Synthesis of Chiral $\alpha$-(N-Sulfoximido) Phosphines, Phosphine Oxides, and Phosphonates through Hydrophosphination and Hydrophosphorylation of N-Vinyl Sulfoximines

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Abstract: The reaction of N-vinyl sulfoximines with HPPh$_2$, HP(O)Ph$_2$, and HP(O)(OMe)$_2$ gave the corresponding $\alpha$-(N-sulfoximido) phosphines, phosphine oxides, and phosphonates, respectively, with high regioselectivity in high yield. The N-vinyl sulfoximines showed an enamine-like regioselectivity in hydrophosphination and hydrophosphorylation (Pudovik reaction). While sulfoximines showed an enamine-like regioselectivity in hydrophosphination and hydrophosphorylation, the corresponding NH-sulfoximine and cyclohexanone, its hydroboration/oxidation afforded the corresponding $N$-(β-hydroxycyclohexenyl) sulfoximine. The structure of an $\alpha$-(N-sulfoximido) phosphine was determined by X-ray crystal structure analysis.

Keywords: Pudovik reaction, N-vinyl sulfoximines, phosphonation, phosphinylation, phosphines, $\alpha$-(N-sulfoximido) phosphines, $\alpha$-(N-sulfoximido) phosphonates, $\alpha$-(N-sulfoximido) phosphine oxides, hydroboration, hydrophosphination

Sulfoximines have emerged as valuable chiral auxiliaries$^{1-4}$ and chiral ligands$^{5,6}$ for asymmetric synthesis. In addition sulfoximines have found important application as enzyme inhibitors$^7$ and peptidomimetics.$^8$ Recently, the N-vinyl sulfoximines I have been described, which are readily available through a palladium-catalyzed or copper-mediated coupling reaction of NH-sulfoximines with the corresponding vinyl halides or triflates (Scheme 1).$^9$

![Scheme 1](image)

We decided to study the hydrophosphination and hydrophosphorylation (Pudovik reaction)$^{10}$ of N-vinyl sulfoximines I with phosphines II. The resulting $\alpha$- or $\beta$-(N-sulfoximido) phosphines, phosphine oxides, and phosphonates III and IV, respectively, should both be of interest as new potential N,P-ligands for transition metals and analogues of $\alpha$- and $\beta$-amino phosphonic acids. N,P-Ligands have found much application, for example, in transition-metal-catalyzed asymmetric synthesis.$^{11}$ Both $\alpha$- and $\beta$-amino phosphonic acids are of significant interest as analogues of $\alpha$- and $\beta$-amino acids.$^{12}$

The N-vinyl sulfoximines 3$^9$ and 5 of 95% purity were obtained through a copper-mediated coupling of the enantiopure $\beta$-configured sulfoximine 1$^3$ with the corresponding bromides 2 and 4 in practically quantitative yields (Scheme 2). Despite their ready availability almost nothing was known about the reactivity of N-vinyl sulfoximines of type I. Specifically, the question whether they behave like enamines as hinted by the polar structure, which is according to ab initio calculations an appropriate representation of the electronic structure of the sulfoximine group,$^4$ or react as electron-withdrawing group activated alkenes, awaited experimental verification. Therefore, the reactivity of sulfoximine 5 towards water and acid was first investigated. The N-vinyl sulfoximine proved to be stable towards water in CDCl$_3$ at room temperature for at least 24 hours as shown by NMR spectroscopy and GC analysis. However, the addition of acetic acid to a mixture of 5 and water in CDCl$_3$ at room temperature resulted within one hour in a complete hydrolysis of the N-vinyl sulfoximine and gave sulfoximine 1 and ketone 6 (Scheme 3). Furthermore, an attempted chromatography of 3 and 5 on silica gel also led to a hydrolysis of the N-vinyl sulfoximines and the isolation of sulfoximine 1. 

![Scheme 2](image)
Having established an enamine like reactivity of 5 towards H₂O/H⁺, the reactions of the acyclic N-vinyl sulfoximine 3 with HPPh₂ (7a), HP(O)Ph₂ (7b) and HP(O)(OMe)₂ (7c) were studied. The treatment of 3 with 1.3 equivalents of neat 7a at 100 °C for 48 hours resulted in complete conversion of the starting sulfoximine and gave, after the addition of BH₃·THF, a mixture of the diastereomeric α-(N-sulfoximido) phosphine–borane adducts (S)-8a·BH₃ and (R)-8b·BH₃ in a ratio of 1:1 in 87% yield (Scheme 4, Table 1). Crystallization and HPLC afforded the pure diastereomers (S)-8aa·BH₃ and (R)-8ab·BH₃. The configuration of (S)-8aa·BH₃ was determined by X-ray crystal structure analysis (Figure 1).[15]

**Scheme 4**

Next the reaction of the cyclic N-vinyl sulfoximine 5 with 7a-c was studied. Surprisingly, the synthesis of phosphine 9a from 5 and 7a could not be achieved. The treatment of 5 with 7a at 100 °C for a prolonged period of time resulted only in a low conversion of the vinyl sulfoximine to 9a (10%) (Scheme 5). Attempts to achieve an addition of HPPh₂·BH₃ to the N-vinyl sulfoximine 5 also failed. Instead, the saturated sulfoximine 10 was directly isolated in 84% yield after chromatography of the crude reaction product on silica gel (Scheme 6). Treatment of 5 with BH₃·THF followed by an oxidation with H₂O₂ in the presence of NaOH gave the β-hydroxy sulfoximine 11 as a mixture of two diastereomers in a ratio of 2:1 in 71% yield. According to ¹H NMR spectroscopy, both diastereomers have the trans-configuration. These results show that BH₃ caused a highly regioselective hydroboration of the N-vinyl sulfoximine 5. In contrast to 7a, the reaction of 7b with 5 at 100 °C proceeded cleanly and gave after a reaction time of 3 hours the α-(N-sulfoximido) phosphine oxide 9b in 86% yield (Table 2). Similarly, the treatment of 5 with 7c at 100 °C for 18 hours afforded the α-(N-sulfoximido) phosphonate 9c in 96% yield. The addition of 7b and 7c to 5 proceeded with high regioselectivity according to NMR spectroscopy of the crude reaction mixtures.

**Scheme 5**

A similar reaction of 3 with 1 equivalent of neat 7b at 100 °C was complete after only 3 hours and gave a mixture of the diastereomeric α-(N-sulfoximido) phosphine oxides 8ba and 8bb in a ratio of 3:2 in 87% yield. Separation by HPLC furnished the pure diastereomers 8ba and 8bb. Finally, the treatment of 3 with 1.5 equivalents of neat 7c at 100 °C for 23 hours gave a mixture of the diastereomeric α-(N-sulfoximido) phosphonates 8ca and 8cb in a ratio of 3:2 in 99% yield. Separation by HPLC afforded the pure diastereomers 8ca and 8cb. The addition of 7a-c to 3 had occurred with high regioselectivity. The NMR spectra of the crude reaction mixtures gave no indication for the formation of regioisomers of type IV. Thus, the N-vinyl sulfoximine 3 showed in the Pudovik reaction with 7a-c an enamine like reactivity[15] and gave the α-adducts of type III with high regioselectivity. The reactivity of 3 decreased in the order HP(O)Ph₂ > HP(O)(OMe)₂ > HPPh₂, which roughly parallels their acidity.[17]
In conclusion, we have shown that the N-vinyl sulfoximines 3 and 5 readily undergo with high regioselectivity a noncatalyzed hydrophosphination and hydrophosphorylation with 7a–c to give α-(N-sulfoximido) phosphines, phosphine oxides and phosphonates of type III in high yields. A complete conversion of 3 and 5 was only observed when the N-vinyl sulfoximines and the phosphines were heated without solvent at elevated temperatures. The asymmetric induction in the addition to the acyclic N-vinyl sulfoximine 3 was only low. It is not known, however, whether the addition of 7a–c to 3 and 5 is kinetically or thermodynamically controlled since it might be reversible under the reaction conditions employed. The reaction of sulfoximines 3 and 5 with 7a–c show the same regioselectivity as that of enamines. However, the Pudovik reaction of enamines has been studied only in a few cases and nothing is known about its mechanism. It has been suggested that the addition of 7a–c to imines, for example, takes place via a four-membered cyclic transition state. Therefore the addition of 7a–c to 3 and 5 may occur by a similar mechanism. We found that the reaction of 3 and 5 with 7a–c in the presence or in the absence of oxygen occurred with a similar high regioselectivity. Thus a radical mechanism for the reaction of 3 and 5 with 7a–c seems unlikely. Because of the successful derivatization of sulfoximine 9b at the S-methyl group via lithiation, the synthesis of interesting functionalized derivatives of III can be envisioned. Finally, it should be noted that hydroboration of 5 occurred readily and showed the same regioselectivity as that of enamines. This suggests a perhaps facile route to cyclic N-(β-hydroxalkyl) sulfoximines which are not easily accessible otherwise.

Table 2 Hydrophosphorylation of the Cyclic N-Vinyl Sulfoximine 5

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPPh₂ (7a)</td>
<td>9a</td>
<td>–^a</td>
</tr>
<tr>
<td>HP(O)Ph₂ (7b)</td>
<td>9b</td>
<td>86</td>
</tr>
<tr>
<td>HP(O)OMe₂ (7c)</td>
<td>9c</td>
<td>96</td>
</tr>
</tbody>
</table>

^a Only a 10% conversion of 5 to 9a was observed.

All reactions were carried out under argon with flame-dried glassware and dried solvents. Reactions involving oxygen sensitive phosphorus compounds were performed with degassed solvents (argon). Solvents were dried and purified by conventional methods before use. THF and toluene were freshly distilled from Na under N₂. Sulfoximine 1, the N-vinyl sulfoximine 3⁴ and bromide 4⁵ were synthesized according to the literature. All other chemicals were obtained from commercial sources. TLC was performed on silica gel 60 F₂₅₄ aluminum sheets (Merck) with UV and iodine detection. Flash chromatography was performed on silica gel 60, 0.040–0.063 mm (Merck). Analytical HPLC was carried out on Waters 600 E UV 481 and Hewlett Packard HP 1050 instruments. Optical rotations were measured on a PerkinElmer P241 polarimeter. NMR spectra were recorded on Varian Mercury 300 and Varian Inova 400 instruments. Chemical shifts are reported relative to TMS. MS spectra were measured on a Finnigan SSQ 7000 (EI, 70 eV or CI, methane or isobutane) instrument and HRMS spectra on a Varian MAT 95 (EI, 70 eV) instrument. IR spectra were run on a Perkin Elmer FTIR 1760 S instrument. Microanalyses were obtained with a Vario EL element analyzer. Melting points were determined on a Leica melting point apparatus and are uncorrected.

(5)-N-Cyclohex-1-enyl-S-methyl-S-phenylsulfoximine (5)

A Schlenk flask was charged with Cu(1.03 g, 5.5 mmol), K₂CO₃ (1.49 g, 10.8 mmol), and (S)-S-methyl-S-phenylsulfoximine (1: 840 mg, 5.4 mmol). Subsequently, the flask was purged with argon and then toluene (50 mL), N,N′-dimethylethlenediamine (1.16 mL, 10.8 mmol), and bromide 4 (1.30 g, 8.1 mmol) were added. The mixture was heated under stirring for 20 h at 110 °C. Then, the mixture was cooled to r.t., Et₂O (50 mL) was added, and the mixture was filtered through a layer of Celite (1 cm) by washing with Et₂O (50 mL). Removal of the solvents under reduced pressure gave the N-vinyl sulfoximine 5 (1.25 g, 98%) as a yellow oil; [α]D<sub>20</sub> +137.6 (c 1.00, CHCl₃).

IR (capillary): 2925 (s), 2839 (m), 1640 (m), 1444 (m), 1366 (w), 1243 (s), 1184 (s), 1093 (m), 1015 (m), 970 (m), 843 (w), 789 (m), 744 (s), 689 cm⁻¹ (m).

1^1H NMR (300 MHz, CDCl₃): δ = 1.24–1.47 (m, 2 H, CH₂), 1.50–1.60 (m, 2 H, CH₂), 1.76–2.05 (m, 2 H, CH₂), 2.28–2.35 (m, 2 H, CH₂), 2.65 (s, 3 H, SCH₃), 5.39–5.44 (m, 1 H, CH), 7.09–7.16 (m, 3 H, ArH), 7.88–7.97 (m, 2 H, ArH).

1^1C NMR (75 MHz, CDCl₃): δ = 22.7 (CH₂), 23.7 (CH₂), 25.1 (CH₂), 32.1 (CH₃), 45.1 (SC(HCl)), 109.9 (CH), 128.6 (CH₉), 129.2 (CH₉), 132.5 (CH₂), 141.0 (C or C₉), 141.4 (C or C₉).

MS (El, 70 eV): m/z (%) = 235 (M⁺, 58), 234 (12), 173 (14), 172 (100), 157 (13), 145 (16), 144 (10), 141 (10), 140 (15), 130 (11), 125 (54), 124 (16).

Anal. Calc'd for C₁₃H₁₄NOS (235.10): C, 64.63; H, 7.28; N, 9.55. Found: C, 66.33; H, 7.37; N, 6.08.

(S)-1-N-[(S)-2-Methylphosphoryl]-(2-methylpropyl)-1-phosphine–Borane Adduct [(S)-Saa-BH₃] and (R)-1-N-[(S)-2-Methylphosphoryl]-(2-methylpropyl)-1-phosphine–Borane Adduct [(R)-Saa-BH₃]

A Schlenk tube (5 mL) with a screw cap was charged with the N-vinyl sulfoximine 3 (500 mg, 2.4 mmol) and PPH₂ (7a; 578 mg, 3.1 mmol). The tube was purged with argon and the mixture was heated for 48 h at 100 °C. After the mixture had cooled to r.t., the mixture was added dropwise to a Schlenk flask. Then borane (6 mL of 1 M in THF, 6.0 mmol) was added dropwise. After the mixture had stirred for 3 h at r.t., it was quenched with the dropwise addition of aq 2 M HCl (3 mL) under ice-bath cooling (formation of H₂ gas!). The mixture was diluted with CH₂Cl₂ (100 mL) and washed successively with aq NaHCO₃ (50 mL) and H₂O (50 mL). The organic layer was dried (MgSO₄) and concentrated under reduced pressure. Purification by flash chromatography (cyclohexane–EtOH, 80:20) gave the phosphine–borane adduct 8aa·BH₃ (885 mg, 87%) as a mixture of diastereomers in a ratio of 1:1 as a viscous colorless oil. Crystallization from cyclohexane–EtOH (92:8) furnished (S)-8aa-BH₃ (230 mg, 23%) as colorless crystals. The mother liquor was concentrated under reduced pressure. Separation by HPLC (Kromasil Si 100; 30 mm × 250 mm; cyclohexane–EtOH, 92:8; 20 mL/min) afforded (R)-8aa-BH₃ (378 mg, 38%) and (S)-8aa-BH₃ (168 mg, 17%) as colorless crystals.

(S)-8aa-BH₃

Mp 95 °C; [α]₀²⁰⁻⁰⁻₃⁹.₃ (c 1.00, CHCl₃); Rf = 0.14 (cyclohexane–EtOH, 4:1).

IR (CHCl₃): 3017 (m), 2974 (w), 2853 (s), 2395 (w), 1459 (w), 1348 (w), 1250 (54), 1249 (s), 1143 (m), 1107 (s), 1097 (s), 950 (w), 874 (s), 837 (w), 747 (s), 695 cm⁻¹ (s).

1^1H NMR (400 MHz, CDCl₃): δ = 0.60–1.00 (m, 3 H, BH₃), 0.85–0.94 (m, 6 H, CH₂), 2.29–2.41 (m, 1 H, CH), 3.05 (s, 3 H, SCH₃), 3.56–3.60 (m, 1 H, CH), 6.96–6.98 (m, 2 H, ArH), 7.24–7.35 (m, 2 H, ArH), 7.37–7.53 (m, 7 H, Ar), 7.65–7.72 (m, 2 H, ArH), 8.15–8.21 (m, 2 H, ArH).

1^1C NMR (100 MHz, CDCl₃): δ = 17.8 (CH₃), 22.9 (d, JCH = 13.7 Hz, CH₃), 30.0 (d, JCH = 7.6 Hz, CH), 45.6 (SC(HCl)), 62.6 (d, JCH = 44.2 Hz, CHNP), 127.8, 127.91, 129.76, 128.05 and 128.15 (5 CH₉), 128.4 (Ca₉), 128.9 (Ca₉), 130.1 (d, JCH = 54.2 Hz, Ca₉), 130.6 (d, JCH = 2.3 Hz, Ca₉), 131.0 (d, JCH = 3.2 Hz, Ca₉), 132.4 (Ca₉), 133.2 (d, JCH = 8.4 Hz, Ca₉), 134.5 (d, JCH = 8.3 Hz, Ca₉), 136.9 (Ca₉).

1^P NMR (162 MHz, CDCl₃): δ = 22.3.

MS (El, 70 eV): m/z (%) = 548 (M⁺–1, 3), 211 (14), 210 (100), 141 (25).


(Major Diastereomer)

H NMR (400 MHz, CDCl₃): δ = 18.0 (d, JCH = 1.8 Hz, CH), 23.2 (d, JCH = 12.6 Hz, CH), 30.6 (d, JCH = 7.8 Hz, CH), 43.7 (SCH₃), 61.0 (d, JCH = 41.3 Hz, CNP), 127.3 (Ca₉), 127.5 (Ca₉), 128.2, 128.4, 128.6 (4 CH₉), 129.0 (Ca₉), 130.7 (d, JCH = 1.8 Hz, CH₉), 131.4 (d, JCH = 1.7 Hz, CH₉), 132.7 (Ca₉), 132.8 (Ca₉), 134.9 (d, JCH = 12.4 Hz, CH₉), 141.57 (Ca₉).

1^P NMR (121 MHz, CDCl₃): δ = 25.7.

MS (El, 70 eV): m/z (%) = 408 (M⁺–1, 3), 211 (14), 210 (100), 141 (25).


1^1H NMR (300 MHz, CDCl₃): δ = 0.60–1.80 (m, 3 H, BH₃), 0.72–0.91 (m, 6 H, CH₂), 2.42–2.44 (m, 4 H, CH and SCH₃), 4.22–4.27 (m, 1 H, CH), 7.43–7.61 (m, 9 H, ArH), 7.67–7.81 (m, 4 H, ArH), 8.14–8.26 (m, 2 H, ArH).

1^1C NMR (75 MHz, CDCl₃): δ = 18.0 (d, JCH = 1.8 Hz, CH), 23.2 (d, JCH = 12.6 Hz, CH), 30.6 (d, JCH = 7.8 Hz, CH), 43.7 (SCH₃), 61.0 (d, JCH = 41.3 Hz, CNP), 127.3 (Ca₉), 127.5 (Ca₉), 128.2, 128.4, 128.6 (4 CH₉), 129.0 (Ca₉), 130.7 (d, JCH = 1.8 Hz, CH₉), 131.4 (d, JCH = 1.7 Hz, CH₉), 132.7 (Ca₉), 132.8 (Ca₉), 134.9 (d, JCH = 12.4 Hz, CH₉), 141.57 (Ca₉).

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Chiral α-(N-Sulfoximido) Phosphines, Phosphine Oxides, and Phosphonates

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IR (KBr): 3058 (w), 2985 (w), 2965 (w), 2906 (m), 1477 (m), 1439 (m), 1340 (w), 1248 (s), 1180 (s), 1142 (s), 1109 (s), 971 (m), 879 (m), 727 (s), 699 cm⁻¹ (s).

1H NMR (300 MHz, CDCl₃): δ = 0.80–0.92 (m, 6 H, CH₃), 2.25–2.38 (m, 1 H, CH₂), 2.46 (s, 3 H, SCH₂), 4.15–4.20 (m, 1 H, CHNH), 7.42–7.60 (m, 9 H, ArH), 7.78–7.92 (m, 4 H, ArH), 8.10–8.22 (m, 2 H, ArH).

13C NMR (75 MHz, CDCl₃): δ = 18.5 (CH₃), 22.5 (d, J₂⁻CH₃ = 12.0 Hz, CH₂), 29.7 (d, J₂⁻CH₂ = 3.0 Hz, CH₃), 44.3 (SCH₂), 60.5 (d, J₂⁻CH₂ = 88.6 Hz, CH₂Ph), 127.1 (CH₂), 128.0, 128.2, 128.3 and 128.5 (4 CH₂), 129.0 (CH₃), 131.0 (C₃H₃), 131.5 and 131.6 (2 CH₂), 132.6 and 132.7 (2 CH₃), 134.0 (d, J₂⁻C₄ = 93.4 Hz, C₄H₄), 142.6 (C₅H₅).

31P NMR (121 MHz, CDCl₃): δ = 32.8.

MS (EI, 70 eV): m/z (%) = 412 (M⁺ + 1, 1), 211 (13), 210 (100), 201 (14), 141 (35).

Found: C, 68.49; H, 6.41; N, 3.02.


1H NMR (300 MHz, CDCl₃): δ = 0.88–1.51 (m, 8 H, CH₂), 1.91–2.03 (m, 3 H, CH₃), 2.08–2.28 (m, 2 H, CH₂), 2.44–2.51 (m, 2 H, CH₂), 3.06 (s, 3 H, CH₃), 3.99 (d, J₁⁻CH₃ = 14.3 Hz, 1 H, CH₃), 4.29 (d, J₁⁻CH₂ = 10.7 Hz, 1 H, ArH), 5.18 (d, J₁⁻CH₃ = 9.6 Hz, 1 H, ArH), 7.13–7.44 (m, 4 H, ArH), 7.40–7.62 (m, 7 H, ArH), 7.96–8.03 (m, 2 H, ArH), 8.27–8.38 (m, 2 H, ArH).

13C NMR (75 MHz, CDCl₃): δ = 21.4 (d, J₂⁻CH₃ = 17.3 Hz, CH₃), 21.4 (CH₂), 25.0 (CH₃), 31.9 (CH₃), 34.0 (CH₃), 48.8 (SCH₂), 63.3 (d, J₂⁻C₄ = 92.2 Hz, C₄), 127.4 (C₅H₅), 127.9, 128.0 and 128.1 (4 CH₂), 128.8 (CH₃), 130.8 (C₆H₅), 131.1 (d, J₂⁻CH₂ = 3.0 Hz, CH₂), 131.4 (d, J₂⁻CH₂ = 2.4 Hz, CH₂), 132.0 (d, J₂⁻CH₂ = 1.8 Hz, CH₂), 132.2 (CH₃), 133.1, 133.2, 133.2 and 133.3 (4 CH₂); 144.2 (C₄H₄).

31P NMR (162 MHz, CDCl₃): δ = 36.7.

MS (EL, 70 eV): m/z (%) = 237 (15), 236 (100), 202 (10), 201 (27), 172 (10), 96 (12), 91 (10).

Found: C, 48.49; H, 7.27; N, 4.56.

1H NMR (300 MHz, CDCl₃): δ = 1.22–2.12 (m, 10 H, CH₃), 3.02 (s, 3 H, SCH₂), 7.14–7.30 (m, 4 H, ArH), 7.40–7.62 (m, 7 H, ArH), 7.96–8.03 (m, 2 H, ArH), 8.27–8.38 (m, 2 H, ArH).

13C NMR (75 MHz, CDCl₃): δ = 21.4 (d, J₂⁻CH₃ = 17.3 Hz, CH₃), 21.4 (CH₂), 25.0 (CH₃), 31.9 (CH₃), 34.0 (CH₃), 48.8 (SCH₂), 63.3 (d, J₂⁻C₄ = 92.2 Hz, C₄), 127.4 (C₅H₅), 127.9, 128.0 and 128.1 (4 CH₂), 128.8 (CH₃), 130.8 (C₆H₅), 131.1 (d, J₂⁻CH₂ = 3.0 Hz, CH₂), 131.4 (d, J₂⁻CH₂ = 2.4 Hz, CH₂), 132.0 (d, J₂⁻CH₂ = 1.8 Hz, CH₂), 132.2 (CH₃), 133.1, 133.2, 133.2 and 133.3 (4 CH₂); 144.2 (C₄H₄).
Vinyl sulfoximine

A Schlenk tube (5 mL) with a screw cap was charged with the solution to 0 °C, it was successively treated with aq NaOH (5 mL, 20%) first for 15 min at 0 °C and then for 2 h at r.t. After cooling the mixture was diluted with CH2Cl2 (20 mL), the organic layer was separated with brine (10 mL), and concentrated under reduced pressure. Purification by flash chromatography (EtOAc) gave the sulfoximine (10) (59 mg, 84%) as a colorless viscous liquid; \[ \delta_{H}^1 = 0.14 (1.00, \text{CHCl}_3); R_f = 0.14 \] (EtOAc).

IR (KBr): 3389 (w), 3017 (w), 2930 (s), 2854 (m), 1146 (m), 1084 (w), 1018 (m), 895 (m), 747 (s), 669 cm–1 (s).

HRMS: m/z calcd for C15H24NO4PS – C2H6O3P: 237.118643; found: 237.118643.

S-N-Cyclohexyl-S-methyl-S-phenylsulfoximine (10)

A Schlenk flask (50 mL) was charged with the solution to 0 °C and HPPb-BH4 (80 mg, 0.40 mmol) was added. After the tube was carefully purged with argon, the mixture was heated for 19 h at 80 °C. Then the mixture was cooled to r.t. to and applied to a silica gel column. Purification by flash chromatography (EtOAc) gave the sulfoximine (10) (59 mg, 84%) as a colorless viscous liquid; \[ \delta_{H}^1 = 0.14 (1.00, \text{CHCl}_3); R_f = 0.14 \] (EtOAc).

IR (CHCl3): 3389 (w), 3017 (w), 2930 (s), 2854 (m), 1146 (m), 1082 (w), 971 (w), 885 (w), 754 (s), 669 cm–1 (s).

HRMS: m/z calcd for C15H24NO4PS – C2H6O3P: 237.118643; found: 237.118643.

A Schlenk tube (5 mL) with a screw cap was charged with the N-vinyl sulfoximine 5 (70 mg, 0.30 mmol) and HPPb-BH4 (80 mg, 0.40 mmol) was added. After the tube was carefully purged with argon, the mixture was heated for 19 h at 80 °C. Then the mixture was cooled to r.t. and applied to a silica gel column. Purification by flash chromatography (EtOAc) gave the sulfoximine (10) (59 mg, 84%) as a colorless viscous liquid; \[ \delta_{H}^1 = 0.14 (1.00, \text{CHCl}_3); R_f = 0.14 \] (EtOAc).

1H NMR (400 MHz, CDCl3): \[ \delta = 1.00–1.55 (m, 6 H, CH_3), 1.60–1.75 (m, 3 H, CH_2), 1.85–1.95 (m, 1 H, CH), 2.82–2.90 (m, 1 H, CH), 3.06 (s, 1 H, SCHO), 7.51–7.64 (m, 3 H, ArH), 7.93–7.97 (m, 2 H, ArH).

13C NMR (100 MHz, CDCl3): \[ \delta = 25.3 (CH_2), 25.5 (CH_2), 25.6 (CH_2), 37.6 (CH_2), 37.6 (CH_2), 45.7 (SCH_2), 54.1 (CH_2), 128.7 (CH_2), 129.1 (CH_2), 132.5 (CH_2), 140.7 (C Ar).

MS (EI, 70 eV): m/z % = 237 (C^14, 17), 194 (50), 142 (10), 141 (100), 130 (37), 125 (29), 114 (10).

HRMS-El: m/z calcd for C_{15}H_{22}NO_5PS (C_{18}H_{20}NO_5S – C_{12}H_{10}OP): 322.184077; found: 322.184045.

Minor Diastereomer

1H NMR (400 MHz, CDCl_3): δ = 0.72 (d, J = 6.9 Hz, 3 H, CH_3), 0.76 (d, J = 6.6 Hz, 3 H, CH_3), 1.00–1.11 (m, 1 H, CH), 1.25–2.01 (m, 12 H, CH_2), 2.95–3.04 (d, J = 6.9 Hz, 3 H, ArH), 7.20–7.32 (m, 5 H, ArH), 7.48–7.65 (m, 6 H, ArH), 7.90–8.10 (m, 2 H, ArH), 8.22–8.34 (m, 2 H, ArH).

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References


(15) Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 662748. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(1223)336033, e-mail: deposit@ccdc.cam.ac.uk, or www.ccdc.cam.ac.uk].


