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Reactions of Diheteroaryl Sulfoxides with Heteroaryllithiums—Ligand Coupling and Exchange Reactions

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ABSTRACT

The reactions of heteroaryl sulfoxides with heteroaryllithiums gave various biheteroaryls and diheteroaryl sulfoxides as ligand coupling and ligand exchange products through sulfurane intermediates. Especially, the reaction of di-2-furyl sulfoxide with 2-pyridyllithium proceeded first by a ligand exchange reaction to form 2-furyllithium and 2-furyl 2-pyridyl sulfoxide, which then underwent ligand coupling with 2-pyridyllithium to afford 2,2'-bipyridyl. Furthermore, it was found that the occurrence of the ligand coupling reaction depends on the stereoisomerism of the sulfurane intermediate formed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Recent studies of hypervalent species have shown numerous synthetic reactivities and reaction patterns. The concept [1] of the ligand coupling reaction at various heteroatoms [1,2], especially the reactivity of the central sulfur atom in a sulfurane, has successfully been developed through investigation of the reactions of sulfoxides, one class of tri-coordinate sulfur compounds. Also, similar reactions of organometallic reagents have been studied in detail [3].

The ligand coupling reaction is interesting both in its theoretical [4] and synthetic aspects. However, until now, the nature of the controlling factors for coupling or exchange have not been well understood. Nevertheless, the synthetic applications have become an important and timely area because ligand coupling leads to otherwise difficult carbon–carbon bond formation reactions. For example, electrically conducting polymers have attracted public attention because copolymers consisting of alternating heterocycles have become quite useful as electronic materials [5]. Also, 2,2'-bipyridyl is a valuable chelating agent, and 4,4'-bipyridyl is an important synthetic precursor of viologens, which are widely used as redox reagents and as an intermediate for the synthesis of insecticides [6]. Ligand coupling has been found to be useful for effecting difficult C–C bond formation.

In order to clarify both synthetic applications and the mechanism of the reaction, various dihet-

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Dedicated to Professor Louis D. Quinn on the occasion of his retirement from the University of Massachusetts at Amherst.

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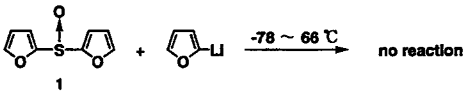
eroaryl sulfoxides have been treated with heteroaryllithium compounds in tetrahydrofuran, wherein the ligands studied were those containing furan, pyridine, and thiophene moieties [7].

RESULTS AND DISCUSSION

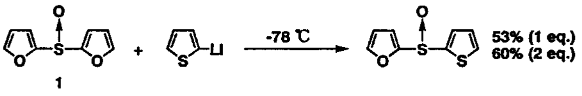
Reactions of bis-(2-Heteroaryl) Sulfoxides with Heteroaryllithiums

The starting sulfoxides can be classified as two types, the first being symmetrical sulfoxides, and the second, unsymmetrical ones.

As the first examples of the use of symmetrical sulfoxides, the reactions of di-2-furyl sulfoxide 1 with 2-furyl-, 2-thienyl-, and 2-pyridyllithiums were carried out at various temperatures, as shown in Equations 1 through 3. The reaction of 1 with 2-furyllithium apparently gave neither ligand exchange nor coupling products even though the temperature was varied from −78 to 66°C. The reaction of 1 with 2-thienyllithium gave 2-furyl 2-thienyl sulfoxide as a ligand exchange product. As shown in Equation 2, the amount of 2-thienyllithium was increased from 1 to 2 equivalents as against 1, but the yield of the exchanged sulfoxide changed but little. The reaction of 1 with 2-pyridyllithium gave 2,2′-bipyridyl, as shown in Equation 3. As shown in Equation 3, changes in the amount of 2-pyridyllithium used relative to 1 caused yields of the ligand coupling product, 2,2′-bipyridyl, to vary from 27% to 73%. Obviously, in this case, ligand exchange takes place prior to the coupling of two 2-pyridyl ligands.



(1)



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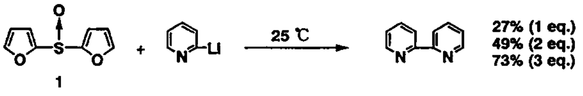
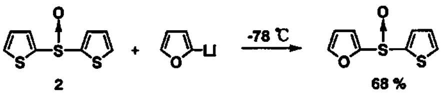


(3)

In the next case of the use of symmetrical sulfoxides, the reactions of di-2-thienyl sulfoxide 2 with 2-furyl-, 2-thienyl-, and 2-pyridyllithium were carried out at −78°C with results as shown in Equations 4 through 6.



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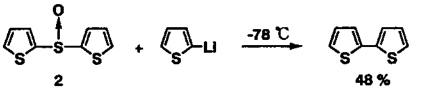

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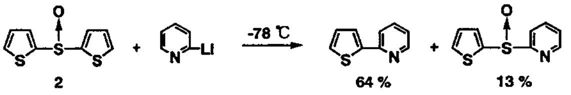
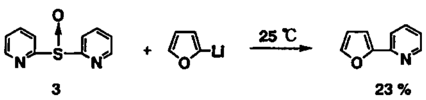


(6)

The reaction of 2 with 2-furyllithium proceeded to give 2-furyl 2-thienyl sulfoxide as the ligand exchange product, as shown in Equation 4. The reaction behaved in the same way as shown in Equation 2, no matter which lithiated heterocycle was used. The reaction of 2 with 2-thienyllithium as reported in a previous article [8] gave only 2,2′-bithienyl as the ligand coupling product, as shown in Equation 5. The reaction of 2 with 2-pyridyllithium proceeded to afford both the ligand coupling and the ligand exchange products, namely, 2-(2-pyridyl)thiophene and 2-pyridyl 2-thienyl sulfoxide, as shown in Equation 6; however, the ligand coupling process prevailed. However, treatment of 2-pyridyl 2-thienyl sulfoxide with 2-pyridyllithium led to no further reaction (Equation 18).

As the last case in which symmetrical sulfoxides were used, the reactions of bis-(2-pyridyl) sulfoxide 3 with 2-furyl-, 2-thienyl-, and 2-pyridyllithiums were carried out with the results shown in Equations 7 through 9. In all cases, only the ligand coupling products were obtained. The reaction of 3 with 2-furyllithium gave 2-(2-furyl)pyridine in a poor yield, as shown in Equation 7. The reaction of 3 with 2-thienyllithium proceeded very well, giving 2-(2′-pyridyl)thiophene quantitatively, as shown in Equation 8. The reaction of 3 with 2-pyridyllithium afforded 2,2′-bipyridyl in an excellent yield, as shown in Equation 9.



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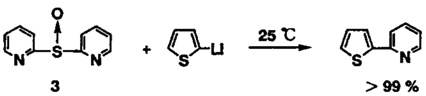

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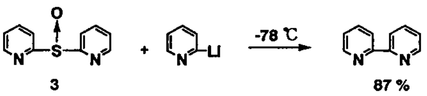
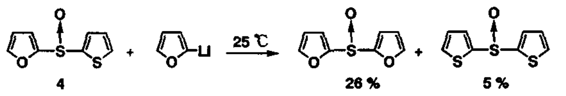


(9)

In general, di-2-furyl sulfoxide only reluctantly couples with any of the lithio-heterocycles; e.g., the reaction with 2-thienyllithium gives only the ligand exchange product, but a facile ligand exchange with 2-pyridyllithium occurs that eventually leads to the coupling product, 2,2'-bipyridyl. Di-2-pyridyl sulfoxide undergoes only the ligand coupling reaction with any of the lithioheterocycles while di-2-thienyl sulfoxide behaves in a manner that lies in between those of the other two sulfoxides.

As the first case of the use of unsymmetrical sulfoxides, the reactions of 2-furyl 2-thienyl sulfoxide **4** with 2-furyl-, 2-thienyl-, and 2-pyridyllithium were carried out with the results as shown in Equations 10 through 12. Reactions of **4** with both 2-furyllithium and 2-thienyllithium gave two kinds of ligand exchange products, namely, di-2-furyl sulfoxide **1** and di-2-thienyl sulfoxide **2** in poor yields as shown in Equations 10 and 11, together with recovery of the original sulfoxide **4**. However, the reaction of **4** with 2-pyridyllithium proceeded to give four different ligand coupling products, namely, 2-(2-furyl)pyridine, 2-(2-furyl)thiophene, 2-(2-pyridyl)thiophene, and 2,2'-bipyridyl, as shown in Equation 12. Obviously, there was a prior ligand exchange reaction of 2-pyridyllithium that led to the formation of 2,2'-bipyridyl.



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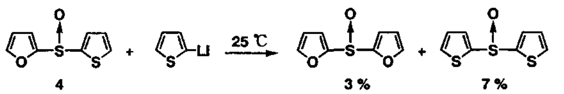

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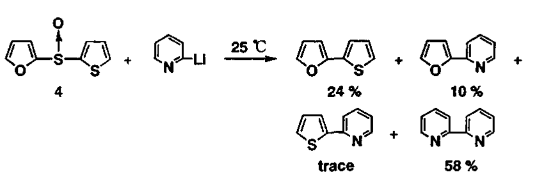
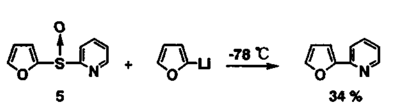


(12)

As the next case of the use of unsymmetrical sulfoxides, the reaction of 2-furyl 2-pyridyl sulfoxide **5** with 2-furyl-, 2-thienyl-, and 2-pyridyllithiums were carried out with the results as shown in Equations 13 through 15. The reaction of **5** with 2-furyllithium gave 2-(2-furyl)pyridine, while the original sulfoxide **5** was recovered to the extent of 52%. The reaction of **5** with 2-thienyllithium gave three ligand coupling products, namely, 2-(2-furyl)pyridine, 2-(2-pyridyl)thiophene, and 2,2'-bipyridyl; 2-pyridyl 2-thienyl sulfoxide is known to undergo the ligand coupling reaction upon treatment with 2-thienyllithium to give 2-(2-pyridyl)thiophene. The reaction of **5** with 2-pyridyllithium gave two ligand coupling products, namely, 2-(2-furyl)pyridine and 2,2'-bipyridyl.



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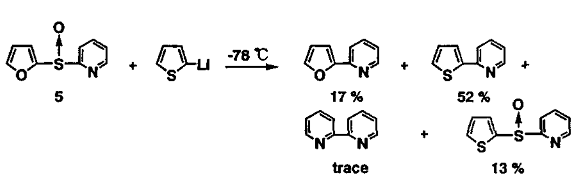

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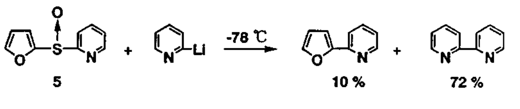
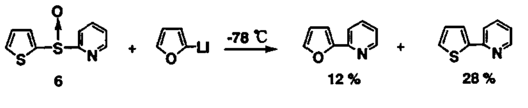


(15)

As the last case of the use of unsymmetrical sulfoxides, the reactions of 2-pyridyl 2-thienyl sulfoxide **6** with 2-furyl-, 2-thienyl-, and 2-pyridyllithiums were carried out with the results as shown in Equations 16 through 18. The reaction of **6** with 2-furyllithium gave two ligand coupling products, namely, 2-(2-furyl)pyridine and 2-(2-pyridyl)thiophene, while the original sulfoxide **6** was recovered in a yield of 14%, as shown in Equation 16. The reaction of **6** with 2-thienyllithium gave two ligand coupling products, namely, 2-(2-pyridyl)thiophene and 2,5-di-(2-pyridyl)thiophene, as shown in Equation 17 [8]. The latter product was presumably formed by first formation of 5-(2-pyridyl)2-thienyllithium, which eventually underwent ligand coupling with 2-thienyl 2-pyridyl sulfoxide **6**. This was confirmed since 2-thienyllithium was found to react in the expected manner with the sulfoxide **6**. The reaction of **6** with 2-pyridyllithium gave no product under normal conditions where the temperatures were raised from −78 to 66°C, even in the presence of crown ether [8]. We do not understand why reaction did not occur since 2-pyridyllithium easily undergoes ligand coupling, while 2-thienyllithium should be replaced readily by 2-pyridyllithium in a ligand exchange reaction.



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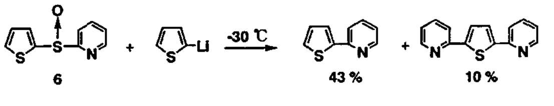

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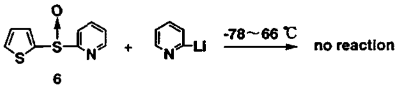


(18)

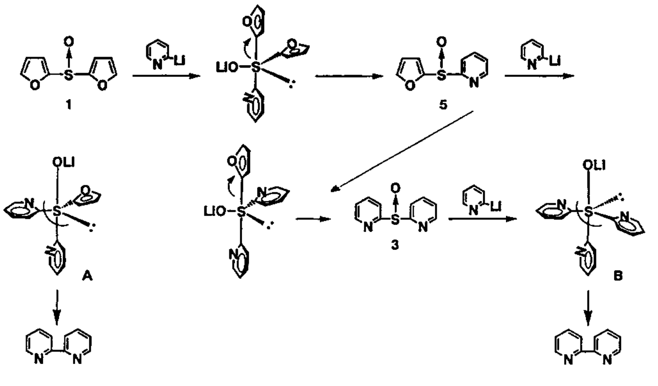
Up until now, we have dealt with the ligand coupling and the ligand exchange reactions of 2-lithio derivatives of furan, thiophene, and pyridine with the respective sulfoxides in order to determine the modes of ligand coupling and exchange in these cases. Next, we will provide interpretations of these results.

Mechanism of the Reaction of di-2-Furyl Sulfoxide with 2-Pyridyllithium

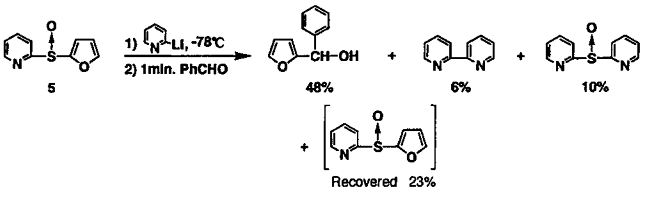
The reaction of di-2-furyl sulfoxide 1 with 2-pyridyllithium gave 2,2′-bipyridyl, as shown in Equation 3; the formation of 2,2′-bipyridyl is believed to be due to ligand coupling occurring within sulfurane **A** and sulfurane **B**, formed by ligand exchange, as shown in Scheme 1.

However, the increase of ligand coupling product with the increase of the amount of 2-pyridyllithium used seems to favor sulfurane **B** as the most important intermediate. If this is the case, it should be possible to detect the formation of 2-furyllithium, the other product of the initial ligand exchange reaction. Thus, in order to provide evidence in support of the mechanism for this reaction, the reaction of 2-furyl 2-pyridyl sulfoxide 5 with 2-pyridyllithium was carried out in the presence of benzaldehyde, as shown in Scheme 2 [9].

Indeed, 2-furylphenylmethanol was obtained, together with di-2-pyridyl sulfoxide 3 and a small amount of 2,2′-bipyridyl, the ligand coupling product. Thus, evidence was provided that the reaction of di-2-furyl sulfoxide 1 with 2-pyridyllithium proceeds to form sulfurane **B**. Scheme 2 also indicates that 2-pyridyllithium first undergoes ligand exchange to give 2-furyllithium, which reacts with benzaldehyde to afford 2-furylphenylmethanol in a good yield, although with relatively small amounts of di-2-pyridyl sulfoxide 3 and 2,2′-bipyridyl also being obtained.



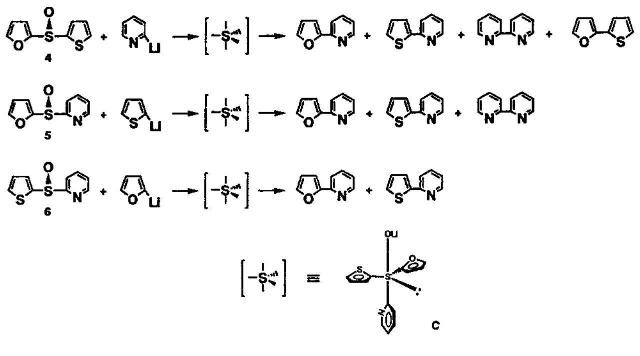
SCHEME 1



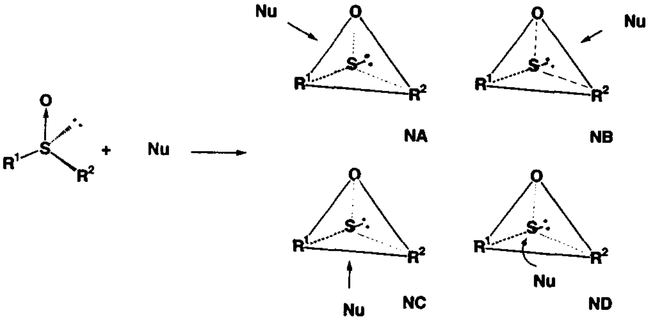
SCHEME 2

Selectivity in the Occurrence of the Ligand Coupling Reactions

As shown in the previous two sections, even if the reaction of an unsymmetrical sulfoxide with an appropriate heteroaryllithium proceeds to give a sulfurane intermediate **C** bearing three different ligands, namely, 2-furyl, 2-thienyl, and 2-pyridyl, the actual reaction in the various cases showed couplings to form 2-(2-furyl)thiophene, 2-(2-furyl)pyridine, or 2-(2-pyridyl)thiophene in addition to 2,2′-bipyridyl, which is the major product as shown in Scheme 3. However, the formation of 2,2′-bipyridyl was noticed in only the two cases depicted in Equations 12 and 14. As shown in Equation 12, a ligand exchange of a 2-thienyl group with 2-pyridyllithium is necessary to form 2-furyl 2-pyridyl sulfoxide 5, some of which undergoes ligand coupling. Subsequently, it is further necessary to exchange 2-furyllithium with 2-pyridyllithium to form the ligand coupling product, 2,2′-bipyridyl. Therefore, we believe that these reactions proceed to form initially different sulfurane intermediates. In other words, when the nucleophile attacks the positively charged sulfur atom, the direction of approach of the nucleophile follows a certain rule to form the sulfurane intermediate. Among the four possible directions of attack of the nucleophile to form the sulfurane, as shown in Scheme 4, there are two possible pathways NA and NB, if we do not consider the possibility of pseudorotation. (Even if we were to consider this possibility, the situation would still be the same.) The



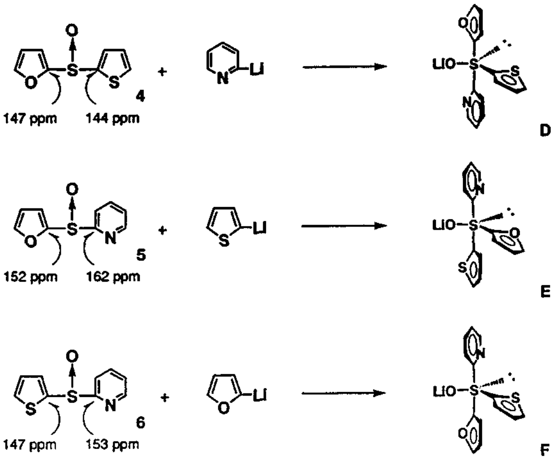
SCHEME 3



SCHEME 4

formation of 2,2′-bipyridyl means that the 2-pyridyllithium on site is necessary in Equation 14, if the R^1 or R^2 ligand is considered to couple. If the difference of NA and NB is considered to reflect the apicophilicity of the ligand in the hypervalent compounds, the apicophilicity should be parallel to the electronegativity of an ipso carbon atom in the heteroaromatic ring [8]. One easy means to find the relative values of electronegativity is to measure the values of the ^{13}C-NMR chemical shift at each ipso carbon of the original sulfoxide, and these values are shown in Scheme 5.

The values for the ipso carbon of the 2-furyl and 2-thienyl ligands in 2-furyl 2-thienyl sulfoxide **4** are 147 and 144 ppm. Therefore, the value of the 2-furyl ligand is higher than that of the 2-thienyl ligand, and therefore, the reaction of **4** with 2-pyridyllithium proceeds to form sulfurane **D**. This means that the 2-furyl ligand is placed in an apical direction in the hypervalent sulfurane. Further, the values of the 2-furyl and 2-pyridyl ligands are 152 and 162 ppm, respectively, and hence the reaction of **5** with 2-thienyllithium proceeds to form sulfurane **E**. In the same way, since the values of the 2-thienyl and 2-pyridyl ligands are 147 and 153 ppm [8], respectively, the reaction of **6** with 2-furyllithium proceeds to form sulfurane F. Among the sulfoxides, the ^{13}C-NMR value of the 2-pyridyl ligand is the highest, and the lowest is that of the 2-furyl ligand. The ease of ligand coupling is the lowest with the 2-furyl ligand. The ligand couplings of 2-thienyl and 2-pyridyl ligands are nearly of the same propensity. Thus, these data seem to indicate that the occurrence of the ligand coupling reaction depends on the conformation of the initially formed sulfurane intermediate.



SCHEME 5

EXPERIMENTAL

All the melting points are uncorrected and were taken on a Yanagimoto melting-point apparatus. Infrared spectra were obtained on a Perkin Elmer FT-IR 1760X spectrometer. The NMR spectra were obtained on a JEOL-PMX60$_{SI}$ or a JEOL-GSX-270 FT-NMR spectrometer, using TMS as the internal standard. All the reactions were monitored by thin-layer chromatography (TLC) (Merck, 60 F 254), gas-liquid chromatography (GLC) (Hitachi 663-30, using a 3% silicon OV-17 on chromosorb W of 60–80 mesh in column), high-pressure liquid chromatography (HPLC) (Shimadzu SPD-6A, OD-ST 5 μm in column). Silica gel used for column chromatography was Wakogel C-200 and C-300. Mass spectra were taken with a Shimadzu GCMS-QP1000(A) mass spectrometer. Elemental analyses were carried out at the Elemental Analysis Center of Wako Pure Chemical Industries Ltd.

Materials

All reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co., and Aldrich Chemical Co. The reagents used and reaction solvents were further purified by general methods.

Synthesis of 2-Furyl 2-Thienyl Sulfoxide 4

A typical experimental procedure for the preparation of 2-furyl 2-thienyl sulfide is as follows. A solution of 2-furyllithium was prepared by adding *n*-butyllithium (57 mmol as a 1.5 M solution in *n*-hexane) to a solution of furan (4.2 mL, 55 mmol) in tetrahydrofuran (400 mL) under an argon atmosphere at −78°C during 4 hours. This solution was added to di-2-thienyl disulfide [8] (11 g, 48 mmol) in tetrahydrofuran (100 mL) under an argon atmosphere at −78°C for 1 hour. After the usual workup, the product was extracted with ether three times. The combined ether layer was washed with water and dried over anhydrous magnesium sulfate. After the solvent had been evaporated, the residues were purified by silica gel column chromatography; elution with *n*-hexane gave 2-furyl 2-thienyl sulfide in 86% yield (7.5 g). 2-Furyl 2-thienyl sulfide: Oil, R_f = 0.45 (*n*-hexane), mass (*m*/*z*); 182 (M^+, 74.5), 153 (62.4), 121 (53.1), 71 (63.9), 39 (100.0%), ^{1}H-NMR (δ, 270 MHz); 6.37 (t, *J* = 3.2 Hz, 1H, 4 furan), 6.61 (d, *J* = 3.1 Hz, 1H, 3 furan), 6.94 (t, *J* = 5.2 Hz, 1H, 4 thiophene), 7.19 (d, 1H, 3 thiophene), 7.31 (d, *J* = 5.2 Hz, 1H, 5 thiophene), 7.47 (d, 1H, 5 furan), ^{13}C-NMR (δ, 270 MHz, DEPT); 111.63, 116.65, 127.45, 129.51, 132.61 (ipso position in thiophene ring), 132.75, 145.09 (ipso position in furan ring), 145.72, HRMS; Calcd. for $C_8H_6OS_2$: 181.98; found: 181.98. A typical experimental procedure for the preparation of 2-furyl 2-thienyl sulfoxide **4** is as follows. To a solution of 2-furyl 2-thienyl sulfide (7.5 g, 41 mmol) in dichloromethane (200 mL) was added dropwise *m*-chloroperbenzoic acid (8.49 g, 49.2 mmol) in dichloromethane (200 mL) at 0°C over 4 hours. The mixture was stirred at 0°C. After 4 hours, a sodium dithionate aqueous solution and then a sodium hydroxide aqueous solution were added. After the usual workup, the product was extracted with chloroform three times. The combined chloroform layer was washed with water and dried over anhydrous magnesium sulfate. After the solvent had been evaporated, the residue was purified by silica gel column chromatography; elution with a 1:1 mixture of *n*-hexane-ethyl acetate (R_f = 0.2) gave 2-furyl 2-thienyl sulfoxide in 98% yield (8.0 g). 2-Furyl 2-thienyl sulfoxide **4**: white plates, mp; 62.5–63.0°C, HRMS; Calcd. for $C_8H_6O_2S_2$: 197.97; found: 197.9802, IR (KBr, cm^{-1}): 1045 (S–O), ^{1}H-NMR (δ, 270 MHz); 6.52 (t, *J* = 3.8 Hz, 1H, 4 furan), 6.94 (d, *J* = 3.8 Hz, 1H, 3 furan), 7.13 (t, *J* = 4.9 Hz, 1H, 4 thiophene), 7.58 (d, 1H, 3 thiophene), 7.63 (d, 1H, 5 furan), 7.68 (d, *J* = 4.9 Hz, 1H, 5 thiophene), ^{13}C-NMR; 111.44, 115.10, 127.35, 130.98, 132.28, 143.97 (ipso position in thiophene ring), 147.05, 153.07 (ipso position in furan ring); anal. Calcd. for $C_8H_6O_2S_2$: C, 48.48; H, 3.03; found: C, 48.64; H, 3.26%.

Synthesis of 2-Furyl 2-Pyridyl Sulfoxide 5

A typical experimental procedure for the preparation of 2-furyl 2-pyridyl sulfide is as follows. A solution of 2-furyllithium was prepared by adding *n*-butyllithium (5.5 mmol as 1.6 M solution in *n*-hexane) to a solution of furan (480 μL, 5.5 mmmol) in tetrahydrofuran (20 mL) under an argon atmosphere at −78°C over 4 hours. To the stirred solution was added a solution of di-2-pyridyl disulfide (1.10 g, 5.0 mmol) in tetrahydrofuran (100 mL) under an argon atmosphere at −78°C during 1 hour. After the usual workup, the product was extracted with ether three times. The combined ether layer was washed with water and dried over anhydrous magnesium sulfate. After the solvent had been evaporated, the residue was purified by silica gel column chromatography; elution with chloroform gave 2-furyl 2-pyridyl sulfide in 83% yield (808 mg). 2-Furyl 2-pyridyl sulfide: oil, R_f = 0.45 (with a mixture of *n*-hexane: ethyl acetate = 9:1), mass (*m*/*z*); 177 (M^+, 48.5), 149 (49.7), 123 (18.2), 104 (21.6), 78 (96.2), 51 (100.0%), ^{1}H-NMR (δ, 270 MHz); 6.54 (t, *J* = 3.2 Hz, 1H, 4 furan), 6.80 (d, *J* = 7.8 Hz, 1H, 3 pyridine), 6.84 (d, *J* = 3.2 Hz, 1H, 3 furan), 7.20 (d, *J* = 5.3 Hz, 1H, 5 pyridine), 7.49 (t, *J* = 7.8 Hz, 1H, 4 pyridine), 7.67 (d, 1H, 5 furan), 8.41 (d, *J* = 5.3 Hz, 1H, 6 pyridine), ^{13}C-NMR (δ, 270 MHz, DEPT); 112.19, 120.25, 120.57, 120.81, 136.93, 141.06 (ipso position in furan ring), 147.09, 149.47, 160.28 (ipso position in pyridine ring), HRMS; calcd. for C_9H_7NOS: 172.022; found: 172.03. A typical experimental procedure for the preparation of 2-furyl 2-pyridyl sulfoxide **5** is as follows. To a solution of 2-furyl 2-pyridyl sulfide (700 mg, 3.95 mmol) in dichloromethane (100 mL) was added dropwise *m*-chloroperbenzoic acid (819 mg, 4.74 mmol) in dichloromethane (100 mL) at 0°C during 4 hours. The mixture was stirred at 0°C. After 4 hours, a sodium dithionate aqueous solution and then a sodium hydroxide aqueous solution were added. After the usual workup, the product was extracted with chloroform three times. The combined chloroform layer was washed with water and dried over anhydrous magnesium sulfate. After the solvent had been evaporated, the residue was purified by recrystallization from ether to give 2-furyl 2-pyridyl sulfoxide in 97% yield (740 mg). 2-Furyl 2-pyridyl sulfoxide **5**: white needles, mp, 114.0–115.0°C, R_f = 0.5 (with chloroform), mass (*m*/*z*); 194 (M^+ + 1, 0.6), 193 (M^+, 0.3), 164 (52.0), 136 (32.9), 111 (21.6), 78 (100.0%), IR (KBr, cm$^+$): 1057 (S–O), ^{1}H-NMR (δ, 270 MHz); 6.48 (t, *J* = 3.4 Hz, 1H, 4 furan), 7.04 (d, *J* = 3.4 Hz, 1H, 3 furan), 7.41 (t, 1H, 5 pyridine), 7.52 (d, *J* = 5.3 Hz, 1H, 5 furan), 8.01 (t, *J* = 7.8 Hz, 1H, 4 pyridine), 8.23 (d, *J* = 7.8 Hz, 1H, 3 pyridine), 8.58 (d, *J* = 5.3 Hz, 1H, 6 pyridine), ^{13}C-NMR (δ, 270 MHz, DEPT); 111.35, 118.06, 120.22, 124.92, 135.12, 147.34, 149.74, 151.97 (ipso position in furan ring), 161.92 (ipso position in pyridine ring); anal. calcd. for $C_9H_7NO_2S$: C, 55.96; H, 3.62; N, 7.25. Found: C, 55.45; H, 3.61; N, 7.11%.

Reaction of di-2-Furyl Sulfoxide 1 *with 2-Thienylithium*

A similar procedure to that described earlier was followed with 2-thienyllithium (3.3 mL, 3.3 mmol), 1

(546 mg, 3.0 mmol) and THF (10 mL) under an argon atmosphere. The yield of **4** is shown in Equation 2.

Reaction of di-2-Furyl Sulfoxide 1 *with 2-Pyridyllithium*

Similarly, we obtained 2,2′-bipyridyl (mp: 68.5°C [Lit. 69.7°C] [10]). The yield of 2,2′-bipyridyl is shown in Equation 3.

Reaction of di-2-Thienyl Sulfoxide 2 *with 2-Furyllithium*

We obtained 2-furyl 2-thienyl sulfoxide **4** similarly. The yield of **4** is shown in Equation 4.

Reaction of di-2-Thienyl Sulfoxide 2 *with 2-Pyridyllithium*

The reaction took place at −78°C for 10 minutes to give 2-(2-pyridyl)thiophene(mp 63°C [Lit. 62°C] [8]) and 2-pyridyl 2-thienyl sulfoxide **6** (mp 89°C [Lit. 89–90°C] [11]). The yields of 2-(2′-pyridyl)thiophene and 2-pyridyl 2-thienyl sulfoxide **6** are shown in Equation 6.

Reaction of di-2-Pyridyl Sulfoxide 3 *with 2-Furyllithium*

A similar reaction proceeded under an argon atmosphere at 25°C for 10 minutes to give 2-(2-furyl)pyridine. The yield of 2-(2-furyl)pyridine is shown in Equation 7. 2-(2-Furyl)pyridine: oil, R_f = 0.52 (*n*-hexane:ethyl acetate = 6:4), mass (*m/z*); 145 (M^+, 100.0), 117 (32.6), 89 (46.0), 78 (15.8%), ^{1}H-NMR (δ, 270 MHz); 6.52 (t, J = 4.8 Hz, 1H, 5 pyridine), 7.05 (d, J = 3.3 Hz, 1H, 3 pyridine), 7.09–7.16 (m, 1H, 4 furan), 7.52 (d, 1H, 3 furan), 7.67 (d, 1H, 5 furan), 7.69 (t, J = 3.3 Hz, 1H, 4 pyridine), 8.59 (d, J = 4.8 Hz, 1H, 6 pyridine), ^{13}C-NMR (δ, 270 MHz, DEPT); 108.48, 111.96, 118.48, 121.81, 136.54, 143.20, 149.28 (ipso position in furan ring), 149.48, 153.48 (ipso position in pyridine ring), 149.48, HRMS; calcd. for C_9H_7NO: 145.05; found: 145.05.

Reaction of di-2-Pyridyl Sulfoxide 3 *with 2-Thienyllithium*

The reaction occurred in THF similarly and gave 2-(2-pyridyl)thiophene in the yield shown in Equation 8.

Reaction of di-2-Pyridyl Sulfoxide 3 *with 2-Pyridyllithium*

A similar reaction gave 2,2′-bipyridyl in the yield shown in Equation 9.

Reaction of 2-Furyl 2-Thienyl Sulfoxide 4 *with 2-Furyllithium*

A similar reaction gave di-2-furyl sulfoxide **1** (mp 85°C [Lit. 85.0–85.5°C] [12]) and also di-2-thienyl sulfoxide **2** [8]. The yields of **1** and **2** are shown in Equation 10.

Reaction of 2-Furyl 2-Thienyl Sulfoxide 4 *with 2-Thienyllithium*

After the reaction mixture had been stirred at 25°C for 10 minutes, we obtained 2,2′-difuryl sulfoxide **1** and di-2-thienyl sulfoxide **2**. The yields of **1** and **2** are shown in Equation 11.

Reaction of 2-Furyl 2-Thienyl Sulfoxide 4 *with 2-Pyridyllithium*

Similarly, 2-(2-furyl)thiophene, 2-(2-furyl)pyridine, 2-(2-pyridyl)thiophene, and 2,2′-bipyridyl were obtained in the yields shown in Equation 12.

Reaction of 2-Furyl 2-Pyridyl Sulfoxide 5 *with 2-Furyllithium*

A similar reaction gave 2-(2-furyl)pyridine in the yield shown in Equation 13.

Reaction of 2-Furyl 2-Pyridyl Sulfoxide 5 *with 2-Thienyllithium*

The reaction mixture was stirred at −78°C for 10 minutes in the usual way, and 2-(2-furyl)pyridine, 2-(2-pyridyl)thiophene, 2,2′-bipyridyl, and 2-pyridyl 2-thienyl sulfoxide **6** were obtained in the yields shown in Equation 14.

Reaction of 2-Furyl 2-Pyridyl Sulfoxide 5 *with 2-Pyridyllithium*

We obtained 2-(2-furyl)pyridine, 2-(2-pyridyl)-thiophene, and 2,2′-bipyridyl in the same way in the yields shown in Equation 15.

Reaction of 2-Pyridyl 2-Thienyl Sulfoxide 6 *with 2-Furyllithium*

In the same way, we obtained 2-(2-furyl)pyridine and 2-(2-pyridyl)thiophen in the yields shown in Equation 16.

Reaction of 1 *with 2-Pyridyllithium in the Presence of Benzaldehyde*

A typical procedure is as follows. A solution of 2-pyridyllithium was prepared by adding *n*-butyllithium (3.4 mL, 5.5 mmol as a 1.6 M solution in *n*-hexane) to a solution of 2-bromopyridine (513 μL, 5.5 mmol) in THF (5 mL) under an argon atmosphere at -78°C during 10 minutes. The solution was added to a solution of **1** (965 mg, 5.0 mmol) in THF (10 mL) under an argon atmosphere. After 1 minute, benzaldehyde (508 μL, 5.0 mmol) was added to the reaction mixture and stirred for 10 minutes. After the usual workup, the products were extracted with ether three times. The combined ether layer was washed with water and dried over anhydrous magnesium sulfate. After the solvent had been evaporated, the residue was purified by silica gel column chromatography with chloroform as eluent to give 2-furylphenylmethanol, di-2-pyridyl, and di-2-pyridyl sulfoxide **3**. The yields of products are shown in Scheme 2. 2-Furylphenylmethanol: oil, mass (*m/z*); 174 (M^+), ^{1}H-NMR (δ, 270 MHz); 2.45 (s, 1H, OH), 5.82 (s, 1H, -CH-), 6.11 (t, J = 3.0 Hz, 1H, 3 furan), 6.31 (dd, J = 3.0 Hz, 1H, 4 furan), 7.21–7.40 (m, 6H, Ph, 5 furan).

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