



α -Phosphoryl Sulfoxides. X. A General Synthesis of Optically Active α -Chlorovinyl Sulfoxides¹.

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Abstract: A general and efficient synthesis of enantiomeric α -chlorovinyl p-tolyl sulfoxides **1** using (+)-(S)_C(S)_S- α -chloro- α -dimethoxyphosphorylmethyl p-tolyl sulfoxide as a key substrate for the Horner-Wittig reaction with carbonyl compounds is described. The *E/Z* ratio of geometrical isomers of **1** was determined and briefly investigated. The X-ray diffraction structures of (*Z*)-1-chloro-1-p-tolylsulfinyl-2-phenyl-ethene and (*Z*)-1-chloro-1-p-tolylsulfinyl-2-(2-thienyl)-ethene are reported. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

α , β -Unsaturated sulfoxides have received a considerable attention as useful chiral reagents in asymmetric synthesis, especially in asymmetric Diels-Alder reactions as chiral dienophiles and in Michael addition reactions as chiral acceptors². However, owing to a low reactivity of simple vinyl sulfoxides, it was necessary to activate the carbon-carbon double bond in vinyl sulfoxides by introduction of an additional electron-withdrawing group at the α - or β - position. Usually, the alkoxycarbonyl³, phosphonate⁴ and sulfonyl⁵ substituents were used to increase the reactivity of vinyl sulfoxides.

α - and β -halovinyl sulfoxides have also found application as Michael acceptors in the reaction with malonates⁶, alkoxide ions⁷, 2-nitropropane⁸ and cuprates⁹. In these cases the addition reaction is followed by dehydrohalogenation or cyclopropanation. Other organometallic reagents, such as alkyllithiums and Grignard reagents, react with α -halovinyl sulfoxides at sulfur affording diaryl or aralkyl sulfoxides and alkynes^{9,10}. The use of optically active (+)-S- α -bromovinyl p-tolyl sulfoxide showed that the reaction with alkylmagnesium halides occurs with inversion of configuration at sulfur and with almost full enantioselectivity¹⁰.

Although optically active halovinyl sulfoxides may advantageously be applied in asymmetric synthesis and stereoselective transformations, there are no general methods of their synthesis which could lead to arbitrarily substituted systems. The synthesis of the above mentioned (+)-(S)- α -bromovinyl p-tolyl sulfoxide¹⁰, obtained by addition of bromine to (+)-(R)-vinyl p-tolyl sulfoxide followed by hydrogen bromide elimination, represents so far the only method of the preparation of this type of chiral, non-racemic sulfoxides.

In the present paper we describe a general and highly efficient synthesis of enantiomeric α -chlorovinyl p-tolyl sulfoxides **1** using (+)-(S)_C(S)_S- α -chloro- α -dimethoxyphosphorylmethyl p-tolyl sulfoxide **2** as a key

substrate for the Horner-Wittig reaction with carbonyl compounds. The latter has recently been prepared in our Laboratory by chlorination of optically active α -dimethoxyphosphorylmethyl *p*-tolyl sulfoxide and the chirality at both stereogenic atoms (carbon and sulfur) in **2** has been determined by X-ray methods¹¹.

RESULTS and DISCUSSION

Metallation of the sulfoxide (+)-**2** was carried out in a tetrahydrofuran solution at -78°C using *n*-butyllithium. A solution of aldehydes in tetrahydrofuran was then added to the lithiated sulfoxide at this low temperature and after raising the temperature of the reaction mixture to 0°C the desired optically active α -chlorovinyl *p*-tolyl sulfoxides **1** were isolated in an usual way. Representative aliphatic and aromatic aldehydes were found to react with (+)-**2** giving in all cases the enantiomerically pure chlorovinyl sulfoxides **1a-f** in good yields^{12a-b}. The results are summarized in Table 1. An inspection of the data in Table 1 reveals that the Horner-Wittig reaction products **1** were usually formed as mixtures of **E** and **Z** geometrical isomers with the ratio mainly dependent on the group R of an aldehyde. The **E/Z** ratio was determined by GC of the crude sulfoxides **1a-f** and in all cases the predominant isomer was that of lower retention time. The crude reaction products were purified by flash chromatography and then the major isomers of **1** were isolated by crystallization or/and chromatography.

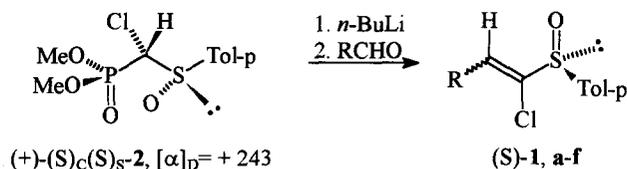


Table 1. Selected Experimental and Spectroscopic Data of 1-Chlorovinyl Sulfoxides **1**.

| 1 | R | Yield ^a % | Z/E ratio | Z-1 [α] _D (acetone) | δ vinyl H (ppm) | |
|---|---|-------------------------|--|--|----------------------------------|----------------------|
| | | | | | Found for Z-1 (E-1) | Calcd for Z-1 E-1 |
| a | Ph | 85 | 1.2:1 ^b | +35 (c, 3.0) ^d | 7.63 ^f | 7.43 7.22 |
| b | <i>p</i> Br-Ph | 92 | 6:1 ^b | +41 (c, 2.1) | 7.56 ^f | 7.45 7.25 |
| c | <i>p</i> NO ₂ -Ph | 78 | 100:0 ^b | +56 (c, 2.4) | 7.71 ^f | 7.55 7.34 |
| d |  | 83 | 1.6:1 ^b | +39 (c, 2.2) ^e | 7.84 (7.30) | - - |
| e | Me | 63 | 2.2:1 ^b 2:1 ^c | +70 (c, 2.5) | 6.83 J=6.8 Hz (6.35 J=7.5 Hz) | 6.50 6.29 |
| f | Am | 72 | 1.6:1 ^c | +47 (c, 1.8) | 6.67 J=7.3 Hz (6.43 J=7.4 Hz) | 6.50 6.29 |

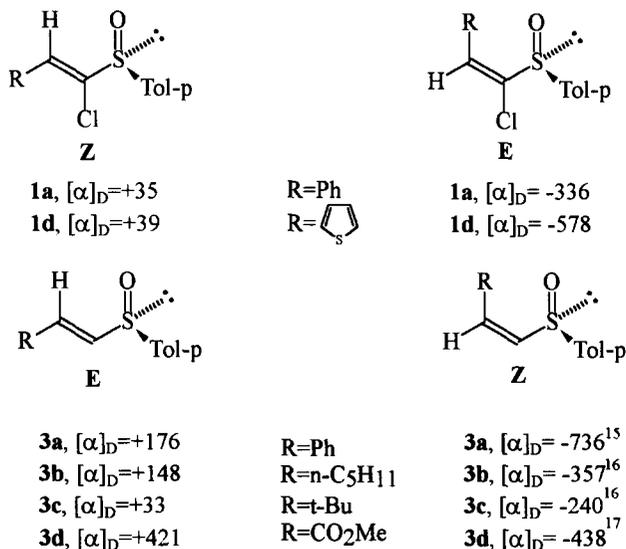
a -chemical yield of both isomers; b -determined by GC; c -determined by ¹H NMR; d -**E-1a**, [α]_D²⁵=336 (c, 2.6); e -the rotation of **E-1d**, [α]_D²⁵=578, was calculated using the value [α]_D²⁵=412 (c, 3.0) for a 27:73 mixture of **Z** and **E** isomers of **1d**; f -vinyl H of the **E** isomer is covered by aromatic protons at $\sim 7.2-7.4$ ppm

In another set of experiments the effect of the Horner-Wittig reaction conditions on the **Z/E** ratio of α -chlorovinyl *p*-tolyl sulfoxide **1a** was briefly investigated. The results obtained (see Table 2) indicate that the nature of a base used for the α -phosphonate carbanion generation has an important influence on the stereochemical outcome of the reaction. Interestingly, the use of LDA results in the formation of **E-1a** as a major isomer in contrast to the reaction with *n*-BuLi leading to the major product with the **Z**-geometry. Similarly, when NaH is used, the prevailing isomer of **1a** formed has the **E**-geometry. However, in this case a mixture of both isomers of **1a** is formed in moderate yield.

Table 2. Results of the Horner-Wittig Reaction of **2** with Benzaldehyde under Different Conditions.

| Entry | Base | Temp. | Yield % | Z/E ratio |
|-------|---|--------------|---------|------------------|
| 1 | <i>n</i> -BuLi | -78° to 0° | 85 | 1.2:1 |
| 2 | NaH | r.t | 39.5 | 1:2.6 |
| 3 | 50% KOH/CH ₂ Cl ₂ | r.t | 75 | 2.1:1 |
| 4 | <i>i</i> -Pr ₂ NLi | -78° to -20° | 76 | 1:2 |

The observed stereochemistry of the reaction under discussion can be rationalized on the basis of the previously proposed mechanism for the Horner-Wittig reaction of α -phosphoryl sulfoxides with carbonyl compounds¹³.



Assignment of the **Z**-configuration to the isolated major isomers of the sulfoxides **1** listed in Table 1 was based in the first instance on the additive increments method¹⁴. The observed and calculated β -vinyl proton resonance positions of **Z-1** and **E-1** corresponding to the proposed configurations are shown in Table 1. Although in some cases there are substantial differences between the calculated and observed δ_H -values, the relative positions of the chemical shift for the β -vinyl proton in **Z-1** and **E-1** were predicted correctly.

Additional arguments in support of the above configurational assignments came from the comparison of the specific rotation values of **Z** and **E** isomers of **1a** and **1d** with those of **E**- and **Z**- β -substituted vinyl sulfoxides **3a-d** having the same **S**-configuration at sulfur and the same relationship between the sulfinyl oxygen and β -vinyl proton. It is noteworthy that all the **Z**-isomers of **1a-f** and the **E**-isomers of **3a-d** are dextrorotatory whereas the **E**-isomers of **1a** and **1d** as well as **Z-3a-d** have a very high negative rotation. If examination of a greater number of examples shows this to be a general rule the sign of optical rotation might allow a rapid assignment of configuration to geometrical isomers of enantiomeric vinyl sulfoxides.

In order to establish unequivocally the **E**, **Z**-geometry and the absolute configuration at the stereogenic sulfur atom in enantiomeric sulfoxides **1** obtained in this work, the crystal and molecular structures of the sulfoxides (+)-**1b**, $[\alpha]_D^{25} = +41$ and (+)-**1d**, $[\alpha]_D^{25} = +39$ were determined by X-ray diffractometric technique. Their molecular structures with the atom numbering system are shown in Fig. 1 and Fig. 2, respectively.

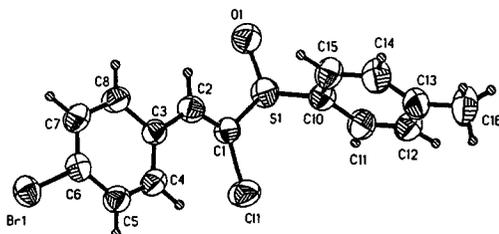


Fig. 1. Thermal ellipsoidal view of the molecule **1b** with atom numbering scheme. Ellipsoids are shown with 50% probability.

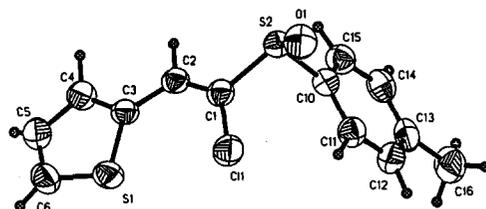


Fig. 2. Thermal ellipsoidal view of the molecule **1d** with atom numbering scheme.

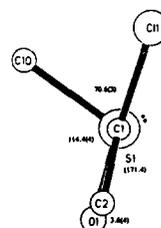


Fig. 3. The Newman projection perpendicular to the C1-S1 bond.

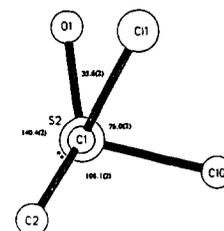


Fig. 4. The Newman projection perpendicular to the C1-S2 bond.

As it is seen, both sulfoxides have the **Z**-geometry around the carbon-carbon double bond and, as expected, the **S**-configuration at sulfur. Fig. 1 shows also that in the solid state conformation of (+)-**1b** there are two short intramolecular contacts. The first is between the sulfinyl oxygen atom O1 and the β -vinyl hydrogen at C2 of 2.41 Å and the second one between the chlorine atom Cl1 and the aromatic hydrogen at C4 of 2.54 Å. An inspection of Fig. 2 reveals that in the case of (+)-**1d** the shortest intramolecular contact is that between Cl1 and the aromatic hydrogen at C11 of 2.77 Å.

In spite of the fact that both sulfoxides are the **Z**-isomers, their solid state conformations are entirely different. The Newman projection around the C1-S1 bond for the sulfoxide (+)-**1b** (Fig. 3) shows that the free electron pair at sulfur is located synclinally with respect to the chlorine atom Cl1. However, in the sulfoxide (+)-**1d** these two

substituents are antiperiplanar as shown in Fig. 4. Most probably these differences are caused by different packing mode. The crystal packing of (+)-**1b** in the unit cell is presented in Fig. 5 which shows that the molecules of this sulfoxide are symmetrically disposed ("head to head" like arrangement) and held together by intermolecular hydrogen bond between the hydrogen at C12 and the sulfinyl oxygen atom O1 of 2.46 Å. The different packing of the molecules of (+)-**1d** in the crystal is depicted in Fig. 6. It clearly reveals that the molecules of (+)-**1d** adopt the unsymmetrical "head to tail" like arrangements and form intermolecular hydrogen bond between the sulfinyl oxygen atom O1 and the thiophene hydrogen at C6 of 2.54 Å.

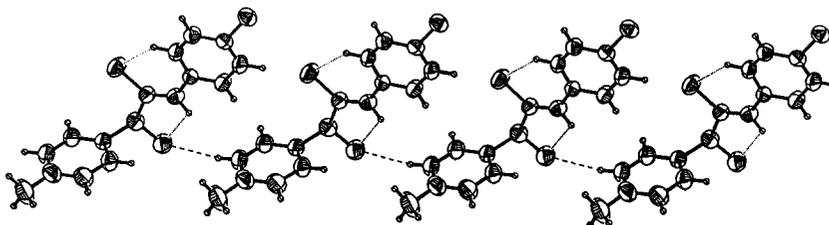


Fig. 5. The crystal packing of (+)-**1b** in the unit cell.

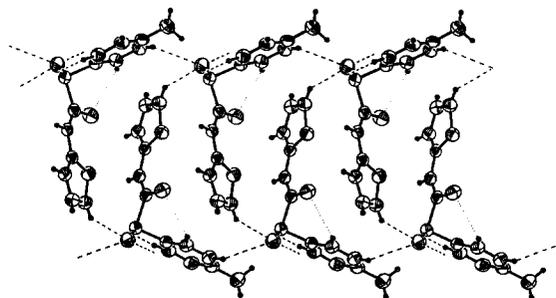


Fig. 6. The crystal packing of (+)-**1d** in the unit cell.

EXPERIMENTAL

NMR spectra were recorded on Bruker MSL 300 and Bruker AC 200 spectrometers in CDCl_3 solution. The microanalyses were performed on Elemental Analyzer EA 1108. Gas chromatography was done on a Hewlett Packard 5890 instrument. Column chromatography was performed using Merck 60 (70-230 mesh) silica gel. The optical rotations were measured on a Perkin-Elmer 241H polarimeter. THF was freshly distilled over potassium/benzophenone.

Synthesis of Optically Active α -Chlorovinyl Sulfoxides-General Procedure.

To a magnetically stirred solution of 2 mmol of (+)- $(S)_C(S)_S$ - α -chloro- α -dimethoxyphosphorylmethyl *p*-tolyl sulfoxide **2** in dry THF (20 ml) at -78° 2.1 mmol *n*-BuLi in hexane was added. After 5 min. of stirring, aldehyde in THF solution was added dropwise. The reaction mixture was allowed to rise 0°C and quenched with aq. NH_4Cl . Extractive work-up afforded crude vinyl sulfoxides as a mixture of *E/Z* isomers determined by GC. The crude products were purified by flash chromatography (CH_2Cl_2 /hexane).

(*Z*)-1-Chloro-1-*p*-tolylsulfinyl-2-phenyl-ethene **1a**

Mp. $86\text{--}87^\circ\text{C}$; δ_{H} : 2.42 (s, 3H, CH_3Ar); 7.33 and 7.64 (A_2B_2 , 4H, CH_3Ar); 7.40 (m, 3H, Ar); 7.63 (s, 1H, vinyl); 7.75

(m, 2H, Ar); δ_c : 21.4 ($\underline{\text{CH}_3\text{Ar}}$); 125.8; 128.6; 128.7; 129.4; 129.7; 129.8; 132.1; 135.3; 138.4; 142.6. Anal. Calcd. for: $\text{C}_{13}\text{H}_{13}\text{ClOS}$: C, 65.09; H, 5.78; S, 11.58 Found: C, 94.88; H, 5.92; S, 11.67.

(E)-1-Chloro-1-p-tolylsulfinyl-2-phenyl-ethene 1a

Mp. 95-96°C; δ_H : 2.42 (s, 3H, $\underline{\text{CH}_3\text{Ar}}$); 7.29-7.62 (m, 10H, vinyl + Ar)

(Z)-1-Chloro-1-p-tolylsulfinyl-2-p-bromophenyl-ethene 1b

Mp. 169-171°C; δ_H : 2.42 (s, 3H, $\underline{\text{CH}_3\text{Ar}}$); 7.33 and 7.63 (A_2B_2 , 4H, $\underline{\text{CH}_3\text{Ar}}$); 7.53 and 7.62 (A_2B_2 , 4H, Br-Ar); 7.56 (1H, vinyl); δ_c : 21.5 ($\underline{\text{CH}_3\text{Ar}}$); 124.6; 125.9; 127.2; 130.0; 131.0; 131.1; 131.9; 132.1; 137.0; 142.9. Anal. Calcd. for: $\text{C}_{15}\text{H}_{12}\text{BrClSO}$: C, 50.65; H, 3.40; S, 9.01 Found: C, 50.75; H, 3.33; S, 9.08.

(Z)-1-Chloro-1-p-tolylsulfinyl-2-p-nitrophenyl-ethene 1c

Mp. 168-169°C; δ_H : 2.43 (s, 3H, $\underline{\text{CH}_3\text{Ar}}$); 7.35 and 7.66 (A_2B_2 , 4H, $\underline{\text{CH}_3\text{Ar}}$); 7.71 (s, 1H vinyl); 7.88 and 8.25 (A_2B_2 , 4h, $\text{NO}_2\text{-Ar}$); δ_c : 21.5 ($\underline{\text{CH}_3\text{Ar}}$); 123.8; 125.3; 126.0; 130.2; 130.3; 137.9; 138.7; 138.3; 140.1; 143.3. Anal. Calcd. for: $\text{C}_{15}\text{H}_{12}\text{ClNO}_3\text{S}$: C, 55.99; H, 3.76; S, 9.96 Found: C, 56.06; H, 3.95; S, 10.11

(Z)-1-chloro-1-p-tolylsulfinyl-2-(2-thienyl)-ethene 1d

Mp. 131-132°C; δ_H : 2.41 (s, 3H, $\underline{\text{CH}_3\text{Ar}}$); 7.12 (dd 1H, $J=3.7$; 5.0 Hz); 7.33 and 7.61 (A_2B_2 4H $\underline{\text{CH}_3\text{Ar}}$); 7.44-7.52 (m, 2H); 7.84 (1H, vinyl); δ_c : 21.5 ($\underline{\text{CH}_3\text{Ar}}$); 123.5; 125.7; 127.0; 129.6; 130.0; 132.4; 135.2; 138.4; 142.4. Anal. Calcd. for: $\text{C}_{13}\text{H}_{11}\text{ClOS}_2$: C, 55.21; H, 3.92; S, 22.67 Found: C, 54.95; H, 4.01

(E)-1-Chloro-1-p-tolylsulfinyl-2-(2-thienyl)-ethene 1d

δ_H : 2.41 (s, 3H, $\underline{\text{CH}_3\text{Ar}}$); 7.08 (dd, 1H, $J=3.7$, 5.2Hz); 7.27 (m, 1H); 7.30 (s, 1H vinyl); 7.32 and 7.60 (A_2B_2 , 4H $\underline{\text{ArCH}_3}$); 7.48 (m, 1H)

(Z)-1-Chloro-1-p-tolylsulfinyl-propene 1e

Liquid; δ_H : 1.94 (d, 3H, $\underline{\text{CH}_3}$, $J=6.8$ Hz); 2.41 (s, 3H, $\underline{\text{CH}_3\text{Ar}}$); 6.83 (q, 1H, $\underline{\text{CH}}=$, $J=6.8$ Hz); 7.31 and 7.55 (A_2B_2 , 4H, $\underline{\text{CH}_3\text{Ar}}$); δ_c : 14.0 ($\underline{\text{CH}_3}$); 21.4 ($\underline{\text{CH}_3\text{Ar}}$); 125.4; 129.7; 129.8; 134.8; 138.0; 142.3. Anal. Calcd. for: $\text{C}_{10}\text{H}_{11}\text{ClOS}$: C, 55.94; H, 5.16; S, 14.93; Found: C, 56.38; H, 5.33; S, 14.64

(E)-1-Chloro-1-p-tolylsulfinyl-propene 1e

Liquid; δ_H : 2.21 (d, 3H, $\underline{\text{CH}_3}$, $J=7.5$ Hz); 2.41 (s, 3H, $\underline{\text{CH}_3\text{Ar}}$); 6.35 (q, 1H, vinyl, $J=7.5$); 7.31 and 7.54 (A_2B_2 , 4H, $\underline{\text{CH}_3\text{Ar}}$)

(Z)-1-Chloro-1-p-tolylsulfinyl-heptene 1f

Liquid; δ_H : 0.87 (m, 3H); 1.24-1.38 (m, 4H); 1.48 (m, 2H); 2.32 (dt, 2H, $J=7.2$, 7.4 Hz); 2.39 (s, 3H, $\underline{\text{CH}_3\text{Ar}}$); 6.77 (t, 1H, $J=7.4$ vinyl); 7.30 and 7.54 (A_2B_2 , 4H, $\underline{\text{CH}_3\text{Ar}}$); δ_c : 13.9; 21.4 $\underline{\text{CH}_3\text{Ar}}$; 22.3; 27.5; 28.3; 31.2; 125.4; 129.8; 134.6; 136.8; 140.3; 142.2. Anal. Calcd. for: $\text{C}_{14}\text{H}_{19}\text{ClOS}$: C, 62.09; H, 7.07; S, 11.84 Found: C, 62.37; H, 6.90.

Crystal Structure Determination of Z-1-p-Tolylsulfinyl-2-p-bromophenyl-ethene 1b.

Crystal and molecular structure of **1b** was determined using data collected at room temperature on a CAD4 diffractometer with graphite monochromatized $\text{CuK}\alpha$ radiation¹⁸. Compound crystallizes in monoclinic system, in space group P2_1 . Lattice constants were refined by least-squares fit of 25 reflections in θ range 12.6-25.7°. The decline in intensities of three standard reflections (-1, -2,5; 1-2,5; -2, -1, -2) was 0.3% during the 34.6 hours. An empirical absorption correction was applied using the ψ -scan method^{19,20}. A total of 1668 observed reflections [with $I \geq 3\sigma(I)$], were used to solve the structure by direct methods and to refine it by full matrix least-squares using F^2 ^{21,22}. Hydrogen atoms were found in a difference Fourier map (except phenyl ring hydrogen atoms) and set as riding. Thermal isotropic parameters of hydrogen atoms were refined. Anisotropic thermal parameters were refined for all nonhydrogen atoms.

The final refinement converged to $R=0.0496$ and $R_w=0.0496$ (see Table 3). The absolute structure of **1b** was determined by three methods: the Rogers η -test^{21,24}, the Hamilton test^{24,25}, and calculation of the Flack parameter x ^{26,27}. The results (Rogers' method: $\eta=1.5(2)$, $\eta_{inv}=-1.3(2)$; Hamilton test: $R_{ratio}=1.0170$, $N=1483$, then probability of opposite (inv) configuration $\alpha \ll 10^{-6}$; Flack x parameter: $x=0.02(4)$) unequivocally confirm the configuration shown in Figure 1. Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre²³.

Table 3. Crystal Data and Experimental Details for (+)-**1b** and (+)-**1d**.

| Molecular formula | $C_{15}H_{12}O_1S_1Br_1Cl_1$ -(+)- 1b | $C_{13}H_{11}O_1S_2Cl_1$ -(+)- 1d |
|---|--|--|
| F(000) | 356 | 584 |
| M_r | 355.67 | 282.8 |
| Crystallographic system | monoclinic | orthorhombic |
| Space group | $P2_1$ | $P2_12_12_1$ |
| a (Å) | 7.986(2) | 5.9337(9) |
| b (Å) | 5.067(2) | 7.400(2) |
| c (Å) | 18.149(9) | 29.258(6) |
| β (°) | 94.09(3) | - |
| V (Å ³) | 732.5(3) | 1284.6(6) |
| Z | 2 | 4 |
| D_c (g/cm ³) | 1.613(2) | 1.462(2) |
| μ (cm ⁻¹) | 68.0 | 55.0 |
| Crystal dimensions (mm) | 0.30, 0.35, 0.50 | 0.30, 0.30, 0.55 |
| Radiation, λ (Å) | CuK α , 1.54184 | CuK α , 1.54184 |
| Diffractometer | Enraf-Nonius CAD4 | Enraf-Nonius CAD4 |
| Scan mode | $\omega/2\theta$ | $\omega/2\theta$ |
| Scan width (°) | $0.88+0.14\tan\theta$ | $0.70+0.14\tan\theta$ |
| Absorption correction min, max, av | 0.8077, 0.9981, 0.9169 | 0.7155, 0.9999, 0.9035 |
| Transmission min, max, av (%) | 65.24, 99.62, 84.07 | 51.19, 99.99, 81.63 |
| Measured reflections | 3349 | 3074 |
| Independent reflections | 1682 | 2637 |
| Observed reflections [$I \geq 3\sigma(I)$] | 1668 | 2604 |
| R_{int} | 0.235 | 0.024 |
| Maximum 2θ (°) | 150 | 150 |
| Ranges h, k, l | -10 to 10, -6 to 0, -22 to 22 | -7 to 0, 0 to 9, -36 to 36 |
| Parameters refined | 185 | 191 |
| Weighting scheme | $w=[\sigma^2(F)+0.009614F^2]^{-1}$ | $w=[\sigma^2(F)+0.004206F^2]^{-1}$ |
| $(\Delta/\sigma)_{max}$ | 0.003 | 0.001 |
| Residual density max, min (eÅ ⁻³) | 0.904, -1.025 | 0.625, -0.691 |
| S | 0.6692 | 0.8654 |
| R_w | 0.0496 | 0.0438 |
| R | 0.0496 | 0.0364 |

Crystal Structure Determination of Z-1-Chloro-1-p-tolylsulfinyl-2-(2-thienyl)-ethene **1d**.

Crystal and molecular structure of **1d** was determined using data collected at room temperature on a CAD4 diffractometer with graphite monochromatized CuK α radiation¹⁸. Compound crystallizes in orthorhombic system, in space group $P2_12_12_1$. Lattice constants were refined by least-squares fit of 25 reflections in θ range 20.5–27.7°. The decline in intensities of three standard reflections (-1, 4, 2; -2, 3, -2; -3, 2, -4) was 0.7% during 37.7 hours. An empirical absorption correction was applied using the ψ -scan method^{19,20}. A total of 2604 observed reflections [with $I \geq 3\sigma(I)$], were used to solve the structure by direct methods and to refine it by full matrix least-squares using F^2 's^{21,22}. Hydrogen atoms

were found in a difference Fourier map (except hydrogen atoms in methyl C16 which were set geometrically and refined as riding) and refined isotropically. Anisotropic thermal parameters were refined for all nonhydrogen atoms. The final refinement converged to $R=0.0364$ and $R_w=0.0438$ (see Table 3). The absolute configuration of **1d** was determined by three methods: the Rogers η -test^{21,24}, the Hamilton test^{24,25}, and calculation of the Flack parameter x ^{26,27}. The results (Rogers' method: $\eta=0.97(3)$, $\eta_{inv} = -0.96(3)$; Hamilton test: $R_{ratio}=1.3118$, $N=2413$, then probability of opposite (inv) configuration $\alpha \ll 10^{-6}$; Flack x parameter: $x=0.01(2)$) unequivocally confirm the configuration shown in Figure 2. Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre²³.

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b) After publication of our paper¹¹ on the α -chlorination of α -phosphoryl sulfoxides, the Horner-Wittig synthesis of racemic chlorovinyl sulfoxides was reported by Van der Gen *et al*; Otten, P.A.; Davies, H.M.; Van der Gen, A.; *Tetrahedron Lett.*, **1995**, *36*, 781.
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