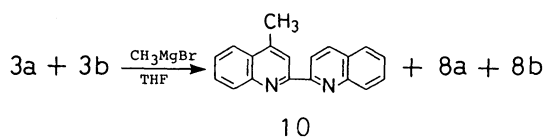
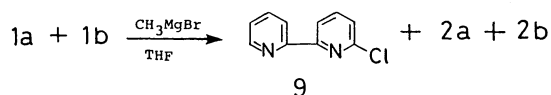


a) Ref. 6. b) Ref. 7. c) Ref. 8. d) Ref. 9. e) Ref. 10. f) Ref. 11.



Scheme 4.

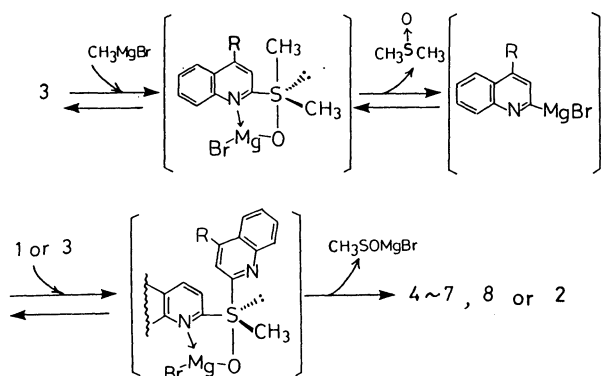
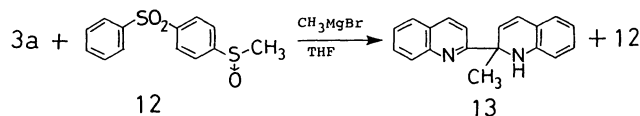


Chart 1.

The mechanism of the reaction has been examined carefully in the cases of 2-(alkylsulfinyl)pyridines and proposed by Oae et al.⁴⁾ According to the mechanism, an initial attack of the methylmagnesium bromide on the sulfur atom of **3** forms a σ -sulfurane intermediate followed by disproportionation to release dimethyl sulfoxide and 2-quinolylmagnesium bromide, which subsequently reacts with another sulfoxide **1** or **3** to promote a normal ligand coupling, and finally affording the cross coupling product **4**—**7** as well as the homo-coupling products **8** and **2**.

The coupling reaction of **3a** with 2-(*t*-butylsulfinyl)pyridine (**11**) also gave the desired cross coupling product **4** in 22% yield along with **8a** in 8% yield but none of **2a** was detected in the reaction mixture.¹³⁾ The rest of the starting sulfoxide **11** was recovered in 71% yield. The result would be due to the steric hindrance of the *t*-butylsulfinyl group, thus the rate of formation of the intermediary σ -sulfurane derived from 2-quinolylmagnesium bromide and **11** is anticipated to be considerably slow. The cross coupling reaction obviously competes with the usual ligand coupling reaction as well as other side reactions involving simple ligand exchange or disulfide formation. Thus the reaction is not simple. In fact, no cross coupling was observed between **3a** and 1-methylsulfinyl-4-(phenylsulfonyl)benzene (**12**). The major product was 2-methyl-1,2-dihydro-2,2'-biquinolyl (**13**) along with 90% recovery of the other sulfoxide **12**. The compound **13** is known to be produced by treatment of two equivalents of methylmagnesium bromide and **3a**.⁵⁾



Scheme 5.

Reactions of **3a** with other substrates, 2-(methylsulfinyl)pyrimidine, methylsulfinylbenzene, and their *t*-butylsulfinyl derivatives gave almost similar results in which no cross coupling product was detected among the reaction mixtures. In the reaction of **1a** and **12**, the dimeric compound **2a** was obtained in 89% yield and the sulfoxide **12** was recovered quantitatively.

Experimental

Melting points were determined with Yanaco micromelting point apparatus and were uncorrected. ¹H NMR spectra were run on JEOL-GX400 spectrometer in CDCl₃ with tetramethylsilane as an internal standard. Chemical shifts are given as σ value. Infrared spectra were obtained with JASCO IR-A spectrometer. Low- and high-resolution mass spectra were taken on JEOL-JMS 303HF spectrometer with a direct inlet method at 70 eV. Only strong and/or structurally important peaks are reported here for IR and MS. Column chromatography was carried out on silica gel (Wako gel 200). THF for the reactions was dried over sodium benzophenone ketyl and freshly distilled just before use. Methylmagnesium bromide was purchased from Kanto Chemical Co. as THF solution.

Typical Procedure of the Cross-Coupling Reaction. To a mixture of sulfoxide (**1** mmol) and another sulfoxide (**1** mmol) in THF (5 ml) was dropped methylmagnesium bromide (2 ml, 1M solution in THF) at room temperature during a min under Argon atmosphere. The reaction mixture was stirred for 15 min at the same temperature. It was quenched with aq. ammonium chloride (2 ml) and extracted with chloroform (60 ml). The extract was washed with water (4 ml×2) and brine (4 ml), dried over MgSO₄ and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel. Characteristic properties of the products are the following.

4: Colorless crystals, mp 98–99°C (EtOH) (lit.⁶⁾ 99°C); ¹H NMR δ =7.36 (1H, td, J =6.4, 1.8 Hz), 7.56 (1H, td, J =7.1, 1.5 Hz), 7.74 (1H, dt, J =7.9, 1.5 Hz), 7.85 (1H, d, J =8.5 Hz), 7.88 (1H, td, J =7.3, 1.9 Hz), 8.19 (1H, d, J =8.7 Hz), 8.29 (1H, d, J =8.2 Hz), 8.56 (1H, d, J =8.2 Hz), 8.66 (1H, dd, J =8.1, 1.1 Hz), 8.75 (1H, ddd, J =4.7, 1.9, 1.1 Hz).

8a: Colorless crystals, mp 193–194°C (EtOH) (lit.⁷⁾ 193–196°C; ¹H NMR δ =7.58 (2H, ddd, J =7.5, 5.0, 1.1 Hz), 7.76 (2H, td, J =8.0, 1.1 Hz), 7.89 (2H, d, J =8.0 Hz), 8.23 (2H, d, J =8.1 Hz), 8.33 (2H, d, J =8.1 Hz), 8.85 (2H, d, J =8.1 Hz).

2a: Colorless crystals, mp 70–73°C (EtOH) (lit.⁸⁾ 69.7°C); ¹H NMR δ =7.31 (2H, ddd, J =7.5, 5.0, 1.3 Hz), 7.82 (2H, td, J =7.7, 1.8 Hz), 8.39 (2H, d, J =8.1 Hz), 8.69 (2H, dd, J =5.0, 0.3 Hz).

5: Colorless crystals, mp 156–158°C (EtOH); ¹H NMR δ =7.57 (1H, td, J =8.1, 1.5 Hz), 7.75 (1H, td, J =8.0, 1.5 Hz), 7.76 (1H, t, J =7.9 Hz), 7.82 (1H, d, J =8.1 Hz), 8.16 (1H, d, J =8.4 Hz), 8.28 (1H, d, J =8.4 Hz), 8.34 (1H, dd, J =7.7, 0.7 Hz), 8.55 (1H, d, J =8.7 Hz), 8.62 (1H, dd, J =7.9, 0.8 Hz); IR(CHCl₃) 2930, 2850, 1600, 1570, 1550, 1410, 1150, 1140

cm⁻¹; MS *m/z*(rel intensity) 240, 242 (M⁺, 67 and 23), 205 (65), 128 (26), 28 (base); Found: C, 69.67; H, 3.78; N, 11.77%. Calcd for C₁₄H₉N₂Cl: C, 69.86; H, 3.77; N, 11.64%.

2b: Colorless crystals, mp 216–219°C (benzene:hexane, 1:1) (lit.⁹) 218–219°C; ¹H NMR δ=7.36 (2H, d, *J*=8.1 Hz), 7.78 (2H, t, δ=7.7 Hz), 8.35 (2H, dd, *J*=7.7, 0.7 Hz).

6: Colorless crystals, mp 64–66°C (petr. ether) (lit.¹⁰) 69–70°C; ¹H NMR δ=2.78 (3H, s), 7.32 (1H, ddd, *J*=7.3, 4.8, 1.1 Hz), 7.56 (1H, td, *J*=8.4, 1.4 Hz), 7.72 (1H, td, *J*=7.7, 1.2 Hz), 7.86 (1H, td, *J*=7.7, 1.8 Hz), 8.01 (1H, d, *J*=8.4 Hz), 8.17 (1H, dd, *J*=8.4, 0.7 Hz), 8.39 (1H, s), 8.63 (1H, dd, *J*=7.0, 1.0 Hz), 8.73 (1H, dm, *J*=4.0 Hz).

8b: Colorless crystals, mp 279–280°C (chloroform) (lit.¹¹) 280°C; ¹H NMR δ=2.85 (6H, s), 7.60 (2H, td, *J*=8.0, 1.1 Hz), 7.76 (2H, td, *J*=7.7, 1.0 Hz), 8.06 (2H, d, *J*=8.4 Hz), 8.25 (2H, d, *J*=8.4 Hz), 8.67 (2H, s).

7: Colorless crystals, mp 110–112°C (EtOH); ¹H NMR δ=2.80 (3H, s), 7.38 (1H, d, *J*=7.0 Hz), 7.58 (1H, td, *J*=7.3, 0.9 Hz), 7.73 (1H, td, *J*=7.3, 1.5 Hz), 7.82 (1H, t, *J*=7.7 Hz), 8.03 (1H, dd, *J*=8.4, 0.7 Hz), 8.15 (1H, d, *J*=8.4 Hz), 8.39 (1H, s), 8.60 (1H, dd, *J*=7.7, 0.7 Hz); IR(CHCl₃) 2960, 2940, 1600, 1585, 1570, 1550, 1440, 1420, 1360, 1160, 1140 cm⁻¹; MS *m/z* (rel intensity) 254, 256 (M⁺, base and 31), 219 (65), 112 (14); Found: C, 70.62; H, 4.50; N, 10.69%. Calcd for C₁₅H₁₁N₂Cl: C, 70.72; H, 4.32; N, 10.99%.

9: Colorless crystals, mp 59–60°C (petr. ether) (lit.¹²) 60–62°C; ¹H NMR δ=7.33 (1H, td, *J*=6.2, 1.1 Hz), 7.34 (1H, dd, *J*=8.0, 0.7 Hz), 7.77 (1H, t, *J*=7.7 Hz), 7.82 (1H, td, *J*=7.9, 1.7 Hz), 8.35 (1H, d, *J*=7.7 Hz), 8.41 (1H, d, *J*=7.7 Hz), 8.67 (1H, dm, *J*=4.4 Hz).

10: ¹H NMR δ=2.85 (3H, s), 7.58 (1H, t, *J*=8.0 Hz), 7.60 (1H, t, *J*=8.0 Hz), 7.75 (1H, t, *J*=8.4 Hz), 7.76 (1H, t, *J*=8.4 Hz), 7.88 (1H, d, *J*=8.0 Hz), 8.06 (1H, d, *J*=8.4 Hz), 8.22 (1H, d, *J*=8.4 Hz), 8.23 (1H, d, *J*=8.4 Hz), 8.32 (1H, d, *J*=8.8 Hz), 8.68 (1H, s), 8.85 (1H, d, *J*=8.8 Hz).

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