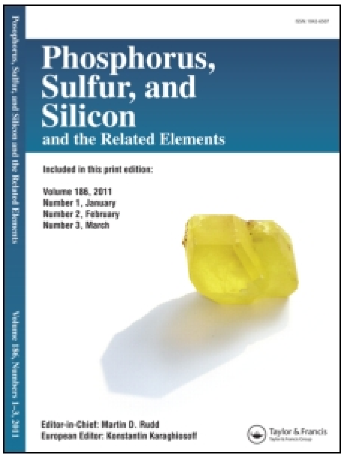

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THE REACTION OF 2,2′-DIPYRIDYL SULFIDE WITH PHENOL

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The reaction of 2,2′-dipyridyl sulfide with phenol affords 2-pyridinethiol and phenyl 2-pyridyl ether, which is the aromatic ipso substitution in 2,2′-dipyridyl sulfide by the phenoxy group. On the other hand. pyridyl tolyl sulfide is formed by the reaction of phenyl pyridyl ether with toluenethiol.

The ipso substitution is the usual process occurring in nucleophilic aromatic substitutions. It is observed that alkyl radicals are capable of effecting the displacement of acyl group in the pyridine, quinoline, and benzothiazole systems.[1] As to disulfides, these sulfur-sulfur bonds are cleaved by the attack of a nucleophile or radical,[2] but little is known concerning the carbon–sulfur bond cleavage of aryl sulfides.[3] This paper reports the cleavage of the carbon–sulfur bond of dipyridyl sulfide, viz, the replacement of the pyridylthio group by the phenoxy group at the 2-position of the pyridine ring.

When a mixture of 2,2′-dipyridyl sulfide (**1**) and a large excess of phenol (**2**) was heated at 200°C for 1 hour in a sealed tube, phenyl 2-pyridyl ether (**3a**) and 2-pyridinethiol (**4**) were formed.

(1)

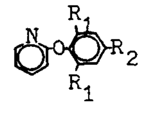
1 **2** **3a** **4**

The yields of the ether formed from several substituted phenols, based on converted **1**, are shown below.

Compound **3a** was also formed in 69% yield by the reaction of 2,2′-dipyridyl disulfide (**5**) with a large excess of **2**. When a mixture of 2-pyridyl tolyl sulfide (**6**) and a large excess of **2** was heated under the same conditions, **3a** and toluenethiol (**7**) were obtained, but phenyl tolyl ether and **4** were not formed. This result indicates that the carbon–sulfur bond between the pyridine ring and sulfur is cleaved, but the carbon–sulfur bond between the tolyl group and sulfur is not cleaved. These

TABLE 1

Compounds number	3a	3b	3c	3d
R_1	H	H	H	Me
R_2	H	Me	MeO	Me
Yields of ether (%)	72	86	81	38



3a–d

observations clearly indicate that ipso substitution occurs only for the pyridine ring. Upon heating of a mixture of **3a** and a large excess of **7**, **2** and **6** were formed quantitatively. In this process, the reverse was found for the reaction of **1** with **2**. Thus, it is considered that the reaction of **1** with **2** is reversible.

When a mixture of **2** and di-*p*-nitrophenyl sulfide (**8**) or dibenzyl sulfide (**9**), both of which are considered to be reactive towards nucleophiles, was heated under the same conditions, no reaction took place. On the other hand, aryl halides bearing electron-withdrawing groups are usually reactive towards alkoxides. Thus, the reaction of **1** with **2** was performed in the presence of potassium *t*-butoxide or acetic acid. The amount of **3a** formed in this reaction was not affected by the presence of alkali or acid. In the presence of a large excess of norbornene (**10**), **1** reacted at 200°C to yield a small amount of norbornyl 2-pyridyl sulfide (**11**) which was considered to be formed by the addition of pyridylthio radical to **10**. However, **8** or **9** was unreactive to **10**. Thus, positional selectivity and reactivity of the sulfide may be attributed to the leaving ability of the substituent such as the pyridylthio group.

EXPERIMENTAL

Gas chromatographic analyses were carried out with a Hitachi 163 instrument, using a 5% OV-1 column (2 m). Nmr spectra were determined on a Hitachi R-600 spectrometer, using tetramethylsilane as internal standard. Mass spectra were recorded on a Hitachi RMU-6M instrument.

Reaction of 2,2'-Dipyridyl Sulfide (**1**) *with Phenol* (**2**). A typical run was carried out as follows. A mixture of **1** (122 mg) and **2** (1248 mg) was heated at 200°C for 1 hour in three sealed tubes. The reaction mixture was chromatographed on silica gel eluting with chloroform to give 79.9 mg of phenyl 2-pyridyl ether (**3a**) and 47.5 mg of 2-pyridinethiol (**4**). The products **3a** and **4** were identified by comparison of spectral data with these of the authentic samples. **3a**: NMR (deuteriochloroform), δ 6.8–7.85 (8 H, multiplet), 8.15–8.36 (1 H, multiplet). Anal. Calcd. for $C_{11}H_9NO$: C, 77.17; H, 5.29; N, 8.18. Found: C, 77.10; H, 5.40; N, 8.37. MS, m/e 171 (M^+), 170 (M^+—H) **4**: NMR (deuteriochloroform), δ 6.65–6.98 (1 H, multiplet), 7.23–7.75 (4 H, multiplet). MS, m/e 111 (M^+). The products **3b**, **3c**, and **3d**, formed under the same reaction conditions as formation of **3a**, were analyzed directly by g.l.c., using biphenyl as internal standard. **3b**: MS, m/e 185 (M^+), 184 (M^+—H). **3c**: MS, m/e 201 (M^+), 200 (M^+—H). **3d**: MS, m/e 213 (M^+).

Reaction of p-Toluenethiol (**7**) *with* **3a**. A mixture of **7** (608.2 mg), **3a** (35.5 mg), and bibenzyl (12.3 mg) as internal standard for g.l.c. was heated at 200°C for 1 hour in a sealed tube and analyzed directly by g.l.c. Compounds **2** and **6** formed in this reaction were identified by comparison of mass spectral degradation patterns with these of the authentic samples.

Reaction of **1** *with* **2** *in the Presence of Potassium t-Butoxide or Acetic Acid*. Three kinds of solutions (A), (B), and (C) were made. Solution (A) contained **1** (103.7 mg), **2** (1315.9 mg), propyl alkol (229 mg) as a solvent, and biphenyl (3.4 mg) as a internal standard of g.l.c. Solution (B) was a mixture of (A) (468.0 mg) and acetic acid (27.6 mg). Solution (C) was a mixture of (A) (512.3 mg) and potassium *t*-butoxide (16.5 mg). Solution (A), (B), and (C) were heated at 200°C for 30 minutes in a sealed tube respectively and analyzed directly by g.l.c. Then, no differences in their tendencies to form **3a** could be detected in three kinds of solvents.

Reaction of **1** *with Norbornene* (**10**). A mixture of **1** (64.7 mg) and **10** (398 mg) was heated at 200°C for 1 hour in a sealed tube and analyzed directly by g.l.c. The mass spectral peaks of product (**11**) were given at m/e 205 (M^+), 111 (M^+–norbornene).

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