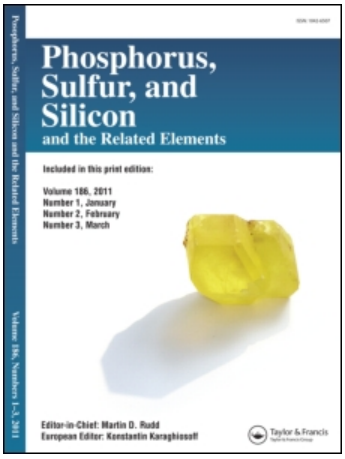

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LIGAND EXCHANGE AND LIGAND COUPLING VIA THE σ-SULFURANE INTERMEDIATE IN THE REACTION OF ALKYL 2-PYRIDYL SULFOXIDE WITH GRIGNARD REAGENTS: CONVENIENT PREPARATION OF 2,2'-BIPYRIDINES

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LIGAND EXCHANGE AND LIGAND COUPLING VIA THE σ-SULFURANE INTERMEDIATE IN THE REACTION OF ALKYL 2-PYRIDYL SULFOXIDE WITH GRIGNARD REAGENTS: CONVENIENT PREPARATION OF 2,2′-BIPYRIDINES[1]

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The reaction between methyl 2-pyridyl sulfoxide (**1**) with Grignard reagents afforded 2,2′-bipyridine (**2**) in moderate yield. The reaction is considered to involve initial ligand exchange to generate 2-pyridylmagnesium halide which in the subsequent step attacks the original sulfoxide to form the σ-sulfurane that undergoes ligand coupling to afford **2**. The reaction of *t*-butyl 2-pyridyl sulfoxide (**3**) with C_6H_5MgBr, however, gave only 2-phenylpyridine (**4**). This may be due to steric hindrance to the initial ligand exchange. Formation of **2** is a convenient process for preparation of 2,2′-bipyridines bearing various substituents.

In our previous papers,[2] we have shown that the reaction of benzylic 2-pyridyl sulfoxides with Grignard reagents or organolithium reagents gives 2-benzylpyridine. It was suggested that this compound is formed by an intramolecular ligand coupling within σ-sulfuranes formed incipiently upon nucleophilic attack of an organometallic species on the tricoordinate sulfur. A number of other ligand couplings of two identical aryl groups have also been found in the reactions of tricoordinate sulfur compounds with either aryl- and alkyllithium or Grignard reagents, all of which have been presumed to proceed via incipiently formed sulfuranes.[3]

There are reactions of other types in the treatment of sulfoxides with organolithium compounds or Grignard reagents,[4,5] which are believed to involve initial proton removal from an α-methyl or methylene group.[6] We have found an interesting reaction that affords 2,2′-bipyridine (**2**) in moderate yield by treating methyl 2-pyridyl sulfoxide (**1**) with Grignard reagents. This reaction is considered to involve initial ligand exchange and subsequent ligand coupling of two identical pyridyl groups within a sulfurane formed upon the nucleophilic attack of 2-pyridyl Grignard reagent on the original sulfoxide **1**. When the heteroaryl group is highly electron withdrawing, such as benzothiazolyl, only the ligand exchange was observed even in the reaction between benzyl 2-benzothiazolyl sulfoxide (**5**) with

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alkyl Grignard reagents. The reaction of *t*-butyl 2-pyridyl sulfoxide (**3**) with C_6H_5MgBr afforded only 2-phenylpyridine (**4**), which is presumed to be the ligand coupling product.

This paper deals with the detailed account of our observations and the mechanistic implications of these reactions.

RESULTS AND DISCUSSION

Prior to the discussion, it may be pertinent to consider briefly the general feature of the reactions of such tricoordinate sulfur compounds as sulfoxides with nucleophiles such as Grignard reagents.

In all the reactions of alkyl 2-pyridyl sulfoxides with such nucleophiles as Grignard reagents or similar oganometallic reagents, the initial step is considered to involve the nucleophilic attack of one of the nucleophilic reagents on the sulfinyl sulfur atom to form incipiently, a σ-sulfurane. This view is supported by the facile formation of stable sulfuranes[7] and the extremely short distance between the weakly nucleophlic oxygen atom of the *o*-nitro group and even the divalent sulfur atom in *o*-nitrobenzenesulfonyl methoxide,[8] and other similar observations.[7]

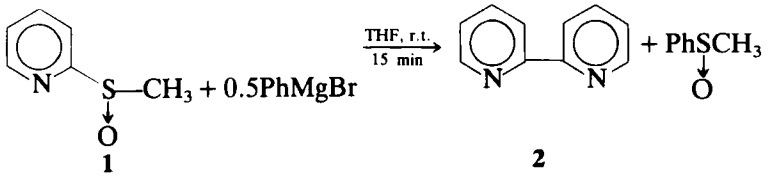
There are three conceivable ways for hypervalent species, such as σ-sulfuranes, to undergo transformation to stable compounds in which the central valence-shell-expanded atom tends to resume the normal valency by extruding a ligand bearing a pair of electrons or a pair of ligands coupled with a pair of electrons, namely, self-decomposition, ligand exchange and ligand coupling.[1]

A typical example of self-decomposition is the Wittig reaction[9] in which the high energy gained by formation of the P=O bond, *ca.* 536–576 kJ, would outweigh other possible reactions. When the leaving ligand is highly electron withdrawing, or the ligand coming from the axial position to form a hypervalent intermediate has a relatively small cohesive interaction with any ligand at the equatorial position, ligand exchange results. However, if there is a certain amount of cohesive interaction between two ligands, i.e., one at an axial and another at an equatorial position, such as overlapping of orbitals, ligand coupling would take place. The extent of the electron-withdrawing effect of a particular carbon-centered ligand combined with the central atom and forming an incipient hypervalent intermediate may be compared roughly by measuring the ^{13}C-nmr. chemical shift of the α-carbon atom of the combined ligand.

Although more data are necessary to predict *a priori* which ligand tends to couple with any other ligand preferentially, our accumulated data have shown that benzylic and allylic groups tend to couple with 2-pyridyl, which seems to couple better with itself rather than a phenyl group, which in turn appears to be a better coupling group than alkyl groups. Although the leaving ability of a certain ligand may be roughly diagnosed on the basis of the ^{13}C-nmr chemical shift of the α-carbon atom, the ease of ligand coupling within the hypervalent intermediate, in this case the σ-sulfurane, has to be tested in each case before we can fully understand the scope and the reaction trend. Hence, we have initiated extensive investigations into the coupling reaction within hypervalent intermediates. Following are some of our findings on the reactions of 2-pyridyl sulfoxides with Grignard reagents.

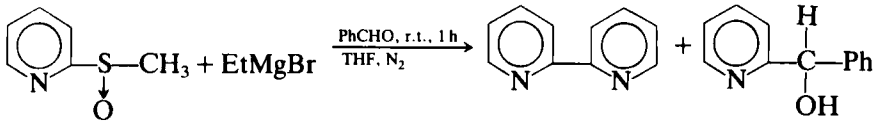
A. *Formation of 2,2'-Bipyridine* (2)

The reaction of **1** with a half equimolar amount of C_6H_5MgBr gave **2** and methyl phenyl sulfoxide (**6**) as shown in Equation 1.



1 2 (1)

The reaction is considered to involve initial ligand exchange to form 2-pyridylmagnesium bromide, which in the subsequent step attacks the original sulfoxide **1** to form the corresponding σ-sulfurane (**7**) that undergoes ligand coupling of two 2-pyridyl groups, affording **2**. Indeed, 2-pyridylmagnesium bromide, though not isolated, can be trapped in the presence of 1.4 equivalent of benzaldehyde to afford phenyl 2-pyridyl methanol (**8**) in 15% yield in addition to **2** as shown in Equation 2. 2,2'-Dipyridyl sulfoxide (**9**) was found to react with



1 2 41% 8 15% (2)

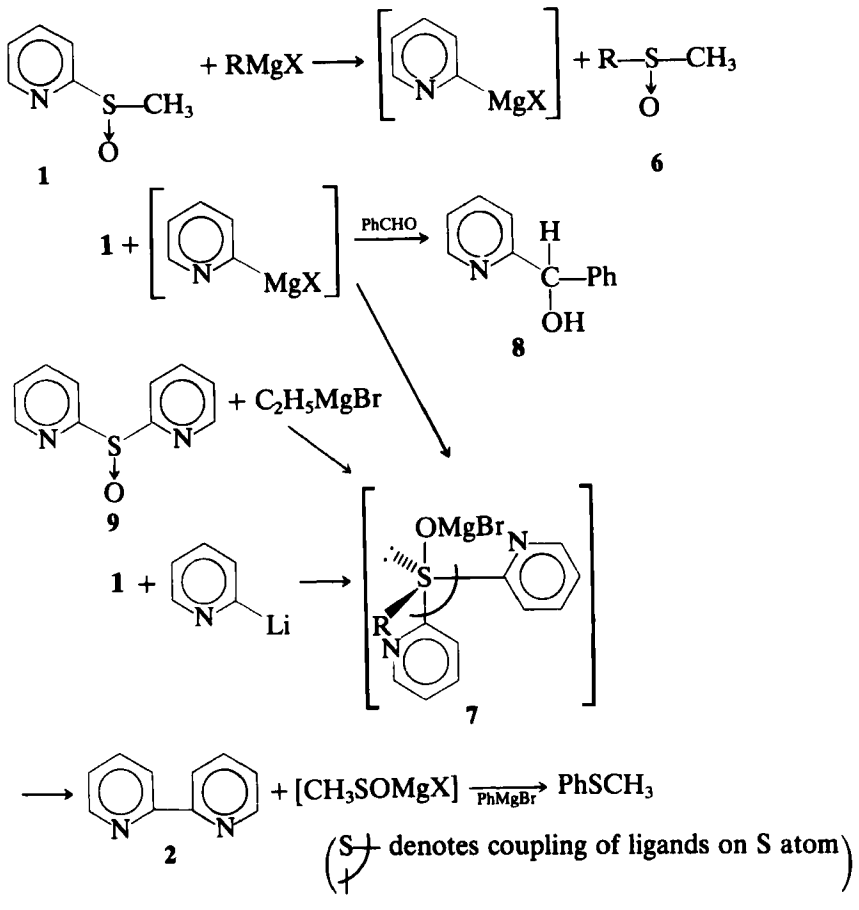
CH_3CH_2MgBr similarly, affording the same product **2**. Since there is no need of initial ligand exchange, two 2-pyridyl groups undergo facile coupling within the same σ-sulfurane intermediate **7**. A similar reaction was found to take place when **1** was treated with 2-pyridyllithium. In this case, methanesulfinylmagnesium bromide is considered to be the counterpart of the ligand coupling reaction and was indeed trapped to give methyl phenyl sulfide upon treatment of the reaction mixture with 1 eq. of C_6H_5MgBr, although the yield was poor (less than 3%)[10]. The mechanistic paths of all these reactions may be illustrated as in the following Scheme 1; representative data are summarized in Tables I and III.

When substituted 2-pyridyl sulfoxides were treated with a half equimolar amount of CH_3CH_2MgBr, various disubstituted 2,2'-bipyridines were obtained in moderate yields as shown in Table II.

A similar coupling of two substituted pyridyl groups was found in the reaction of di-2-pyridylphenylphosphine oxide with alkoxide.[11] Our procedure will be as useful as this reaction and perhaps more facile for the preparation of various substituted 2,2'-bipyridines.

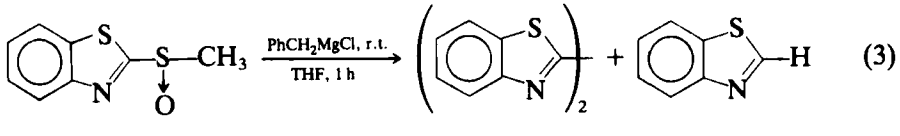
B. *Concurrent Ligand Exchange and Ligand Coupling*

As in the reaction of **1** with Grignard reagents, the reaction of alkyl 2-benzothiazolyl sulfoxides with Grignard reagents gave 2,2'-bisbenzothiazolyl. However, the main product was benzothiazole, the ligand exchange product, in

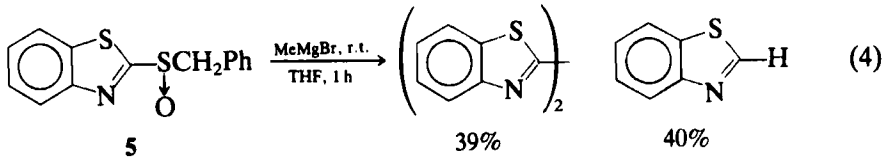


SCHEME 1

the reaction of methyl 2-benzothiazolyl sulfoxide (**10**) with $C_6H_5CH_2MgCl$ despite the apparently facile coupling of a benzyl group with heteroaryl or aryl groups bearing electron-withdrawing substituents.[12] Even in the reaction between **5** with CH_3MgBr, no 2-benzylbenzothiazole was obtained, as shown in Equations 3 and 4.



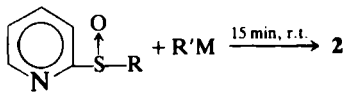
(3)

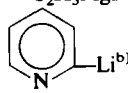


(4)

TABLE I

Preparation of bipyridyl



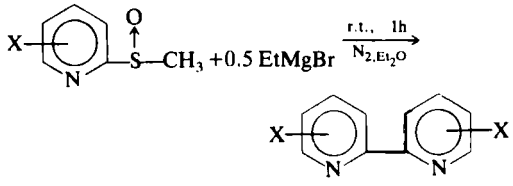
R	R'M	Yield of **2** (%)
CH_3	CH_3MgBr[a]	73
CH_3	C_2H_5MgBr	57
CH_3		59[c,d]
C_2H_5	C_2H_5MgBr[a]	55[d]
Ph	C_2H_5MgBr[a]	42[d]
	CH_2H_5MgBr[a]	63

[a] Molar ratio; sulfoxide: R'M = 1:0.5.
[b] Molar ratio; sulfoxide: R'M = 1:1.
[c] At −18°C.
[d] By g.l.c. analysis

Since the 2-benzothiazolyl group is somewhat more electron withdrawing than the 2-pyridyl group, as expected from the higher value of the ^{13}C-nmr chemical shift of the 2-position of the 2-benzothiazolyl group, 176.9 ppm, than that of the 2-pyridyl group, 163.6 ppm, ligand exchange would be more facile for a 2-benzothiazolyl group than a 2-pyridyl group, but the former would be less nucleophilic than the latter in attacking the sulfinyl sulfur atom. This may be the

TABLE II

Preparation of Substituted Bipyridyls



X	Yield (%)	mp (°C)
H	30[a]	69·5–71
6-SCH_3	61	130–131
5-Cl	40	200–202
6-Cl	55[b]	216–217
6-Br	50	228–229
3,5-Cl_2	52	103–104

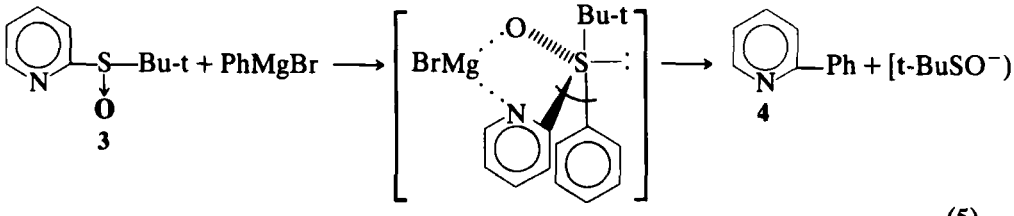
[a] In THF, yield 60–80%.
[b] In THF, yield 20–30%

main cause for the predominant ligand exchange in the reaction of 2-benzothiazolyl sulfoxide.

^{13}C-nmr chemical shifts appear to offer a rough diagnosis of the occurrence of ligand coupling. For example, the *p*-benzenesulfonylphenyl group, which has a ^{13}C-nmr chemical shift of the ipso carbon atom of 151.9 ppm, undergoes ligand coupling like the 4-pyridyl group, which has a chemical shift at the 4-position of 153.1 ppm. However, the phenyl group, having the shift of the ipso carbon atom at 146.3 ppm, may not be electron withdrawing enough for the coupling reaction to proceed.

C. *Steric Hindrance in Ligand Exchange in the Reaction of Alkyl 2-Pyridyl Sulfoxides with C_6H_5MgBr*

In the reactions of methyl, ethyl and isopropyl 2-pyridyl sulfoxides with C_6H_5MgBr, **2** and **4** were obtained as the main products along with alkyl phenyl sulfoxides as major by-products. However, in the case of **3**, no **2** was obtained but the major product was **4** which is presumed to be formed by coupling of the incoming phenyl group and a 2-pyridyl group within the σ-sulfurane (**11**) formed by the nucleophilic attack of C_6H_5MgBr as shown in Equation 5.



(5)

All these results are listed in Table III.

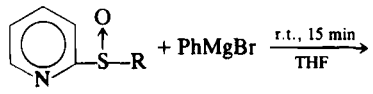
It is interesting to note that as the bulkiness of the alkyl group, *R*, increases, the direct ligand coupling of 2-pyridyl and the incoming phenyl to afford **4** starts competing with the consecutive reaction of ligand exchange to generate 2-pyridylmagnesium bromide which undergoes coupling with another 2-pyridyl group of the starting sulfoxide. When *R* is *t*-butyl, the only reaction observed was the direct coupling between 2-pyridyl group and phenyl.[13] This is considered to result mainly owing to the bulkiness of the *t*-butyl group which would be present at an axial position, as in **11**, rather than at an equatorial position where the readily exchangeable 2-pyridyl group would be located for facile ligand coupling.

EXPERIMENTAL

General. All the melting points were uncorrected and were taken on Yanaco micro melting-point apparatus. The IR spectra were obtained on a Jasco A-3 spectrometer and the nmr spectra were obtained on a Hitachi R-600 FT-nmr spectrometer or a JEOL LNM-MH-100 spectrometer in $CDCl_3$ or CCl_4 using TMS as an internal standard. All the reactions were monitored by TLC(Merck, Kieselgel 60-GF254, aluminum oxide 60GF254), GLC, (Hitachi 163, using a 5% silicon GE SE-30 on 60–80 mesh or 2% silicon OV-1 chromosorb W on 80–100 mesh in column). Silica gel used for column chromatography was Merck Kieselgel 60. Alumina used for column chromatography was

TABLE III

Reaction of 2-Pyridyl Sulfoxide with PhMgBr



R	PhMgBr (equivalent)	Products (%) 2	4	Others
CH_3	0.5	79[a]		$PhS(O)CH_3$ 36[a]
CH_3	1.0	78[b]		$PhS(O)CH_3$ 39[a]
CH_3	1.0	68	9	$PhS(O)CH_3$ 30[a] PhSMe 23
C_2H_5	0.5	56	4	PhS(O)Et 30
C_2H_5	1.0	56	6	EtSS(O)Et 8 PhS(O)Et 52 PhSEt 20
i-Pr	1.0	59	17	PhS(O)Pr-i 42 i-PrSS(O)Pr-i 23
t-Bu	1.0	0	85	t-BuSS(O)Bu-t 63

[a] By g.l.c. analysis.
[b] In all reactions, 2-alkylpyridine was not obtained.

Wako activated aluminum oxide about 200 mesh. Mass spectra were taken with a Hitachi RMU-6MG mass spectrometer. Elemental analyses were carried out at the Chemical Analysis Center in this University.

Materials. All reagents were obtained from Wako Pure Chemical Industrial Ltd., Tokyo Kasei Co., or Aldrich Chemical Co. The reagents used and reaction solvents were further purified by general methods. Starting sulfoxides were prepared by oxidation of the corresponding sulfide with hydrogen peroxide or *m*-chloroperbenzoic acid, according to our previously reported procedure.[14]

Reaction of sulfoxides with Grignard reagents. A typical experimental procedure is as follows. To a solution of **1** (200 mg, 1.56 mmol) in 5 ml THF, CH_3MgBr (1.16 ml, 1.6 mmol) in 1.0 mmol/ml THF solution was added through a 1 ml syringe with stirring under N_2 at room temperature. Stirring was continued for 15 min. Then, water was added to the reaction mixture and the solution was neutralized with dil. HCl solution and extracted three times with CH_2Cl_2. The combined CH_2Cl_2 layer was washed with water and dried over anhydrous $MgSO_4$. After the solvent was evaporated, the resulting residue was separated through activated alumina column chromatography using benzene as an eluent. **2** (90 mg, 73%) was obtained. Methyl, ethyl, isopropyl, *t*-butyl, phenyl and 2-pyridyl derivatives were allowed to react with Grignard reagents in the same way, as shown in Tables I and III. Compounds **2**, **4**, the sulfides, the sulfoxides and the thiosulfinate were isolated by chromatography through an activated alumina column using benzene and chloroform as first and second eluents and then identified by comparing the spectroscopic data with those of authentic samples.

Reaction of **1** *with 2-pyridyllithium.* To a solution of **1** (170 mg, 1.21 mmol) in 3 ml THF, 2-pyridyllithium which was prepared from 2-bromopyridine (0.16 ml, 1.68 mmol) and 15% BuLi-hexane solution (1.21 ml, 1.81 mmol) in 2 ml THF, was added with stirring under N_2 at −18°C when the solution turned red. Stirring was continued for 15 min at −18°C. After the reaction mixture was warmed at room temperature, water was added which was then extracted three times with CH_2Cl_2. The combined CH_2Cl_2 layer was washed with water and dried over anhyd. $MgSO_4$. After the solvent was filtered, the yield of **2** was 59% determined by glc.

Reaction of **1** *with* CH_3CH_2MgBr *in the presence of benzaldehyde.* To a solution of **1** (1 g, 7.1 mmol) in 20 ml THF, a solution of CH_3CH_2MgBr (7.1 mmol) in 20 ml THF was added with stirring under N_2 at room temperature. After 1 min, benzaldehyde (1 ml, 9.84 mmol) was added and stirring was continued for 1 h. Then, water was added to reaction mixture and the solution was extracted three

times with CH_2Cl_2. The combined CH_2Cl_2 layer was washed with water and dried over anhyd. $MgSO_4$. After the solvent was evaporated, the residue was distilled under reduced pressure using a Kugelrohr. At first, excess benzaldehyde was removed at 60°C under 5 mm Hg. **2** (277 mg, 41%) of bp 120–130°C/4 mm Hg and **8**[15] (198 mg, 15%) of bp 130–140 °C/4 mm Hg were obtained.

Preparation of substituted 2-methylsulfenylpyridines. Starting substituted 2-halopyridines were commercial reagents except for 3,5-dichloro-2-bromopyridine. Preparation of 3,5-dichloro-2-bromopyridine is as follows. 2-Amino-3,5-dichloropyridine (24 g, 0.15 mol) was carefully added to a 47% HBr solution (62 ml) in a 2 l three-necked flask equipped with a mechanical stirrer, cooled with crushed ice and NaCl below 0°C. After the addition, the solution was warmed at 60–70°C in a water bath until the solid 2-amino-3,5-dichloropyridine was dissolved. Then, the solution was cooled with crushed ice and NaCl below 0°C again and Br_2 (26 ml, 0.51 mol) was added dropwise to the solution, affording precipitation as a bromine adduct. Then, a solution of $NaNO_2$ (29 g, 0.42 mol) in 38 ml water was carefully added dropwise to this solution, while stirring and keeping the solution below 0°C. During the addition, gas was formed vigorously and temperature increased up to 5°C to 10°C. After the reaction was complete, a solution of 63 g NaOH in 138 ml water added, keeping the temperature below 25°C. After the solution was extracted with hexane, the combined hexane layer was washed with water and dried over anhyd. $MgSO_4$. After the solvent was evaporated, the residue was purified by recrystallization from ethanol and water, and 3,5-dichloro-2-bromopyridine was obtained. Yield 89%, mp 41–42°C (lit. mp 41.5°C).[16]

5-Chloro-, 6-chloro-, 6-bromo- and 3,5-dichloro-2-methyl-sulfenylpyridines were prepared by treating the corresponding 2-halopyridines with methanethiolate under phase-transfer conditions, according to our procedure.[17] The data for these substituted 2-methylsulfenylpyridines are listed as follows.

5-Chloro-2-methylsulfenylpyridine. Yield 92%; bp 115–117°C/24 mm Hg; (Found: C, 44.90; H, 3.76; N, 8.74. Calcd. for C_6H_6ClNS; C, 45.14; H, 3.78; N, 8.77%), ^{1}H-nmr($CDCl_3$) $\delta = 2.54$ (3H, s, CH_3), 7.03–7.54 (2H, m, 3,4-PyrH), 8.35–8.41 (1H, m, 6-PyrH).

6-Chloro-2-methylsulfenylpyridine. Yield 98%; bp 105–107°C/14 mm Hg; (Found: C, 45.23; H, 3.82; N, 8.99. Calcd. for C_6H_6ClNS; C, 45.14; H, 3.78; N, 8.77%), ^{1}H-nmr ($CDCl_3$) $\delta = 2.74$ (3H, s, CH_3), 6.60–7.73 (3H, m, 3,4,5-PyrH).

6-Bromo-2-methylsulfenylpyridine. Yield 97%; bp 128–132°C/16 mm Hg; (Found: C, 35.66; H, 2.94; N, 6.95. Calcd. for C_6H_6BrNS; C, 35.31; H, 2.96; N, 6.86%), ^{1}H-nmr($CDCl_3$) $\delta = 2.62$ (3H, s, CH_3), 6.87–7.43 (3H, m, 3,4,5-PyrH).

3,5-Dichloro-2-methylsulfenylpyridine. Yield 77% mp 63–64°C; (Found: C, 37.02; H, 2.58; N, 7.11. Calcd. for $C_6H_5Cl_2NS$; C, 37.13; H, 2.59; N, 7.21), ^{1}H-nmr ($CDCl_3$) $\delta = 2.54$ (3H, s, CH_3), 7.55 (1H, d, $J = 2$Hz, 4-PyrH), 8.33 (1H, d, $J = 2$Hz, 6-PyrH).

2,6-dimethylsulfenylpyridine. To a solution of 200 ml ethanol containing dissolved sodium metal (6.9 g, 0.3 mol), methanethiol (14.34 g, 0.3 mol), which were prepared from aqueous solution of 15% sodium methanethiolate and dil. H_2SO_4 solution, and 6-chloro-2-methylsulfenylpyridine (23.88 g, 0.51 mol) were added. The reaction mixture was refluxed under N_2 for 12 h. The mixture was cooled, water was added, and the solution was extracted with benzene. The extract was washed with water and dried over anhyd. Na_2SO_4. After the solvent was evaporated, the residue was purified by distillation under reduced pressure, 2,6-dimethylsulfenyl-pyridine (21.33 g) was obtained. Yield 83%; bp 95°C/3 mm Hg; (Found: C, 49.29; H, 5.24; N, 8.41. Calcd. for $C_7H_9NS_2$; C, 49.08; H, 5.29; N, 8.17%), ^{1}H-nmr ($CDCl_3$) $\delta = 2.83$ (6H, s, CH_3), 6.90-7.51 (3H, m, 3,4,5-PyrH).

Preparation of substituted 2-methylsulfinylpyridines. A typical procedure is as follows. To a solution of 5-chloro-2-methylsulfenylpyridine (3.2 g, 0.02 mol) in 10 ml acetic acid, 30% hydrogen peroxide (2.7 g, 0.024 mol) was added dropwise. After the mixture was stirred for 24 h, CH_2Cl_2 was added and then the solution cooled with an ice-water bath was neutralized with aqueous ammonia. After the solution was extracted with CH_2Cl_2, the extract was washed with water and dried over anhyd. $MgSO_4$. After the solution was filtered and evaporated, the residue was recrystallized from cyclohexane-ether-methanol.

5-Chloro-2-methylsulfinylpyridine (2.99 g) was obtained. Yield 65%; mp 52–53°C; (Found: C, 40.93; H, 3.39; N, 7.90. Calcd. for C_6H_6ClONS; C, 41.03; H, 3.44; N, 7.97%), ^{1}H-nmr ($CDCl_3$) $\delta = 2.85$ (3 H, s, CH_3), 7.94–7.98 (2 H, m, 4,5-PyrH), 8.56–8.61 (1 H, m, 2-PyrH).

6-Chloro-2-methylsulfinylpyridine. Yield 95%, mp 66.0–66.5°C; (Found: C, 41.0; H, 3.45; N, 8.0. Calcd. for C_6H_6ClNOS; C, 41.0; H, 3.4; N, 8.0%), ^{1}H-nmr ($CDCl_3$) $\delta = 2.74$ (3H, s, CH_3), 7.11–7.80 (3H, m, 3,4,5-PyrH).

6-Bromo-2-methylsulfinylpyridine. Yield 61%, mp 76.5–77.0°C; (Found: C, 32.90; H, 2.67; N, 6.38. Calcd. for C_6H_6BrNOS; C, 32.74; H, 2.74; N, 6.36%), ^{1}H-nmr ($CDCl_3$) $\delta = 2.74$ (3H, s, CH_3), 7.25–7.86 (3H, m, 3,4,5-PyrH).

3,5-Dichloro-2-methylsulfinylpyridine. Yield 77%, mp 95–96°C; (Found: C, 34.26; H, 2.35; N, 6.55. Calcd. for $C_6H_5Cl_2NOS$; C, 34.30; H, 2.39; N, 6.66%), ^{1}H-nmr ($CDCl_3$) $\delta = 2.89$ (3H, s, CH_3), 7.82 (1 H, d, $J = 2$ Hz, 4-PyrH), 8.69 (1 H, d, $J = 2$ Hz, 6-PyrH).

6-Methylsulfenyl-2-methylsulfinylpyridine. Yield 54%, bp 134–137°C/4 mm Hg; (Found: C, 44.85; H, 4.88; N, 7.59. Calcd. for $C_7H_9NOS_2$; C, 44.89; H, 4.84; N, 7.47%), ^{1}H-nmr ($CDCl_3$) $\delta = 2.50$ (3H, s, SCH_3), 2.80 (3 H, s, $S(O)CH_3$), 7.01–7.23 (1 H, m, 5-PyrH), 7.47–7.87 (2 H, m, 3,4-PyrH).

Preparation of bis substituted 2,2'-bipyridine. A typical procedure is as follows. To a stirred solution of 2-methylsulfenyl-6-methanesulfinylpyridine (471.5 mg 2.25 mmol) in 20 ml ether cooled in an ice-water bath, CH_3CH_2MgBr (1.5 ml, 1.5 mmol) in 1.0 mmol/ml THF solution was added using a 2 ml syringe. After adding the CH_3CH_2MgBr solution, this solution was warmed to room temperature and stirred for 1 h. Then water was added to the reaction mixture and the solution was neutralized with dil. HCl solution and extracted three times with benzene. The combined layer was washed with water and dried over anhyd. Na_2SO_4. After the solvent was evaporated, the residue was separated through activated alumina chromatography column with benzene as an eluent.

6,6-Dimethylsulfenyl-2,2'-bipyridine (192 mg) was obtained. Yield 61%, mp 130–131°C; (Found; C, 57.78; H, 4.48; N, 11.14. Calcd. for $C_{12}H_{12}N_2S_2$; C, 58.03; H, 4.87; N, 11.27%), ^{1}H-nmr ($CDCl_3$) $\delta = 2.67$ (6H, s, CH_3), 7.71 (2H, dd, $J = 8.1$ Hz, 5-PyrH), 7.61 (2H, t, $J = 8$ Hz, 4-PyrH), 8.17 (2H, dd, $J = 7.1$ Hz, 3, PyrH).

5,5'-Dichloro-2,2'-bipyridine. Yield 40%, mp 200–202°C (lit. 199–200°C[18]); ^{1}H-nmr ($CDCl_3$) $\delta = 7.77$ (2H, dd, $J = 9$ Hz, 3 Hz, 3,3'-PyrH), 8.35 (2H, dd, $J = 9$ Hz, 1 Hz, 4,4'-PyrH), 8.59–8.63 (2H, m, 6.6'-PyrH).

6,6'-Dichloro-2,2'-bipyridine. Yield 55%, mp 216–217°C (lit. 218–219°C[19]); ^{1}H-nmr($CDCl_3$) $\delta =$ 7.35 (2H, dd, $J = 8$ Hz, 1 HZ, 5,5'-PyrH), 8.36 (2H, dd, $J = 7$ Hz, 1 Hz, 3,3'-PyrH).

6,6'-Dibromo-2,2'-bipyridine. Yield 50% mp 228–229°C(lit. 221–223°C[20]); ^{1}H-nmr ($CDCl_3$) $\delta =$ 7.84 (2H, dd, $J = 8$ Hz, 2 Hz, 5,5'-PyrH), 7.68 (2H, t, $J = 8$ Hz, 4,4'-PyrH), 8.36 (2H, dd, $J = 8$ Hz, 2 Hz, 3,3'-PyrH).

3,3',5,5'-Tetrachloro-2,2'-bipyridine. Yield 52%, mp 103–104°C; ^{1}H-nmr($CDCl_3$) $\delta = 7.87$ (2H, d, $J = 2$ Hz, 4,4'-PyrH), 8.60 (2H, d, $J = 2$ Hz, 6,6'-PyrH).

Reaction of **5** *with* CH_3MgBr. To a solution of **5** (255 mg, 0.93 mmol) in 8 ml THF, CH_3MgBr (0.9 ml, 0.9 mmol) in 1.0 mmol/ml THF solution was added through a 1 ml syringe with stirring under N_2 at room temperature. Stirring was continued for 1 h. Then, water was added to the reaction mixture and the solution was neutralized with dil. HCl solution and extracted three times CH_2Cl_2. The CH_2Cl_2 layer was washed with water and dried over anhyd. $MgSO_4$. After the solvent was evaporated, the resulting residue was distilled under reduced pressure using a Kugelrohr. 2-Benzothiazol (51 mg, 40%) of (110–120°C/16 mm Hg) and 2,2'-dibenzothiazolyl (51 mg, 39%) were obtained from the residue (solid. 2,2'-Dibenzothiazolyl; mp 303–305°C (lit. 303–304°C[21]).

Reaction of **10** *with* $C_6H_5CH_2MgCl$. **10** (200 mg, 1.01 mmol) was treated with $PhCH_2MgCl$ (1.2 ml, 1.2 mmol) in 8 ml THF as in the above manner, benzothiazol (89.2 mg, 65%) and 2,2'-dibenzothiazolyl (7.8 mg, 6%) were obtained.

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