = 0.90$ ,  $T_{\max} = 0.93$   
 2487 measured reflections  
 2380 independent reflections  
 1337 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.047$   
 $\theta_{\max} = 25^\circ$   
 $h = 0 \rightarrow 15$   
 $k = 0 \rightarrow 8$   
 $l = -17 \rightarrow 16$   
 3 standard reflections every 200 reflections  
 intensity decay:  $<0.1\%$

Table 2

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (IIIa).

S1—C1	1.805 (4)	N1—N2	1.425 (4)
S1—C3	1.872 (3)	N1—C10	1.455 (4)
O1—C3	1.413 (4)	N2—C12	1.366 (4)
O1—C2	1.417 (4)	N2—C7	1.460 (4)
O2—C11	1.210 (4)	N3—C11	1.378 (4)
O3—C12	1.215 (4)	N3—C12	1.388 (4)
N1—C11	1.379 (4)	N3—C13	1.454 (4)
C1—S1—C3	91.56 (17)	C12—N2—C7	123.7 (3)
C3—O1—C2	110.5 (3)	N1—N2—C7	116.7 (2)
C11—N1—N2	107.3 (3)	C11—N3—C12	111.3 (3)
C11—N1—C10	123.0 (3)	C11—N3—C13	125.0 (3)
N2—N1—C10	114.8 (2)	C12—N3—C13	123.6 (3)
C12—N2—N1	107.8 (2)		

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.042$   
 $wR(F^2) = 0.130$   
 $S = 1.00$   
 2380 reflections  
 182 parameters  
 H-atom parameters constrained

Compound (IVb)

Crystal data

$\text{C}_{16}\text{H}_{20}\text{O}_5\text{S}$   
 $M_r = 324.38$   
 Triclinic,  $P\bar{1}$   
 $a = 6.812 (3) \text{ \AA}$   
 $b = 10.494 (7) \text{ \AA}$   
 $c = 11.023 (5) \text{ \AA}$   
 $\alpha = 96.014 (7)^\circ$   
 $\beta = 90.97 (1)^\circ$   
 $\gamma = 90.21 (2)^\circ$   
 $V = 783.5 (7) \text{ \AA}^3$

$Z = 2$   
 $D_x = 1.375 \text{ Mg m}^{-3}$   
 Cu  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 20\text{--}25^\circ$   
 $\mu = 2.03 \text{ mm}^{-1}$   
 $T = 293 (2) \text{ K}$   
 Prismatic, colourless  
 $0.38 \times 0.25 \times 0.09 \text{ mm}$

Data collection

Enraf-Nonius CAD-4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: empirical via  $\psi$  scan (3 reflections; North *et al.*, 1968)  
 $T_{\min} = 0.51$ ,  $T_{\max} = 0.84$   
 3104 measured reflections  
 2843 independent reflections

2323 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.012$   
 $\theta_{\max} = 68^\circ$   
 $h = 0 \rightarrow 8$   
 $k = -12 \rightarrow 12$   
 $l = -13 \rightarrow 13$   
 3 standard reflections every 200 reflections  
 intensity decay:  $<0.1\%$

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.054$   
 $wR(F^2) = 0.170$   
 $S = 1.06$   
 2843 reflections  
 201 parameters  
 H-atom parameters constrained

Table 3

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (IVb).

S1—C1	1.793 (4)	O3—C13	1.332 (3)
S1—C3	1.848 (3)	O3—C14	1.439 (3)
O1—C2	1.423 (3)	O4—C15	1.191 (3)
O1—C3	1.425 (3)	O5—C15	1.323 (3)
O2—C13	1.195 (3)	O5—C16	1.448 (3)
C1—S1—C3	92.04 (14)	C13—O3—C14	115.9 (2)
C2—O1—C3	108.8 (2)	C15—O5—C16	115.5 (2)

For compounds (IIa), (IIIa) and (IVb), the space groups  $P2_1$ ,  $P2_1/c$  and  $P\bar{1}$ , respectively, were determined from the systematic absences, packing considerations, a statistical analysis of intensity distribution and the successful solution and refinement of the structures. In all three structures, most of the H atoms were located from difference maps and all H atoms were placed at geometrically idealized positions ( $\text{C—H} = 0.93\text{--}1.00 \text{ \AA}$ ) utilizing riding models, with torsional parameters refined for each methyl group in (IIIa) and (IVb). No Friedel reflections were measured for (IIa).

For compounds (IIa) and (IVb), data collection: *CAD-4 Software* (Enraf–Nonius, 1989); for compound (IIIa), data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); for compounds (IIa) and (IVb), cell refinement: *CAD-4 Software*; for compound (IIIa), cell refinement: *MSC/AFC Diffractometer Control Software*; for all three 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*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1148). Services for accessing these data are described at the back of the journal.

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