

C228	-0.3608 (2)	0.1093 (2)	0.11122 (15)	0.0241 (7)
C229	-0.2798 (2)	0.0480 (2)	0.1344 (2)	0.0252 (7)
C230	-0.3211 (2)	-0.0447 (2)	0.12429 (14)	0.0206 (6)
C231	-0.2046 (2)	0.2062 (2)	0.3563 (2)	0.0279 (7)
C232	-0.2237 (2)	0.1630 (2)	0.4159 (2)	0.0280 (7)
C233	-0.3172 (3)	0.1977 (2)	0.4291 (2)	0.0285 (7)
C234	-0.3562 (3)	0.2629 (2)	0.3774 (2)	0.0278 (7)
C235	-0.2862 (2)	0.2679 (2)	0.3325 (2)	0.0286 (7)
C236	-0.1629 (2)	0.1562 (2)	0.3070 (2)	0.0289 (7)
C237	-0.2014 (2)	0.1656 (2)	0.2315 (2)	0.0283 (7)
C238	-0.2014 (2)	0.0757 (2)	0.1933 (2)	0.0260 (7)
C239	-0.1633 (2)	0.0122 (2)	0.2449 (2)	0.0268 (7)
C240	-0.1393 (2)	0.0614 (2)	0.3148 (2)	0.0277 (7)
C241	-0.2013 (2)	0.0710 (2)	0.4235 (2)	0.0274 (7)
C242	-0.1578 (2)	0.0199 (2)	0.3720 (2)	0.0274 (7)
C243	-0.2009 (2)	-0.0723 (2)	0.3617 (2)	0.0261 (7)
C244	-0.2708 (2)	-0.0782 (2)	0.40618 (15)	0.0250 (7)
C245	-0.2710 (2)	0.0111 (2)	0.44458 (15)	0.0278 (7)
C246	-0.3839 (3)	0.1400 (2)	0.44958 (15)	0.0301 (8)
C247	-0.3595 (3)	0.0447 (2)	0.45778 (15)	0.0282 (7)
C248	-0.4528 (2)	-0.0098 (2)	0.43225 (15)	0.0267 (7)
C249	-0.5346 (2)	0.0521 (2)	0.4086 (2)	0.0277 (7)
C250	-0.4922 (2)	0.1444 (2)	0.4196 (2)	0.0277 (7)
C251	-0.4590 (3)	0.2672 (2)	0.3489 (2)	0.0287 (7)
C252	-0.5293 (2)	0.2070 (2)	0.3700 (2)	0.0290 (7)
C253	-0.6097 (2)	0.1791 (2)	0.3085 (2)	0.0283 (7)
C254	-0.5905 (2)	0.2218 (2)	0.2488 (2)	0.0289 (7)
C255	-0.4974 (2)	0.2767 (2)	0.2737 (2)	0.0279 (7)
C256	-0.3224 (2)	0.2768 (2)	0.2603 (2)	0.0270 (7)
C257	-0.4298 (3)	0.2812 (2)	0.2307 (2)	0.0277 (7)
C258	-0.4532 (3)	0.2310 (2)	0.1608 (2)	0.0275 (7)
C259	-0.3609 (2)	0.1958 (2)	0.1471 (2)	0.0257 (7)
C260	-0.2794 (2)	0.2243 (2)	0.2090 (2)	0.0275 (7)
C261	-0.4063 (2)	-0.2541 (2)	0.13936 (15)	0.0241 (7)
C262	-0.3903 (2)	-0.2627 (2)	0.0649 (2)	0.0260 (7)
C263	-0.2738 (3)	-0.3046 (3)	-0.0035 (2)	0.0476 (11)
C264	-0.2198 (4)	-0.2203 (4)	-0.0145 (2)	0.0569 (12)
C265	-0.4236 (3)	-0.3452 (2)	0.1664 (2)	0.0282 (7)
C266	-0.4639 (5)	-0.5029 (2)	0.1290 (3)	0.098 (2)
C267	-0.4191 (5)	-0.5601 (3)	0.0855 (3)	0.093 (2)
O21	-0.4530 (2)	-0.2442 (2)	0.01329 (11)	0.0371 (6)
O22	-0.2993 (2)	-0.2931 (2)	0.06487 (11)	0.0414 (6)
O23	-0.4161 (2)	-0.3586 (2)	0.22603 (13)	0.0583 (8)
O24	-0.4477 (3)	-0.4081 (2)	0.11365 (13)	0.0778 (11)
C111	0.23956 (7)	0.16721 (5)	0.42762 (4)	0.0351 (2)
C112	0.05230 (7)	0.14908 (8)	0.46774 (5)	0.0526 (3)
C113	0.11899 (8)	-0.00036 (6)	0.38398 (6)	0.0578 (3)
C1	0.1168 (3)	0.1190 (2)	0.4016 (2)	0.0324 (8)
Cl21	-0.25251 (6)	-0.33583 (5)	0.42978 (4)	0.0329 (2)
Cl22	-0.38478 (8)	-0.49729 (6)	0.38741 (5)	0.0478 (2)
Cl23	-0.44317 (7)	-0.33913 (7)	0.46707 (5)	0.0475 (2)
C2	-0.3783 (3)	-0.3767 (2)	0.4026 (2)	0.0298 (7)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: SE1063). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## (-)-(S,S)- $\alpha$ -Phenyl-2-(p-tolylsulfinyl)-3-furanmethanol

R. RETOUX

*Laboratoire des Fluorures, URA 449,  
 Faculté des Sciences, Université du Maine,  
 72017 Le Mans CEDEX, France*

L. GIRODIER AND F. ROUESSAC

*Laboratoire de Synthèse Organique, URA 482,  
 Faculté des Sciences, Université du Maine,  
 72017 Le Mans CEDEX, France*

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## Abstract

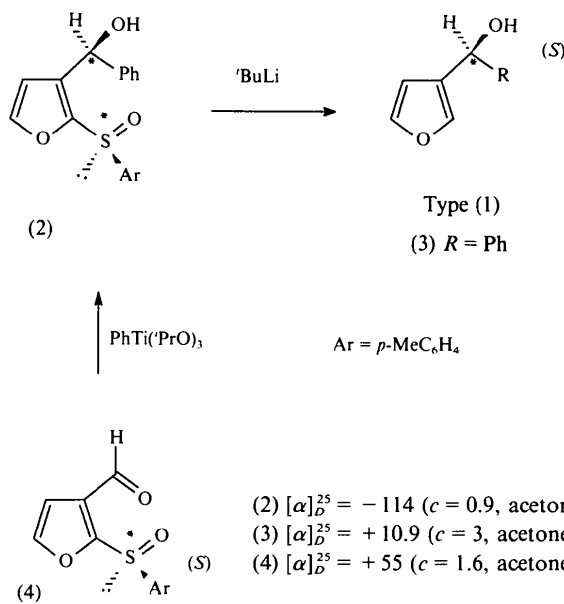
The structure determination of the title compound, C<sub>18</sub>H<sub>16</sub>O<sub>3</sub>S, based on X-ray single crystal diffraction data, confirms that the absolute configuration is *S* at the two asymmetric centres; it facilitated the establishment of the absolute configuration of the chiral C centre of the parent molecule, after cleavage of the sulfoxide group, which had been postulated but not confirmed in the literature until now.

Although  $\langle |E^2 - 1| \rangle$  was 1.04, the phase problem could be solved only in the non-centrosymmetric space group *P1* with four molecules of fullerene per unit cell. In the course of the investigation it was found that one molecule of chloroform crystallizes with one molecule of fullerene and that the structure has, in reality, the centrosymmetric space group *P* $\bar{1}$ . During parameter refinement in the non-centrosymmetric space group it was not possible to distinguish between single and double bonds in the fullerene molecule without extensive use of restraints. Refinement in the correct space group, however, produced average bond lengths with relatively low e.s.d.'s for the single and double bonds at a 'respectful' distance from the cyclopropane ring [1.453 (4) and 1.393 (5) Å].

Siemens *P3* diffractometer software was used for data collection, data reduction and cell refinement. *SHELXS86* (Sheldrick, 1990) was used for the solution of the phase problem and *SHELXL93* (Sheldrick, 1993) was used for the refinement of parameters. *SHELXTL-Plus* (Sheldrick, 1991) was used for molecular graphics and *SHELXL93* for the preparation of the published material.

### Comment

Optically pure 3-furyl alcohols of type (1) are versatile synthetic molecules, with two functional groups which may be manipulated easily to give a wide range of other homochiral products. They find use as intermediates in the synthesis of pharmaceuticals or natural compounds of the sesquiterpenoid class.



There are two known routes to obtain compounds of type (1). One consists of the kinetic resolution of racemic 3-furyl alcohols by Sharpless oxidation (Kusakabe, Kitano, Kobayashi & Sato, 1989) and the other involves the enantioselective aminoalcohol-catalysed addition of alkyl- or arylzinc to 3-furaldehyde (Soai, Kawase & Niwa, 1989; Yoshioka, Kawakita, & Ohno, 1989; Takahashi, Kawakita, Yoshioka, Kobayashi & Ohno, 1989). The absolute configuration of the asymmetric centre was thought to be *S*, judging from the products of the reaction with 2-furaldehyde, obtained in the same manner and giving a known configuration (Joshi, Srebnik & Brown, 1989; Soai & Kawase, 1990; Hayashi, Kaneko & Oguni, 1991; Thompson, Humphrey, DeMarco, Mathre & Grabowski, 1993).

To overcome this uncertainty, we prepared compound (3), a molecule representative of type (1) ( $R = \text{Ph}$ ), by cleavage of the title compound (2) (with  $\text{'BuLi}$ ), for which X-ray structure determination was possible. Compound (2) was obtained as the major diastereoisomer formed by the addition of phenyltriisopropoxytitanium to a solution of the optically pure (*S*)-sulfoxide aldehyde (4), of known absolute configuration (Girodier, Maignan & Rouessac, 1992). The structure determination of (2), after purification by liquid chromatography and recrystallization, revealed the absolute configuration; the

structure is consistent with a transition state under the influence of the interaction between the aryl group of (4) and the bulky titanate. If this is the case, the attack of the nucleophile must occur *trans* to the  $\text{S—Ar}$  bond in order to give rise to the observed major (*S*)-(2) diastereoisomer.

Finally, this work confirms the assignment made by Soai, Kawase & Niwa (1989) and shows that the (*S*)-sulfoxide group could induce optical activity on the aldehydic prochiral C atom, despite the distance between the two sites.

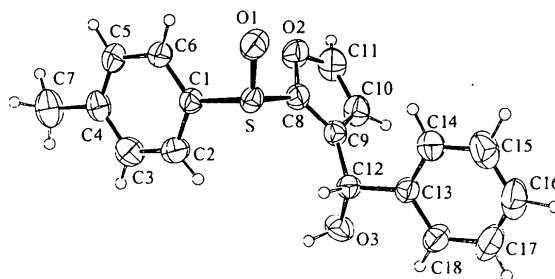


Fig. 1. ORTEP plot of  $\text{C}_{18}\text{H}_{16}\text{O}_3\text{S}$ . The displacement parameters of the H atoms have been divided by ten for the sake of clarity. Displacement ellipsoids are plotted at the 50% probability level.

### Experimental

Recrystallization from ethyl ether gave (2) as colourless needles. Slow evaporation from ethyl ether gave suitable crystals for X-ray analysis. A parallelepipedic crystal was chosen and its quality tested using Laue photographs.

#### Crystal data

$\text{C}_{18}\text{H}_{16}\text{O}_3\text{S}$   
 $M_r = 312.37$   
 Monoclinic  
 $P2_1$   
 $a = 8.2513$  (8) Å  
 $b = 10.5006$  (13) Å  
 $c = 9.3090$  (8) Å  
 $\beta = 102.849$  (11)°  
 $V = 786.37$  (14) Å<sup>3</sup>  
 $Z = 2$   
 $D_x = 1.319$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 $\lambda = 0.71069$  Å  
 Cell parameters from 32 reflections  
 $\theta = 14.1\text{--}15.8^\circ$   
 $\mu = 0.205$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Plate  
 $0.722 \times 0.523 \times 0.323$  mm  
 Colourless

#### Data collection

Stoe Siemens AED-2 diffractometer  
 $\omega$ - $2\theta$  scans  
 Absorption correction: none  
 4806 measured reflections  
 4575 independent reflections  
 3894 observed reflections  
 $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0126$   
 $\theta_{\text{max}} = 29.99^\circ$   
 $h = -11 \rightarrow 11$   
 $k = -14 \rightarrow 14$   
 $l = -13 \rightarrow 13$   
 3 standard reflections  
 frequency: 60 min  
 intensity variation: 4%

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.0329$   
 $wR(F^2) = 0.0912$   
 $S = 1.071$   
 4573 reflections  
 243 parameters  
 $w = 1/[\sigma^2(F_o^2) + (0.0687P)^2 + 0.0067P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = -0.004$   
 $\Delta\rho_{\max} = 0.222 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.168 \text{ e } \text{Å}^{-3}$

Extinction correction:

SHELXL93

(Sheldrick, 1993)

Extinction coefficient:

0.0235 (41)

Atomic scattering factors

from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Absolute configuration:

Flack (1983)

C1—C6—C5	119.1 (2)	C16—C15—C14	120.0 (2)
C9—C8—O2	111.74 (14)	C17—C16—C15	119.2 (2)
C9—C8—S	129.43 (12)	C16—C17—C18	121.1 (2)
O2—C8—S	118.80 (11)	C13—C18—C17	120.0 (2)
C8—C9—C10	104.89 (14)		

The well known absolute configuration of (4) allowed the absolute configuration determination; the method described by Flack (1983) was used to confirm the absolute configuration [ $\chi = 0.00(5)$ ] in the calculations performed on the final structure factors after refinement [SHELXL93 option applied to non-centrosymmetric space groups (Sheldrick, 1993)].

H atoms were first found using Fourier difference peaks after calculations with all S, C and O atoms placed in the structure. They were ultimately refined as rigid groups using the AFIX card of SHELXL93.

Data collection and cell refinement: DIF4 (Stoe & Cie, 1988a). Data reduction: REDU4 (Stoe & Cie, 1988b). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93. Molecular graphics: ORTEP (Johnson, 1965).

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{Å}^2$ )

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \cdot a_i \cdot a_j$$

	x	y	z	$U_{\text{eq}}$
S	0.07295 (4)	0.05817 (3)	0.52006 (3)	0.03954 (9)
O1	0.1839 (2)	0.16781 (14)	0.50422 (14)	0.0564 (3)
O2	-0.1703 (2)	0.22078 (12)	0.55000 (13)	0.0533 (3)
O3	-0.3894 (2)	-0.14417 (12)	0.3441 (2)	0.0528 (3)
C1	0.0931 (2)	0.02814 (13)	0.71234 (15)	0.0384 (3)
C2	0.0284 (2)	-0.0845 (2)	0.7536 (2)	0.0529 (4)
C3	0.0457 (2)	-0.1104 (2)	0.9014 (2)	0.0570 (4)
C4	0.1301 (2)	-0.0273 (2)	1.0094 (2)	0.0485 (3)
C5	0.1946 (2)	0.0838 (2)	0.9652 (2)	0.0518 (4)
C6	0.1772 (2)	0.1124 (2)	0.8168 (2)	0.0483 (3)
C7	0.1544 (3)	-0.0576 (3)	1.1706 (2)	0.0702 (6)
C8	-0.1329 (2)	0.11340 (15)	0.4803 (2)	0.0401 (3)
C9	-0.2698 (2)	0.0628 (2)	0.39027 (13)	0.0381 (2)
C10	-0.4039 (2)	0.1446 (2)	0.4063 (2)	0.0532 (4)
C11	-0.3377 (3)	0.2365 (2)	0.5014 (2)	0.0599 (5)
C12	-0.2790 (2)	-0.05633 (13)	0.2992 (2)	0.0374 (3)
C13	-0.3331 (2)	-0.03146 (14)	0.1344 (2)	0.0388 (3)
C14	-0.2717 (2)	0.0723 (2)	0.0714 (2)	0.0553 (4)
C15	-0.3086 (3)	0.0893 (2)	-0.0808 (2)	0.0704 (6)
C16	-0.4093 (3)	0.0026 (3)	-0.1714 (2)	0.0753 (7)
C17	-0.4729 (3)	-0.0993 (3)	-0.1090 (3)	0.0742 (7)
C18	-0.4350 (2)	-0.1178 (2)	0.0428 (2)	0.0544 (4)

The authors thank Professor M. Leblanc, University of Maine, for helpful discussions.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: PA1114). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 2. Selected geometric parameters ( $\text{Å}$ ,  $^\circ$ )

S—O1	1.4982 (13)	C9—C10	1.435 (2)
S—C8	1.754 (2)	C9—C12	1.504 (2)
S—C1	1.7884 (14)	C10—C11	1.341 (3)
C1—C6	1.382 (2)	C11—O2	1.364 (2)
C1—C2	1.386 (2)	C12—O3	1.423 (2)
C2—C3	1.379 (3)	C12—C13	1.523 (2)
C3—C4	1.395 (3)	C13—C14	1.385 (3)
C4—C5	1.381 (3)	C13—C18	1.391 (2)
C4—C7	1.504 (2)	C14—C15	1.393 (3)
C5—C6	1.390 (2)	C15—C16	1.385 (4)
C8—C9	1.357 (2)	C16—C17	1.376 (4)
C8—O2	1.370 (2)	C17—C18	1.392 (3)
O1—S—C8	108.00 (8)	C8—C9—C12	127.21 (13)
O1—S—C1	108.12 (7)	C10—C9—C12	127.84 (13)
C8—S—C1	98.02 (7)	C11—C10—C9	106.8 (2)
C6—C1—C2	121.02 (14)	C10—C11—O2	111.44 (15)
C6—C1—S	120.78 (12)	C11—O2—C8	105.12 (13)
C2—C1—S	118.14 (11)	O3—C12—C9	109.23 (12)
C3—C2—C1	119.0 (2)	O3—C12—C13	110.12 (11)
C2—C3—C4	121.3 (2)	C9—C12—C13	113.09 (11)
C5—C4—C3	118.53 (15)	C14—C13—C18	118.8 (2)
C5—C4—C7	120.1 (2)	C14—C13—C12	120.56 (13)
C3—C4—C7	121.4 (2)	C18—C13—C12	120.48 (14)
C4—C5—C6	121.1 (2)	C13—C14—C15	120.9 (2)