On the Additions of Lithium Methyl \textit{p}-Tolyl Sulfoxide to \textit{N}-(PMP)Arylaldimines

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Abstract: The results presented in this paper confirm that the stereochemical outcome of the reversible additions of lithium (\textit{R})-methyl \textit{p}-tolyl sulfoxide to \textit{N}-arylidene-\textit{p}-anisidines (\textit{N}-PMP imines) depends on: (a) the reaction conditions used and (b) the electronic properties of the arylidene moiety on the starting imine. In particular, we show that under kinetic control (-70 °C) the additions involving electron-rich \textit{N}-arylidene groups occur with very high stereocontrol in favor of (2\textit{S},\textit{R}S)-\textit{β}-aminosulfoxides with decreasing the number of fluorine atoms on the \textit{N}-arylidene groups [2]. This observation, supported by previous literature reports [3], led us to

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Introduction

Additions of chiral lithium sulfoxides to imines represent a powerful tool in asymmetric synthesis [1]. We have recently reported that kinetically controlled additions (-70 °C) of lithium methyl \textit{p}-tolyl sulfoxide (2) (Scheme 1) to \textit{N}-PMP(amines) (PMP = \textit{p}-methoxyphenyl) derived from a series of aromatic aldehydes having a variable degree of fluorination occur with a progressively higher stereocontrol in favor of (2\textit{S},\textit{R}S)-\textit{β}-aminosulfoxides 3 with decreasing the number of fluorine atoms on the \textit{N}-arylidene groups [2]. This observation, supported by previous literature reports [3], led us to
propose that the presence of electron-rich N-arylidene groups was responsible for the very high kinetic stereocontrol in favor of the \((2S,R_S)\)-diastereomers, whereas an electron-deficient group should favor the opposite stereochemical outcome. In this paper we present a complementary part of work, in which the additions of \((R)-2\) are extended to a number of variously substituted \(N\-arylidene-p\-anisidines \(1\).

**Results and Discussion**

The starting \(N\)-(PMP)arylimines \(1a-g\) were prepared in good yields through acid catalyzed condensation of the corresponding aldehyde and \(p\-anisidine\) (Scheme 1) [2]. All imines \(1a-g\) were obtained as geometrically \((E)\)-homogeneous compounds, according to their \(^1\)H-NMR spectra. First, we studied the stereochemical outcome of reactions between lithium sulfoxide \((R)-2\) and \(p\-methoxy-imine \(1a\) (Table 1).

\[
\begin{align*}
\text{Ar} & \quad \text{O} \\
\text{H} & \quad \text{Ar} \quad \text{N} \\
\text{H} & \quad \text{PMP} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{N-}\text{PMP}, \text{C}_6\text{H}_6 & \quad \text{DOWEX-50W} \\
\text{Dean-Stark} & \quad \text{Li} \quad \text{Tol-S} \\
\end{align*}
\]

\[
\begin{align*}
\text{Ar} & \quad \text{O} \\
\text{H} & \quad \text{Ar} \quad \text{N} \\
\text{PMP} & \quad \text{NH-PMP} \\
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{H} \\
(2S,R_S) & \quad \text{Ar} \\
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{H} \\
(2R,R_S) & \quad \text{Ar} \\
\end{align*}
\]

**Scheme 1.** Additions carried out at \(-70^\circ\text{C}\) under kinetic control.

We have already demonstrated [2] that the additions of \((R)-2\) to \(N\)-(PMP)arylimines are reversible processes and that the diastereomeric products like \(3\) and \(4\) readily equilibrate at 0 \(^\circ\text{C}\). Thus, in order to ensure kinetic control, all the reactions in Table 1 were carried out at \(-70\ \text{°C}\). The only exception can be found in entry 1, because imine \(1a\) did not undergo addition of \((R)-2\) at that temperature (entry 2). However, the addition proceeded smoothly within \(-40\ \text{and} -50\ \text{°C}\), providing the diastereomer \(3a\) with excellent stereoselectively, evidently under kinetic control. Next we examined the imine \(1b\) derived from 3,4-(methylenedioxy)benzaldehyde (entry 3). Due to the presence of an additional alkoxy substituent in \(meta\)-position this imine was expected to be more electrophilic than \(1a\). In fact, addition of \((R)-2\) took place even at \(-70\ \text{°C}\), although rather slowly. After 60 min, 34\% yield was obtained, and the d.r. \(3:4\) decreased in comparison to \(1a\). Imine \(1c\) derived from \(p\-CF_3\-benzaldehyde\) featured a further decrease of stereoselectivity (entry 4) and, as expected, increased reactivity, the addition being nearly complete after 30 min. With imine \(1d\) (entry 5), obtained from 2-naphthaldehyde both isolated yield and the observed diastereocontrol were slightly lower than that of \(1c\). A further decrease of stereoselectivity was observed with the \(p\-nitrobenzaldehyde\)-derived imine \(1e\) (entry 6) and \((2,6\-difluorophenyl)imine 1f, which provided the lowest \(3:4\) d.r. (ca. 3:1, entry 7). Finally, no reaction was achieved with imine \(1g\) derived from mesitaldehyde (entry 8), as a likely result of a strong steric hindrance.
The stereochemical assignments were carried out as follows. β-Sulfinyl-amines 3 and 4a,e are known compounds [3b], whereas the stereochemistry of 3f was determined through X-ray diffraction of a suitable single crystal (Figure 1) [4]. In the remaining three cases the stereochemistry was confidentially assigned exploiting some unambiguous chemical-physical similarities existing among the major diastereomers 3 in comparison with the minor ones 4. In particular, in the ¹H-NMR spectra of 4 the methylene signals invariably appeared as well defined ABX systems with eight lines and large ∆ν between the diastereotopic protons (see Spectral Data section). In contrast, the corresponding signals of the major diastereomers 3 showed a contracted pattern with smaller ∆ν. In addition, all the diastereomers 3 displayed lower tᵣ and higher Rᵣ than diastereomers 4 by HPLC and TLC analyses, respectively.

The data summarized in Table 1 confirm [2] that an increase of electron-deficiency of the benzylidene aromatic group of imines 1 brings about a decrease of kinetic selectivity (namely, the d.r. 3:4). This means that electron-releasing substituents, which enhance the ring electron density, produce a much better stereocletion than electron-withdrawing groups. Such a picture might be rationalized by supposing two possible transition states A (leading to the diastereomers 3) and B (leading to 4) (Figure

| Entry | Ar | Time (min) | Yield (%)<sup>a</sup> | (2S,R₅)-3 (%)<sup>b</sup> | (2R,R₅)-4 (%)<sup>b</sup> |
|-------|----|------------|-----------------------|---------------------------|---------------------------|
| 1<sup>c</sup> (a) | ![Ar structure](image) | 80 | 91 | 95.0 | 5.0 |
| 2 (a) | ![Ar structure](image) | 80 | < 2 | Not determined | Not determined |
| 3 (b) | ![Ar structure](image) | 60 | 34 | 91.7 | 8.3 |
| 4 (c) | ![Ar structure](image) | 30 | 88 | 83.8 | 16.2 |
| 5 (d) | ![Ar structure](image) | 30 | 76 | 81.6 | 18.4 |
| 6 (e) | ![Ar structure](image) | 40 | 83 | 76.5 | 23.5 |
| 7 (f) | ![Ar structure](image) | 30 | 86 | 73.7 | 26.3 |
| 8 (g) | ![Ar structure](image) | 90 | < 2 | Not determined | Not determined |

Key: <sup>a</sup> Isolated yields. <sup>b</sup> Determined by ¹H-NMR and HPLC. <sup>c</sup> Carried out at –50/-40 °C.
2). The former (chair-like) could be mainly operating in the case of imines having an electron-rich benzylidene ring, whereas the latter (boat-like) becomes competitive with electron-poor rings.

**Figure 1.** ORTEP view of (2S,R_S)-3f showing the atomic labeling scheme. Only non hydrogen atoms are shown, using 30% thermal ellipsoids.

In fact, in the case of electron-rich Ar, TS-B experiences a repulsive steric flagpole interaction with the sulfinyl oxygen, that is absent in TS-A, where in addition the unfavorable steric interactions are minimized. However, in the case of electron-poor Ar an attractive π-p interaction with the sulfinyl oxygen may be invoked to stabilize TS-B lowering its energy, as well as the 3:4 ratio [5].

![Diagram](image-url)

**Figure 2.**
Conclusions

The data coming out from this investigation confirm the validity of the previously proposed picture [2], which appears to be valid beyond the realm of fluorinated compounds. Thus, a general and predictive rationale for the highly synthetically useful additions of chiral lithium sulfoxides to arylimines is now available.

Experimental

General.

For general experimental details see Ref. 2. Coupling constants (J) are reported in Hertz. HPLC analyses were performed using a LiChrosorb Si60 prepacked column. Retention times (t_r) are expressed in minutes.

Representative procedure for the additions of (R)-2 to 1. To a solution of (R)-methyl-p-tolyl sulfoxide (1 mmol) in dry THF (2.7 mL) cooled to –70 °C, a 1.5 M solution of LDA⋅THF in cyclohexane was added dropwise. After 15 min at the same temperature, a suspension of imine 1a (1.2 mmol) in 2.3 mL of dry THF was added dropwise. The temperature was allowed to raise up to –50 °C, then maintained in the range –50/-40 °C, and the mixture was magnetically stirred for 80 min. The reaction was quenched at the same temperature with a saturated NH₄Cl solution, and the mixture was allowed to warm up to r.t.. The phases were separated, and the aqueous phase was extracted three times with AcOEt. The collected organic phases were dried over anhydrous Na₂SO₄, filtered, then the solvent was removed in vacuo. Purification by flash chromatography (Hex/AcOEt 7:3) afforded the diastereomerically pure products 3a and 4a in overall 91% yield.

Spectral Data

3a: R_f (Hex/AcOEt 6:4) 0.27; t_r 11.49 (Hex/AcOEt 1:1, 1 mL/min); [α]_D^{20} +179.7 (CHCl₃, c 1.22); m.p. (AcOEt) 180.5-181.5 °C; ¹H-NMR (CDCl₃) δ 7.49 (2H, d, J = 8.2), 7.27 (4H, m), 6.82 (2H, d, J = 8.6), 6.68 (2H, d, J = 9.0), 6.58 (2H, d, J = 9.0), 4.70 (1H, dd, J = 3.4 and 9.4), 3.76 (3H, s), 3.70 (3H, s), 3.30 (1H, dd, J = 9.4 and 13.9), 3.11 (1H, dd, J = 3.4 and 13.9), 2.40 (3H, s); ¹³C-NMR (CDCl₃) δ 159.1, 152.6, 141.7, 140.2, 139.9, 133.0, 130.0, 127.6, 124.0, 115.7, 114.6, 114.3, 63.9, 55.2, 55.0, 21.4; MS (EI, 70 eV) m/Z (%) 395 (M⁺, 63), 255 (88), 242 (39), 134 (92), 122 (100), 91 (81); FT IR (cm⁻¹) 3449 (br), 1510, 1241, 1035, 808.

4a: R_f (Hex/AcOEt 6:4) 0.21; t_r 15.64 (Hex/AcOEt 1:1, 1 mL/min); [α]_D^{20} +64.2 (CHCl₃, c 0.47); ¹H-NMR (CDCl₃) δ 7.52 (2H, d, J = 7.9), 7.30 (4H, m), 6.84 (2H, d, J = 8.6), 6.68 (2H, d, J = 9.0), 6.54 (2H, d, J = 9.0), 5.28 (1H, s), 4.74 (1H, dd, J = 5.2 and 9.4), 3.76 (3H, s), 3.69 (3H, s), 3.32 (1H, dd, J = 9.4 and 13.5), 2.94 (1H, dd, J = 5.2 and 13.5), 2.40 (3H, s).
3b: \( R_f \) (Hex/AcOEt 6:4) 0.29; \( t_r \) 9.98 (Hex/AcOEt 1:1, 1 mL/min); \( [\alpha]_D^{20} +168.2 \) (CHCl₃, c 1.18); m.p. (MeOH) 182-184 °C; \(^1\)H-NMR (CDCl₃) \( \delta \) 7.49 (2H, d, \( J = 8.1 \)), 7.30 (2H, d, \( J = 8.1 \)), 6.85 (1H, d, \( J = 1.5 \)), 6.77 (1H, d, \( J = 1.5 \)), 6.70 (3H, m), 6.60 (2H, d, \( J = 8.9 \)), 5.91 (2H, m), 4.64 (1H, dd, \( J = 2.7 \) and 8.9), 3.70 (3H, s), 3.31 (1H, m), 3.08 (1H, dd, \( J = 3.5 \) and 13.9), 2.41 (3H, s); \(^{13}\)C-NMR (CDCl₃) \( \delta \) 141.7, 139.7, 130.1, 124.0, 119.7, 115.6, 114.7, 108.6, 106.8, 101.1, 63.7, 55.7, 55.4, 21.4; MS (EI, 70 eV) \( m/Z \) (%) 409 (M⁺, 10), 269 (100), 256 (66), 148 (65), 122 (77), 91 (8); FT IR (cm⁻¹) 3448 (br), 3307, 1510, 1239, 1035, 817.

3c: \( R_f \) (Hex/AcOEt 6:4) 0.39; \( t_r \) 8.07 (Hex/AcOEt 1:1, 1 mL/min); \( [\alpha]_D^{20} +160.8 \) (CHCl₃, c 1.04); m.p. (MeOH) 184-185 °C; \(^1\)H-NMR (CDCl₃) \( \delta \) 7.48 (6H, m), 7.27 (2H, d, \( J = 8.1 \)), 6.69 (2H, d, \( J = 8.5 \)), 6.59 (2H, d, \( J = 8.5 \)), 4.82 (1H, dd, \( J = 3.5 \) and 8.9), 3.70 (3H, s), 3.38 (1H, dd, \( J = 8.9 \) and 13.5), 3.14 (1H, dd, \( J = 3.5 \) and 13.5), 2.39 (3H, s); \(^{13}\)C NMR (CDCl₃) \( \delta \) 152.6, 145.7, 141.9, 140.1, 139.4, 136.6, 126.8, 125.9, 124.0, 115.3, 114.7, 63.4, 55.6, 55.1, 21.4; 19F NMR (CDCl₃) \( \delta \) -63.6 (s); MS (EI, 70 eV) \( m/Z \) (%) 433 (M⁺, 12), 293 (100), 280 (30), 172 (11), 122 (51); FT IR (cm⁻¹) 3629, 3020, 2977, 2901, 2829, 1542, 1511, 1396, 1243, 1014, 825.

4b: \( R_f \) (Hex/AcOEt 6:4) 0.23; \( t_r \) 13.80 (Hex/AcOEt 1:1, 1 mL/min); \(^1\)H-NMR (CDCl₃) \( \delta \) 7.53 (2H, m), 7.30 (2H, d, \( J = 78.1 \)), 6.90 (4H, m), 6.71 (4H, m), 5.91 (2H, m), 4.70 (1H, dd, \( J = 5.4 \) and 9.3), 3.70 (3H, s), 3.35 (1H, dd, \( J = 9.3 \) and 13.5), 2.95 (1H, dd, \( J = 5.4 \) and 13.5), 2.40 (3H, s).

3d: \( R_f \) (Hex/AcOEt 6:4) 0.39; \( t_r \) 8.49 (Hex/AcOEt 1:1, 1 mL/min); \( [\alpha]_D^{20} +111.1 \) (CHCl₃, c 1.04); m.p. (i-PrOH) 220-225 °C; \(^1\)H-NMR (CDCl₃) \( \delta \) 7.78 (5H, m), 7.44 (5H, m), 7.32 (1H, d, \( J = 8.1 \)), 7.21 (2H, d, \( J = 7.3 \)), 6.65 (2H, d, \( J = 8.9 \)), 4.89 (1H, dd, \( J = 4.2 \) and 7.3), 3.67 (3H, s), 3.28 (2H, m), 2.33 (3H, s); MS (EI, 70 eV) \( m/Z \) (%) 415 (M⁺, 3), 275 (75), 260 (25), 154 (42), 122 (100), 91 (33); FT IR (cm⁻¹) 3304, 3052, 2939, 2829, 1542, 1511, 1396, 1243, 1014, 825.

4d: \( R_f \) (Hex/AcOEt 6:4) 0.33; \( t_r \) 10.94 (Hex/AcOEt 1:1, 1 mL/min); \(^1\)H-NMR (CDCl₃) \( \delta \) 7.76 (5H, m), 7.51 (5H, m), 7.29 (2H, d, \( J = 8.1 \)), 6.63 (3H, m), 4.94 (1H, m), 3.69 (3H, s), 3.52 (1H, m), 3.08 (1H, m), 2.41 (3H, s).

3e: \( R_f \) (Hex/AcOEt 6:4) 0.25; \( t_r \) 12.25 (Hex/AcOEt 1:1, 1 mL/min); \( [\alpha]_D^{20} +133.4 \) (CHCl₃, c 0.68); m.p. (MeOH): 191-193 °C; \(^1\)H-NMR (CDCl₃) \( \delta \) 8.11 (2H, d, \( J = 8.3 \)), 7.53 (2H, d, \( J = 8.3 \)), 7.44 (2H, d, \( J = 7.9 \)), 7.30 (2H, d, \( J = 9.4 \)), 6.68 (4H, m), 4.86 (1H, br m), 3.71 (3H, s), 3.48 (1H, br m), 3.15 (1H, br m), 2.40 (3H, s); \(^{13}\)C-NMR (CDCl₃) \( \delta \) 149.3, 142.1, 139.9, 139.2, 130.2, 127.4, 124.3, 115.3,
114.8, 62.8, 55.6, 55.2, 29.7; MS (EI, 70 eV) m/z (%) 410 (M⁺, 12), 270 (100), 255 (41), 209 (20), 139 (30), 122 (54), 91 (39); FT IR (cm⁻¹) 3307, 2923, 1520, 1348, 1238, 1036, 1014, 809.

4e: Rf (Hex/AcOEt 6:4) 0.19; t, 16.11 (Hex/AcOEt 1:1, 1 mL/min); [α]D 20 +44.0 (CHCl₃, c 0.47);
\[^1^H-NMR\] (CDCl₃) δ 8.17 (2H, d, J = 8.3), 7.64 (2H, d, J = 8.7), 7.53 (2H, d, J = 8.3), 7.32 (2H, d, J = 7.9), 6.68 (2H, d, J = 8.7), 6.54 (2H, d, J = 8.7), 4.91 (1H, m), 3.70 (3H, s), 3.38 (1H, m), 3.04 (1H, m), 2.41 (3H, s).

3f: Rf (Hex/AcOEt 6:4) 0.25; t, 7.53 (Hex/AcOEt 1:1, 1 mL/min); [α]D 20 +285.0 (CHCl₃, c 0.77);
m.p. (MeOH) 210-212 °C; \[^1^H-NMR\] (CDCl₃) δ 7.56 (2H, d, J = 8.3), 7.29 (2H, d, J = 7.9), 7.14 (1H, m), 6.76 (6H, m), 4.42 (1H, dd, J = 4.8 and 9.9), 3.70 (3H, s), 3.41 (1H, dd, J = 9.9 and 13.0), 3.19 (1H, dd, J = 4.8 and 13.0), 2.39 (3H, s); \[^1^3^C-NMR\] (CDCl₃) δ 163.1, 159.2, 154.0, 141.6, 140.7, 130.0, 124.1, 117.1, 114.7, 112.0, 111.7, 62.1, 55.6, 46.0, 21.4; \[^1^9^F-NMR\] (CDCl₃) δ -115.5 (s); MS (EI, 70 eV) m/z (%) 401 (M⁺, 6), 261 (100), 248 (19), 139 (82), 122 (99); FT IR (cm⁻¹) 3446 (br), 1510, 1241, 1035, 808.

4f: Rf (Hex/AcOEt 6:4) 0.15; t, 14.07 (Hex/AcOEt 1:1, 1 mL/min); [α]D 20 +285.0 (CHCl₃, c 0.77);
m.p. (MeOH) 210-212 °C; \[^1^H-NMR\] (CDCl₃) δ 7.55 (2H, m), 7.29 (2H, m), 7.15 (1H, m), 6.71 (6H, m), 5.43 (1H, m), 3.68 (3H, s), 3.36 (1H, m), 3.13 (1H, m), 2.41 (3H, s); \[^1^9^F-NMR\] (CDCl₃) δ -116.1 (s).

Crystal data for 3f. C₄₄H₄₂F₄N₂O₄S₂, f.w. 802.92, Triclinic, space group P1, a = 5.641(1) Å, b = 11.685(2) Å, c = 15.701(3) Å, α = 92.94(1)°, β = 98.34(1)°, γ = 101.75(1)°, V = 999.0(3) Å³, Z = 1, Dc = 1.335 g/cm³, μ = 1.749 mm⁻¹, F(000) = 420.

Data collection. X-ray diffraction data were collected from a colourless prismatic crystal of (2S,RS)-3f (size 0.2 x 0.2 x 0.1), with graphite monochromated Cu-Kα radiation (λ = 1.5418 Å) on a Siemens P4 diffractometer (θ-2θ scan technique). 6624 Reflections were collected (2.85<θ<67.99; +h,+k,+l and –h,-k,-l), 6624 unique; 3 standard reflections, measured every 100 reflections, showed no significant decay. Data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied.

Structure analysis and refinement. The structure was solved by direct methods using SIR92 [6] and refined by full-matrix least squares on F2 using SHELXL97 [7]. Non hydrogen atoms were refined anisotropically. All hydrogen atoms have been included at calculated positions and refined with group temperature factors. Final values of the residual R1 for reflections with I>2σ and for all reflections were respectively 0.050 and 0.061. The highest peak and hole in the final difference-Fourier map were 0.263 and -0.291 eÅ³. The refined value of Flack’s parameter [8] was –0.004(19).
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4. Selected molecular dimensions of (2S,R$_5$)-3f are reported in Table 2. Bond lengths and angles fall all in the expected range (Allen, F.M.; Kennard, O; Watson, D.G.; Brammer, L.; Orpen, A.G.; Taylor, R.J.; *J. Chem. Soc., Perkin Trans. 2*, 1987, S1-S19). The two molecules in the unit cell are configurationally identical but not related by any symmetry operation. The angles found on atoms N1 and N2 suggest a planar arrangement, which is common for aromatic amines. The high thermal parameters and the corresponding elongated thermal ellipsoids of atom C(3) and C(6) suggest disorder involving these atoms. In the crystal, the molecules of (2S,R$_5$)-3f pack arranging the aromatic rings of adjacent molecules with a favourable herringbone interaction geometry.

| Bond lengths (Å)       | Bond angles (°)       |
|------------------------|----------------------|
| S(1)−O(1)              | 1.501(3)             |
| S(2)−O(3)              | 1.479(4)             |
| N(1)−C(31)             | 1.376(5)             |
| N(1)−C(2)              | 1.453(5)             |
| N(2)−C(61)             | 1.390(5)             |
| N(2)−C(5)              | 1.442(5)             |
| C(52)−F(4)             | 1.345(6)             |
| C(56)−F(3)             | 1.358(5)             |
| C(26)−F(2)             | 1.356(5)             |
| C(22)−F(1)             | 1.351(6)             |
| S(1)−O(1)−C(11)−C(1)   | 107.3(2)             |
| S(2)−O(3)−C(41)−C(4)   | 108.1(2)             |
| N(1)−C(31)−C(11)−C(1)  | 96.69(17)            |
| N(2)−C(61)−C(41)−C(4)  | 97.08(18)            |

**Table 2**
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Sample Availability: Available from the authors.

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