Pergamon

Tetrahedron: Asymmetry Vol. 6, No. 8, pp. 2045-2052, 1995
Elsevier Science Ltd
Printed in Great Britain
0957-4166/95 $9.50+0.00

0957-4166(95)00266-9

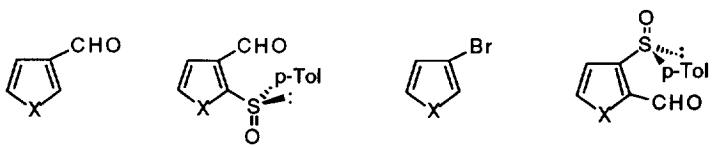
Preparation of optically active 2-(or 3)(p-tolylsulfinyl)-3(or 2)furyl- or thienylcarboxaldehydes

Laurent D. GIRODIER, Christian S. MAIGNAN, Francis P. ROUESSAC

Laboratoire de Synthèse Organique (URA 482), Université du Maine,
Avenue Olivier Messiaen, BP 535, F-72017 Le Mans, France, e-mail: lso@lola.univ-lemans.fr

Abstract: The preparation of the four enantiomerically pure title compounds is described by reaction of (l)-(-)-Ss-menthyl-p-toluenesulfinate on furan or thiophene precursors.

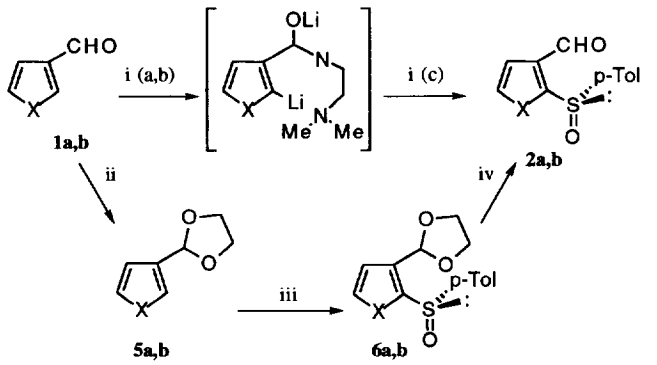
In a previous publication[1] we have reported an approach to α-alkyl-2- and 3-furylcarbinols by an intramolecular diastereoselective reaction induced by optically active precursor aldehydes **2a** and **4a**. Our procedure appeared different from other reports that essentially focused on the choice of optically active amino alcohols[2]. The chiral sulfoxide group of known configuration was used for this purpose[3]. Here we would like to report some details of our studies directed toward the enantioselective preparation of aldehydes **2** and **4** including thiophene derivatives.



1a/b **2a,b** **3a/b** **4a,b**

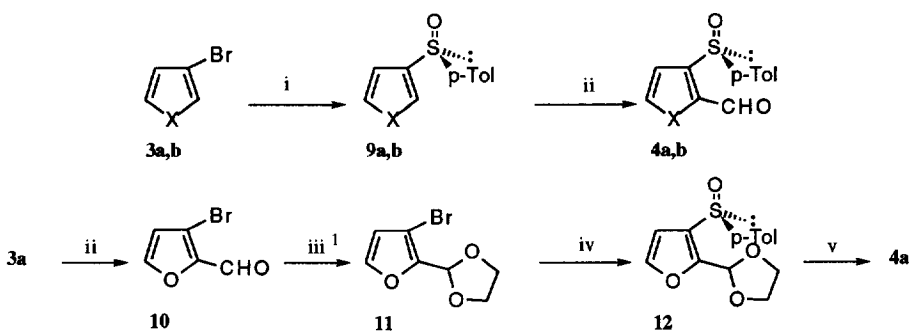
for a, X = O
for b, X = S

In the early stage, we tried to get aldehyde **2a** through unprotected **1a** (scheme 1, **1a** → i → **2a**) by application of a method developed by Comins[4]. When **1a** was treated with lithiated N,N,N'-trimethylethylenediamine (LTMDA) an α-aminoalkoxide was formed which was metallated *in situ* and reacted with (-)-Ss-menthyl-p-toluenesulfinate to give **2a** on workup, in 36% yield only (table 1, entry 2). This reaction gave also by-products difficult to separate and was then forsaken.



Scheme 1 : i, a) LiTMDA, THF b) BuLi c) (-)-(Ss)-menthyl-p-toluenesulfinate, ii, 1,2-ethanediol, PTSA, benzene iii, a) BuLi, THF, b) $MgBr_2.Et_2O$, Et_2O c) (-)-(Ss)-menthyl-p-toluenesulfinate, iv, acetone, H_2O, PPTS.

So, we explored an alternative (scheme 1, ii, iii, iv). The reaction of **1a/b** with ethyleneglycol in the presence of PTSA gave **5a/b**. In the next step ortho-directing effect of the dioxolane group[5] gave only the 2-lithiated derivative which was transformed into the Grignard reagent with anhydrous magnesium dibromide etherate before being reacted with (-)-Ss-menthyl-p-toluenesulfinate (table 1, entries 3 and 4). Finally **6a/b** was submitted to a transacetalisation reaction in the presence of acetone to give aldehyde **2a/b** (table 2, entries 10 and 12)[6]. The preparation of aldehydes **4a/b** from bromide **3a/b** is described in scheme 2.



Scheme 2 : i, a) BuLi, THF, b) $MgBr_2.Et_2O$, Et_2O c) (-)-(Ss)-menthyl-p-toluenesulfinate, ii, a) LDA, THF b) DMF, iii, 1,2-ethanediol, PTSA, benzene, iv, a) BuLi, THF, b) $MgBr_2.Et_2O$, Et_2O c) (-)-(Ss)-menthyl-p-toluenesulfinate, v, acetone, H_2O, PPTS.

Aldehydes **4a/b** were prepared from commercially available 3-bromofuran **3a** or 3-bromothiophene **3b**. Two sequences were used. The bromide (**3a** or **3b**) was reacted with BuLi, then converted into sulfoxide **9a** or **9b** in the presence of anhydrous $MgBr_2$,Et_2O in ether (see table 1, entries 5 and 6) followed by formylation to **4a** (or **4b**), (table 3, entries 13 and 14) The isolated yields were 71% for **4a** from **3a** and 83% for **4b** from **3b**. In an alternative 4-step reaction sequence performed to obtain **4a**, **3a** was formylated to **10**, then protected to **11** and transformed to the sulfoxide **12** (table 1, entry 7). The dioxolan of **12** was removed by PPTS (table 2, entry 11). The enantiomeric excesses of optically active sulfoxides were confirmed by NMR shift reagent [$Eu(hfc)_3$] and by HPLC with a DAICEL-Chiracel-OB column.

Table 1 : Formation of enantiomerically pure furyl and thienyl p-tolyl sufoxides

Entry	Substr.	Reaction conditions : Temperature T (°C) and Reaction time t (min)						Product	Yield (%)	$[\alpha]_D^{24}$
		Lithiation		Magnesium[d]		Reaction[e]				
		T1	t1	T2	t2	T3	t3			
1	**3a**[b]	-15	25	-15	15	-15	60	**7**	54	- 92
2	**1a**[c]	-78	120	x	x	-78[f]	90	**2a**	36[g]	+47[g]
3	**5a**[a]	-20	20	-20	20	-20	60	**6a**	86	- 52
4	**5b**[a]	-20	30	-30	30	-20	45	**6b**	57	- 32
5	**3a**[a]	-78	30	-40	15	-40	45	**9a**	94	+31
6	**3b**[a]	-78	20	-30	10	-30	45	**9b**	90	+40
7	**11**[a]	-78	15	-50	10	-35	45	**12**	44	- 152
8	**13a**[a,h]	-20	30	-20	15	-20	60	**14a**	96	+106
9	**13b**[a,h]	-20	20	-20	15	-20	30	**14b**	74	+110

a : BuLi/THF, b : LDA/THF, c : 1) LiTMDA/THF 2) BuLi, d : $MgBr_2.Et_2O/Et_2O$, e : (-)-(Ss)-menthyl-p-toluenesulfinate/THF, f : The reaction mixture was warmed up to -25°C before treatment, g : The presence of by-products explains the low yield and the value of $[\alpha]_D$ (+55 for pure compound), h : see reference 7.

Table 2 : Acetal cleavage of 1,3-dioxolan compounds

Entry	Substrate	Reaction[a] time t (h)	Product	Yield (%)	$[\alpha]_D^{24}$
10	**6a**	120	**2a**	80	+55
11	**12**	48	**4a**	73	- 209
12	**6b**	56	**2b**	93	- 129

a : acetone/water/PPTS/reflux.

Table 3 : Introduction of carboxaldehyde group

Entry	Substrate	Temperature T (°C) and Reaction time t (min)			Product	Yield (%)	$[\alpha]_D^{24}$
		Lithiation[a]		Reaction[b]			
		T1	t1	T2			
13	**9a**	-30 → 0	60	-78→ -30	**4a**	75	- 209
14	**9b**	-30	30	-78→ -30	**4b**	92	- 200
15	**3a**	-30 → 0	30	-78→ -30	**10**	66	-

a : LDA/THF, b : DMF.

Further investigations are under way dealing with new applications of the furyl and thienyl sulfoxides described in this paper.

EXPERIMENTAL SECTION

General Methods

Melting points were determined on a Reichert apparatus and are uncorrected. Optical rotations were taken on a Perkin Elmer 241 polarimeter. IR spectra were recorded on a Nicolet 5DX or Genesis (Mattson) spectrometers. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectra were obtained for solutions in $CDCl_3$ on a Bruker AC400 spectrometer. Chemical shifts are reported in ppm (δ) relative to Me_4Si as internal standard, coupling contants (J) are given in Hz with the following abbreviations for splitting patterns : s singlet, d doublet, q quadruplet, m multiplet, b broad. Elemental analyses were performed by the Service de Microanalyse du CNRS (Gif sur Yvette).

All moisture-sensitive reactions were carried out under a nitrogen atmosphere. THF and diethyl ether were distilled from sodium/benzophenoneketyl immediately prior to use. *Standard aqueous work up* involved addition of aqueous ammonium chloride and extraction with CH_2Cl_2, the extracts were dried over $MgSO_4$ and evaporated under reduced presure. Column Chromatography was carried out on 230-400 Mesh SDS silica gel 60 ACC.

General Procedures :

Procedure A : Introduction of p-tolylsulfinyl group : To a stirred solution of butyllithium (11.2 mmol, 7 mL of a 1.6 M solution in hexane) in anhydrous THF (20 mL) was added dropwise at **T1** °C (cf Table 1) the heterocycle (10 mmol). After **t1** min. (cf Table 1) the reaction mixture was allowed to reach **T2** °C (cf Table 1) then a mixture of magnesium bromide etherate* in dry diethyl ether was added with vigorous stirring. During this addition (taking about 3 min.) the temperature was kept at **T2** ± 5 °C. After **t2** min. (cf Table 1) of stirring, a solution of (-)-(Ss)-menthyl-p-toluenesulfinate (10 mmol, 2.94 g) in anhydrous THF (20 mL) was added dropwise over 20 min and the temperature was maintained to **T3** °C (cf Table 1) for an additionnal period of **t3** min.(cf Table 1). Then *standard aqueous work up* was applied.

**Magnesium bromide etherate* ($MgBr_2.Et_2O$)[8] : To a mixture of magnesium (33 mmol, 0.8 g) and diethyl ether was added dropwise over 15 minutes 1,2-dibromoethane (15 mmol, 1.3 mL). Then 5 mL of diethyl ether was added. The resulting mixture was stirred vigorously and heated to reflux for 15 minutes. After cooling the grey underlayer of $MgBr_2.Et_2O$ and the supernatant ether were decanted from the excess of magnesium and added to the lithium derivative.

Procedure B : 1,3-dioxolan cleavage : To a solution of the acetal (2.5 mmol) in acetone (25 mL) was added water (3 drops) and pyridinium tosylate (0.85 mmol, 215 mg). The reaction mixture was refluxed for **t** hours (cf Table 2). Then excess of solvent was removed under vacuo, diluted in diethyl ether, washed successively with saturated $NaHCO_3$ and saturatedbrine. The organic layer was dried over $MgSO_4$ and diethyl ether removed under vacuo to give the pure aldehyde.

Procedure C : Introduction of carboxaldehyde group : A solution of butyllithium (11.2 mmol, 7 mL of a 1.6 M solution in hexane) was added dropwise at -20 °C to a stirred solution of diisopropylamine (12 mmol, 1.7 mL) in dry THF (20 mL). After 30 min. a solution of the heterocycle (10 mmol) in dry THF (10 mL) was added dropwise over 15 min. The reaction mixture was maintained at **T1**°C (cf Table 2) for **t1** min. (cf Table 3) then cooled at -78°C. Dimethylformamide (15 mmol, 1.1 mL) was added in one go, the cooling bath was removed and when the temperature had risen to -30°C the standard work up was applied.

(Ss)-2-(p-tolylsulfinyl)-3-formylfurane **2a** : This compound was prepared by 2 methods :

- (cf Table 1, entry 2). To a stirred solution of N,N,N'-trimethylethylenediamine (6 mmol, 0.76 mL) in dry THF (10 mL) was added butyllithium (5.4 mmol, 3.4 mL of a 1.6 M solution in hexane) at -78°C. After 20 min., freshly distilled 3-furfural (5 mmol, 0.43 mL) was added dropwise. The reaction mixture was stirred at -78°C for 20 min. and butyllithium (5.4 mmol, 3.4 mL of a 1.6 M solution in hexane) was added dropwise. After 2 hours of stirring, a solution of (-)-(Ss)-menthyl-p-toluenesulfinate (5 mmol, 1.47 g) in dry THF (10 mL) was added dropwise over 20 min, then the temperature was slowly warmed up to -25 °C over an additional period of 90 min. and *standard aqueous work up* was then applied. The crude product was purified by silica gel chromatography (eluent cyclohexane/ethyl acetate 90/10) to give **2a** (420 mg). Yield : 36%.

- Procedure **B** (cf Table 2, entry 10). The crude product was purified by silica gel chromatography (eluent cyclohexane/ethyl acetate 90/10). Yield : 80%. Pale yellow crystals ; m.p. = 91-92.5 °C (ether/pentane). $[\alpha]_D^{24}$ = +55 (c = 1.6 ; acetone). IR (KBr) : 3113 ; 1684 ; 1485 ; 1161 ; 1117 ; 1081 ; 1050 ; 1024 ; 808 ; 786 ; 753 cm^{-1}. ^{1}H-NMR : 2.43 (s, 3H, CH_3Ar) ; 6.85 (d, J_{4-5} = 1.8 Hz, 1H , H_4) ; 7.37-7.67 (q, AA'BB' system, J = 8.1 Hz, 4H, HAr) ; 7.51 (d, J_{5-4} = 1.8 Hz, 1H, H_5) ; 10.42 (s, 1H, CHO). ^{13}C-NMR : 21.5 (q, C_{10}) ; 109.3 (d, C_4) ; 125.1 (d, C_7 and $C_{7'}$) ; 129.7 (C_3) ; 130.4 (d, C_8 and $C_{8'}$) ; 137.8 (s, C_6) ; 143.0 (s, C_9) ; 146.7 (d, C_5) ; 158.9 (s, C_2) ; 183.9 (d, CHO). Analysis : Calculated for $C_{12}H_{10}O_3S$: C 61.52 H 4.30 S 13.68 ; Found C 61.35 H 4.60 S 13.53.

(Ss)-3-(p-tolylsulfinyl)-2-formylfurane **4a** : This compound was prepared by 2 methods :

- Procedure **B** (cf Table 2, entry 11). The crude product was purified by simple recrystallisation. Yield : 73 %. White crystals ; m.p. = 71.5 °C (ether). $[\alpha]_D^{24}$ = -209 (c = 1.3 ; acetone). IR (KBr) : 3117 ; 2911 ; 1676 ; 1550 ; 1464 ; 1404 ; 1351 ; 1191 ; 1079 ; 1045 ; 1005 ; 886 ; 806 ; 786 ; 780 ; 700 cm^{-1}. ^{1}H-NMR : 2.39 (s, 3H, CH_3Ar) ; 6.84 (d, J_{4-5} = 1.7 Hz, 1H , H_4) ; 7.30-7.67 (q, AA'BB' system, J = 8.1 Hz, 4H, HAr) ; 7.64 (d, J_{5-4} = 1.7 Hz, 1H, H_5) ; 9.96 (s, 1H, CHO). ^{13}C-NMR : 21.4 (q, C_{10}) ; 109.8 (d, C_4) ; 124.8 (d, C_7 and $C_{7'}$) ; 130.1 (d, C_8 and $C_{8'}$) ; 140.7 (s) ; 140.9 (s) ; 142.4 (s) ; 147.5 (d, C_5) ; 148.3 (s C_2) ; 178.2 (d, CHO). Analysis : Calculated for $C_{12}H_{10}O_3S$: C 61.52 H 4.30 S 13.68; Found C 61.55 H 4.32 S 13.56.

- Procedure **C** (cf Table 3, entry 13). The crude product was purified by silica gel chromatography (eluent cyclohexane/ethyl acetate 85/15). Yield : 75 %.

(Ss)-2-[2-(p-tolylsulfinyl)-3-furyl]-1,3-dioxolane **6a** : The reaction was performed using the procedure **A**, (cf Table 1, entry 3). The crude product was purified by silica gel chromatography (eluent cyclohexane/ethyl acetate 85/15). Yield : 86 %. White crystals ; m.p. = 71-71.5 °C (ether/pentane). $[\alpha]_D^{24}$ = -52 (c = 1.5 ; acetone). IR (KBr) : 3137 ; 2896 ; 1478 ; 1350 ; 1120 ; 1108 ; 1084 ; 1042 ; 1016 ; 967 ; 934 ; 818 ; 786 cm^{-1}. ^{1}H-NMR : 2.39 (s, 3H, CH_3Ar) ; 4.06 (m, 2H, CH_2) ; 4.12 (m, 1H, CH_2) ; 4.17 (m, 1H, CH_2) ; 6.14 (s, 1H, CH) ; 6.53 (d, J_{4-5} = 1.7 Hz, 1H , H_4) ; 7.31-7.60 (q, AA'BB' system, J = 8.0 Hz, 4H, HAr) ; 7.44 (d, J_{5-4} = 1.7 Hz, 1H, H_5). ^{13}C-NMR : 21.4 (q, C_{10}) ; 65.3 (t, $\underline{C}H_2O$) ; 65.5 (t, $\underline{C}H_2O$) ; 96.2 (d, $\underline{C}H$) ; 110.3 (d, C_4) ; 124.8 (d, C_7 and $C_{7'}$) ; 129.7 (s, C_3) ; 129.9 (d, C_8 and $C_{8'}$) ; 138.3 (s, C_6) ; 141.5 (s, C_9) ; 146.5 (d, C_5) ; 149.9 (s, C_2).Analysis : Calculated for $C_{14}H_{14}O_4S$: C 60.42 H 5.07 S 11.52 ; Found C 60.65 H 5.27 S 11.26.

(Ss)-3-bromo-2-(p-tolylsulfinyl)-furane **7** : The reaction was performed using the procedure **A**, with Lithium diisopropylamide (cf Table 1, entry 1). The crude product was purified by silica gel chromatography (eluent cyclohexane/ethyl acetate 85/15).Yield : 54 %. White crystals ; m.p. = 98-99 °C (ether/pentane). $[\alpha]_D^{24}$ = -92 (c = 0.9 ; acetone). IR (KBr) : 3116 ; 1540 ; 1360 ; 1122 ; 1082 ; 1041 ; 963 ; 819 ; 765 cm^{-1}. ^{1}H-NMR : 2.42 (s, 3H, CH_3Ar) ; 6.51 (d, J_{4-5} = 1.9 Hz, 1H , H_4) ; 7.33-7.60 (q, AA'BB' system, J = 8.1 Hz, 4H, HAr) ; 7.45 (d, J_{5-4} = 1.9 Hz, 1H, H_5). ^{13}C-NMR : 21.4 (q, C_{10}) ; 106.9 (s, C_3) ; 115.4 (d, C_4) ; 124.7 (d, C_7 and $C_{7'}$) ; 130.1 (d, C_8 and $C_{8'}$) ; 138.0 (s, C_6) ; 141.9 (s, C_9) ; 147.1 (s, C_5) ; 150.3 (s, C_2). Analysis : Calculated for $C_{11}H_9O_2SBr$: C 46.33 H 3.18 S 11.24 ; Found C 46.48 H 3.26 S 11.40. MS[EI 70 eV, m/z (% rel.int.)] : 270 (100, [M-16]) ; 269 (57) ; 268 (32) ; 189 (62) ; 162 (48) ; 161 (96) ; 70 (49) ; 69 (89) ; 65 (40).

(Ss)-3-(p-tolylsulfinyl)-furane **9a** : The reaction was performed using the procedure **A**, (cf Table 1, entry 5). The crude product was purified by silica gel chromatography (eluent cyclohexane/ethyl acetate 85/15). Yield : 94 %. White needles ; m.p. = 81 °C (ether/pentane). $[\alpha]_D^{24}$ = +31 (c = 2.5 ; acetone). IR (KBr) : 3130 ; 1490 ; 1138 ; 1085 ; 1045 ; 1012 ; 999 ; 873 ; 813 ; 800 cm^{-1}. ^{1}H-NMR : 2.41 (s, 3H, CH_3Ar) ; 6.39 (m, 1H , H_4) ; 7.32 and 7.55 (q, AA'BB' system, J = 8.1 Hz, 4H, HAr) ; 7.43 (m, 1H, H_5) ; 7.78 (m , 1H, H_2). ^{13}C-NMR : 21.4 (q, C_{10}) ; 107.4 (d, C_4) ; 124.6 (d, C_7 and $C_{7'}$) ; 129.9 (d, C_8 and $C_{8'}$) ; 131.3 (s, C_3) ; 140.8 (s, C_6) ; 141.6 (s, C_9) ; 143.9 (d, C_2) ; 144.9 (d, C_5). Analysis : Calculated for $C_{11}H_{10}O_2S$: C 64.06 H 4.89 S 15.54 Found C 63.96 H 4.88 S 15.38. MS[EI 70 eV, m/z (% rel.int.)] :190 (100, [M-16]) ; 161 (61) ; 147 (19) ; 129 (20) ; 91 (18) ; 65 (21).

(Ss)-2-[3-(p-tolylsulfinyl)-2-furyl]-1,3-dioxolane **12** : The reaction was performed using the procedure **A**, (cf Table 1, entry 7). The crude product was purified by silica gel chromatography (eluent cyclohexane/ethyl acetate 85/15). Yield : 44 %. White crystals ; m.p. = 67-68°C °C (ether/pentane). $[\alpha]_D^{24}$ = -152 (c = 2.6 ; acetone). IR (KBr) : 3111 ; 2891 ; 1497 ; 1224 ; 1138 ; 1085 ; 1045 ; 1012 ; 826 ; 800 ; 760 cm^{-1}. ^{1}H-NMR : 2.39 (s, 3H, CH_3Ar) ; 4.09 (m, 2H, CH_2) ; 4.17 (m, 1H, CH_2) ; 4.25 (m, 1H, CH_2) ; 6.22 (s, 1H, CH) ; 6.41 (d, J_{4-5} = 1.8 Hz, 1H, H_4) ; 7.29-7.55 (q, AA'BB' system, J = 8.1 Hz, 4H, HAr) ; 7.36 (d, J_{5-4} = 1.8 Hz, 1H, H_5). ^{13}C-NMR : 21.4 (C_{10}) ; 65.4 ($\underline{C}H_2O$) ; 65.7 ($\underline{C}H_2O$) ; 96.7 ($\underline{C}H$) ; 107.8 (C_4) ; 124.4 (C_7 and $C_{7'}$) ; 129.1 (C_3) ; 129.9 (C_8 and $C_{8'}$) ; 141.2 (C_6 or C_9) ; 141.3 (C_6 or C_9) ; 143.8 (C_5) ; 151.6 (C_2). Analysis : Calculated for $C_{14}H_{14}O_4S$: C 60.42 H 5.07 S 11.52 ; Found C 60.57 H 4.87 S 11.48.

(Ss)-2-(p-tolylsulfinyl)-furane **14a** : The reaction was performed using the procedure **A**, (cf Table 1, entry 8). The crude product was purified by silica gel chromatography (eluent cyclohexane/ethyl acetate 85/15). Yield : 96%. White needles ; m.p. = 43.5-44°C (ether/pentane). $[\alpha]_D^{24}$ = +106 (c = 2.5 ; acetone). IR (KBr) : 3117 ; 1454 ; 1139 ; 1082 ; 1042 ; 1014 ; 911 ; 808 ; 785 cm^{-1}. ^{1}H-NMR : 2.41 (s, 3H, CH_3Ar) ; 6.44 (dd, J_{3-4} = 3.3 Hz, J_{4-5} = 1.7 Hz, 1H, H_4) ; 6.79 (d, J_{3-4} = 3.3 Hz, 1H, H_3) ; 7.32-7.59 (q, AA'BB' system, J = 8.1 Hz, 4H, HAr) ; 7.53 (d, J_{4-5} = 1.7 Hz, 1H, H_5). ^{13}C-NMR : 21.3 (q, C_{10}) ; 111.1 (d, C_4) ; 115.6 (d, C_3) ; 124.8 (d, C_7 and $C_{7'}$) ; 129.8 (d, C_8 and $C_{8'}$) ; 138.3 (s, C_6) ; 141.7 (s, C_9) ; 147.0 (d, C_5) ; 153.5 (s, C_2). Analysis : Calculated for $C_{11}H_{10}O_2S$: C 64.06 H 4.89 S 15.54 ; Found C 64.63 H 4.92 S 15.83. MS[EI 70 eV, m/z (% rel.int.)] :190 (100, [M-16]) ; 161 (43) ; 147 (20) ; 129 (60) ; 91 (19) ; 65 (23).

(Ss)-2-(p-tolylsulfinyl)-3-formylthiophene **2b** : The reaction was performed using the procedure **B** (cf Table 2, entry 12). The crude product was purified by simple recrystallisation. Yield : 93 %. White needles ; m.p. = 80.5-81 °C (ether/pentane). $[\alpha]_D^{24}$ = -129 (c = 1.2 ; acetone). IR (KBr) : 1685 ; 1668 ; 1504 ;

1376 ; 1218 ; 1095 ; 1081 ; 1049 ; 808 ; 755 ; 748 cm^{-1}. ^{1}H-NMR : 2.39 (s, 3H, CH_3Ar) ; 7.29-7.73 (q, AA'BB' system, J = 8.1 Hz, 4H, HAr) ; 7.49 (d, J = 5.2 Hz, 1H) ; 7.58 (d, J = 5.2 Hz, 1H) ; 10.09 (s, 1H, CHO). ^{13}C-NMR : 21.5 (q, C_{10}) ; 125.4 (d, C_7 and $C_{7'}$) ; 129.2 (d) ; 130.1 (d, C_8 and $C_{8'}$) ; 130.3 (d) ; 139.5 (s) ; 141.7 (s) ; 142.6 (s) ; 159.9 (s) ; 183.4 (d, CHO). Analysis : Calculated for $C_{12}H_{10}O_2S_2$: C 57.58 H 4.03 S 25.61 Found C 57.41 H 3.96 S 25.41.

(Ss)-3-(p-tolylsulfinyl)-2-formylthiophene **4b** : The reaction was performed using the procedure **C** (cf Table 3, entry 14). The crude product was purified by silica gel chromatography (eluent cyclohexane/ethyl acetate 85/15). Yield : 92 %. Yellow crystals ; m.p. = 77.5-78 °C (ether/pentane). $[\alpha]_D^{24}$ = -200 (c = 1.0 ; acetone). IR (KBr) : 1668 ; 1415 ; 1207 ; 1081 ; 1047 ; 808 ; 786 ; 755 cm^{-1}. ^{1}H-NMR : 2.39 (s, 3H, CH_3Ar) ; 7.30-7.62 (q, AA'BB' system, J = 8.1 Hz, 4H, HAr) ; 7.45 (d, J = 5.2 Hz, 1H) ; 7.74 (d, J = 5.2 Hz, 1H) ; 10.29 (s, 1H, CHO). ^{13}C-NMR : 21.4 (q, C_{10}) ; 125.0 (d, C_7 and $C_{7'}$) ; 126.6 (d) ; 130.3 (d, C_8 and $C_{8'}$) ; 134.9 (d) ; 140.6 (s) ; 141.3 (s) ; 142.2 (s) ; 152.3 (s) ; 181.0 (d, CHO). Analysis : Calculated for $C_{12}H_{10}O_2S_2$: C 57.58 H 4.03 S 25.61 ; Found C 57.55 H 4.07 S 25.54.

(Ss)-2-[2-(p-tolylsulfinyl)-3-thienyl]-1,3-dioxolane **6b** : The reaction was performed using the procedure **A**, (cf Table 1, entry 4). The crude product was purified by silica gel chromatography (eluent hexane/ethyl acetate 85/15). Yield : 57 %. White crystals ; m.p. = 115-115.5 °C (CH_2Cl_2/pentane). $[\alpha]_D^{24}$ = -32 (c = 1,1 ; acetone). IR (KBr) : 3083 ; 1396 ; 1110 ; 1079 ; 1039 ; 1014 ; 825 ; 763 cm^{-1}. ^{1}H-NMR : 2.39 (s, 3H, CH_3Ar) ; 4.06 and 4.15 (m, 3H and 1H, $2CH_2$) ; 6.16 (s, 1H, CH) ; 7.10 (d, J_{4-5} = 5.2 Hz, 1H , H_4) ; 7.28-7.64 (q, AA'BB' system, J = 8.1 Hz, 4H, HAr) ; 7.49 (d, J_{5-4} = 5.2 Hz, 1H, H_5). ^{13}C-NMR : .21.4 (q, C_{10}) ; 65.3 (t, $\underline{C}H_2O$) ; 65.4 (t, $\underline{C}H_2O$) ; 99.0 (d, $\underline{C}H$) ; 124.7 (d, C_7 and $C_{7'}$) ; 127.0 (d) ; 129.7 (d, C_8 and $C_{8'}$) ; 130.8 (d) ; 141.5 (s) ; 142.2 (s) ; 142.4 (s) ; 147.4 (s).Analysis : Calculated for $C_{14}H_{14}O_3S_2$: C 57.12 H 4.79 S 21.78 ; Found C 57.11 H 4.73 S 21.68.

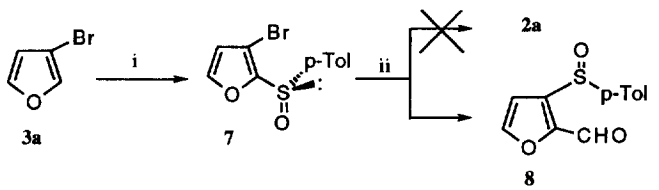
(Ss)-3-(p-tolylsulfinyl)-thiophene **9b** : The reaction was performed using the procedure **A** (cf Table 1, entry 6). The crude product was purified by silica gel chromatography (eluent cyclohexane/ethyl acetate 85/15).Yield : 90 %. White needles ; m.p. = 69-71 °C (ether). $[\alpha]_D^{24}$ = +40 (c = 2.5 ; acetone). IR (KBr) : 3064 ; 1490 ; 1397 ; 1095 ; 1083 ; 1039 ; 1014 ; 853 ; 803 cm^{-1}. ^{1}H-NMR : 2.39 (s, 3H, CH_3Ar) ; 7,05 (d, J_{4-5} = 5,1 Hz, 1H, H_4) ; 7.29 and 7.54 (q, AA'BB' system, J = 8.0 Hz, 4H, HAr) ; 7.37 (dd, J_{5-4} = 5.1 Hz, J_{5-2} = 3.0 Hz, 1H, H_5) ; 7.75 (d, J_{2-5} = 3.0 Hz, 1H, H_2). ^{13}C-NMR : 21.4 (q, C_{10}) ; 124.1 (d, C_4 or C_5) ; 124.4 (s, C_3) ; 124.8 (d, C_7 and $C_{7'}$) ; 126.8 (d, C_4 or C_5) ; 128.2 (d, C_2) ; 130.0 (d, C_8 and $C_{8'}$) ; 141.6 (s, C_9) ; 145.2 (s, C_6). Analysis : Calculated for $C_{11}H_{10}OS_2$: C 59.43 H 4.53 S 28.84 ; Found C 59.42 H 4.61 S 28.71. MS[EI 70 eV, m/z (% rel.int.)] :206 (100, [M-16]) ; 191 (23) ; 173 (17) ; 161 (10) ; 129 (18) ; 115 (15) ; 71 (32) ; 65 (26).

(Ss)-2-(p-tolylsulfinyl)-thiophene **14b** : The reaction was performed using the procedure **A**, (cf Table 1, entry 9). The crude product was purified by silica gel chromatography (eluent cyclohexane/ethyl acetate 85/15). Yield : 74 %. White crystals ; m.p. = 62-66 °C (ether/pentane). $[\alpha]_D^{24}$ = +110 (c = 2.5 ; acetone). IR (KBr) : 3071 ; 1490 ; 1450 ; 1397 ; 1218 ; 1085 ; 1045 ; 1012 ; 959 ; 853 ; 813 cm^{-1}. ^{1}H-NMR : 2.41 (s, 3H, CH_3Ar) ; 7.06 (dd, J_{4-5} = 4.9 Hz, J_{4-3} = 3.8 Hz, 1H, H_4) ; 7.31-7.59 (q, AA'BB' system, J = 8.1 Hz, 4H, HAr) ; 7.54 (dd, J_{3-4} = 3.8 Hz, J_{3-5} = 1.2 Hz, 1H, H_3) ; 7.57 (m, 1H, H_5). ^{13}C-NMR : 21.4 (q, C_{10}) ; 124.4 (d, C_7 and $C_{7'}$) ; 127.2 (d, C_3) ; 129.9 (d, C_8 and $C_{8'}$) ; 130.9 (d, C_4 or C_5) ; 132.0 (d, C_4 or C_5) ; 141.7 (s,

C_9) ; 142.2 (s, C_6) ; 148.6 (s, C_2). Analysis : Calculated for $C_{11}H_{10}OS_2$: C 59.43 H 4.53 S 28.84; Found C 59.27 H 4.36 S 28.75. MS[EI 70 eV, m/z (% rel.int.)] :206 (100, [M-16]) ; 191 (32) ; 173 (13) ; 161 (17) ; 129 (14) ; 115 (13) ; 91 (17) ; 71 (18) ; 65 (23).

REFERENCES AND NOTES

1. Girodier, L.; Rouessac, F. *Tetrahedron: Asym.* **1994**, 5 (7), 1203-1206.
2. (a) Soai, K.; Kawase, Y.; Niwa, S. *Heterocycles* **1989**, 29 (11), 2219. (b) Joshi, N. N.; Srebnik,M.; Brown, H. C. *Tetrahedron lett.* **1989**, 30(41), 5551-5554. (c) Soai, K.; Niwa, S. *Chem. Rev.* **1992**, 833-856. (d) Hayashi, M.; Kaneko, T.; Oguni, N. *J. Chem. Soc., Perkin Trans. 1*, **1991**, (1), 25-28. (e) Chelucci, G.; Conti, S.; Falorni, M.; Giacomelli, G. *Tetrahedron* **1991**, 47(38), 8251-8258. (f) Wally, H.; Widhalm, M.; Weissensteiner, W.; Schlögl, K. *Tetrahedron: Asym.* **1993**, 4(3), 285-288. (g) Wallbaum, S.; Martens, J. *Tetrahedron: Asym.* **1993**, 4(4), 637-640.
3. The well-known methodology of Andersen was used, *see* Andersen, K.K.*J. Org. Chem.* **1964**, 29, 1953.
4. Comins, D. L.; Killpack, M. O. *J. Org. Chem.* **1987**, 52, 104-109.
5. (a) Zaluski, M. C.; Robba, M.; Bonhomme, M. *Bull. Soc. Chim. Fr.* **1970**, (5), 1838-1846. (b) Fournié-Zaluski, M. C.; Chatain-Cathaud, C. *Bull. Soc. Chim. Fr.* **1974**, (7-8), 1571-1574.
6. In order to obtain **2a** by one alternative route, **3a** was transformed to **7** (table 1, entry 1) which was reacted with N,N-dimethylformamide as indicated below. Unfortunately, in the course of this reaction we observed a migration of the sulfoxide group allied to a racemization. The sulfoxide **8** was formed in 24 % yield together with racemic **14a** as the major product. A rearrangement during the course of this reaction is probably the origin of the racemic compound **8**.



i, a) LDA, THF b) $MgBr_2.Et_2O$, Et_2O c) (-)-(Ss)-menthyl-p-toluenesulfinate, ii, a) BuLi, THF, b) DMF.

7. Furan (**13a**) and thiophene (**13b**) have also been transformed to sulfoxides **14a** or **14b** by the same reaction. These two compounds appeared in Girodier, L.; Maignan, C.; Rouessac, F. *Tetrahedron: Asym.* **1992**, 3 (7), 857-858.

i, a) BuLi, THF b) $MgBr_2.Et_2O$, Et_2O c) (-)-(Ss)-menthyl-p-toluenesulfinate.

8. Brandsma, L.; Verkruijsse, H. *"Preparative polar organometallic chemistry 1"*, Springer-Verlag, **1987**.

(*Received in UK* 22 *June* 1995)