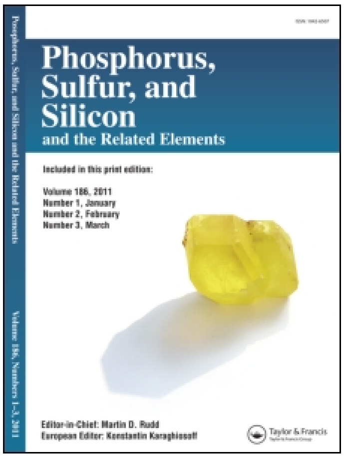

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THIONYL CHLORIDE—A GOOD LIGAND COUPLING REAGENT

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THIONYL CHLORIDE—A GOOD LIGAND COUPLING REAGENT*

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Thionyl chloride was found to react with phenylethynyllithium and heteroaryllithium affording 1,4-diphenylbutadiyne and biheteroaryl, and the corresponding sulfoxides and sulfides, respectively. Apparently, ligand coupling proceeded within the intermediary sulfurane. The occurrence of ligand coupling was estimated from the pKa value of the carbon acid as a nucleophile. Furthermore, it was found that the presence of *p*-orbital, i.e., π-bond, is preferable at the ipso carbon atom of the nucleophile for a good ligand coupling reaction, while for alkyllithiums and alkylmagnesium chloride do not give bialkyl as the main coupling product, but others, which are different from the organic lithiums or magnesium chloride used.

Key words: Thionyl chloride, hypervalent, ligand coupling, sulfurane

INTRODUCTION

Since the first example of the ligand coupling reaction within hypervalent species was found, more than 25 years has passed.[1] The concept was introduced[2] and has been found to be applicable to many hypervalent species of various heteroatoms.[3] Especially, the ligand coupling reaction on the sulfur atom in the sulfoxide has been reported in detail.[4]

As an extension of the ligand coupling reaction, treatments of thionyl chloride with organolithium compounds has been carried out at this time. Thionyl chloride is known to have a pyramidal structure,[5] and is known to be a good chlorinating reagent of aliphatic alcohols, amides, carbonylates, epoxides, oximes, sulfonic acids and various others.[6] Thionyl chloride has also been known to be a good deoxygenating reagent for the sulfoxides.[7] Dimethyl sulfoxide reacted with thionyl chloride to give a rearrangement product, as shown in Scheme I.[8]

However, only a few reactions have been known for the reactions of organometallics with thionyl chloride. Representative reactions are shown in Scheme II.[9] In our previous papers,[10] the reaction of thionyl chloride with 2-thienyllithium was reported to afford bi-2-thienyl as a ligand coupling product through a sulfurane

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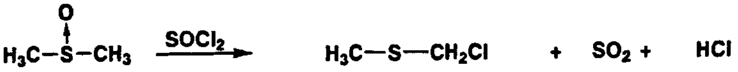
*Dedicated to Professor Reinhard Schmutzler's 60th birthday.



$$H_3C-\overset{\overset{O}{\uparrow}}{S}-CH_3 \xrightarrow{SOCl_2} H_3C-S-CH_2Cl + SO_2 + HCl$$

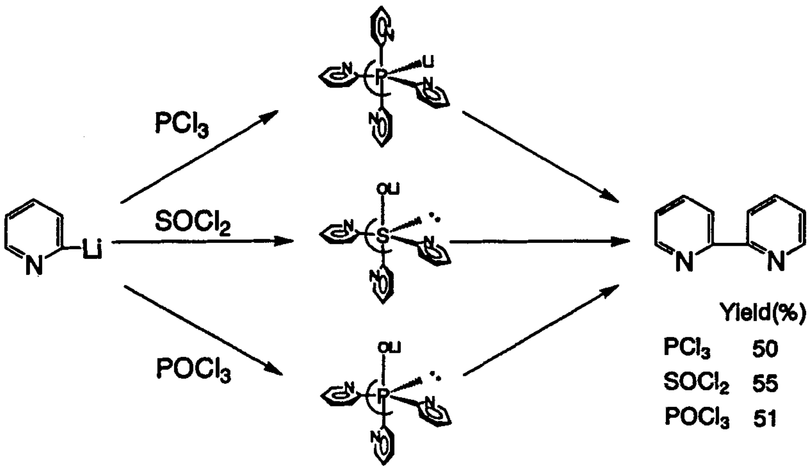
SCHEME I

$$R_4Pb \xrightarrow{SOCl_2} R_3PbCl + R_2PbCl_2 + RSOCl + R\text{-}S(O)\text{-}R$$

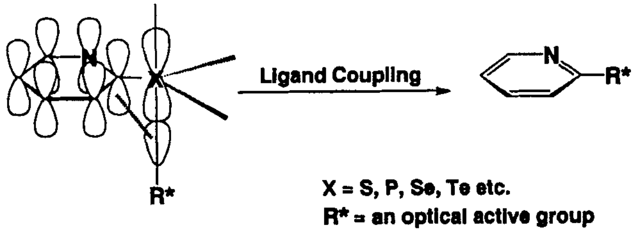
$$Hg(SCF_3)_2 \xrightarrow{SOCl_2} CF_3SSCF_3 + SO_2 + HgCl_2$$

$$2RMgBr \xrightarrow{SOCl_2} R\text{-}S(O)\text{-}R + MgCl_2 + MgBr_2$$

SCHEME II



SCHEME III



SCHEME IV

intermediate. One can use not only thionyl chloride but also other chlorinating reagents to achieve the same coupling reactions, as shown in Scheme III.[11]

We have suggested that the ligand coupling reaction is considered to take place between an equatorial ligand of sp^2 hybrid orbitals and an axial one which is of p-orbital in the hypervalent sulfurane, as shown in Scheme IV.

Recently Morokuma *et al.* suggested that there is a certain amount of interaction between axial and equatorial ligands in the hypervalent intermediate based on their calculation.[12]

Up until now we have used only one sp^2 carbon atom for the occurrence of the ligand coupling reaction. We do not know this can be extended to other systems.

Thus, in order to clarify if a *p*-orbital at the ipso carbon is absolutely necessary for the ligand coupling reactions, we have carried out the reactions of thionyl chloride with various organometallics and found a few interesting results.

RESULTS AND DISCUSSION

A. Formation of 1,4-diphenylbutadiyne from β-styryllithium in the Treatment with Thionyl Chloride

While we were attempting to study the stereochemistry at the ipso carbon in the coupling product and treated *β*-styryllithium which would be formed between the mixture of cis and trans *β*-bromostyrene and *n*-BuLi with thionyl chloride. This reaction would give 3 isomers (cis-cis, cis-trans and trans-trans) of 1,4-diphenyl-1,3-butadiene. However, we found the first step to be the formation of phenylethyne **1**, which then further treatment with *n*-BuLi to form *ω*-phenylethynyllithium. Thus the newly formed *ω*-phenylethynyllithium reacted with thionyl chloride to give 1,4-diphenylbutadiyne **2**, as shown in Scheme V and Table I.

Consequently, the treatment of thionyl chloride with *ω*-phenylethynyllithium gave 1,4-diphenylbutadiyne **2**. As one expects the yield of the coupling product, namely, 1,4-diphenyl-butadiyne **2** would increase as a mole ratio of *ω*-phenylethynyllithium increases. This was found to be true and we obtained the maximum yield when 3 moles of phenylethynyllithium was used, as shown in Scheme VI.

B. Formation of Biheteroaryls by Treatment of 2-lithiated-heteroaryls with Thionyl Chloride

Earlier, in order to make the symmetrical sulfoxide, we used a standard procedure,[13] of using imidazole and thionyl chloride, as shown in Scheme VII, however

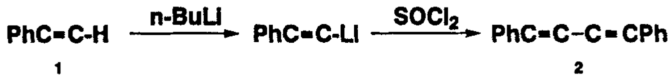
SCHEME V

TABLE I

Reaction of thionyl chloride with *β*-bromostyrene and *n*-BuLi

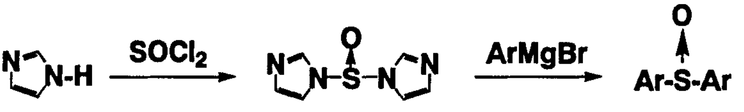
β-Bromostyrene[a)]	n-BuLi[a)]	Products(%)	
		1	2
1	1	trace	trace
1	2	8	trace
2	4	3	5
4	8	31	7
6	12	39	9

a) molar ratio to $SOCl_2$



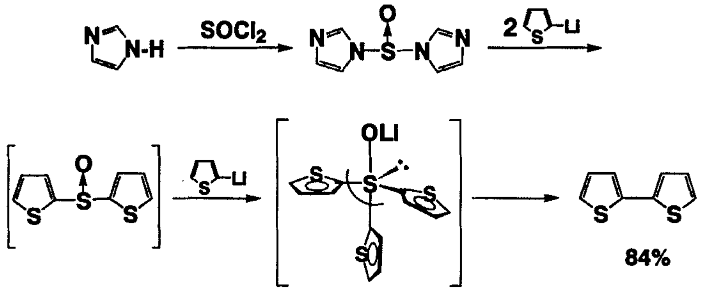
(1 quiv. to SOCl$_2$)	12%
(2 equiv. to SOCl$_2$)	24%
(3 equiv. to SOCl$_2$)	96%

SCHEME VI



Ar	Ar-S(O)-Ar (%)
Ph	35
p-Tolyl	40
p-Anisyl	60
Mesityl	84

SCHEME VII



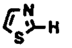
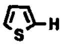
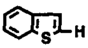
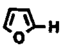
SCHEME VIII

we could not find di-2-thienyl sulfoxide among the product, but found a direct ligand coupling reaction, as shown in Scheme VIII.

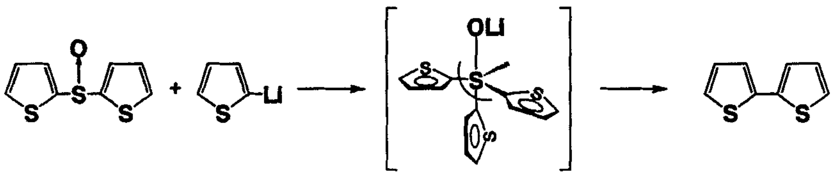
Up until now when we were dealing the ligand coupling reaction between aryl alkyl sulfoxides and benzylmagnesium halides, we believed that the ipso carbon atom of the aryl group would be in between 177.5 and 150 ppm by ^{13}C nmr scale for the successful ligand coupling.[14] It was a useful empirical rule to diagnose the reaction path. We have found away from both sides of 177.5 and 150 ppm by ^{13}C nmr scale range the ligand exchange seems to prevail. Now that we have treated 2-thienyllithium and other 2-lithiated heteroaryls with thionyl chloride, we cannot use our old diagnose. Therefore, we have shifted to use the pKa value of the ipso carbon atom of the sulfoxide. As shown in Table II, it has been quite successful. The range of successful ligand coupling lies in between pKa 28.3 to 33.2. Not only thiophene but also 2-thiazole (pKa = 28.3),[15] benzothiazole (pKa = 27.8–28.9)[15] and benzo[2,3-b]furan (pKa = 33.2)[15] were found to couple each other. However 2-furyllithium (pKa of 2-furyl group = 35.6)[15] did not undergo any coupling. Since the pKa value of the 2 position of thiophene is 33.0 while ^{13}C nmr chemical shift of di-2-thienyl sulfoxide is just in the range of ligand coupling, we have treated di-2-thienyl sulfoxide with 2-thienyllithium and indeed a nice ligand coupling took place, as shown in Scheme IX.

TABLE II

Reaction of thionyl chloride with R-Li

R-H	Value of pKa	Products (%) a) R-R	R-S-R	R-$\overset{\text{O}}{\text{S}}$-R	Value of chemical shift b)	Chemical mode
	15.7	-	-	-	-	
	28.3	33	15	17	172.97	L. C.c)
	27.8 28.9	29	11	19	177.97	L. C.c)
	33.0	48	-	-	150.30	L. C.c)
	33.2	48	27	17	152.65	L. C.c)
	32.4 33.5	-	-	34	141.97	Formation of sulfoxide
	35.6	-	-	45	151.44	Formation of sulfoxide

a) Yields were based on using 3 equiv. R-Li to $SOCl_2$. b) ipso carbon in the sulfoxide detected by ^{13}C-NMR (DEPT)
c) L. C.; ligand coupling reaction

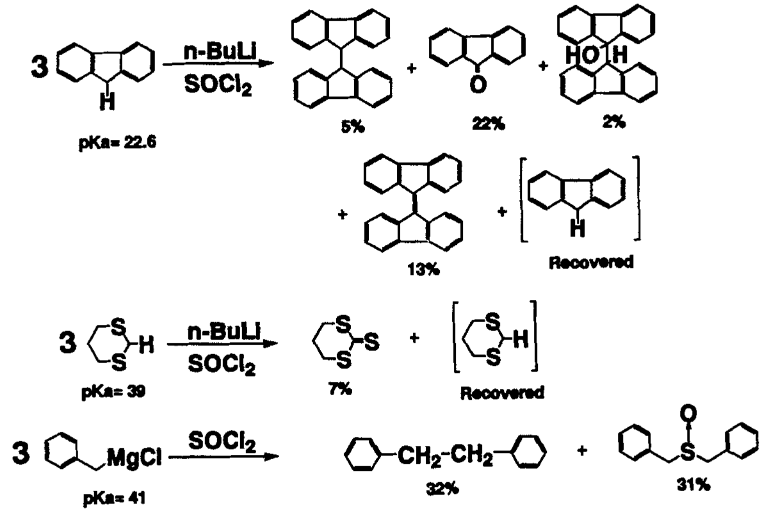


SCHEME IX

When 2-furyllithium compound was allowed to react with di-2-furyl sulfoxide under various conditions, as described in the experimental section, 2-furyllithium was found not to react with the sulfoxide to give bi-2-furyl. 2-Furyllithium, however, was found to react with thionyl chloride to give di-2-furyl sulfoxide in a fair yield.

C. Reaction of Thionyl Chloride with Alkylmetallic Reagents Formed from sp^3 Carbon Acid

We believe that thionyl chloride is a good ligand coupling reagent for many 2-lithiated heteroaromatic compounds and ω-phenylethynyllithium. However, for lithiated carbon of sp^3 species whose pKa values are not in the range of ligand coupling reaction, even the formation of symmetrical sulfoxides does not necessarily applicable, as shown in Scheme X. For example, lithiated fluorene (pKa of 9-fluorene = 22.6)[16] reacts with thionyl chloride but the products are rather complicated, while the benzyl Grignard reagent (pKa of ω position of toluene = 43)[16] affords dibenzyl in small yields. These require some further study to clarify the nature of the reaction.



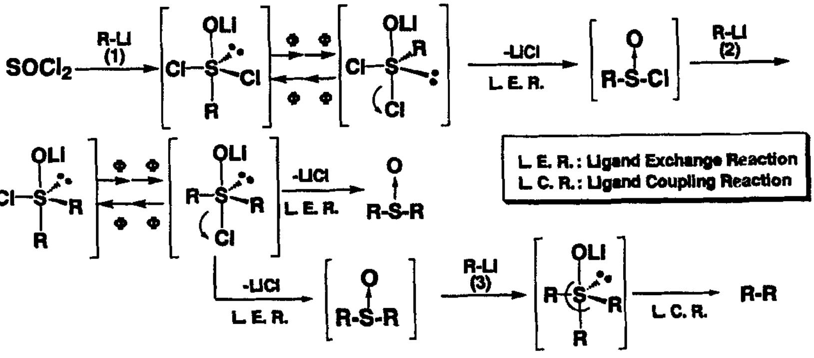
SCHEME X

CONCLUSION

The reaction of thionyl chloride with alkynyllithium and aryllithium gave the corresponding coupling products, sulfoxides and sulfides, respectively.

Thus, the mechanism is considered as follows. Initially the ligand exchange reaction of thionyl chloride with the first nucleophile takes place to give the sulfinyl chloride. The sulfinyl chloride thus formed reacts with the second nucleophile to give the symmetrical sulfoxide, as shown in Scheme XI.

If we assumed that the facile ligand coupling reaction occurs only the 2-lithiated substituted ipso carbon atom of sp^2, i.e., π-bond, of a suitable pKa value in the newly formed sulfoxide, this is an interesting behavior of the sulfurane species. However no straight forward ligand coupling products were formed for alkyllithiums and alkylmagnesium chloride.



SCHEME XI

EXPERIMENTAL

General. All the melting points were uncorrected and were taken on a Yanagimotò melting-point apparatus. IR spectra were obtained on a Jasco-IRA-202 and Perkin Elmer FT-IR 1760X spectrometers. NMR spectra were obtained on a JEOL-PMX60SI or a JEOL-GSX-270 FT-NMR spectrometer in $CDCl_3$ using TMS as an internal standard. All the reactions were monitored by TLC (Merck, Kieselgel 60 F254), GLC (Hitachi 163 and 663-30, using a 3% silicon OV-17 chromosorb W, a 30% silicon gum SE-30 or a 30% polyethylene glycol 20 M on 60–80 mesh), HPLC (Shimadzu SPD-6A, OD-ST). The 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 in Wako Pure Chemical Industries, LTD.

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

Reaction of thionyl chloride with β-bromostyrene and n-BuLi

A typical experimental procedure is as follows. A solution of phenyl ethynyllithium was prepared by adding *n*-BuLi (7.1 mL, 11 mmol as 1.5 M a solution in *n*-hexane) to a solution of *β*-bromostyrene (1.3 mL, 10 mmol) in THF (30 mL). Thionyl chloride (0.4 mL, 5.0 mmol) was added to a stirred above solution at −78°C for 10 min under an argon atmosphere when the solution turned to red. The reaction mixture was quenched by MeOH (1 mL).

The products were extracted with ether three times. The combined ether layer was washed with water and dried over anhyd. $MgSO_4$. After the solvent was evaporated, the residue was purified by silica gel column chromatography eluting for *n*-hexane. The relative yield of phenylethyne **1** (bp; 143–146°C)[17] was and that of 1,4-diphenylbutadiyne **2** (mp; 87.0–88.0°C)[18] was shown in Table I upon determination of glc analysis by using *n*-tridecane (100 μL) as an internal standard.

Reaction of thionyl chloride with phenylethynyllithium

A similar procedure to that described above was followed with 1.5 M *n*-BuLi (0.29 mL, 5.1 mmol), phenylethyne (0.60 mL, 5.0 mmol), THF (30 mL) and thionyl chloride (0.4 mL, 5.0 mmol) to give **2**. The yield of **2** was shown in Scheme VI upon determination of glc analysis by using *n*-tridecane (100 μL) as an internal standard.

Reaction of di-1-imidazolyl sulfoxide with 2-thienyllithium

A typical experimental procedure is as follows. Thionyl chloride (0.4 mL, 5.0 mmol) was added to a solution of imidazole (272 mg, 4.0 mmol) in THF (100 mL) at 0°C for 30 min. After 30 min, the precipitate was filtered under an argon atmosphere. The filtrate was added to 2-thienyllithium which was prepared by adding *n*-BuLi (8.6 mL, 12.0 mmol as 1.5 M a solution in *n*-hexane) to a solution of 2-bromothiophene (1.2 mL, 12 mmol) in THF (100 mL) at −78°C for 1 h. The reaction mixture was quenched by MeOH (1 mL). The product was extracted with ether three times. The ether layer was washed with water and dried over anhyd. $MgSO_4$. The solvent was evaporated, the residue was purified by silica gel column chromatography eluting for *n*-hexane. The yield of di-2-thienyl (mp: 30°C)[10] was shown in Scheme VIII.

Reaction of thionyl chloride with 2-thiazolyllithium

A typical experimental procedure is as follows. 2-Thiazolyllithium was prepared by adding *n*-BuLi (2.0 mL, 3.0 mmol, a 1.5 M solution in *n*-hexane) to thiazole (213 μL, 3.0 mmol) in THF (5 mL) at −78°C for 5 min under an argon atmosphere when the solution turned to yellow. To the above 2-thiazolyllithium solution thionyl chloride (0.1 mL, 1.0 mmol) was added at −78°C for 10 min when the solution immediately turned to red. The reaction mixture was quenched by MeOH (1 mL). The products were extracted with ether three times. The ether layer was washed with water and dried over anhyd. $MgSO_4$. The solvent was evaporated, the residue was purified by silica gel column chromatography eluting for $CHCl_3$. The yields of di-2-thiazolyl, di-2-thiazolyl sulfide and di-2-thiazolyl sulfoxide were shown in Table II.

di-2-thiazolyl; mp; 103.5–104.0°C. MS (m/z); 168 (M^+, 5.6), 149 (18.3), 132 (25.6), 85 (100%). ^1H-NMR (δppm); 7.44 (d, J = 2.7 Hz, 2 H, 5,5'Thiazol), 7.90 (d, J = 2.7 Hz, 2 H, 4,4'Thiazol). ^{13}C-NMR (δppm); 161.65 (at ipso position on Thiazol), 143.90, 120.93. Anal. Calcd. for $C_6H_4N_2S_2$: C, 42.84%; H, 2.38%; N, 16.66%. Found: C, 42.52%; H, 1.98%; N, 16.51%.

di-2-thiazolyl sulfide; Oil. MS (m/z); 200 (M^+, 100), 124 (22.7), 58 (94.0%). ^{1}H-NMR (δppm); 7.42 (d, *J* = 3.3 Hz, 2 H, 5,5'Thiazol), 7.85 (d, *J* = 3.3 Hz, 2 H, 4,4'Thiazol). ^{13}C-NMR (δppm); 158.93 (at ipso position on Thiazol), 143.79, 122.93. Anal. Calcd. for $C_6H_4N_2S_3$: C, 35.98%; H, 2.00%; N, 13.99%. Found: C, 35.50%; H, 1.87%; N, 16.66%.

di-2-thiazolyl sulfoxide; MS (m/z); 216 (M^+, 1.9), 68 (32.2), 58 (100%). ^{1}H-NMR (δppm); 7.79 (d, *J* = 3.0 Hz, 2 H, 5,5'Thiazol), 7.99 (d, *J* = 3.0 Hz, 2 H, 4,4'Thiazol). ^{13}C-NMR (δppm); 172.97, (at ipso position on Thiazol), 145.12, 124.64. Anal. Calcd. for $C_6H_4N_2OS_3$: C, 33.32%; H, 1.85%; N, 12.95%. Found: C, 33.19%; H, 1.69%; N, 12.84%.

Reaction of thionyl chloride with 2-benzothiazolyllithium

A similar procedure to that described above was followed with 1.5 M *n*-BuLi (2.0 mL, 3.0 mmol), benzothiazole (213 μL, 3.0 mmol), THF (5 mL) and thionyl chloride (0.1 mL, 1.0 mmol) to give di-2-benzothiazolyl, di-2-benzothiazolyl sulfide and di-2-benzothiazolyl sulfoxide. The products were purified by silica gel column chromatography eluting for $CHCl_3$. The yields of di-2-benzothiazolyl, di-2-benzothiazolyl sulfide and di-2-benzothiazolyl sulfoxide were shown in Table II.

di-2-benzothiazolyl; Oil. ^{1}H-NMR (δppm); 7.41 (dd, *J* = 8.0, 7.6 Hz, 2 H, 6,6'Btz), 7.47 (dd, *J* = 8.4, 7.2 Hz, 2 H, 5,5'Btz), 7.88 (d, *J* = 7.2 Hz, 2 H, 4,4'Btz), 7.99 (d, *J* = 8.0 Hz, 2 H, 7,7'Btz). ^{13}C-NMR (δppm); 121.22, 123.06, 125.71, 126.63, 136.63, 152.91, 159.97. Anal. Calcd. for $C_{14}H_8N_2S_2$: C, 62.67%; H, 2.98%; N, 10.44%. Found: C, 62.11%; H, 2.55%; N, 10.45%.

di-2-benzothiazolyl sulfide; Oil. ^{1}H-NMR (δppm); 7.24 (dd, *J* = 8.0 Hz, 8.0, 2 H, 6,6'Bt), 7.38 (dd, *J* = 7.4, 8.1 Hz, 2H, 5,5'Btz), 7.62 (d, *J* = 8.1 Hz, 2H, 4,4'Btz), 7.86 (d, *J* = 8.0 Hz, 2 H, 7,7'Btz). Anal. Calcd. for $C_{14}H_8N_2S_3$: C, 55.98% H, 2.66%; N, 9.33%. Found: C, 55.53%; H, 2.42%; N, 8.96%.

di-2-benzothiazolyl sulfoxide; Oil. ^{1}H-NMR (δppm); 7.42 (dd, *J* = 7.8, 8.3 Hz, 2H, 6,6'Bt), 7.52 (dd, *J* = 8.2, 7.8 Hz, 2H, 5,5'Bt), 7.85 (d, *J* = 8.2 Hz, 2H, 4,4'Btz), 8.06 (d, *J* = 8.3, 2H, 7,7'Bt). Anal. Calcd. for $C_{14}H_8N_2OS_3$: C, 53.15%; H, 2.53%; N, 8.86%. Found: C, 52.89%; H, 2.42%; N, 8.77%.

Reaction of thionyl chloride with 2-thienyllithium

A similar procedure to that described above was followed with 1.5 M *n*-BuLi (2.10 mL, 3.0 mmol), 2-bromothiophene (291 μL, 3.0 mmol), THF (50 mL) and thionyl chloride (0.22 mL, 3.0 mmol) to give bi-2-thienyl. The yield of di-2-thienyl was shown Table II upon determination of glc analysis by using *n*-tridecane (500 μL) as an internal standard.

Reaction of thionyl chloride with 2-benzo[2,3-b]furanyllithium

A similar procedure to that described above was followed with 1.5 M *n*-BuLi (2.0 mL, 3.0 mmol), benzo[2,3-b]furan (331 μL, 3.0 mmol), THF (5 mL) and thionyl chloride (0.1 mL, 1.0 mmol) to give di-2-benzo[2,3-b]furyl, di-2-benzo[2,3-b]furyl sulfide and di-2-benzo[2,3-b]furyl sulfoxide. The products were purified by silica gel column chromatography eluting for $CHCl_3$. The yields of di-2-benzo[2,3-b]furyl, di-2-benzo[2,3-b]furyl sulfide and di-2-benzo[2,3-b]furyl sulfoxide were shown in Table II.

di-2-benzo[2,3-b]furyl; mp; 108.0–108.5°C. MS (m/z); 234 (M^+, 100), 205 (19.3), 176 (7.8), 152 (5.0), 117 (10.6%). ^{1}H-NMR (δppm); 7.31 (dd, *J* = 7.3, 7.6 Hz, 2 H, 5,5'Bf), 7.41 (dd, *J* = 7.1, 7.7 Hz, 2 H, 6,6'Bf), 7.47 (s, 2 H, 3,3'Bf), 7.51 (d, *J* = 7.3 Hz, 2 H, 4,4'Bf), 7.69 (d, *J* = 7.7 Hz, 2 H, 7,7'Bf). ^{13}C-NMR (δppm); 156.81 (at 9 position on Bf), 152.65 (at 2 position on Bf), 127.18, 126.55 (at 8 position on Bf), 123.97, 122.50, 112.69, 112.22. Anal. Calcd. for $C_{16}H_{10}O_2$: C, 82.06%; H, 4.27% Found: C, 81.68%; H, 3.95%.

di-2-benzo[2,3-b]furyl sulfide; mp; 119.5–120.0°C, MS (m/z); 266 (M^+, 100). 237 (46.4), 205 (38.0), 121 (14.2), 89 (14.6%), ^{1}H-NMR (δppm); 7.03 (s, 2 H, 3,3'Bf), 7.21 (dd, *J* = 4.3, 3.8 Hz, 2 H, 5,5'Bf), 7.29 (dd, *J* = 3.9, 4.1 Hz, 2 H, 6,6'Bf), 7.44 (d, *J* = 3.8 Hz, 2 H), 7.53 (d, *J* = 3.9 Hz, 2 H, 7,7'Bf). ^{13}C-NMR (δppm); 156.67 (at 9 position on Bf), 145.72 (at 2 position on Bf), 128.32 (at 8 position on Bf), 125.25, 123.18, 120.97, 113.02, 111.41. Anal. Calcd. for $C_{16}H_{10}O_2S$: C, 72.18%; H, 3.76%. Found: C, 71.90%; H, 3.58%.

di-2-benzo[2,3-b]furyl sulfoxide; mp; 195.5–196.0°C. MS (m/z); 282 (M^+, 1.5), 266 (5.7), 234 (100), 205 (15.7%). ^{1}H-NMR (δppm); 7.17 (s, 2 H, 3,3'Bf), 7.27 (dd, *J* = 8.0, 7.5 Hz, 2 H, 6,6'Bf), 7.34 (dd, *J* = 7.3, 8.6 Hz, 2 H, 5,5'Bf), 7.55 (d, *J* = 8.6 Hz, 4,4'Bf), 7.63 (d, *J* = 7.5 Hz, 2 H, 7,7'Bf). ^{13}C-NMR (δppm); 155.23 (at 9 position on Bf), 147.81 (at 2 position on Bf), 128.62 (at 8 position on Bf), 125.11, 123.38, 121.39, 111.31, 103.74. Anal. Calcd. for $C_{16}H_{10}O_3S$: C, 68.08%; H, 3.54%. Found: C, 67.86%; H, 3.15%.

Reaction of thionyl chloride with 2-benzo[2,3-b]thienyllithium

A similar procedure to that described above was followed with 1.5 M *n*-BuLi (2.0 mL, 3.0 mmol), benzo[2,3-b]thiophene (402 μL, 3.0 mmol), THF (5 mL) and thionyl chloride (0.1 mL, 1.0 mmol) to give di-2-benzo[2,3-b]thienyl sulfoxide. The product was purified by silica gel column chromatography eluting for *n*-hexane-ether mixture. The yield of di-2-benzo[2,3-b]thienyl sulfoxide was shown in Table II.

di-2-benzo[2,3-b]thienyl sulfoxide; Oil. MS (m/z); 316 ($[M + 2]^+$, 4.0), 298 (100), 266 (16.4), 221 (40.2), 121 (18.9%). ^{1}H-NMR (δppm); 7.40 (d, *J* = 6.4 Hz, 4 H, 4,4'Bt, 7,7'Bt), 7.81 (t, *J* = 5.9 Hz, 2 H, 5,5'Bt), 7.82 (t, *J* = 6.6 Hz, 2 H, 6,6'Bt), 7.85 (s, 2 H, 3,3'Bt). ^{13}C-NMR (δppm); 147.75 (at 9 position on Bt), 141.97 (at 2 position on Bt), 137.99 (at 8 position on Bt), 127.01, 126.56, 125.19, 125.16, 122.80. IR (KBr, cm^{-1}); 1070 (S → O). Anal. Calcd. for $C_{16}H_{10}OS_3$: C, 61.13%; H, 3.18%. Found: C, 60.95%; H, 2.89%.

Reaction of thionyl chloride with 2-furyllithium

A similar procedure to that described above was followed with 1.3 M *n*-BuLi (1.72 mL, 2.2 mmol), furan (0.20 mL, 2.0 mmol), THF (10 mL) and thionyl chloride (0.14 mL, 2.0 mmol) to give di-2-furyl sulfoxide. The sulfoxide was purified by recrystallization from ether. The yield was shown in Table II upon determination of glc analysis by using dibenzyl (300 μg) as an internal standard.

di-2-furyl sulfoxide; mp: 85.0–85.5°C. MS (m/z): 182 (M^+). ^{1}H-NMR (δppm): 6.55 (dd, *J* = 1.6, 3.2 Hz, 2 H, 4,4'Fu), 7.00 (d, *J* = 3.2 Hz, 2 H, 3,3'Fu), 7.65 (d, *J* = 1.6 Hz, 2 H, 5,5'Fu). ^{13}C-NMR (δppm): 150.73 (at ipso position), 147.24, 116.16, 111.56. IR (KBr, cm^{-1}): 1058 (S → O). Anal. Calcd. for $C_8H_6O_3S$: C, 52.77%; H, 3.33%. Found: C, 52.27%; H, 2.95%.

Reaction of di-2-furyl sulfoxide with 2-furyllithium

A similar procedure to that described above was followed with 1.5 M *n*-BuLi (0.73 mL, 1.1 mmol), furan (80 μL, 1.1 mmol), THF (5 mL) and di-2-furyl sulfoxide (182 mg, 1.0 mmol) and THF (10 mL). The reaction temperature was maintained at −78°C. The conversion of di-2-furyl sulfoxide was determined by HPLC analysis, while di-2-furyl sulfoxide used as a starting material was recovered quantitatively. Even at −78°C, 25°C, and 66°C, the reaction did not proceed and only di-2-furyl sulfoxide was recovered quantitatively.

Reaction of thionyl chloride with 9-fluorenyllithium

A similar procedure to that described above was followed with 1.6 M *n*-BuLi (4.1 mL, 6.6 mmol), fluorene (997 mg, 6.0 mmol), THF (30 mL) and thionyl chloride (0.15 mL, 2.0 mmol) to give di-9-fluorenyl (mp: 242.0°C),[19] 9-fluorenone (mp: 82.0°C),[19] 9-hydroxy-di-9-fluorenyl (mp: 118.0–119.0°C)[19] and di-9-fluorenylidene (mp: 196.0–197.0°C),[19] while fluorene as a starting material was recovered in a yield of 41%. The products were purified by silica gel column chromatography eluting for *n*-hexane-ether mixture. The yields of products were shown in Scheme X.

Reaction of thionyl chloride with 2-lithio-1,3-dithiane

A similar procedure to that described above was followed with 0.8 M *n*-BuLi (7.9 mL, 6.3 mmol), 1,3-dithiane (721 mg, 6.0 mmol), THF (30 mL) and thionyl chloride (0.15 mL, 2.0 mmol) to give 1,3-dithiane-2-thione, while 1,3-dithiane as a starting material was recovered in a yield of 37%. The products were purified by silica gel column chromatography eluting for n-hexane. The yield of the product was shown in Scheme X.

1,3-dithiane-2-thione; Oil. MS (m/z): 150 (M^+, 71.2), 106 (66.3), 46 (100%). ^{1}H-NMR (δppm): 2.45 (5, *J* = 6.1 Hz, 2 H, 5 dithiane), 3.23 (t, *J* = 6.1 Hz, 4 H, 4, 6 dithiane). ^{13}C-NMR (δppm): 20.53, 34.31, 221.19. Anal. Calcd. for $C_4H_6OS_3$: C, 31.98%; H, 3.99%. Found: C, 31.87%; H, 3.43%.

Reaction of thionyl chloride with benzylmagnesium chloride

A similar procedure to that described above was followed with 1.0 M benzylmagnesium chloride (6.0 mL, 6.0 mmol), THF (10 mL) and thionyl chloride (0.15 mL, 2.0 mmol) to give dibenzyl (mp: 50.0°C)[20] nd benzyl sulfoxide (mp: 133°C).[21] The products were purified by silica gel column chromatography eluting for *n*-hexane. The yield of product was shown in Scheme X.

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