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Reactions of Tris(2-pyridyl)phosphine Oxides with Electrophiles: Formation of 5-Substituted 2,2′-Bipyridyls

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ABSTRACT: *The reaction of tris(2-pyridyl)phosphine oxides with benzeneselenenyl chloride in methanol gave the corresponding 5-phenylseleno-2,2′-bipyridyls together with a small amount of 2,2′-bipyridyls. Similarly, the reaction with arenesulfenyl chlorides in aqueous acetonitrile afforded two kinds of coupling products, 5-phenylthio-2,2′-bipyridyls and 2,2′-bipyridyls. While in the reaction with arenesulfinyl chlorides in aqueous acetonitrile, four corresponding bipyridyl derivatives, 2,2′-bipyridyls, 5-arylthio-2,2′-bipyridyls, 5-arylsulfinyl-2,2′-bipyridyls, and 5-arylsulfonyl-2,2′-bipyridyls, were formed.* Heteroatom Chem 14:72–81, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10085

INTRODUCTION

Tris(2-pyridyl)phosphine oxide is an interesting compound, which readily undergoes ligand coupling by treating with 2-pyridyllithium or phenyllithium in THF, or with dilute hydrochloric acid, giving 2,2′-bipyridyl in good yield [1]. Recently, we reported the novel ligand coupling reactions of tris(2-pyridyl) phosphine oxides, in which the corresponding 5-substituted 2,2′-bipyridyls and 2,2′-bipyridyls were formed by treatment with some electrophiles [2]. Thus, the reactions of tris(2-pyridyl)phosphine oxide (**1a**) with chlorine, bromine, deuterium chloride, or benzenediazonium chloride gave mainly 5-chloro-, 5-bromo-, 5-deuterio-, or 5-phenylazo-2,2′-bipyridyl as the ligand coupling products, respectively. The 5-substituted 2,2′-bipyridyls were considered to be formed by electrophilic substitution of a pentacoordinate intermediate followed by a ligand coupling reaction.

Since most electrophilic substitutions of pyridine are inhibited by the electron-withdrawing effect of the nitrogen atom, it is noted that electrophilic reactions took place on the pyridine ring under mild conditions. In particular, the formation of azo compounds in the reaction with benzenediazonium chloride suggests that the pyridine ring is considerably activated in the pentacoordinate intermediate because arenediazonium salts are effective electrophiles toward activated aromatic compounds such as phenols and arylamines. We are interested in the pentacoordinate intermediate generated from tris(2-pyridyl)phosphine oxide in acid media owing to its facility for electrophilic substitution and ligand coupling.

Benzeneselenenyl chloride is a representative selenenylating reagent and many reactions of this compound have been reported [3]. The electrophilic reactivity of areneselenenyl chlorides toward aromatic compounds is well emphasized by their reactions with activated benzene derivatives, such as phenols, naphthol, anisole, *N,N*-dimethylaniline, acetanilide,

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and 1,3,5-trimethylbenzene under mild conditions to give selenides [4].

Arenesulfenyl chlorides also react with activated aromatic compounds. For example, anisole, *m*-xylene, and diphenyl ether are sulfenylated with benzenesulfenyl chloride in the presence of iron powder in the dark [5]. The reaction of 1-phenylpyrazole with *o*-nitrobenzenesulfenyl chloride proceeds without catalysis under refluxing in ethylene dichloride [6].

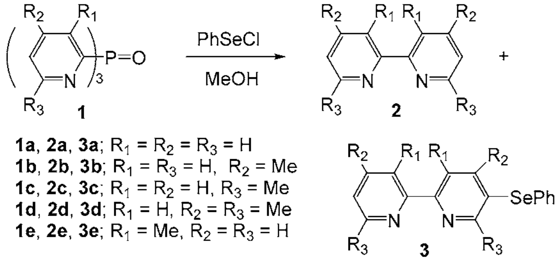
We have further extended our previous study on the reaction of tris(2-pyridyl)phosphine oxide with electrophiles to study the behavior of the respective pentacoordinate intermediates. In the present study, benzeneselenenyl chloride, arenesulfenyl chlorides, and arenesulfinyl chlorides were used as the electrophile in the reactions with **1**.

RESULTS AND DISCUSSION

*Reaction of Tris(2-pyridyl)phosphine Oxide (***1a***) with Benzeneselenenyl Chloride*

First, we examined the reaction of **1a** with benzeneselenenyl chloride. The reaction was carried out in methanol with 2–10 equiv of benzeneselenenyl chloride for 24 h at room temperature. 5-Phenylseleno-2,2′-bipyridyl (**3a**) was obtained as a major coupling product, together with 2,2′-bipyridyl **2a**. The coupling products could be isolated easily from the reaction mixture by extraction with concentrated hydrochloric acid, followed by making the extract alkaline in order to regenerate the products. Then each coupling product was separated by silica gel column chromatography. The structure of **3a** was assigned on the basis of ^{1}H NMR and MS spectral data and elemental analyses. The yields of **3a** increased with an increasing molar ratio of benzeneselenenyl chloride to the phosphine oxide. The results are summarized in Table 1. When **1a** was treated with 10 equiv of benzeneselenenyl chloride, the yield of **3a** increased to 88%.

The 5-substituted 2,2′-bipyridyl was not formed and 2,2′-bipyridyl **2a** was recovered when it was treated with 3 equiv of benzeneselenenyl chloride under the same conditions as those of the reaction with **1a**. This result demonstrates that **2a** is not an intermediate in the formation of **3a** and suggests that **3a** was formed by the same mechanism reported in a previous article [2] for the reactions of **1a** with some electrophiles.



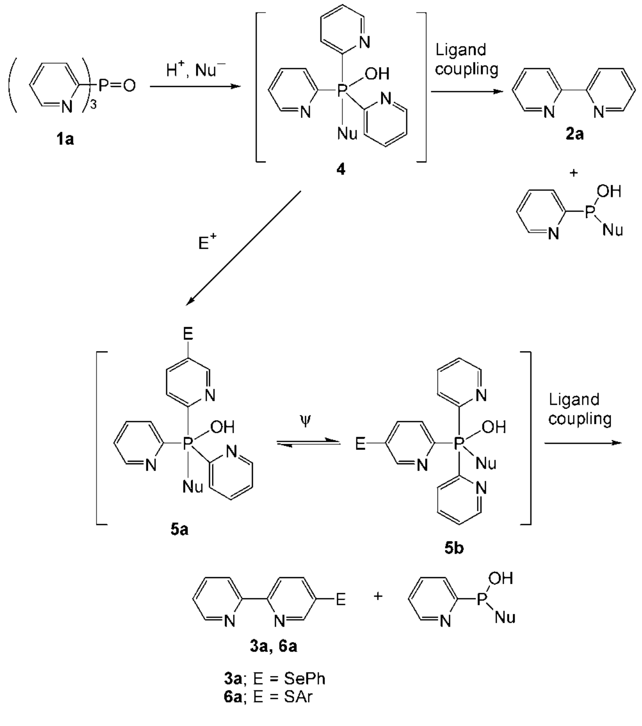
1a, **2a**, **3a**; $R_1 = R_2 = R_3 = H$
1b, **2b**, **3b**; $R_1 = R_3 = H$, $R_2 = Me$
1c, **2c**, **3c**; $R_1 = R_2 = H$, $R_3 = Me$
1d, **2d**, **3d**; $R_1 = H$, $R_2 = R_3 = Me$
1e, **2e**, **3e**; $R_1 = Me$, $R_2 = R_3 = H$

(1)

In a previous article, we postulated a possible mechanism for the formation of 5-substituted 2,2′-bipyridyls [2]. The mechanism involves a pentacoordinate phosphorus intermediate **4**, which undergoes either electrophilic substitution on an axial pyridine ring or ligand coupling to give substituted intermediates **5a** and **5b** or **2a**, respectively, as shown in Scheme 1. The substituted pyridyl ligand couples with another pyridyl ligand to afford the 5-substituted 2,2′-bipyridyl and a trivalent phosphorus compound. Although benzenephosphinic acid, a tautomer of benzenephophonous acid, had earlier been isolated as the phosphorus portion in the ligand coupling reaction of phenylbis(2-pyridyl)phosphine oxide in aqueous acid media [1], we did not succeed in isolating the phosphorus-containing product in the present study.

Reactions of Substituted Tris(2-pyridyl)-phosphine Oxides with Benzeneselenenyl Chloride

The reactions of some tris(2-pyridyl)phosphine oxides **1b–e** bearing methyl group(s) on the pyridine



3a; E = SePh
6a; E = SAr

SCHEME 1 Reaction mechanism of the formation of 5-substituted 2,2′-bipyridyl.

TABLE 1 Reactions of Phosphine Oxides **1** with Benzeneselenenyl Chloride

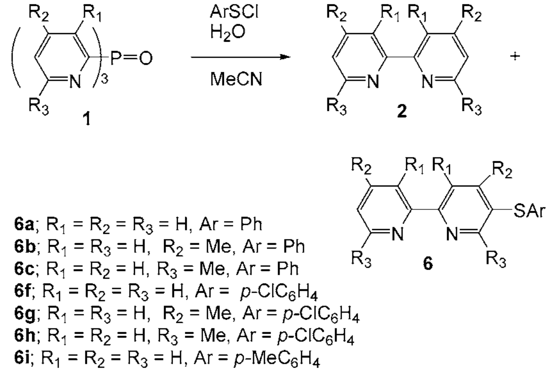
Phosphine Oxide					*Product Yield (%)*[b]	
	R$_1$	*R*$_2$	*R*$_3$	*PhSeCl/1*[a]	**2**	**3**
1a	H	H	H	2	36	57
1a	H	H	H	3	22	78
1a	H	H	H	5	18	81
1a	H	H	H	10	12	88
1b	H	Me	H	3	28	56
1c	H	H	Me	3	20	79
1d	H	Me	Me	3	56	33
1e	Me	H	H	3	18[c]	8[c]

[a] Mol ratio.
[b] Isolated yield.
[c] After the reaction for 4 days.

rings with 3 equiv of benzeneselenenyl chloride were carried out in methanol. The corresponding 5-phenylseleno-2, 2′-bipyridyls **3b–e** and 2, 2′-bipyridyls **2b–e** were formed as the coupling products. These results are summarized in Table 1. In these reactions, the coupling products, **2** plus **3**, were obtained in good yields except in the reaction with **1e**. The reaction of **1e** with benzeneselenenyl chloride proceeded very slowly. In this reaction, a small amount of 3, 3′-dimethyl-2, 2′-bipyridyl (**2e**) and 3, 3′-dimethyl-5-phenylseleno-2, 2′-bipyridyl (**3e**) were formed, and 45% of **1e** was recovered after the reaction had been carried out for 4 days. The slow reaction of **1e** is attributed to steric effects. The equatorial pyridine rings in the intermediate **4** formed from **1e** are sterically hindered by the methyl group at the 3 position of the axial pyridine ring. Such steric hindrance would inhibit both formation of intermediate **4** and a favorable arrangement of the pyridine rings for ligand coupling.

Reactions of Tris(2-pyridyl)phosphine Oxide with Arenesulfenyl Chlorides

Next, we examined the reaction of **1** with benzenesulfenyl chloride, in which a similar coupling reaction to that described earlier in this article was expected to take place. The reaction of **1a** with 5 equiv of benzenesulfenyl chloride in methanol did not afford a sulfur analogue, 5-phenylthio-2, 2′-bipyridyl (**6a**), but instead 2, 2′-bipyridyl **2a** in 95% yield. However, the reaction in acetonitrile containing water afforded two coupling products, **2a** and **6a**, together with diphenyl disulfide and phenyl benzenethiolsulfonate formed by hydrolysis of benzenesulfenyl chloride. Thus, when 6.6 equiv of water were slowly added dropwise into a solution of **1a** and 5 equiv of benzenesulfenyl chloride in acetonitrile for 6 h with stirring at room temperature, **2a** and **6a** were formed in 15% and 38% yields, respectively. Slow addition of methanol instead of water also gave **6a** and **2a** in 6% and 58% yields, respectively.



6a; R$_1$ = R$_2$ = R$_3$ = H, Ar = Ph
6b; R$_1$ = R$_3$ = H, R$_2$ = Me, Ar = Ph
6c; R$_1$ = R$_2$ = H, R$_3$ = Me, Ar = Ph
6f; R$_1$ = R$_2$ = R$_3$ = H, Ar = *p*-ClC$_6$H$_4$
6g; R$_1$ = R$_3$ = H, R$_2$ = Me, Ar = *p*-ClC$_6$H$_4$
6h; R$_1$ = R$_2$ = H, R$_3$ = Me, Ar = *p*-ClC$_6$H$_4$
6i; R$_1$ = R$_2$ = R$_3$ = H, Ar = *p*-MeC$_6$H$_4$

(2)

The reactions of **1a** with *p*-chlorobenzenesulfenyl chloride and with *p*-methylbenzensulfenyl chloride gave 5-(*p*-chlorophenylthio)-2, 2′-bipyridyl (**6f**) and 5-(*p*-methylphenylthio)-2, 2′-bipyridyl (**6i**), respectively, in moderately yields, together with **2a**. The structures of the 5-substituted products were assigned on the basis of ^{1}H NMR and MS spectral data and elemental analyses. The reactions of **1b** and **1c** with benzenesulfenyl chloride or *p*-chlorobenzenesulfenyl chloride were also examined. The results are summarized in Table 2. In these reactions, the predominant coupling products were **2b** and **2c**, respectively.

When **1a** was added to the reaction mixture of 5 equiv of benzenesulfenyl chloride and 6 equiv of water in acetonitrile, the only coupling product isolated was **2a**. The result shows that in the reaction of **1** with benzenesulfenyl chlorides the sulfenylating reagent is benzenesulfenyl chloride, not diphenyl disulfide or phenyl benzenethiolsulfonate formed from benzenesulfenyl chloride by hydrolysis.

When **2a** was treated with benzenesulfenyl chloride in aqueous acetonitrile, again, **2a** was

TABLE 2 Reactions of Phosphine Oxides **1** with Arenesulfenyl Chlorides

Phosphine Oxide				*ArSCl*	*Product Yield (%)*[a]			
	R$_1$	*R*$_2$	*R*$_3$	*Ar*				
1a	H	H	H	Ph	**2a**	15	**6a**	38
1a	H	H	H	*p*-ClC$_6$H$_4$	**2a**	17	**6f**	47
1a	H	H	H	*p*-MeC$_6$H$_4$	**2a**	30	**6i**	46
1b	H	Me	H	Ph	**2b**	47	**6b**	14
1b	H	Me	H	*p*-ClC$_6$H$_4$	**2b**	41	**6g**	17
1c	H	H	Me	Ph	**2c**	55	**6c**	8
1c	H	H	Me	*p*-ClC$_6$H$_4$	**2c**	37	**6h**	15

[a] Isolated yields.

completely recovered. Therefore, the reaction of **1** with arenesulfenyl chlorides is considered to proceed by a similar mechanism to that of the reaction with benzeneselenenyl chloride described previously in this article with some of the electrophiles shown in Scheme 1.

In the reaction of **1** with arenesulfenyl chlorides in acetonitrile in the presence of water or methanol, water or methanol is considered to act as a nucleophile to form intermediate **4**. In the reaction of **1a** with benzenesulfenyl chloride in acetonitrile in the absence of water, **2a** and **6a** were obtained in poor yields. In this case, these coupling products might have been formed during workup. In the reaction of **1a** with benzenesulfenyl chloride in methanol, however, methanolysis of benzenesulfenyl chloride takes place prior to substitution on the pyridine ring of the intermediate **4** and only **2a** would be formed as the coupling product from the intermediate **4**.

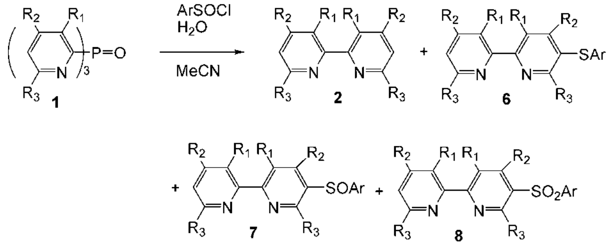
Reactions of Tris(2-pyridyl)phosphine Oxide with Arenesulfinyl Chlorides

The reaction of **1a** with benzenesulfinyl chloride was carried out in aqueous acetonitrile, as described earlier in this article. When **1a** was treated with 5 equiv of benzenesulfinyl chloride and 6 equiv of water in acetonitrile at 30°C for 24 h, four different coupling products, **2a, 6a**, 5-phenylsulfinyl-2,2′-bipyridyl (**7a**), and 5-phenylsulfonyl-2,2′-bipyridyl (**8a**), were formed in 27, 33, 3, and 6% yields, respectively. The results are summarized in Table 3. The product distribution depended on the reaction temperature, as shown in Table 3. Thus, under refluxing, the predominant coupling product was **2a**. The phosphine oxide **1a** readily undergoes ligand coupling under acidic conditions to form **2a** in good yield, as reported previously [1]. Therefore, hydrogen chloride formed, by rapid hydrolysis of benzenesulfinyl chloride, would accelerate the formation of **2a** at higher temperatures.

TABLE 3 Reaction of **1a** with Benzenesulfinyl Chloride

Phosphine Oxide	*PhSOCl/1*[a]	*Temp (°C)*	*Product Yield (%)*[b]			
			2a	***6a***	***7a***	***8a***
1a	2.5	30	52	4	3	1
1a	5	30	27	33	3	6
1a	10	30	12	35	3	3
1a	5	50	49	11	2	2
1a	5	Reflux	76	3	<1	<1

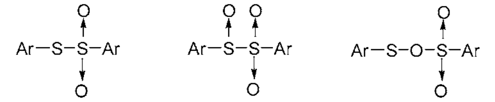
[a] Mol ratio.
[b] Isolated yield.



6a, **7a**, **8a**; $R_1 = R_2 = R_3 = H$, Ar = Ph
6b, **7b**, **8b**; $R_1 = R_3 = H$, $R_2 = Me$, Ar = Ph
6c, **7c**, **8c**; $R_1 = R_2 = H$, $R_3 = Me$, Ar = Ph
6f, **7f**, **8f**; $R_1 = R_2 = R_3 = H$, Ar = *p*-ClC_6H_4
6i, **7i**, **8i**; $R_1 = R_2 = R_3 = H$, Ar = *p*-MeC_6H_4
6j, **7j**, **8j**; $R_1 = R_2 = R_3 = H$, Ar = *p*-$MeOC_6H_4$
6k, **7k**, **8k**; $R_1 = R_2 = R_3 = H$, Ar = *p*-$O_2NC_6H_4$

(3)

The reactions of **1b** and **1c** with benzenesulfinyl chloride also gave the corresponding four coupling products. The reactions of **1a** with some *p*-substituted benzenesulfinyl chlorides also gave similar results, as shown in Table 4. Arenesulfinyl chlorides are known to react with water to yield the corresponding sulfonyl chloride and thiolsulfonate **9**, via intermediates such as arenesulfinic acid, sulfinyl sulfone **10**, and sulfenyl sulfonate **11** [7]. To elucidate the mechanism for the formation of the 5-substituted 2,2′-bipyridyls, the reactions of **1a** with *p*-toluenesulfonyl chloride in aqueous acetonitrile, and with *p*-tolyl *p*-toluenethiolsulfonate (**9a**) in acetonitrile in the presence of hydrochloric acid, were performed. Both reactions afforded **2a** as a coupling product, but no 5-substituted 2,2′-bipyridyls were formed.



9 **10** **11**

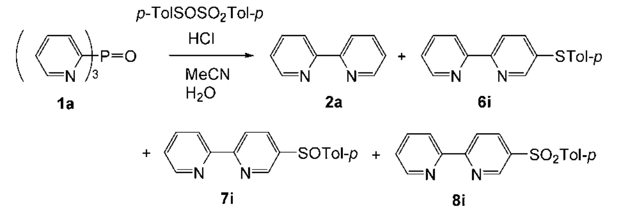
9a, **10a**, **11a**; Ar = *p*-Tol

TABLE 4 Reactions of Phosphine Oxides **1** with Arenesulfinyl Chlorides

Phosphine Oxide	*ArSOCl Ar*	*ArSOCl/1*[a]	*Product Yield (%)*[b]			
1b	Ph	5	**2b** 50	**6b** 13	**7b** 3	**8b** 1
1c	Ph	5	**2c** 25	**6c** 30	**7c** 3	**8c** 3
1a	*p*-ClC_6H_4	5	**2a** 36	**6f** 30	**7f** 4	**8f** 4
1a	*p*-MeC_6H_4	5	**2a** 39	**6i** 29	**7i** 4	**8i** 4
1a	*p*-$MeOC_6H_4$	5	**2a** 47	**6j** 30	**7j** 2	**8j** 4
1a	*p*-$O_2NC_6H_4$	5	**2a** 33	**6k** 11	**7k** 9	**8k** 2

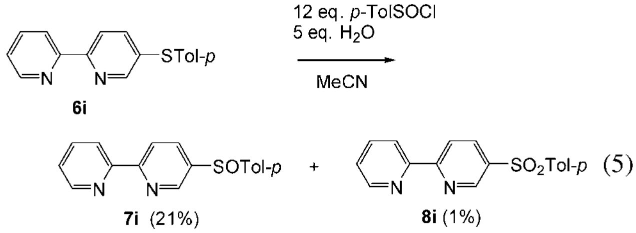
[a] Mol ratio.
[b] Isolated yield.

Furthermore, the reaction of **1a** with 2.5 equiv of *p*-toluenesulfinyl *p*-tolyl sulfone (**10a**) in acetonitrile in the presence of a small amount of hydrochloric acid also gave the 5-substituted 2,2′-bipyridyls, **6i, 7i**, and **8i**, together with **2a**. The results are shown in Table 5.

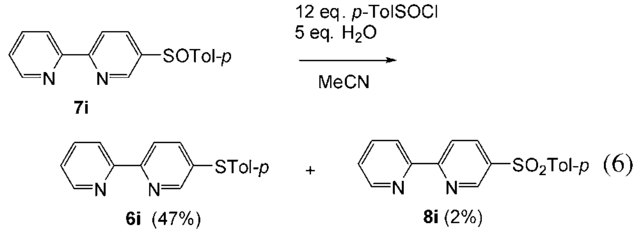


(4)

Table 5 shows that a prolonged reaction time leads to a decrease in the yield of **6i** but increases the yields of **7i** and **8i**. The result suggests that in the reaction of **1a** with **10a**, the sulfide **6i** is a primary coupling product, which is converted to the sulfoxide **7i** and the sulfone **8i**. To verify that **7i** and **8i** are formed from **6i** under the conditions of the reaction of **1a** with *p*-toluenesulfinyl chloride, the reaction of **6i** with *p*-toluenesulfonyl chloride was examined. When **6i** was treated with 12 equiv of *p*-toluenesulfinyl chloride and 5 equiv of water in acetonitrile, **7i** and **8i** were obtained in 21% and 1% yields, respectively, and 67% of **6i** was recovered.



(5)



(6)

It was also found that **7i** is converted to **6i** and **8i** under the same conditions. Thus, in the reaction of **7i** with 12 equiv of *p*-toluenenesulfinyl chloride and 5 equiv of water in acetonitrile, **6i** and **8i** were obtained in 47% and 2% yields, respectively, and 43% of **7i** was recovered.

For the formation of the 5-substituted 2,2′-bipyridyls in the reaction of phosphine oxides **1** with arenesulfinyl chlorides, the most likely conceivable mechanism involves initial formation of sulfides **6** by ligand coupling, followed by oxidation of **6** to give **7** and **8**. In the reaction with arenesufinyl chlorides, a possible sulfinylating agent is sulfenyl sulfonate **11**, formed by hydrolysis of the arenesulfinyl chlorides. An alternative mechanism that involves initial formation of **7** by ligand coupling is less probable, since the yields of **7** to **6** are relatively low, as shown in Tables 3 and 4.

TABLE 5 Reaction of Phosphine Oxide **1a** with *p*-Toluenesulfinyl *p*-Tolyl Sulfone **10a**

		Product Yield (%)[a]			
Run	*Time (h)*	***2a***	***6i***	***7i***	***8i***
1	2	35	14	4	1
2	20	47	7	12	2

[a]Isolated yields.

EXPERIMENTAL

General

All the melting points are uncorrected. Mass spectra were recorded on a JEOL JMS-AX505W spectrometer at 70 eV. NMR spectra were recorded on a Varian Unity-300 NMR spectrometer in CDCl$_3$ solution, using tetramethylsilane as an internal standard.

Phosphine Oxides

Tris(2-pyridyl)phosphine oxide (**1a**) and methyl substituted tris(2-pyridyl)phosphine oxides **1b–e** were prepared according to the procedure reported previously [1b, 2].

Reaction of Tris(2-pyridyl)phosphines (1) with Benzeneselenenyl Chloride

A typical procedure for the reaction of **1** with benzeneselenenyl chloride is as follows: A solution of **1a** (281 mg, 1 mmol) and benzeneselenenyl chloride (576 mg, 3 mmol) in methanol (10 ml) was kept for 24 h at room temperature. The methanol was removed under reduced pressure. The residue was made alkaline with aqueous NaOH solution and the whole mixture was extracted with chloroform (30 ml). The chloroform solution was extracted with concentrated hydrochloric acid (50 ml). The extract was made alkaline with NaOH and extracted with chloroform (30 ml). The combined extracts were washed with water, dried over Na$_2$SO$_4$, and concentrated. Purification by column cromatograpy (silica gel, chloroform) of the residue gave **3a** (244 mg, 78%) and **2a** (34 mg, 22%), which were recrystallized from methanol.

5-Phenylseleno-2,2′-bipyridyl (**3a**). mp 63.5–65.5°C. MS: *m/z* (rel. intensity); 314 (19), 313 (29), 312 (M$^+$, 100), 311 (70), 310 (50), 309 (51), 308 (29), 307 (12), 232 (48), 231 (20), 204 (11), 128 (12), 78 (21). ^{1}H NMR(CDCl$_3$): $\delta = 7.28$–7.33 (4H,m), 7.48–7.56 (2H, m), 7.80 (1H, ddd, $J = 7.8$, 7.5, 1.8 Hz), 7.86 (1H, dd, $J = 8.4$, 2.4 Hz), 8.30 (1H, dd, $J = 8.4$, 0.6 Hz), 8.36 (1H, ddd, $J = 7.8$, 1.8, 0.6 Hz), 8.66 (1H, ddd, $J = 4.8$, 1.8, 0.6 Hz), 8.69 (1H, dd, $J = 2.4$, 0.6 Hz). Anal calcd for $C_{16}H_{12}N_2Se$: C, 61.74; H, 3.89; N, 9.00. Found: C, 61.79; H, 3.93; N, 8.77.

4,4′-Dimethyl-5-phenylseleno-2,2′-bipyridyl (**3b**). mp 104.0–105.0°C. MS: *m/z* (rel. intensity); 342 (20), 341 (31), 340 (M$^+$, 100), 339 (73), 338 (52), 337 (50), 336 (29), 335 (12), 260 (20), 259 (27), 184 (43), 183 (35), 182 (10), 156 (11). ^{1}H NMR(CDCl$_3$): $\delta = 2.42$ (3H, s), 2.46 (3H, s), 7.13 (1H, dd, $J = 4.8$, 1.8 Hz), 7.26–7.36 (3H, m), 7.40–7.47 (2H, m), 8.20 (1H, d, $J = 1.8$ Hz), 8.27 (1H, s), 8.52 (1H, $J = 4.8$, Hz), 8.54 (1H, s). Anal calcd for $C_{18}H_{16}N_2Se$: C; 63.72; H, 4.75; N, 8.26. Found: C, 63.52; H, 4.76; N, 8.02.

6,6′-Dimethyl-5-phenylseleno-2,2′-bipyridyl (**3c**). mp 111.0–112.0°C. MS: *m/z* (rel. intensity); 342 (20), 341 (25), 340 (M$^+$, 100), 339 (43), 338 (52), 337 (34), 336 (25), 260 (49), 259 (72), 258 (13), 183 (11). ^{1}H NMR(CDCl$_3$): $\delta = 2.60$ (3H, s), 2.70 (3H, s), 7.15 (1H, d, $J = 7.5$ Hz), 7.30–7.34 (3H, m), 7.43–7.51 (2H, m), 7.61 (1H, d, $J = 8.4$ Hz), 7 68 (1H, dd, $J = 7.8$, 7.5 Hz), 8.07 (1H, d, $J = 8.4$ Hz), 8.18 (1H, d, $J = 7.8$ Hz). Anal calcd for $C_{18}H_{16}N_2Se$: C, 63.72; H, 4.75; N, 8.26. Found: C, 63.76; H, 4.79; N, 8.08.

4,4′,6,6′-Tetramethyl-5-phenylseleno-2,2′-bipyridyl (**3d**). mp 89.5–90.5°C. MS: *m/z* (rel. intensity); 370 (21), 369 (28), 368 (M$^+$, 100), 367 (29), 366 (52), 365 (29), 364 (23), 288 (37), 287 (48), 211 (13), 170 (12). ^{1}H NMR (CDCl$_3$): $\delta = 2.39$ (3H, s), 2.52 (3H, s), 2.59 (3H, s), 2.81 (3H, s), 7.00 (1H, s), 7.04–7.19 (5H, m), 8.05 (1H, s), 8.16 (1H, s). Anal calc for $C_{20}H_{20}N_2Se$: C, 65.39; H, 5.49; 7.63. Found: C, 65.19; H, 5.50; N, 7.41.

3,3′-Dimethyl-5-phenylseleno-2,2′-bipyridyl (**3e**). MS: *m/z* (rel. intensity); 342 (19), 341 (18), 340 (M$^+$, 77), 339 (29), 338 (45), 337 (26), 336 (18), 327 (21), 326 (19), 325 (100), 324 (11), 323 (49), 322 (19), 321 (14), 248 (12), 182 (18), 181 (13), 168 (48), 130 (14). ^{1}H NMR (CDCl$_3$): $\delta = 2.12$ (3H, s), 2.18 (3H, s), 7.24 (1H, dd, $J = 7.8$, 4.8 Hz), 7.28–7.33 (3H, m), 7.48–7.54 (2H, m), 7.62 (1H, dd, $J = 7.8$, 1.8 Hz), 7.71 (1H, d, $J = 2.1$ Hz), 8.51 (1H, dd, $J = 4.8$, 1.8 Hz), 8.58 (1H, d, $J = 2.1$ Hz).

Reaction of Tris(2-pyridyl)phosphine Oxides (**1**) *with Arenesulfenyl Chlorides*

A typical procedure is as follows: Water (20 μl) was added 6 times at an interval of 1 h into a solution of **1a** (281 mg, 1 mmol) and benzenesulfenyl chloride (725 mg, 5 mmol) in acetonitrile (20 ml) with stirring at room temperature. After the reaction mixture had been allowed to stand overnight, the solvent was removed under reduced pressure, and the residue was made alkaline with aqueous NaOH solution, and the whole mixture was extracted with chloroform (30 ml). The extract was washed with water, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel by using chloroform as an eluent to give **6a** (100 mg, 38%) and **2a** (23 mg, 15%), which were recrystallized from methanol.

Reaction of Tris(2-pyridyl)phosphine Oxides (**1**) *with Arenesulfinyl Chlorides*

A typical procedure is as follows: Water (90 μl) was added 5 times at an interval of 1 h into a solution of **1a** (1.40 mg, 5 mmol) and benzenesulfinyl chloride (4.02 mg, 25 mmol) in acetonitrile (100 ml) with stirring at 30°C. After the reaction mixture had been allowed to stand overnight at room temperature, the solvent was removed under reduced pressure, and the residue was dissolved in chloroform (50 ml). The chloroform solution was extracted with concentrated hydrochloric acid (100 ml). The extract was made alkaline with NaOH and extracted with dichloromethane (100 ml). The extract was washed with water, dried over Na_2SO_4, and concentrated. Column chromatography of the residue on silica gel (chloroform) and on alumina (petroleum ether/ethyl acetate 5:1) gave **2a** (206 mg, 27%), **6a** (430 mg, 33%), **7a** (39 mg, 3%), and **8a** (87 mg, 6%), which were recrystallized from methanol.

5-Phenylthio-2,2′-bipyridyl (**6a**). mp 63.0–64.0°C. MS: *m/z* (rel. intensity); 266 (8), 265 (25), 264 (M$^+$, 100), 263 (45). ^{1}H NMR(CDCl$_3$): $\delta = 7.30$ (1H, ddd, $J = 7.5$, 4.8, 0.9 Hz), 7.32–7.44 (5H, m), 7.71 (1H, dd, $J = 8.4$, 2.4 Hz), 7.80 (1H, ddd, $J = 8.1$, 7.5, 1.8 Hz), 8.33 (1H, dd, $J = 8.4$, 0.6 Hz), 8.37 (1H, ddd, $J = 8.1$, 2.4, 0.9 Hz), 8.58 (1H, dd, $J = 2.4$, 0.6 Hz), 8.66 (1H, ddd, $J = 4.8$, 1.8, 0.9 Hz). Anal calcd for $C_{16}H_{12}N_2S$: C, 72.70; H, 4.58; N, 10.60. Found: C, 72.40; H, 4.69; N, 10.46.

4,4′-Dimethyl-5-phenylthio-2,2′-bipyridyl (**6b**). mp 81.0–81.5°C. MS: *m/z* (rel. intensity); 294 (7), 293 (24), 292 (M$^+$, 100), 291 (30). ^{1}H NMR(CDCl$_3$): $\delta = 2.44$ (3H, s), 2.47 (3H, s), 7.15 (1H, d, $J = 5.1$ Hz), 7.21–7.33 (5H, m), 8.23 (1H, s), 8.32 (1H, s), 8.48 (1H, d, $J = 5.1$ Hz), 8.54 (1H, s). Anal calcd for $C_{18}H_{16}N_2S$: C, 73.94; H, 5.52; N, 9.58. Found: C, 73.66; H, 5.59; N, 9.39.

*6,6′-Dimethyl-5-phenylthio-2,2′-bipyridyl (**6c**).* mp 104.0–105.0°C. MS: m/z (rel. intensity); 294 (7), 293 (24), 292 (M$^+$, 100), 291 (27). ^{1}H NMR ($CDCl_3$): $\delta = 2.61$ (3H, s), 2.68 (3H, s), 7.15 (1H, d, $J = 7.8$ Hz), 7.24–7.36 (5H, m), 7.55 (1H, d, $J = 8.4$ Hz), 7.68 (1H, t, $J = 7.8$ Hz), 8.15 (1H, dd, $J = 8.4$ Hz), 8.19 (1H, d, $J = 7.8$ Hz). Anal calcd for $C_{18}H_{16}N_2S$: C, 73.94; H, 5.52; N, 9.58. Found: C, 73.92; H, 5.56; N, 9.39.

*5-(p-Chlorophenylthio)-2,2′-bipyridyl (**6f**).* mp 78.5–79.5°C. MS: m/z (rel. intensity); 301 (8), 300 (41), 299 (33), 298 (M$^+$, 100), 297 (36), 78 (10). ^{1}H NMR ($CDCl_3$): $\delta = 7.30$ (2H, d, $J = 8.7$ Hz), 7.31 (1H, ddd, $J = 7.5$, 4.8, 0.9 Hz), 7.33 (2H, d, $J = 8.7$ Hz), 7.72 (1H, dd, $J = 8.4$, 2.4 Hz), 7.81 (1H, ddd, $J = 8.1$, 7.5, 1.8 Hz), 8.35 (1H, dd, $J = 8.4$, 0.9 Hz), 8.38 (1H, dt, $J = 8.1$, 0.9 Hz), 8.58 (1H, dd, $J = 2.4$, 0.9 Hz), 8.67 (1H, ddd, $J = 4.8$, 1.8, 0.9 Hz). Anal. calcd for $C_{16}H_{11}ClN_2S$: C, 64.32; H, 3.71; N, 9.38. Found: C, 64.11; H, 3.86; N, 9.29.

*5-(p-Chlorophenylthio)-4,4′-dimethyl-2,2′-bipyridyl (**6g**).* mp 109.0–109.5°C. MS: m/z (rel. intensity); 329 (8), 328 (44), 327 (38), 326 (M$^+$, 100), 325 (30). ^{1}H NMR ($CDCl_3$): $\delta = 2.43$ (3H, s), 2.44 (3H, s), 7.14 (1H, d, $J = 5.1$ Hz), 7.16 (2H, d, $J = 8.7$ Hz), 7.26 (2H, d, $J = 8.7$ Hz), 8.22 (1H, s), 8.31 (1H, s), 8.51 (1H, s), 8.53 (1H, d, $J = 5.1$ Hz). Anal calcd for $C_{18}H_{15}ClN_2S$: C, 66.15; H, 4.63; N, 8.57. Found: C, 66.18; H, 4.76; N, 8.51.

*5-(p-Chlorophenylthio)-6,6′-dimethyl-2,2′-bipyridyl (**6h**).* mp 103.0–104.0°C. MS: m/z (rel. intensity); 329 (7), 328 (35), 327 (30), 326 (100), 325 (19). ^{1}H NMR ($CDCl_3$): $\delta = 2.62$ (3H, s), 2.67 (3H, s), 7.16 (1H, d, $J = 7.8$ Hz), 7.20 (2H, d, $J = 8.7$ Hz), 7.46 (2H, d, $J = 8.7$ Hz), 7.58 (1H, d, $J = 8.1$ Hz), 7.69 (1H, dd, $J = 7.8$ Hz), 8.18 (1H, d, $J = 8.1$ Hz), 8.18 (1H, d, $J = 7.8$ Hz). Anal calcd for $C_{18}H_{15}ClN_2S$: C, 66.15; H, 4.63%; N, 8.57. Found: C, 66.10; H, 4.70; N, 8.55.

*5-(p-Tolylthio)-2,2′-bipyridyl (**6i**).* mp 83.0–84.0°C. MS: m/z (rel. intensity) 280 (7), 279 (23), 278 (M$^+$, 100), 277 (38). ^{1}H NMR ($CDCl_3$): $\delta = 2.36$ (3H, s), 7.17 (2H, d, $J = 8.1$ Hz), 7.28 (1H, ddd, $J = 7.5$, 4.8, 1.2 Hz), 7.36 (2H, d, $J = 8.1$ Hz), 7.63 (1H, dd, $J = 8.4$, 2.1 Hz), 7.78 (1H, ddd, $J = 8.1$, 7.5, 1.8 Hz), 8.28 (1H, dd, $J = 8.4$, 0.6 Hz), 8.34 (1H, ddd, $J = 8.1$, 1.2, 0.9 Hz), 8.52 (1H, dd, $J = 2.1$, 0.6 Hz), 8.65 (1H, ddd, $J = 4.8$, 1.8, 0.9 Hz). Anal calcd for $C_{17}H_{14}N_2S$: C, 73.35; H, 5.07; N, 10.06. Found: C, 73.37; H, 5.16; N, 9.97.

*5-(p-Methoxyphenylthio)-2,2′-bipyridyl (**6j**).* mp 67.0–68.0°C. MS: m/z (rel. intensity); 296 (7), 295 (22), 294 (M$^+$, 100), 293 (16), 279 (18), 264 (30), 263 (19), 78 (10). ^{1}H NMR ($CDCl_3$): $\delta = 3.83$ (3H, s), 6.93 (2H, d, $J = 8.7$ Hz), 7.27 (1H, ddd, $J = 7.5$, 4.8, 1.2 Hz), 7.46 (2H, d, $J = 8.7$ Hz), 7.54 (1H, dd, $J = 8.4$, 2.4 Hz), 7.78 (1H, ddd, $J = 7.8$, 7.5, 1.8 Hz), 8.26 (1H, dd, $J = 8.4$, 0.9 Hz), 8.33 (1H, ddd, $J = 7.8$, 1.2, 0.9 Hz), 8.45 (1H, dd, $J = 2.4$, 0.9 Hz), 8.64 (1H, ddd, $J = 4.8$, 1.8, 0.9 Hz). Anal calcd for $C_{17}H_{14}N_2OS$: C, 69.36; H, 4.79; N, 9.52. Found: C, 69.27; H, 4.86; N, 9.35.

*5-(p-Nitrophenylthio)-2,2′-bipyridyl (**6k**).* mp 124.5–125.5°C. MS: m/z (rel. intensity); 311 (7), 310 (21), 309 (M$^+$, 100), 263 (24), 262 (12), 78 (19). ^{1}H NMR ($CDCl_3$): $\delta = 7.27$ (2H, d, $J = 9.0$ Hz), 7.36 (1H, ddd, $J = 7.5$, 4.8, 1.2 Hz), 7.86 (1H, ddd, $J = 8.1$, 7.5, 1.8 Hz), 7.96 (1H, dd, $J = 8.4$, 2.4 Hz), 8.11 (2H, d, $J = 9.0$ Hz), 8.44 (1H, ddd, $J = 8.1$, 1.2, 0.9 Hz), 8.51 (1H, dd, $J = 8.4$, 0.6 Hz), 8.71 (1H, ddd, $J = 4.8$, 1.8, 0.9 Hz), 8.77 (1H, dd, $J = 2.4$, 0.6 Hz). Anal calcd for $C_{16}H_{11}N_3O_2S$: C, 62.12; H, 3.58; N, 13.58. Found: C, 62.24; H, 3.68; N, 13.51.

*5-Phenylsulfinyl-2,2′-bipyridyl (**7a**).* mp 132.5–133.0°C. MS: m/z (rel. intensity); 282 (2), 281 (8), 280 (M$^+$, 40), 265 (20), 264 (100), 263 (70), 232 (33), 188 (15), 187 (17), 171 (32), 155 (10), 116 (16), 78 (20). ^{1}H NMR ($CDCl_3$): $\delta = 7.33$ (1H, ddd, $J = 7.5$, 4.8, 1.2 Hz), 7.45–7.54 (3H, m), 7.68–7.72 (2H, m), 7.81 (1H, ddd, $J = 8.1$, 7.5, 1.8 Hz), 8.08 (1H, dd, $J = 8.4$, 2.4 Hz), 8.41 (1H, ddd, $J = 8.1$, 1.2, 0.9 Hz), 8.53 (1H, dd, $J = 8.4$, 0.9 Hz), 8.67 (1H, ddd, $J = 4.8$, 1.8, 0.9 Hz), 8.85 (1H, dd, $J = 2.4$, 0.9 Hz). Anal calcd for $C_{16}H_{12}N_2OS$: C, 68.55; H, 4.31; N, 9.99. Found: C, 68.46; H, 4.41; N, 9.89.

*4,4′-Dimethyl-5-phenylsulfinyl-2,2′-bipyridyl (**7b**).* mp 145.0–146.0°C. MS: m/z (rel. intensity); 310(2), 309 (7), 308 (M$^+$, 30), 293 (17), 292 (71), 291 (100), 259 (12), 199 (18), 171 (20), 156 (13), 144 (15), 92 (13). ^{1}H NMR ($CDCl_3$): $\delta = 2.44$ (6H, s), 7.17 (1H, d, $J = 4.8$ Hz), 7.46–7.53 (3H, m), 7.63–7.69 (2H, m), 8.24(1H, s), 8.28 (1H, s), 8.52 (1H, d, $J = 4.8$ Hz), 9.02 (1H, s). Anal calcd for $C_{16}H_{12}ON_2S$: C, 70.10; H, 5.23; N, 9.08. Found: C, 70.08; H, 5.28; N, 8.81.

*6,6′-Dimethyl-5-phenylsulfinyl-2,2′-bipyridyl (**7c**).* mp 136.5–137.5°C. MS: m/z (rel. intensity); 310 (5), 309 (19), 308 (M$^+$, 50), 293 (12), 292 (42), 291 (100), 260 (23), 259 (23), 215 (14), 199 (68), 183 (26), 171 (38), 141 (15), 131 (18), 130 (60), 92 (31), 77 (28). ^{1}H NMR (CDCl$_3$): $\delta = 2.61$ (3H, s), 2.63 (3H, s), 7.19 (1H, dd, $J = 7.8$ Hz), 7.43–7.48 (3H, m), 7.60–7.65 (2H, m), 7.69 (1H, t, $J = 7.8$ Hz), 8.19 (1H, d, $J = 8.1$ Hz), 8.36 (1H, d, $J = 7.8$ Hz), 8.47 (1H, d, $J = 8.1$ Hz). Anal calcd for $C_{16}H_{12}N_2OS$: C, 70.10; H, 5.23; N, 9.08. Found: C, 70.22; H, 5.28; N, 8.87.

*5-(p-Chlorophenylsulfinyl)-2,2′-bipyridyl (***7f***).* mp 156.0–157.0°C. MS: *m/z* (rel. intensity); 316 (14), 315 (7), 314 (M$^+$, 39), 300 (39), 299 (42), 298 (100), 297 (59), 268 (20), 267 (12), 266 (55), 118 (10), 187 (25), 171 (43), 155 (15), 128 (12), 116 (13), 78 (22). ^{1}H NMR (CDCl$_3$): $\delta = 7.35$ (1H, ddd, $J = 7.5$, 4.8, 1.2 Hz), 7.484 (2H, d, $J = 8.4$ Hz), 7.64 (2H, d, $J = 8.4$ Hz), 7.83 (1H, ddd, $J = 7.8$, 7.5, 1.8 Hz), 8.06 (1H, dd, $J = 8.4$, 2.4 Hz), 8.41 (1H, ddd, $J = 7.8$, 1.2, 0.9 Hz), 8.54 (1H, dd, $J = 8.4$, 0.9 Hz), 8.68 (1H, ddd, $J = 4.8$, 1.8, 0.9 Hz), 8.84 (1H, dd, $J = 2.4$, 0.9 Hz). Anal calcd for $C_{16}H_{11}ClN_2OS$: C, 61.05; H, 3.52; N, 8.90. Found: C, 61.15; H, 3.67; N, 8.75.

*5-(p-Tolylsulfinyl)-2,2′-bipyridyl (***7i***).* mp 129.5–130.5°C. MS: *m/z* (rel. intensity); 296 (3), 295 (9), 294 (M$^+$, 44), 278 (16), 277 (39), 247 (18), 246 (100), 245 (16), 188 (13), 187 (17), 171 (52), 123 (22), 116 (12), 78 (28). ^{1}H NMR (CDCl$_3$): $\delta = 2.38$ (3H, s), 7.30 (2H, $J = 8.1$ Hz), 7.34 (1H, ddd, $J = 7.5$, 4.8, 1.2 Hz m), 7.58 (2H, d, $J = 8.1$ Hz), 7.82 (1H, ddd, $J = 8.1$, 7.5, 1.8 Hz), 8.07 (1H, dd, $J = 8.4$, 2.4 Hz), 8.40 (1H, ddd, $J = 8.1$, 1.2, 0.9 Hz), 8.52 (1H, dd, $J = 8.4$, 0.9 Hz), 8.67 (1H, ddd, $J = 4.8$, 1.8, 0.9 Hz), 8.82 (1H, dd, $J = 2.4$, 0.9 Hz). Anal calcd for $C_{17}H_{14}N_2OS$: C, 69.36; H, 4.79; N, 9.52. Found: C, 69.50; H, 4.86; N, 9.38.

*5-(p-Methoxyphenylsulfinyl)-2,2′-bipyridyl (***7j***).* mp 120.5–121.5°C. MS: *m/z* (rel. intensity); 312 (1), 311 (3), 310 (M$^+$, 12), 294 (34), 263 (21), 262 (100), 247 (19), 155 (32), 139 (28), 123 (22), 78 (16). ^{1}H NMR (CDCl$_3$): $\delta = 3.83$ (3H, s), 7.00 (2H, d, $J = 9.0$ Hz), 7.34 (1H, ddd, $J = 7.8$, 4.8, 1.2 Hz), 7.63 (2H, d, $J = 9.0$ Hz), 7.82 (1H, td, $J = 7.8$, 1.8 Hz), 8.06 (1H, dd, $J = 8.4$, 2.4 Hz), 8.41 (1H, ddd, $J = 7.8$, 1.2, 0.9 Hz), 8.52 (1H, dd, $J = 8.4$, 0.6 Hz), 8.68 (1H, ddd, $J = 4.8$, 1.8, 0.9 Hz), 8.79 (1H, $J = 2.4$, 0.6 Hz). Anal calcd for $C_{17}H_{14}N_2O_2S$: C, 65.79; H, 4.55; N, 9.03. Found: C, 65.65; H, 4.64; N, 8.81.

*5-(p-Nitrophenylsulfinyl)-2,2′-bipyridyl (***7k***).* mp 226.0–227.0°C. MS: *m/z* (rel. intensity); 327 (2), 326 (7), 325 (M$^+$, 39), 309 (22), 308 (21), 278 (12), 277 (60), 263 (17), 262 (66), 261 (13), 231 (16), 203 (33), 187 (35), 172 (11), 171 (100), 155 (49), 143 (39), 128 (31), 116 (43), 89 (11), 78 (70). ^{1}H NMR (CDCl$_3$): $\delta = 7.36$ (1H, ddd, $J = 7.5$, 4.8, 1.2 Hz), 7.35 (1H, ddd, $J = 8.1$, 7.5, 1.8 Hz), 7.80 (2H, d, $J = 9.0$ Hz), 8.09 (1H, dd, $J = 8.4$, 2.4 Hz), 8.36 (2H, d, $J = 9.0$ Hz), 8.42 (1H, ddd, $J = 8.1$, 1.2, 0.9 Hz), 8.57 (1H, dd, $J = 8.4$, 0.6 Hz), 8.69 (1H, ddd, $J = 4.8$, 1.8, 0.9 Hz), 8.91 (1H, dd, $J = 2.4$, 0.6 Hz). Anal calcd for $C_{16}H_{11}N_3O_3S$: C, 59.07; H, 3.41; N, 12.92. Found: C, 59.14; H, 3.56; N, 12.73.

*5-Phenylsulfonyl-2,2′-bipyridyl (***8a***).* mp 198.5–199.5°C. MS: *m/z* (rel. intensity); 298 (8), 297 (19), 296 (M$^+$, 100), 295 (24), 264 (31), 263 (15), 203 (19), 171 (22), 155 (18), 143 (14), 128 (11), 125 (13), 116 (123), 78 (23), 77 (11). ^{1}H NMR (CDCl$_3$): $\delta = 7.37$ (1H, ddd, $J = 7.5$, 4.8, 1.2 Hz), 7.51–7.640 (3H, m), 7.84 (1H, ddd, $J = 8.1$, 7.5, 1.8 Hz), 7.99–8.03 (2H, m), 8.30 (1H, dd, $J = 8.4$, 2.4 Hz), 8.45 (1H, dt, $J = 8.1$, 1.2 Hz), 8.57 (1H, dd, $J = 8.4$, 0.9 Hz), 8.69 (1H, ddd, $J = 4.8$, 1.8, 0.9 Hz), 9.17 (1H, dd, $J =$ 2.4, 0.9 Hz). Anal calcd for $C_{16}H_{12}N_2O_2S$: C, 64.85; H, 4.08; N, 9.45. Found: C, 64.82; H, 4.20; N, 9.30.

*4,4′-Dimethyl-5-phenylsulfonyl-2,2′-bipyridyl (***8b***).* mp 175.0–176.0°C. MS: *m/z* (rel. intensity); 326 (10), 325 (28), 324 (M$^+$, 100), 323 (40), 306 (16), 289 (11), 260 (12), 259 (58), 258 (25), 183 (26), 171 (21), 156 (25), 155 (12), 154 (14), 144 (15), 141 (17), 92 (18), 77 (23). ^{1}H NMR (CDCl$_3$): $\delta = 2.46$ (3H, s), 2.56 (3H, s), 7.19 (1H, d, $J = 4.8$ Hz), 7.51–7.65 (3H, m), 7.92–7.96 (2H, m), 8.30 (1H, s), 8.32 (1H, s), 8.53 (1H, d, $J = 4.8$ Hz), 9.31 (1H, s). Anal calcd for $C_{18}H_{16}N_2O_2S$: C, 66.64; H, 4.97; N, 8.64. Found: C, 66.62; H, 5.03; N, 8.41.

*6,6′-Dimethyl-5-phenylsulfonyl-2,2′-bipyridyl (***8c***).* mp 138.5–139.5°C. MS: *m/z* (rel. intensity); 326 (12), 325 (23), 324 (M$^+$, 100), 290 (14), 260 (13), 259 (59), 199 (12), 183 (14), 130 (14), 92 (12), 77 (10). ^{1}H NMR(CDCl$_3$): $\delta = 2.63$ (3H, s), 2.73 (3H, s), 7.21 (1H, d, $J = 7.8$ Hz), 7.50–7.64 (3H, m), 7.70 (1H, t, $J = 7.8$ Hz), 7.88–7.92 (2H, m), 8.22 (1H, d, $J = 7.8$ Hz), 8.47 (1H, d, $J = 7.8$ Hz), 8.56 (1H, d, $J = 7.8$ Hz). Anal calcd for $C_{18}H_{16}N_2O_2S$: C, 66.64; H, 4.97; N, 8.64. Found: C, 66.56; H, 5.05; N, 8.41.

*5-(p-Chlorophenylsulfonyl)-2,2′-bipyridyl (***8f***).* mp 213.5–214.5°C. MS: *m/z* (rel. intensity); 333 (7), 332 (38), 331 (26), 330 (M$^+$, 100), 329 (17), 293 (19), 292 (73), 291 (42), 203 (33), 171 (27), 159 (12), 155 (23), 143 (18), 128 (13), 116 (13), 78 (27). ^{1}H NMR (CDCl$_3$): $\delta = 7.38$ (1H, ddd, $J = 7.8$, 4.8, 1.2 Hz), 7.52 (2H, d, $J = 8.7$ Hz), 7.85 (1H, ddd, $J = 7.8$, 7.5, 1.8 Hz), 7.93 (2H, d, $J = 8.7$ Hz), 8.28 (1H, dd,

$J = 8.4$, 2.4 Hz), 8.46 (1H, ddd, $J = 7.5$, 1.2, 0.9 Hz), 8.59 (1H, dd, $J = 8.4$, 0.6 Hz), 8.70 (1H, ddd, $J = 4.8$, 1.8, 0.9 Hz), 9.16 (1H, dd, $J = 2.4$, 0.6 Hz). Anal calcd for $C_{16}H_{11}ClN_2O_2S$: C, 58.09; H, 3.35; N, 8.47. Found: C, 57.81; H, 3.49; N, 8.30.

5-(p-Tosyl)-2,2′-bipyridyl (**8i**). mp 224.0–225.0°C. MS: *m/z* (rel. intensity); 312 (7), 311 (19), 310 (M^+, 100), 309 (10), 278 (17), 203 (19), 155 (10), 139 (34), 78 (14). ^1H NMR ($CDCl_3$): $\delta = 2.41$ (3H, s), 7.33 (2H, d, $J = 8.4$ Hz), 7.36 (1H, ddd, $J = 7.8$, 4.8, 1.2 Hz), 7.84 (1H, td, $J = 7.8$, 1.8 Hz), 7.87 (2H, d, $J = 8.4$ Hz), 8.28 (1H, dd, $J = 8.4$, 2.4 Hz), 8.44 (1H, ddd, $J = 7.8$, 1.2, 0.9 Hz), 8.55 (1H dd, $J = 8.4$, 0.9 Hz), 8.69 (1H, ddd, $J = 4.8$, 1.8, 0.9 Hz), 9.15 (1H, dd, $J = 2.4$, 0.9 Hz). Anal calcd for $C_{17}H_{14}N_2O_2S$: C, 65.79; H, 4.55; N, 9.03. Found: C, 65.78; H, 4.64; N, 8.94.

5-(p-Methoxyphenylsulfonyl)-2,2′-bipyridyl (**8j**). mp 188.0–189.0°C. MS: *m/z* (rel. intensity); 328 (6), 327 (18), 326 (M^+, 100), 325 (12), 155 (58), 128 (13), 123 (49), 107 (12), 92 (16), 78 (36), 77 (22). ^1H NMR($CDCl_3$): $\delta = 3.85$ (3H, s), 7.00 (2H, d, $J = 9.0$ Hz), 7.36 (1H, ddd, $J = 7.8$, 4.8, 1.2 Hz), 7.83 (1H, ddd, $J = 8.1$, 7.8, 1.8 Hz), 7.93 (2H, d, $J = 9.0$ Hz), 8.27 (1H, dd, $J = 8.4$, 2.4 Hz), 8.44 (1H, ddd, $J = 8.1$, 1.2, 0.9 Hz), 8.55 (1H, dd, $J = 8.4$, 0.6 Hz), 8.68 (1H, ddd, $J = 4.8$, 1.8, 0.9 Hz), 9.14 (1H, dd, $J = 2.4$, 0.6 Hz). Anal calcd for $C_{17}11_{14}N_2O_3S$: C, 62.56; H, 4.32; N, 8.58. Found: C, 62.65; H, 4.35; N, 8.39.

5-(p-Nitrophenylsulfonyl)-2,2′-bipyridyl (**8k**). mp 288.0–289.0°C. MS: *m/z* (rel. intensity) 343 (7), 342 (22), 341 (M^+, 100), 340 (11), 203 (17), 171 (21), 155 (49), 143 (20), 128 (23), 116 (17), 78 (36). ^1H NMR($CDCl_3$): $\delta = 7.39$ (1H, ddd, $J = 7.5$, 4.8, 1.2 Hz), 7.86 (1H, ddd, $J = 7.8$, 7.5, 1.8 Hz), 8.19 (2H, d, $J = 9.0$ Hz), 8.32 (1H, dd, $J = 8.4$, 2.4 Hz), 8.39 (2H, d, $J = 9.0$ Hz), 8.47 (1H, ddd, $J = 7.8$, 1.2, 0.9 Hz), 8.63 (1H, dd, $J = 8.4$, 0.6 Hz), 8.71 (1H, ddd, $J = 4.8$, 1.8, 0.9 Hz), 9.20 (1H, dd, $J = 2.4$, 0.6 Hz). Anal calcd for $C_{16}H_{11}N_3O_3S$: C, 56.30; H, 3.25; N, 12.31. Found: C, 56.25; H, 3.40; N, 12.18.

*Reaction of Tris(2-pyridyl)phosphine Oxide (**1a**) with p-Toluenesulfinyl p-Tolyl Sulfone (**10a**)*

Hydrochloric acid (0.4 ml) was added to a solution of **1a** (283 mg, 1 mmol) and **10a** (1.502 g, 5.1 mmol) in acetonitrile (20 ml) with stirring. After stirring of the reaction mixture for 20 h at room temperature, the solvent was removed under reduced pressure, and the residue was dissolved in chloroform (30 ml). After the same treatment of the chloroform solution as described in the reaction of **1a** with arenesulfinyl chloride, column chromatography of the product mixture on silica gel (chloroform) and on alumina (petroleum ether/ethyl acetate 5:1) gave **2a** (74 mg, 47%), **6i** (19 mg, 7%), **7i** (36 mg, 12%), and **8i** (6 mg, 2%).

*Reaction of 5-(p-Tolylsulfinyl)-2,2′-bipyridyl (**7i**) with p-Toluenesulfinyl Chloride*

Water (18 μl) was added 5 times at an interval of 1 h into a solution of **7i** (118 mg, 0.4 mmol) and *p*-toluenesulfinyl chloride (874 mg, 5 mmol) in acetonitrile (20 ml) with stirring at 30°C. After the reaction mixture had been kept overnight at room temperature, the solvent was removed under reduced pressure, and the residue was dissolved in chloroform (30 ml). After the same treatment of the chloroform solution as described in the reaction of **1a** with arenesulfinyl chloride, column chromatography of the product mixture on silica gel (chloroform) and on alumina (petroleum ether/ethyl acetate 5:1) gave **6i** (53 mg, 47%), **7i** (50 mg, 43%), and **8i** (3 mg, 2%).

*Reaction of 5-(p-Tolylthio)-2,2′-bipyridyl (**6i**) with p-Toluenesulfinyl Chloride*

Water (18 μl) was added 5 times at an interval of 1 h to a solution of **6i** (113 mg, 0.4 mmol) and *p*-toluenesulfinyl chloride (873 mg, 5 mmol) in acetonitrile (20 ml) with stirring at 30°C. After the reaction mixture had been kept overnight at room temperature, the solvent was removed under reduced pressure, and the residue was dissolved in chloroform (30 ml). After the same treatment of the chloroform solution as described in the reaction of **1a** with arenesulfinyl chloride, column chromatography of the product mixture on silica gel (chloroform) and on alumina (petroleum ether/ethyl acetate 5:1) gave **6i** (75 mg, 67%), **7i** (24 mg, 21%), and **8i** (1 mg, 1%).

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