

mass spectrum,  $m/e$ , 283 ( $M^+$ ).

**Registry No.** 1, 6630-99-5; 2a, 94324-70-6; 2b, 94295-50-8; 2c, 94295-51-9; 2e, 94295-52-0; 2f, 7523-57-1; 4a, 94295-53-1; 4d, 94295-54-2; 4e, 94295-55-3; 5, 94295-72-4; 6 ( $R^1 = Me$ ), 52098-72-3; 6 ( $R^1 = Et$ ), 52098-73-4; 6 ( $R^1 = Bu$ ), 80650-17-5; 6 ( $R^1 = Ph$ ), 13078-30-3; 6 ( $R^1 = 4-C_6H_4$ ), 13078-27-8; 6 ( $R^1 = 4-FC_6H_4$ ), 1544-80-5; 6 ( $R^1 = 4-MeC_6H_4$ ), 13078-28-9; 7a, 94295-56-4; 7b, 94295-57-5; 7c, 94295-58-6; 7d, 94295-59-7; 7e, 94295-60-0; 7f, 94295-61-1; 7g, 94295-62-2; 7h, 94295-63-3; 7i, 94295-64-4; 7j, 94324-71-7; 7k, 94295-65-5; 7l, 94295-66-6; 7m, 94295-67-7; 8g, 94295-68-8; 8h, 94295-69-9; 8i, 94295-70-2; 8m, 94295-71-3; 8n, 35488-66-5; 8o, 40145-58-2; 9, 94295-74-6; 10, 34551-29-6; 11, 94295-75-7; PhOCN, 1122-85-6; *o*-ClC<sub>6</sub>H<sub>4</sub>OCN, 1123-90-6; *m*-MeC<sub>6</sub>H<sub>4</sub>OCN, 1124-36-3; *p*-MeOC<sub>6</sub>H<sub>4</sub>OCN, 2983-74-6; Cl<sub>3</sub>CCN, 545-06-2; *p*-MeC<sub>6</sub>H<sub>4</sub>OCN, 1124-58-9; 2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OCN, 1601-46-3; CCl<sub>3</sub>CH<sub>2</sub>OCN, 1118-44-1; H<sub>2</sub>NNH<sub>2</sub>·H<sub>2</sub>O, 7803-57-8; *p*-MeOC<sub>6</sub>H<sub>4</sub>OC(S)Cl, 940-58-9; *p*-MeOC<sub>6</sub>H<sub>4</sub>OC(S)NHNH<sub>2</sub>, 94295-73-5; piperidine, 110-89-4.

**Supplementary Material Available:** <sup>13</sup>C NMR peaks for 2e, 2f, 5, 7e, 8g, and 11; X-ray bond angles and interatomic distances for 7i (6 pages). Ordering information is given on any current masthead page.

### Ipsso Substitution in Dipyrindyl Sulfide by the Phenylthio Radical

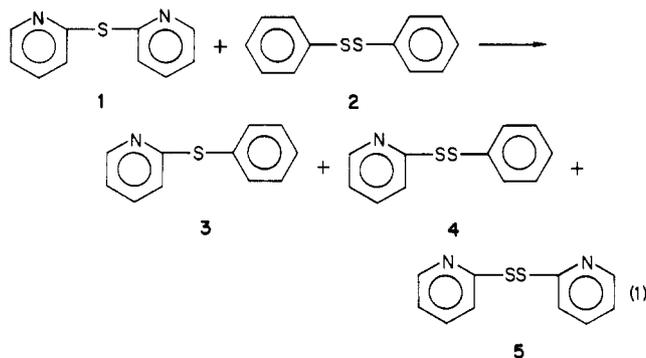
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Many examples of synthetically useful radical ipso substitution have been observed, and this reaction has, therefore, been investigated in some detail. For example, some substituents in aromatic rings such as nitro,<sup>1</sup> acyl,<sup>2</sup> and halogen<sup>3</sup> are replaced by the attack of alkyl or chloro radicals. The positional selectivity of these reactions is interesting from a mechanistic point of view and synthetic applications. It is believed that the polar character of the aromatic substrate and attacking radical is important in determining the positional selectivity.<sup>4</sup> As to disulfide, its sulfur-sulfur bond is easily cleaved by the attack of nucleophile or radical,<sup>5</sup> but little is known about the carbon-sulfur bond cleavage of aryl sulfide. This note reports the carbon-sulfur bond cleavage of 2,2'-dipyrindyl sulfide by the attack of the phenylthio radical.

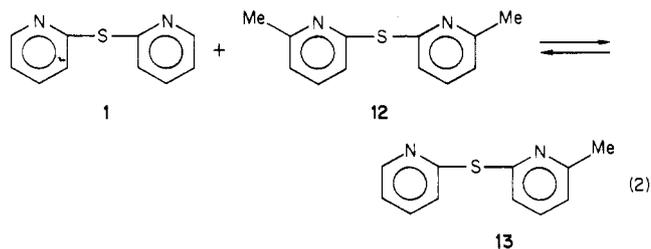
The equimolar reaction of 2,2'-dipyrindyl sulfide (1) with diphenyl disulfide (2) at 180 °C for 1 h in a sealed tube afforded a mixture of phenyl 2-pyrindyl sulfide (3), phenyl 2-pyrindyl disulfide (4), and 2,2'-dipyrindyl disulfide (5) in 49%, 18%, and 6% yields, respectively. The starting materials, 1 and 2 remained in 8% and 17%. In this reaction, it is considered that 3 was formed in the course of the ipso substitution in 1 by the phenylthio radical which was formed in the thermal decomposition of 2, for phenylthio radical produced by the thermal decomposition of 2 is known to effect displacement of halogen atom in



aromatic compounds,<sup>6</sup> phenylthio radical and pyridylthio radical, which was formed from 1, combined directly to produce 4; 5 and 2 were formed by the disproportionation of 4. In general, disproportionation reactions between two varieties of disulfide are well-known.<sup>7</sup> In fact, upon heating of 4 at 180 °C for 5 min, 5 and 2 were formed in 23% and 23% yields, respectively, together with the starting compound and a small amount of 3. Contrary to this reaction, 4 was also formed by heating a mixture of 5 and 2 under the same conditions. Upon prolonged heating of this mixture, 3 was formed, which is also considered to be ipso substitution in 5 by the phenylthio radical.

When an equimolar mixture of 2-pyrindyl tolyl sulfide (6) and 2 was heated at 180 °C for 1 h, 3, phenyl tolyl disulfide (7), and ditolyl disulfide (8) were formed quantitatively. However, phenyl tolyl sulfide and 4 were not formed. This observation indicates that the carbon-sulfur bond between the tolyl group and sulfur does not cleave but only the carbon-sulfur bond between the pyridine ring and sulfur cleaves in this reaction. In fact, 2 did not react with substituted diphenyl sulfides such as dinitrophenyl sulfide (9). On the other hand, dibenzyl sulfide (10) or 2-bromopyridine (11), both of which are considered to be reactive toward nucleophiles such as phenylthiolate, did not react with 2 under the same reaction conditions.

It is generally accepted that the radical ipso substitution in aromatic compounds occurs via the addition-elimination mechanism in a  $\sigma$  complex intermediate and positional selectivity is governed by the polar effects which operate during the addition step.<sup>4</sup> But it is not clear if the mechanism of the general type mentioned above is applicable to the reaction of 1 with 2. The new fact that the carbon-sulfur bond of 1 cleaves easily upon heating was observed. When an equimolar mixture of 1 and 6,6'-dimethyl-2,2'-thiodipyrindine (12) was heated at 180 °C for 1 h, 6-methyl-2,2'-thiodipyrindine (13), which would result from disproportionation reaction, viz., fission and recombination of the carbon-sulfur bond of 1 and 12, was obtained together with the starting compounds. Then, the



molar quantities of 1, 13, and 12 resulted in the ratio of

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1:2:1 which remained unaltered by long periods of heating. This observation refers to an equilibrium reaction involving the pyridylthio radical, i.e., cleavage of the carbon-sulfur bond of 1, which also applies to the reaction of 1 with 2 at the same reaction temperature. However, no disproportionation reaction occurred between diphenyl sulfide (14) and substituted diphenyl sulfide, which indicates that no carbon-sulfur bond of 14 or substituted diphenyl sulfide cleaves upon heating. This observation is responsible for the fact that 2 did not react with substituted diphenyl sulfide. It may be concluded that the sulfide becomes feasible to react with 2, only when carbon-sulfur bond of the sulfide cleave upon heating. That is to say, favorable release of the pyridylthio group from the pyridine ring may enable the positional selectivity of the ipso substitution in 1. If the reactivity of 1 with 2 is attributed to polar effects of substrate, 9 must also undergo the similar reaction as 1 even slightly because the polar effect of nitrophenyl group does not differ too greatly from pyridyl group. Thus, it is considered that the positional selectivity and reactivity of this ipso substitution are attributed to the leaving ability of substituent.

### Experimental Section

VPC analyses were carried out with a Hitachi 163 gas chromatograph, using a 5% OV-1 column (2 m).  $^1\text{H}$  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 Diphenyl Disulfide (2).** Material 1 was prepared from 2-bromopyridine and potassium pyridinethiolate.<sup>8</sup> Material 2 and reference compound 2,2'-dipyridyl disulfide (5) were obtained commercially. A mixture of 1 (789.8 mg, 4.2 mmol) and 2 (913.1 mg, 4.2 mmol) was heated at 180 °C for 1 h in four sealed tubes. The resulting mixture was chromatographed on silica gel, eluting with chloroform to afford 1, 2, phenyl 2-pyridyl sulfide (3), phenyl 2-pyridyl disulfide (4), and 5. The products were identified by comparison of spectral data with those of the authentic samples. 3:  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 6.71-7.71 (8 H, m), 8.28-8.49 (1 H, m); ms,  $m/e$  186 ( $\text{M}^+ - \text{H}$ ). 4:  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 6.89-7.67 (8 H, m), 8.32-8.51 (1 H, m); ms,  $m/e$  219 ( $\text{M}^+$ ), 218 ( $\text{M}^+ - \text{H}$ ), 186 ( $\text{M}^+ - \text{SH}$ ). 5:  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 7.24-8.14 (6 H, m), 8.65-8.94 (2 H, m); ms,  $m/e$  220 ( $\text{M}^+$ ), 187 ( $\text{M}^+ - \text{SH}$ ), 156 ( $\text{M}^+ - 2\text{S}$ ).

**Disproportionation Reaction between 2 and 5.** Compound 4 was formed upon heating a mixture of 2 (365.6 mg, 1.6 mmol) and 5 (366.8 mg, 1.6 mmol) at 180 °C for 5 min in a sealed tube. When heating of this mixture was prolonged, 3 and phenyl pyridyl trisulfide, which was identified only by mass spectroscopy, were formed simultaneously. Phenyl pyridyl trisulfide: ms,  $m/e$  250 ( $\text{M}^+ - \text{H}$ ), 218 ( $\text{M}^+ - \text{SH}$ ), 186 ( $\text{M}^+ - \text{SSH}$ ), 154 ( $\text{M}^+ - \text{SSSH}$ ), 141 ( $\text{M}^+ - \text{PhSH}$ ), 109 ( $\text{M}^+ - \text{PhSSH}$ ). Disulfide 4 (70.3 mg) was heated at 180 °C for 5 min in a sealed tube and analyzed directly by VPC. In this reaction, 2 and 5 were formed together with 4.

**Reaction of 2 with 2-Pyridyl Toluyl Sulfide (6).** Material 6 was prepared from 2-bromopyridine and potassium toluenethiolate.<sup>8</sup> A mixture of 6 (75.2 mg, 0.37 mmol) and 2 (80.3 mg, 0.37 mmol) was heated at 180 °C for 1 h in a sealed tube. Thus, phenyl tolyl disulfide (7), ditolyl disulfide (8), and 3 were identified by comparison of mass spectral degradation patterns with those of the authentic samples. 7: ms,  $m/e$  232 ( $\text{M}^+$ ), 123 ( $\text{M}^+ - \text{PhS}$ ). 8: ms,  $m/e$  246 ( $\text{M}^+$ ), 123 ( $\text{M}^+ - \text{TolS}$ ).

**Disproportionation Reaction between 1 and 6,6'-Dimethyl-2,2'-thiodipyridine (12).** Material 12 was obtained in a low yield by the reaction of 2-methyl-2'-bromopyridine and 2-methyl-2'-mercaptopyridine.<sup>8</sup> 2-Methyl-2'-bromopyridine was formed from 2-methyl-2'-aminopyridine and bromine.<sup>9</sup> 2-Methyl-2'-mercaptopyridine was formed from 2-methyl-2'-bromopyridine and thiourea.<sup>10</sup> A mixture of 1 (73.1 mg, 0.38

mmol) and 12 (82.3 mg, 0.38 mmol) was heated at 180 °C for 1 h in a sealed tube and analyzed directly by VPC. 6-Methyl-2,2'-thiodipyridine (13) was obtained together with 1 and 12. Retention time of 13 was intermediate between 1 and 12. The mass spectral peak was given at  $m/e$  201 ( $\text{M}^+ - \text{H}$ ).

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**Registry No.** 1, 4262-06-0; 2, 882-33-7; 3, 3111-54-4; 4, 24367-35-9; 5, 2127-03-9; 6, 95156-42-6; 7, 95156-44-8; 8, 61886-58-6; 12, 85060-42-0; 2-bromopyridine, 109-04-6; potassium pyridinethiolate, 79236-86-5; potassium toluenethiolate, 95156-43-7; 2-methyl-6-bromopyridine, 5315-25-3; 2-methyl-6-mercaptopyridine, 18368-57-5; 2-methyl-6-aminopyridine, 1824-81-3; thiourea, 62-56-6; 6-methyl-2,2'-thiodipyridine, 95193-22-9; phenyl pyridyl trisulfide, 95193-23-0.

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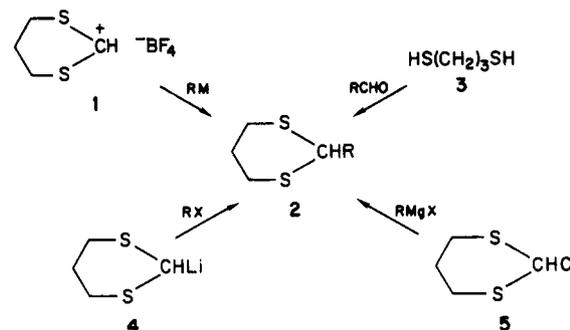
### Reaction of Allylic Aluminum Reagents with 1,3-Dithienium Tetrafluoroborate and with 2-Chloro-1,3-dithiane: Preparation of 2-Substituted 1,3-Dithianes

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1,3-Dithienium tetrafluoroborate (1) is readily prepared<sup>1</sup> from the reaction of 1,3-dithiane with trityl tetrafluoroborate. This easily handled and stable dithio carbocation is highly electrophilic: it reacts easily with trimethylsilyl enol ethers to give  $\alpha$ -1,3-dithianyl ketones<sup>2,3</sup> and with allylic silanes to give 2-alken-2-yl-1,3-dithianes.<sup>4</sup> Therefore, it seemed reasonable that it should undergo reaction with organometallic reagents to give 2-substituted 1,3-dithianes 2. Up to now, most of the known dithianes 2 have been prepared either from the reaction of aldehydes with propane-1,3-dithiol (3)<sup>5</sup> or from the reaction of alkyl halides with 2-lithio-1,3-dithiane (4);<sup>6</sup> some of them have been obtained from Grignard reagents and 2-chloro-1,3-dithiane (5).<sup>7</sup>



During the course of a study about the reactivity of 1,3-dithienium tetrafluoroborate (1) toward organometallic

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