Pyridyl and Furyl Epoxides of More Than 99% Enantiomeric Purities: The Use of a Phosphazene Base

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trans-1-(2-Pyridyl)-, *trans*-1-(3-pyridyl)-, *trans*-1(2-furyl)-, and *trans*-1(3-furyl)-2-phenyl epoxides with enantiomeric purities ranging from 96.8 to 99.8% [in favor of the (+, EtOH)-isomer] are obtained in two steps from pure (*R,R,R*)-oxathiane which is recovered (85–90%) and reused. The chiral bidentate ligand 2-phenyl-(*S*)-1-(2-pyridyl)ethanol with 99.6% *ee* was obtained in three steps and 67% overall isolated yield.

Introduction

Chiral pyridyl alcohols have numerous applications, as ligands in asymmetric metal catalysis,[1] as resolving agents[2] or as starting materials for the preparation of more advanced chiral ligands.[3] They can be prepared by enantioselective reduction of the corresponding pyridyl ketones. Similarly, chiral furyl hydroperoxides have been used for the asymmetric epoxidation of allylic alcohols[4] and sulfides;[5] they are obtained by direct enzymatic resolution.

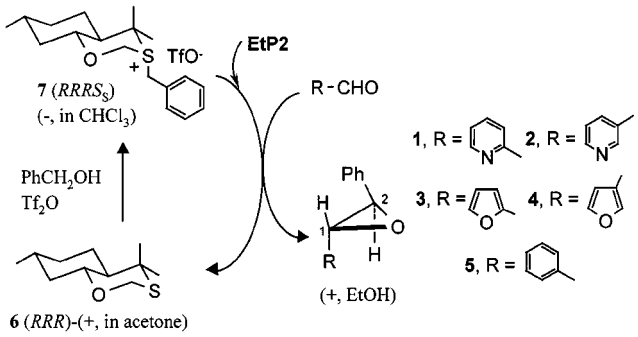
As an application of our asymmetric synthesis of diaromatic epoxides,[6] which has been shown to give almost total enantioselectivities, we present here the asymmetric synthesis and characterization of the pyridyl and furyl epoxides **1–4** as well as the first attempts of the ring-opening of 2-pyridyl epoxide and 2-furyl epoxide.

Results

Asymmetric Synthesis of Epoxides 1–4 with EtP2 as Base

Until now the 2- and 3-pyridyl epoxides **1** and **2** have only been prepared in their racemic form,[7] as has the only known 2-furyl epoxide **3**.[8] Asymmetric synthesis of the epoxides **1–4** has been successfully performed following our method from the pure (*R,R,R,S*$_S$)-(–)-sulfonium salt **7**,[9] the corresponding commercially available aldehydes (Scheme 1) and a phosphazene base [EtP2 = Et–N=P(NMe$_2$)$_2$(N=P(NMe$_2$)$_3$] to generate the ylide.

Alkylation of pure (*R,R,R*)-(+)-oxathiane **6** was performed in 90% conversion (68% isolated yield) using Vedej's triflate method.[10] Use of the phosphazene base EtP2 instead of NaH to generate the ylide gave, even at –78 °C, a very high percentage of conversion into the desired



Scheme 1

epoxides (95%) and in much shorter reaction times (30 min instead of 1 to 2 days). The results are gathered in Table 1.

When the reaction was complete, 1:1 mixtures of the starting chiral auxiliary **6** and the desired epoxide (**1–5**) were obtained (as seen from the ^{1}H NMR spectrum of the crude product of the reaction) which could be separated by chromatography. The chiral auxiliary was recovered pure in 85–90% yield and was reused.

It is worth noting that only the *trans*-epoxide was formed, in agreement with previous results concerning diaromatic epoxides[6,11] obtained with NaH as base; only in the case of 2-pyridyl epoxide **(1)** was 12% of the *cis*-isomer obtained.

The 2-furyl epoxide **(3)** is very reactive/unstable and was lost on the column during chromatography, although enough compound was recovered to measure the optical rotation. However, in situ ring-opening of this epoxide (in the presence of the oxathiane and before purification) can be performed (*cf.* below) which allows to overcome this difficulty. The known epoxide **5** was reprepared as a reference.

Enantiomeric Purities and Absolute Configurations of Epoxides 1–5

The enantiomeric purities (Table 1) were determined by chiral HPLC and the conditions used are gathered in Table 3 (Experimental Section). It is interesting to note that EtP2

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Table 1. Asymmetric synthesis of epoxides **1–5** from the sulfonium salt **7** using EtP2 as base; reaction time = 30 min

Epox.	Temp. (°C)	Conv.[a] (%)	Yield[b] (%)	*trans*/*cis*[a]	*ee*-*trans*[c] (config.) (%)	*ee*-*cis*[c] (config.) (%)	$[\alpha]_D^{20}$, (*c*)[d] *trans*
1	–78	>95	94	88/12	99.2 (1*R*,2*R*)	99.9 (1*S*,2*R*)	+285(1)
2	–78	>95	81	100/0	96.8 (1*R*,2*R*)		+285.5 (1)
3	–78	>95	11	100/0	99.2 (1*S*,2*R*)		+246 (0.18)
4	–78	>95	82	100/0	99.8 (1*R*,2*R*)		+199(1)
5	–40	85	69	100/0	97.0 (1*R*,2*R*)		+281 (1)

[a] Determined by ^{1}H NMR spectroscopy of the crude product of the reaction. – [b] After preparative chromatography of quantities ranging from 500 mg to 2 g (silica gel or Alox). – [c] Determined by chiral HPLC (cf. below). – [d] Measured in EtOH, *c* = concentration in g/100 mL.

also provides exceptionally high enantioselectivities: >99% *ee* for epoxides **1**,**3**,**4** and 97% *ee* for epoxides **2** and **5**.

The *R,R*-configuration was assigned to the *trans*-stilbene oxide **5** on the basis of the positive sign of its optical rotation in EtOH and at 589 nm as in our previous papers.[6,9,11] It thus appeared that EtP2 leads to the same configuration as NaH and one can postulate that the model[9,12] shown in Figure 1 holds. Therefore the same structure was assigned to the (+, EtOH)-isomers obtained for the new and unknown *trans*-epoxides **1**,**2**,**3** and **4:** (1*R*,2*R*)-**1**, (1*R*,2*R*)-**2**, (1*S*,2*R*)-**3** and (1*R*,2*R*)-**4**. Similarly the configuration at C-2 being *R* due to the preferred direction of approach (*cf.* Model in Figure 1), it can be concluded that the configuration at C-1 is *S* in the *cis*-isomer (Table 1, line 1).

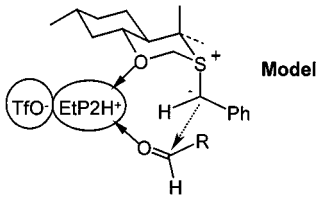
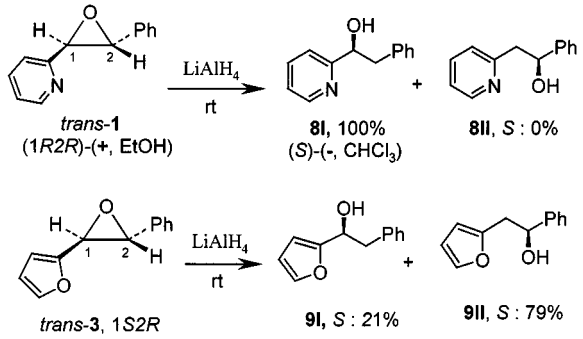


Figure 1

Ring Opening of Epoxides 1 and 2

The first attempts at ring opening of these epoxides were performed with $LiAlH_4$ in Et_2O (Scheme 2 and Table 2).

trans-Epoxide **1** (isolated by chromatography) is opened regioselectively to give alcohol **8I** (Scheme 2) with 99.6% enantiomeric purity. From the known configuration of the starting epoxide (1*R*,2*R*, cf. Table 1), the absolute configuration of the resulting alcohol **8I** was assigned to be: (–, $CHCl_3$) = (*S*). The structure of alcohol **8I** was confirmed through the nonambiguous synthesis of alcohol **8II** (addition of α-picolyllithium to benzaldehyde).



Scheme 2

Ring opening of the 2-furyl epoxide **3** was performed on the crude oxathiane/epoxide mixture and provided the alcohol in high isolated yield (80%), while 90% of the oxathiane was recovered. It is worth noting that although lower regioselectivities were expected, the observed inversion of the regioselectivity in favor of isomers **II** (**9II** = major) was surprising. Both alcohols have, of course, high enantioselectivities (99% *ee*). The structure of **9II** was determined from the unambiguous preparation of *racemic*-**9I** (addition of benzyl Grignard reagent to 2-furylaldehyde).

In conclusion, 1-(2-pyridyl), 1-(3-pyridyl), 1-(2-furyl) and 1-(3-furyl)-2-phenylepoxides **1-4**-*trans* with enantiomeric purities ranging from 96.8 to 99.8% [in favor of the (+, EtOH) isomer] have been obtained for the first time in only two steps, the chiral auxiliary being recovered in 85–90% yield and reused.

A potentially important bidentate chiral ligand, the (*S*)-2-pyridyl alcohol **8I** with 99.6% *ee*, was obtained in three steps and 67% overall isolated yield.

Table 2. Opening of epoxides **1** and **3** with $LiAlH_4$ in Et_2O

Alcohol	*T* (°C)	React. time	Yield (%)	**I/II**	**I** *ee* (conf.)	**I** $[\alpha]_D^{22}$	**II** *ee* (conf.)
8 (2-pyr)	Room temp.	30 min	81	100/0	99.6 (*S*)	-17.5 [a]	-
9 (2-fur)	Room temp.	1 h	91	21/79	99.0 (*S*)[b]		99.0 (*S*)[b]

[a] *c* = 1, $CHCl_3$. – [b] Same conditions as for **8I** (*cf.* Table 3, experimental section).

EtP2H$^+$/TfO$^-$ was recovered by varying the solvent polarity;[13] the expensive base EtP2 can thus be regenerated.

It is worth noting that the epoxides **1–4** are not available from direct asymmetric epoxidation[14] of the corresponding olefins because of side oxidation reactions of the heterocyclic rings. Attempts to make this method catalytic[15] through the use of phenyldiazomethane (dangerous on large scale) have been done, however, because of the possible direct reaction of the diazo compound with the aldehyde *prior* to formation of the desired chiral ylide, the enantiomeric purity obtained is often lower.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 (200 MHz) or a Bruker Avance (400 MHz) spectrometer with $CDCl_3$ as the solvent. Chemical shifts (δ) are given in ppm downfield from an internal standard of TMS. – Optical rotation measurements were carried out with a Perkin–Elmer 241 MC polarimeter. – Melting points were determined with a Reichert melting point apparatus, and are not corrected. – TLC was performed on Merck glass plates with silica gel 60 F_{254}. Silica gel for column chromatography (Merck) was used for the chromatographic purifications, as was aluminium oxide (Fluka, type 5016A basic). – HPLC was performed with a Knauer HPLC pump 64 and Knauer Variable wavelength monitor, equipped with a PC. – Analytical chiral columns were: Chiralcel OD-H, Chiralpak AS (all 25 cm × 4.6 mm I.D., Daicel, Japan). – The (*R,R,R*)-oxathiane **6** was prepared from (+)-pulegone following Eliel's method:[16] $[\alpha]_D^{22}$ = +12 (*c* = 2.1, acetone). The sulfonium salt **7** was prepared following Vedej's method:[10] white powder, m.p. 136–139 °C. – $[\alpha]_D^{22}$ = –222 (*c* = 1.04, $CHCl_3$), one diastereomer by ^{1}H NMR spectroscopy.[6,11]

ucts were found to be 1:1 mixtures of the epoxide **1** (or **2, 3, 4** or **5**) and the oxathiane **6** (as seen from ^{1}H NMR spectroscopy).

[*trans*-(1*R*,2*R*)]-1: Chromatographic purification on silica gel ($CHCl_3$/Et_2O, 7:3; R_f = 0.56) of the crude product yielded 94% of the pure epoxide as pale yellow crystals, m.p. 51–53 °C. – $[\alpha]_D^{20}$ = +285.2 (*c* = 1, EtOH); $[\alpha]_D^{20}$ = +326 (*c* = 1, benzene); *ee* = 99.2% (*cf.* Table 1 and 2). – ^{1}H NMR ($CDCl_3$/TMS): δ = 4.05 (br. s, 2 H), 7.25 (m, 2 H), 7.35 (br. m, 5 H), 7.70 (td, ^3J = 7 Hz, 7 Hz, ^4J = 2 Hz, 1 H), 8.60 (dd, ^3J = 5 Hz, ^4J = 2 Hz, 1 H). – ^{13}C NMR ($CDCl_3$/TMS): δ = 61.8, 62.9 (CH epox), 120.2, 123.3, 125.8, 128.5, 128.6, 136.9, 149.6 (CH rings), 136.8, 156.4 (C).

[*cis*-(1*S*,2*R*)]-1: (R_f = 0.34, $CHCl_3$/Et_2O 7:3) was obtained in 86% yield as pale yellow crystals, m.p. 30–32 °C. – $[\alpha]_D^{20}$ = +63 (*c* = 0.36, EtOH); $[\alpha]_D^{20}$ = +82 (*c* = 0.36, benzene); *ee* = 99.9% (*cf.* Table 1 and 2). – ^{1}H NMR ($CDCl_3$/TMS): δ = 4.45 (br. s, 2 H), 7.05 (m, 2 H), 7.15 (bm, 6 H), 7.45 (td, ^3J = 7 Hz, 7 Hz, ^4J = 2 Hz, 1 H), 8.40 (dd, ^3J = 5 Hz, ^4J = 2 Hz, 1 H). – ^{13}C NMR ($CDCl_3$/TMS): δ = 59.9, 60.0 (CH epox), 121.3, 122.4, 135.2, 147.8 (CH pyr), 126.3, 127.0 (CH arom), 133.3, 154.0 (C).

[*trans*-(1*R*,2*R*)]-2: Chromatographic purification on silica gel (EtOAc/Et_2O, 1:1; R_f = 0.49) of the crude product yielded 81% of the pure epoxide as white crystals, m.p. 47–50 °C. – $[\alpha]_D^{20}$ = +285.5 (*c* = 1, EtOH); $[\alpha]_D^{20}$ = +365.9 (*c* = 1, benzene); *ee* = 96.8% (*cf.* Table 1 and 2). – ^{1}H NMR ($CDCl_3$/TMS): δ = 3.90 (br. s, 2 H), 7.25 (m, 1 H), 7.35 (bm, 5 H), 7.62 (dt, ^3J = 7 Hz, ^4J = 1.5 Hz, 1.5 Hz, 1 H), 8.59 (dd, ^3J = 5 Hz, ^4J = 1.5 Hz, 1 H), 8.63 (d, ^4J = 1.5 Hz, 1 H). – ^{13}C NMR ($CDCl_3$/TMS): δ = 60.7, 62.8 (CH epox), 123.6, 125.6, 128.7, 132.8, 147.9, 149.8 (CH), 132.8, 136.5 (C).

[*trans*-(1*S*,2*R*)]-3: Chromatographic isolation was done on Al_2O_3 (*n*-hexane/Et_2O, 9:1) of the crude product (see above) yield: 11% of pure epoxide as pale yellow crystals, m.p. 29–33 °C. – $[\alpha]_D^{20}$ = +246 (*c* = 0.18, EtOH), $[\alpha]_D^{20}$ = +280 (*c* = 0.18, benzene); *ee* = 99.2% (*cf.* Table 1 and 2). – ^{1}H NMR ($CDCl_3$/TMS): δ = 3.88 (d, ^3J = 3 Hz, 1 H), 4.35 (d, ^3J = 3 Hz, 1 H), 6.43 (AB of an ABX, $\Delta\nu_{AB}$ = 17 Hz, $^3J_{AB}$ = 4 Hz, ^3J = 1.5 Hz, ^4J = 0, 2 H), 7.35 (bm, 5 H), 7.42 (X of the ABX, 1 H). – ^{13}C NMR ($CDCl_3$/TMS): δ = 56.6, 60.0 (CH epox), 110.2, 111.2, 143.3 (CH furyl), 126.0, 128.8, 128.9 (CH arom), 136.9, 150.3 (C).

[*trans*-(1*R*,2*R*]-4: Chromatographic purification on silica gel (CH_2Cl_2; R_f = 0.85) of the crude product yielded 82% of the pure epoxide as pale yellow crystals, m.p. 49–52 °C. – $[\alpha]_D^{20}$ = +199 (*c* = 1, EtOH); $[\alpha]_D^{20}$ = +267 (*c* = 1, benzene); *ee* = 99.8% (*cf.* Table 1 and 2). – ^{1}H NMR ($CDCl_3$/TMS): δ = 3.80 (d, ^3J = 3 Hz, 1 H), 3.98 (d, ^3J = 3 Hz, 1 H), 6.40 (br. s, 1 H), 7.35 (bm, 5 H), 7.43 (br. s, 1 H), 7.57 (br. s, 1 H). – ^{13}C NMR ($CDCl_3$/TMS): δ = 56.6, 61.3

Table 3. Conditions and parameters for HPLC analyses of epoxides **1–4** on chiral columns (for analysis of epoxide **5** see ref.[6b])

	1 *trans*	**1** *cis*	**2**	**3**	**4**	**8I**
Column	Chiralcel OD-H	Chiralpak AS	Chiralcel OD-H	Chiralcel OD-H	Chiralcel OD-H	Chiralcel OD-H
Mobile phase	10% *i*PrOH, 90% hexane	10% *i*PrOH, 90% hexane	10% *i*PrOH, 90% hexane	10% *i*PrOH, 90% hexane	10% *i*PrOH, 90% hexane	20% *i*PrOH, 80% hexane
Flow (mL/min)	1.0	1.0	1.0	0.5	1.0	1.0
R_t (min), major	16.9	7.7	23.6	15.9	14.1	7.4
R_t (min), minor	9.9	11.5	26.0	12.4	17.7	8.8
k_1'	2.83	2.20	4.90	0.59	3.70	1.11
k_2'	4.83	3.29	5.50	1.01	4.80	1.51
α	1.71	1.50	1.12	1.71	1.30	1.36
R_s	6.67	6.13	1.78	4.12	2.06	1.86

General Procedure for the Synthesis of Epoxides 1–5: To a stirred solution of the benzylic sulfonium salt **7** (1 equiv., 1.5 mmol) in anhydrous CH_2Cl_2 (5 mL) was added 1 equiv. of the commercially available phosphazene base EtP2 at –78 °C. After stirring for 10 to 15 min the desired aldehyde (1 equiv.) was added dropwise. The reaction was then stirred for 30 min at –78 °C. After addition of a saturated solution of NaCl in water (1 mL), the organic phase was separated and the aqueous phase extracted with CH_2Cl_2 (3 × 5 mL). The organic phases were combined, dried over Na_2SO_4 and concentrated under vacuum. The remaining phosphazene-base salt EtP$_2$H$^+$TfO$^-$ was precipitated by addition of a 1:1 mixture of ether/*n*-hexane and filtered off. After evaporation the crude prod-

(CH epox), 108.1, 141.4, 143.7, (CH furyl), 125.6, 128.5, 128.7 (CH arom), 123.0, 137.0 (C).

General Procedure for $LiAlH_4$ Opening of Epoxides: To a solution of 1 equiv. of the desired epoxide (pure or oxathiane/epoxide mixture) in 2 mL of dry ether (under argon) was added dropwise 1.5 equiv. of $LiAlH_4$ (1 M in ether), the mixture was stirred at the desired temperature and the reaction monitored by TLC. After completion of the reaction, water was added dropwise and the precipitate was filtered off and washed with ether. The filtrate was dried over Na_2SO_4 and the solvent was evaporated under vacuum.

(*S*)-2-Pyridyl Alcohol 8I: 81%; R_f = 0.3, Et_2O. – $[\alpha]_D^{20}$ = –17.6 (*c* = 1, $CHCl_3$), *ee* = 99.6%, m.p. 89–94 °C. – ^{1}H NMR ($CDCl_3$/TMS): δ = 3.10 (AB of an ABX, $\Delta\tilde{\nu}$ = 35 Hz, $^2J_{AB}$ = 14 Hz, ^3J = 7.5 Hz, 5 Hz, 2 H), 5.00 (X of the ABX, dd, 1 H), 7.20 (m, 7 H), 7.62 (td, ^3J = 7 Hz, 7 Hz, ^4J = 1 Hz, 1 H), 8.52 (dd, ^3J = 5 Hz, ^4J = 1 Hz, 1 H). – ^{13}C NMR ($CDCl_3$/TMS): δ = 45.5 (CH_2), 74.6 (CH), 121.1, 122.2, 136.8, 148.8 (CH pyr), 126.8, 128.7, 130.0 (CH arom), 138.2, 161.8 (C).

Racemic 2-Pyridyl Alcohol 8II: Prepared by addition of α-picolyllithium to benzaldehyde. – ^{1}H NMR ($CDCl_3$/TMS): δ = 3.1 (degenerate AB of an ABX, 2 H), 5.17 (X of the ABX, dd, 1 H), 7.10 (bd, ^3J = 7 Hz, 1 H), 7.30 (bm, 6 H), 7.62 (td, ^3J = 7 Hz, 7 Hz, ^4J = 1 Hz, 1 H), 8.52 (dd, ^3J = 5 Hz, ^4J = 1 Hz, 1 H).
Addition of *racemic*-**8II** thus prepared into a sample of (*S*)-**8I** obtained from opening of the epoxide lead to a spectrum which was a superposition of both spectra described above, mainly two different ABX systems.

(*S*)-2-Furyl Alcohol 9I/9II (9I/9II, 21:79). – 9II (*major*): ^{1}H NMR ($CDCl_3$/TMS): δ = 3.05 (A_2, d, ^3J = 7 Hz, 2 H), 5.03 (t, ^3J = 7 Hz, 1 H), 6.15 (br. s, 1 H), 6.35 (br. s, 1 H), 7.35 (bm, 6 H). – **9I (*minor*):** ^{1}H NMR ($CDCl_3$/TMS): 3.19 (AB of an ABX, Δν = 33 Hz, ^2J = 14 Hz, ^3J = 8 Hz, 5.5 Hz, 2 H), 4.94 (X of the ABX, bdd, 1 H), 6.29 (br. s, 1 H), 6.35 (br. s, 1 H), 7.35 (bm, 6 H).

Identification of **9I** and **9II** was done by addition of *racemic*-**9I** (prepared by addition of benzylmagnesium bromide to 2-furyl aldehyde) to the mixture.

The enantiomeric purity of **9I** and **9II** was determined from the mixture using a Chiralcel OD-H column (20% 2-propanol/80% hexane, flow rate = 1.0 mL/min).

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