Available online at www.sciencedirect.com
SCIENCE DIRECT®
Tetrahedron: Asymmetry
Tetrahedron: *Asymmetry* 16 (2005) 651–655

Asymmetric synthesis of α-sulfinylphosphonates in the thiolane series

Piotr Kielbasinski,[a,*] Piotr Lyzwa,[a] Marian Mikolajczyk,[a] Mihaela Gulea,[b,*] Margareth Lemarié[b] and Serge Masson[b]

[a]*Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland*
[b]*Laboratory of Molecular and Thio-Organic Chemistry (UMR CNRS 6507), ENSICAEN—University of Caen, 6, Bd Maréchal Juin, 14050 Caen, France*

Received 12 October 2004; accepted 10 November 2004
Available online 8 January 2005

Abstract—A series of enantiomerically enriched 2-phosphonothiolane sulfoxides were obtained by diastereoselective S-oxidation combined with kinetic resolution using a chiral oxaziridine. Enantioselective oxidation of the corresponding 2-phosphono-2,3-dihydrothiolanes with the same oxidizing agent led to the corresponding sulfoxides with ee up to 98%.

1. Introduction

Non-racemic α,β-unsaturated sulfoxides are known to be interesting synthetic intermediates as asymmetric Michael acceptors or dienophiles.[1,2] They can be obtained, among others, via a Horner–Wadsworth–Emmons olefination using α-sulfinylphosphonates.[3] In particular, syntheses and synthetic applications of enantiopure α-sulfinylphosphonates **A**[4] and α-sulfinylvinylphosphonates **B**[5] have been published. On the contrary, non-racemic cyclic α-sulfinylphosphonates (**C**, **D**) have been less studied[6] (Fig. 1).

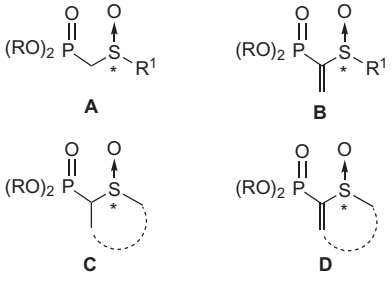
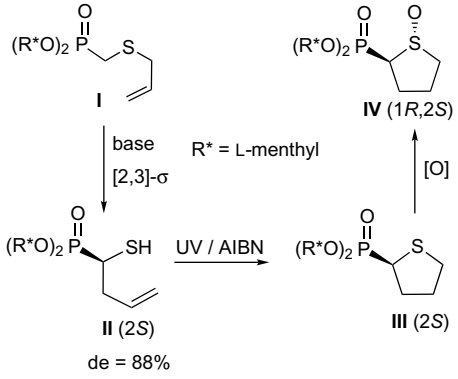


Figure 1.

In a preceding paper,[7] some of us have described an asymmetric synthesis of 2-dimenthylphosphonothiolane S-oxide **IV** in three steps: a diastereoselective [2,3]-sigmatropic rearrangement of the carbanion of O,O′-dimenthyl allylsulfenylmethanephosphonate **I**, a radical cyclization of the intermediate (2-mercapto)but-3-enylphosphonate **II** and then a stereoselective *trans*-S-oxidation of **III** (Scheme 1).

Moreover, in another previous paper,[8] we have described a new convenient method of preparation of racemic 2-dialkylphosphonothiolane S-oxides *rac*-**2**, with different R groups, which consists of a

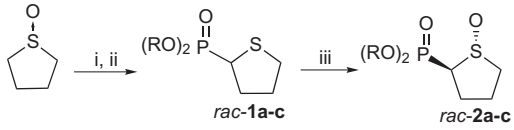


Scheme 1.

* Corresponding authors. E-mail addresses: piokiel@bilbo.cbmm.lodz.pl; mihaela.gulea@ensicaen.fr

0957-4166/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetasy.2004.11.019

Pummerer-phosphorylation of 1-oxothiolane with trialkylphosphites, followed by a *trans*-oxidation of phosphonothiolanes *rac*-**1** (Scheme 2).

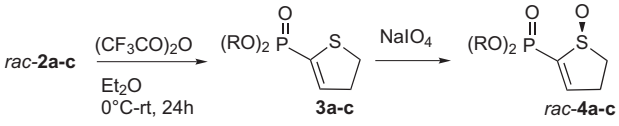


i: $(CF_3CO)_2O$; ii: $(RO)_3P$; iii: $NaIO_4$

a: R = Et, b: R = iPr, c: $(RO)_2 = Me_2C(CH_2O)_2$

Scheme 2.

Due to the potential applicability of the non-racemic cyclic α-sulfinylphosphonate **IV** as a chiral HWE reagent, it would be desirable to develop a more general method of their preparation. This encouraged us to investigate another asymmetric approach, that is, a direct asymmetric S-oxidation of racemic sulfides **1** (*rac*-**1**), using chiral oxidizing agents. Moreover, starting from **2**, we could also easily obtain[8] the racemic unsaturated cyclic sulfoxides *rac*-**4** in two steps: treatment of *rac*-**2** with trifluoroacetic anhydride (conditions of the Pummerer reaction) leading to the formation of the 2-phosphonodidehydrothiolanes **3** (via a β-elimination at the thionium ion step)[9] and S-oxidation with $NaIO_4$ (Scheme 3). Prepared in enantiomerically pure form, the α,β-unsaturated sulfoxides **4** could be interesting chiral Michael acceptors.



Scheme 3.

This paper describes our results concerning a stereoselective S-oxidation of the phosphonothiolanes *rac*-**1** under kinetic resolution conditions and also an enantioselective oxidation of their unsaturated derivatives 2-phosphono-2,3-didehydrothiolanes **3**, both using as a chiral oxidizing agent (+)-(2*S*,8a*R*)-8,8-dichloro-camphorsulfonyloxaziridine, developed by Davis et al.[10]

2. Results and discussion

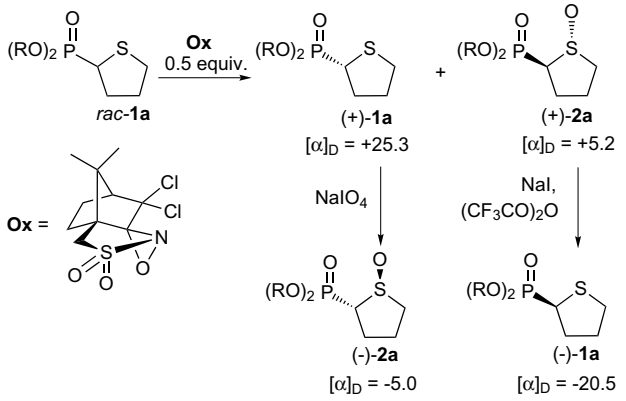
The starting 2-phosphonothiolanes *rac*-**1a**–**c** were prepared from 1-oxothiolane according to the Pummerer-phosphorylation reaction[8] mentioned above (Scheme 2). The only conceivable way to get enantioenriched sulfoxides from the racemic chiral thiolanes **1** is a kinetic resolution based on a preferential oxidation of one of the two enantiomers, together with the exclusive formation of the *trans*-sulfoxide. To our knowledge, kinetic resolution of sulfides by incomplete enantioselective oxidation into sulfoxides has been reported only in a few cases. However, two diastereomeric sulfoxides have been obtained when the starting sulfide already contained a stereogenic center[11] (kinetic resolution strategies using non-enzymatic procedures have been recently reviewed[12]). To this end, compound **1a** was treated with half an equivalent of oxaziridine (noted here **Ox**) in carbon tetrachloride at room temperature. The reaction led to the enantiomerically enriched product (+)-**2a** and unreacted sulfide (+)-**1a**, both with enantiomeric excesses of about 43% (Table 1, Scheme 4).

Table 1. Asymmetric oxidation of phosphonothiolanes **1**

Racemic sulfide **1**	Recovered sulfide (+)-**1**			Sulfoxide (+)-**2**		
	Yield (%)	$[\alpha]_D$[a]	Ee (%)	Yield (%)	$[\alpha]_D$[a]	Ee (%)
1a	49	+25.3	43[b,c]	46	+5.2	44[b]
1b	40	+4.9	75[b]	45	+6.9	nd[d]
1c	35	+18.8	25[b]	48	+8.0	24[c]

[a] See experimental part for the measurements conditions.
[b] Determined by HPLC.
[c] Determined by NMR.
[d] Not determined, but by extrapolation, ee should be close to (+)-**1b**.

To correlate the ee values of both compounds, the recovered enantioenriched sulfide (+)-**1a** was oxidized with $NaIO_4$ to the corresponding sulfoxide (-)-**2a** of a nearly the same $[\alpha]_D$ (but with an opposite sign) as the sulfoxide (+)-**2a** obtained by oxidative kinetic resolution (Scheme 4). Similarly, nearly the same specific rotation with an opposite sign was also observed for the unreacted sulfide **1a** and the sulfide obtained by deoxygenation of the enantioenriched sulfoxide (+)-**2a** with the system $NaI/(CF_3CO)_2O$ (Scheme 4).[13] Although the enantiomeric excesses are moderate, it is noteworthy that such a transformation which combines a kinetic resolution and a simultaneous full diastereoselectivity is not common.

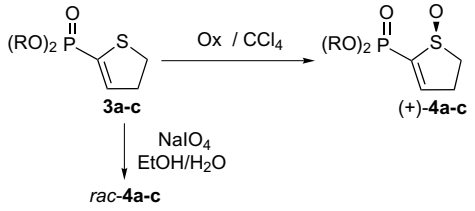


Scheme 4. Absolute configurations are arbitrarily drawn.

The same conditions for the kinetic resolution were then applied to the compounds *rac*-**1b**,**c**. Yields and enantiomeric excesses of the unreacted sulfides and sulfoxides obtained from the three racemic substrates *rac*-**1a**–**c** are listed in Table 1. Half an equivalent of chiral oxidant **Ox** was used in order to stop the conversion at about 50% which was confirmed by ^{31}P NMR of the crude

mixture of **2** and unreacted **1**. Since in all cases, no trace of the corresponding sulfone resulting from dioxidation of sulfide **1**, has been detected in the crude mixture (^{31}P NMR and TLC), no kinetic resolution occurring by a possible sulfoxide to sulfone oxidation has been considered.[14]

In the second part of our study, we examined the S-oxidation of the 2-phosphono-2,3-dehydrothiolanes **3a–c** with the same oxaziridine **Ox** (Scheme 5). The racemic sulfoxides samples of *rac*-**4a–c** were prepared by oxidation of the corresponding **3a–c** with sodium periodate. Yields, specific rotation values and enantiomeric excesses of non-racemic unsaturated sulfoxides **4a–c** are listed in Table 2. It should be pointed out that in contrast to the oxidation of racemic **1a–c** excellent enantiomeric excesses up to 98%, were observed in these cases.



Scheme 5.

We succeeded in the isolation of a single crystal of sulfoxide (+)-**4c** and determined its structure by X-ray diffraction analysis (Fig. 2). We thus were able to assign the (*S*)-configuration at the sulfur atom for (+)-**4c**.

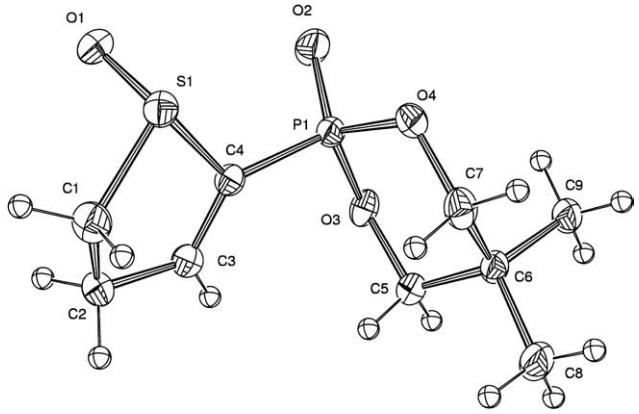


Figure 2. X-ray structure of sulfoxide (+)-**4c**.

In conclusion, a series of enantiomerically enriched 2-phosphonothiolane sulfoxides were obtained by diastereoselective S-oxidation combined with kinetic resolution using a chiral oxaziridine. Enantioselective oxidation of the corresponding 2-phosphono-2,3-didehydrothiolanes with the same oxidizing agent led to the corresponding sulfoxides with ee up to 98%. Investigations related to the use of the latter as Michael acceptors are in progress in our laboratories.

Table 2. Asymmetric oxidation of phosphono(didehydrothiolanes) **3**

Sulfide **3**	Sulfoxide (+)-**4**			
	Product	Yield (%)	$[\alpha]_D$[a]	Ee (%)
3a	**4a**	70	+ 76.7	90[b]
3b	**4b**	78	+ 64.8	83[b]
3c	**4c**	76	+ 60.5	>98[b]

[a] See experimental part for the measurements conditions.
[b] Determined by NMR.

3. Experimental

3.1. General remarks

Most of reactions were carried out under nitrogen with magnetic stirring, unless otherwise specified and monitored by TLC using silica plates. Synthesized products were purified by column chromatography on silica gel or crystallized if necessary. Solvents were dried by distillation prior to use. The NMR spectra were recorded in $CDCl_3$, with a 'Bruker DPX 250', 'Bruker AV 200' or a 'Bruker DRX 400' spectrometer. The chemical shifts (δ) are expressed in ppm relative to TMS for ^{1}H, ^{13}C nuclei, the coupling constants (J) are given in Hz; conventional abbreviations are used. Optical rotation values were measured on a Perkin-Elmer-241 photopolarimeter for the sodium D line at 20 °C. The infrared spectra were recorded with a spectrometer ATI Mattson Infinity 60 AR FTIR on the liquid film, ν (cm^{-1}) are given. Mass spectra were recorded with a Finnigan MAT 95 Voyager Elite spectrometer in chemical ionization. Enantiomeric excesses of non-racemic compounds were determined by NMR spectroscopy using (*R*)-(+)-*t*-butyl(phenyl)phosphinothioic acid[15] as a chiral solvating agent or have been measured by chiral HPLC.

3.2. Synthesis of 2-phosphono-2,3-didehydrothiolanes 3. General procedure

The 2-phosphonothiolane S-oxide **2** (2 mmol) was dissolved in dry ether (10 mL) under nitrogen and cooled to 0 °C. To this solution, trifluoroacetic anhydride (0.57 mL, 4 mmol) was added dropwise with stirring. The cooling bath was removed and the resulting solution was stirred overnight at room temperature. The solution was then poured to a 10% solution of $NaHCO_3$ (ca. 15 mL) and the resulted mixture was stirred for 15 min. The layers were separated and the aqueous layer was extracted with ethyl ether. The combined organic solutions were dried over $MgSO_4$ and evaporated. The crude product was purified by column chromatography using CH_2Cl_2/MeOH in gradient as eluent, or used directly in the oxidation reactions.

3.2.1. 2-Diethoxyphosphono-2,3-didehydrothiolane 3a. Yellow oil, yield = 89%. ^{31}P NMR (161.98 MHz, $CDCl_3$) δ = 12.6 ^{1}H NMR (250 MHz, $CDCl_3$) δ = 1.36 and 1.35 (2t, J = 7.1, 6H, 2 × CH_3), 2.94 (m, 2H, CH_2), 3.37 (t, J = 8.8, 2H, CH_2), 4.07 (m, 4H, 2 × OCH_2), 6.47 (dt, J = 14.8, 3.3, 1H, C=CH). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ = 15.9 (d, J = 6.5, 2 × CH_3), 31.4 (d, J = 6.7, CH_2), 36.2 (d, J = 19.6,

*C*H$_2$), 63.4 (d, J = 5.6, 2 × O*C*H$_2$), 129.4 (d, J = 200.1, P*C*), 139.9 (d, J = 12.9, PC=*C*H). HRMS (MH$^+$) Calcd for $C_8H_{16}PSO_3$: 223.0557 Found: 223.0552.

3.2.2. 2-Diisopropoxyphosphono-2,3-didehydrothiolane 3b. Yellow oil, yield = 95%. ^{31}P NMR (161.98 MHz, $CDCl_3$) δ = 12.4 ^{1}H NMR (250 MHz, $CDCl_3$) δ = 1.33 and 1.36 (2d, J = 6.3, 12H, 4 × C*H*$_3$), 2.90 (m, 2H, C*H*$_2$), 3.34 (t, J = 8.7, 2H, C*H*$_2$), 4.70 (m, 2H, 2 × OC*H*), 6.45 (dt, J = 11.9, 3.1, 1H, C=C*H*). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ = 23.5 (d, J = 5.0, 2 × *C*H$_3$), 23.7 (d, J = 4.0, 2 × *C*H$_3$), 31.4 (d, J = 6.7, *C*H$_2$), 37.2 (d, J = 19.7, *C*H$_2$), 72.9 (d, J = 5.8, 2 × O*C*H), 130.6 (d, J = 202.0, P*C*), 139.6 (d, J = 13.1, PC=*C*H).

3.2.3. 2-[2′-(5,5-Dimethyl-1,3,2-dioxaphosphorinano]-2,3-didehydrothiolane 3c. Yellow solid, mp = 102 °C, yield = 96%. ^{31}P NMR (161.98 MHz, $CDCl_3$) δ = 7.2 ^{1}H NMR (250 MHz, $CDCl_3$) δ = 1.12 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 2.96 (m, 2H, C*H*$_2$), 3.40 (t, J = 8.8, 2H, C*H*$_2$), 4.17 (m, 4H, 2 × OC*H*$_2$), 6.56 (dt, J = 11.8, 2.9, 1H, C=C*H*). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ = 21.5 (s, *C*H$_3$), 21.8 (s, *C*H$_3$), 32.7 (d, J = 6.3, *C*CH$_3$), 34.4 (d, J = 6.7, *C*H$_2$), 37.3 (d, J = 19.4.7, *C*H$_2$), 76.5 (d, J = 4.5, 2 × O*C*H$_2$), 129.7 (d, J = 196.2, P*C*), 139.8 (d, J = 12.7, PC=*C*H). IR (KBr): 2967, 2937, 2876, 1582, 1257, 1032, 988, 793, 631 cm^{-1}. HRMS (MH$^+$) Calcd for $C_9H_{16}PSO_3$: 235.0557 Found: 235.0552.

3.3. Oxidation of 2-phosphonothiolanes 1 under kinetic resolution. General procedure

The 2-phosphonothiolane **1** (1 mmol) was dissolved in dry carbon tetrachloride (20 mL) and the oxaziridine (149 mg, 0.5 mmol) was added in small portions with stirring, at room temperature. The resulting mixture was stirred overnight. The solvent was evaporated and the residue was separated by column chromatography using CH_2Cl_2/MeOH in gradient as eluent, affording unreacted 2-phosphonothiolane **1** (as the first fraction) and 2-phosphonothiolane S-oxide **2** (as the second fraction). These two compounds, previously described in racemic form,[8] were identified by NMR (^{1}H and ^{31}P) and their enantiomeric excesses determined by chiral HPLC or by NMR spectroscopy.

3.3.1. 2-Diethoxyphosphonothiolane (+)-1a. Yield = 49%, $[\alpha]_D$ = +25.3 (*c* 1.0, acetone). HPLC: Daicel Chiralpak AD-RH column (25/75 MeCN/H_2O, flow rate 0.3 mL/min, 198 nm, t = 25 °C), t_1 = 21.081 min, t_2 = 24.346 min. ^{31}P NMR (161.98 MHz, C_6D_6) in the presence of (+)-*t*-BuPhP(O)SH: δ = 27.37 (minor) and 27.33 (major).

3.3.2. 2-Diethoxyphosphonothiolane 1-oxide (+)-2a. Yield = 46%, $[\alpha]_D$ = +5.2 (*c* 1.6, acetone). HPLC: Daicel Chiralpak AD column (100% MeOH, flow rate 0.5 mL/min, 204 nm), t_1 = 8.961 min, t_2 = 9.514 min.

3.3.3. 2-Diisopropoxyphosphonothiolane (+)-1b. Yield = 40%, $[\alpha]_D$ = +4.9 (*c* 2.0, acetone). HPLC: Daicel Chiralpak AD-RH column (25/75 MeCN/H_2O, flow rate 0.3 mL/min, 193 nm, t = 25 °C), t_1 = 41.094 min, t_2 = 44.662 min.

3.3.4. 2-Diisopropoxyphosphonothiolane 1-oxide (+)-2b. Yield = 45%; $[\alpha]_D$ = +6.9 (*c* 3.0, acetone).

3.3.5. 2-[2′-(5,5-Dimethyl-1,3,2-dioxaphosphorinano)]thiolane (+)-1c. Yield = 35%; $[\alpha]_D$ = +18.8 (*c* 0.8, acetone). HPLC: Daicel Chiralpak AD-RH column (40/60 MeCN/H_2O, flow rate 0.2 mL/min, 198 nm, t = 25 °C), t_1 = 19.474 min, t_2 = 20.947 min.

3.3.6. 2–[2′-(5,5-Dimethyl-1,3,2-dioxaphosphorinano)]thiolane 1-oxide (+)-2c. Yield = 48%; $[\alpha]_D$ = +8.0 (*c* 0.6, $CHCl_3$). ^{31}P NMR (161.98 MHz, C_6D_6) in the presence of (+)-*t*-BuPhP(O)SH: δ = 16.28 (major) and 16.26 (minor).

3.4. Oxidation of 2-phosphono-2,3-didehydrothiolanes 3: Synthesis of racemic 2-phosphono-2,3-didehydrothiolane-1-oxides 4. General procedure

Sodium metaperiodate (1.1 equiv, 1.1 mmol) was dissolved in a 1/1 mixture of water/EtOH (8 mL) and under stirring a solution of 2-phosphono-2,3-didehydrothiolane **3** (1.0 mmol) in EtOH (4 mL) was slowly added at room temperature. The reaction was followed by TLC (CH_2Cl_2/MeOH: 15/1). After reaction completion (~3 h) the solvents were evaporated. Then 2 mL of water were added, and the solution was extracted with dichloromethane. The combined organic layers were dried with $MgSO_4$, and evaporated to afford the compound **4**.

3.4.1. 2-Diethoxyphosphono-2,3-didehydrothiolane 1-oxide rac-4a. Yellow oil, yield = 78%. ^{31}P NMR (161.98 MHz, $CDCl_3$) δ = 9.3. ^{1}H NMR (250 MHz, $CDCl_3$) δ = 1.39 (t, J = 7.1, 6H, 2 × C*H*$_3$), 2.80–3.75 (m, 4H, SC*H*$_2$, C*H*$_2$), 4.05–4.30 (m, 4H, 2 × OC*H*$_2$), 7.50 (dt, J = 11.3, 2.8, 1H, C=C*H*). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ = 16.1 (d, J = 6.5, *C*H$_3$), 16.2 (d, J = 6.3, *C*H$_3$), 34.7 (d, J = 12.2, *C*H$_2$), 52.5 (d, J = 7.0, *C*H$_2$), 62.8 (d, J = 5.8, O*C*H$_2$), 63.1 (d, J = 5.3, O*C*H$_2$), 141.1 (d, J = 190.7, P*C*), 156.7 (d, J = 12.6, PC=*C*H). HRMS (MH$^+$) Calcd for $C_8H_{16}PSO_4$: 239.0506 Found: 239.0509.

3.4.2. 2-Diisopropoxyphosphono-2,3-didehydrothiolane 1-oxide rac-4b. Yellow oil, yield = 70%. ^{31}P NMR (161.98 MHz, $CDCl_3$) δ = 7.8 ^{1}H NMR (250 MHz, $CDCl_3$) δ = 1.29–1.41 (m, 12H, 4 × C*H*$_3$), 2.80–3.60 (m, 4H, SC*H*$_2$, C*H*$_2$), 4.62–4.87 (m, 2H, 2 × OC*H*), 7.45 (dt, J = 11.2, 2.7, 1H, C=C*H*). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ = 23.5 (d, J = 5.5, *C*H$_3$), 23.6 (d, J = 5.1, *C*H$_3$), 23.8 (d, J = 4.0, 2 × *C*H$_3$), 34.5 (d, J = 18.1, *C*H$_2$), 52.4 (d, J = 6.9, *C*H$_2$), 71.9 (d, J = 6.0, O*C*H), 72.3 (d, J = 5.7, O*C*H),142.0 (d, J = 192.6, P*C*), 156.0 (d, J = 12.7, PC=*C*H). HRMS (MH$^+$) Calcd for $C_{10}H_{20}PSO_4$: 267.0819 Found: 267.0813.

3.4.3. 2-[2′-(5,5-Dimethyl-1,3,2-dioxaphosphorinano]-2,3-didehydrothiolane 1-oxide rac-4c. White solid, mp = 116 °C, yield = 79%. ^{31}P NMR (161.98 MHz, $CDCl_3$) δ = 4.2 ^{1}H NMR (250 MHz, $CDCl_3$) δ = 1.05

(s, 3H, CH_3), 1.24 (s, 3H, CH_3), 3.00–3.65 (m, 4H, SCH_2, CH_2), 3.98–4.40 (m, 4H, $2 \times OCH_2$), 7.55 (dt, $J = 11.5$, 2.3, 1H, C=C*H*). ^{13}C NMR (50.3 MHz, $CDCl_3$) $\delta = 20.7$ (s, CH_3), 21.7 (s, CH_3), 32.3 (d, $J = 6.8$, CCH_3), 34.9 (d, $J = 18.2$, CH_2), 52.3 (d, $J = 7.0$, CH_2), 76.5 (d, $J = 6.5$, OCH_2), 77.4 (d, $J = 6.4$, OCH_2), 140.1 (d, $J = 187.4$, P*C*), 157.4 (d, $J = 12.7$, PC=*C*H). IR (KBr): 3441, 2972, 2897, 1645, 1594, 1474, 1263, 1056, 843, 786 cm^{-1}. HRMS (MH^+) Calcd for $C_9H_{16}PSO_4$: 251.0506 Found: 251.0509.

3.5. Asymmetric oxidation of 2-phosphono-2,3-didehydrothiolanes 3: synthesis of non-racemic 2-phosphono-2,3-didehydrothiolanes 1-oxide 4. General procedure

The oxaziridine (149 mg, 0.5 mmol) was dissolved in dry carbon tetrachloride (8 mL) and under stirring a solution of 2-phosphono-2,3-didehydrothiolanes **3** (0.5 mmol) in carbon tetrachloride (2 mL) was slowly added at room temperature. The reaction was followed by TLC (CH_2Cl_2/MeOH: 15/1). After reaction completion ($\sim$3 h) the solvent was evaporated and the residue purified by column chromatography (CH_2Cl_2/MeOH: 50/1), affording the compound **4**.

3.5.1. 2-Diethoxyphosphono-2,3-didehydrothiolane 1-oxide (+)-4a. Yellow oil, yield = 70%, $[\alpha]_D = +76.7$ (*c* 2.2, acetone). ^{31}P NMR (161.98 MHz, C_6D_6) in the presence of (+)-*t*-BuPhP(O)SH: $\delta = 9.48$ (minor) and 9.44 (major).

3.5.2. 2-Diisopropoxyphosphono-2,3-didehydrothiolane 1-oxide (+)-4b. Yellow oil, yield = 78%, $[\alpha]_D = +64.8$ (*c* 1.0, acetone). ^1H NMR (250 MHz, C_6D_6) in the presence of (+)-*t*-BuPhP(O)SH: $\delta = 7.30$ (m, C=C*H* major) and 7.24 (m, C=C*H* minor).

3.5.3. 2-[2′-(5,5-Dimethyl-1,3,2-dioxaphosphorinano]-2,3-didehydrothiolane 1-oxide (+)-4c. White solid, yield = 77%, $[\alpha]_D = +60.5$ (*c* 1.0, acetone). ^{31}P NMR (161.98 MHz, C_6D_6) in the presence of (+)-*t*-BuPhP(O)SH: $\delta = 4.37$ (minor non detected) and 4.28 (major).

The crystal structure of (+)-**4c** has been registered at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 240024.

Acknowledgements

This work was carried out with the support of the European Community within the fifth framework programme (contract ICA-CT-2000-70021-Centre of Excellence), of the French CNRS and the Polish Academy of Sciences. Authors thank Dr. L. Toupet (University of Rennes) for the X-ray crystal diffraction analysis.

References

1. Posner, G. H. *Acc. Chem. Res.* **1987**, *20*, 72–78.
2. (a) Arai, Y.; Koizumi, T. *Sulfur Rep.* **1993**, *15*, 41–65; (b) Carreño, C. *Chem. Rev.* **1995**, *95*, 1717–1760; (c) Lee, A. W. M.; Chan, W. H. *Top. Curr. Chem.* **1997**, *190*, 103–126; (d) Garcia-Ruano, J. L.; Cid de la Plata, B. *Top. Curr. Chem.* **1999**, *204*, 1–126; (e) Delouvrié, B.; Fensterbank, L.; Nájera, F.; Malacria, M. *Eur. J. Org. Chem.* **2002**, 3507–3525.
3. Mikolajczyk, M.; Midura, W.; Grzejszczak, S.; Zatorski, A. *J. Org. Chem.* **1978**, *43*, 473–478.
4. (a) Mikolajczyk, M.; Balczewski, P. In *Advances in Sulfur Chemistry*; Block, E., Ed.; JAI, Stanford, CT, USA, 1994; Vol. 1, pp 41–96; (b) Gulea, M.; Masson, S. *Top. Curr. Chem.* **2003**, *229*, 161–198; (c) Capozzi, M. A. M.; Cardellicchio, C.; Naso, F. *Eur. J. Org. Chem.* **2004**, 1855–1863.
5. (a) Midura, W. H.; Krysiak, J. A.; Mikolajczyk, M. *Tetrahedron* **1999**, *55*, 14791–14802; (b) Midura, W. H.; Krysiak, J. A.; Wieczorek, M. W.; Majzner, W. R.; Mikolajczyk, M. *Chem. Commun.* **1998**, 1109–1110; (c) Midura, W. H.; Mikolajczyk, M. *Tetrahedron Lett.* **2002**, 3061–3065.
6. (a) Aggarwal, V. K.; Barrell, J. K.; Worrall, J. M.; Alexander, R. *J. Org. Chem.* **1998**, *63*, 7128–7129; (b) Aggarwal, V. K.; Barrell, J. K.; Worrall, J. M.; Alexander, R. *Phosphorus, Sulfur and Silicon* **1999**, *153/154*, 337–338.
7. Marchand, P.; Gulea, M.; Masson, S.; Saquet, M.; Collignon, N. *Org. Lett.* **2000**, 3757–3759.
8. Marchand, P.; Gulea, M.; Masson, S.; Averbuch-Pouchot, M.-T. *Synthesis* **2001**, 1623–1626.
9. Marchand, P., PhD thesis, University of Caen, France, 1999.
10. (a) Davis, F. A.; Thimma Reddy, R.; Weismiller, M. C. *J. Am. Chem. Soc.* **1989**, *111*, 5964; (b) Davis, F. A.; Thimma Reddy, R.; McCauley, J. P., Jr.; Przeslawski, R. M.; Harakal, M. E.; Carroll, P. J. *J. Org. Chem.* **1991**, *56*, 809–815.
11. (a) Phillips, M. L.; Berry, D. M.; Panetta, J. A. *J. Org. Chem.* **1992**, *57*, 4047–4049; (b) Phillips, M. L.; Panetta, J. A. *Tetrahedron: Asymmetry* **1997**, *13*, 2109–2114; (c) Nemecek, C.; Kagan, H. B. *Pol. J. Chem.* **1994**, *68*, 2467–2475; (d) Griffiths, S. L.; Perrio, S.; Thomas, S. E. *Tetrahedron: Asymmetry* **1994**, *5*, 1847–1864.
12. Robinson, D. E. J. E.; Bull, S. D. *Tetrahedron: Asymmetry* **2003**, *14*, 1407–1446.
13. Drabowicz, J.; Oae, S. *Synthesis* **1977**, 404–406.
14. (a) Scettri, A.; Bonadies, F.; Lattanzi, A.; Senatore, A.; Soriente, A. *Tetrahedron: Asymmetry* **1996**, *7*, 657–658; (b) Komatsu, N.; Hashizume, M.; Sugita, T.; Uemura, S. *J. Org. Chem.* **1993**, *58*, 7624–7626.
15. (a) Omelanczuk, J.; Mikolajczyk, M. *Tetrahedron: Asymmetry* **1996**, *7*, 2687–2694; (b) Hammerschmidt, F.; Kahlig, H.; Schmidt, S.; Wuggenig, F. *Phosphorus Sulfur Silicon Relat. Elem.* **1998**, *140*, 79–93.