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## The Cyanide-Ion Cleavage of Organic Disulfides

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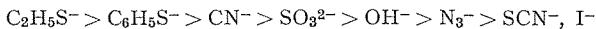
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### I. INTRODUCTION

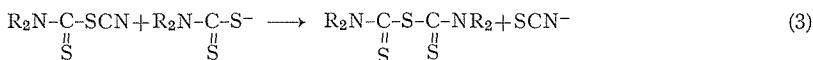
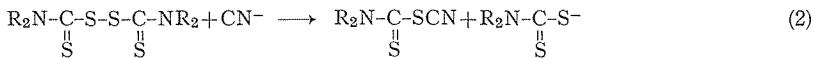
The scission of the sulfur-sulfur bond takes place when an attacking nucleophile,  $Y^-$ , has a greater affinity for sulfur than the displaced group,  $R'S^-$  (Eq. 1). This affinity for sulfur



is called "S-nucleophilicity" or "thiophilicity".<sup>1)</sup> The reactions of nitro-substituted aromatic disulfides with various S-nucleophiles were reported by Parker and Kharasch.<sup>2)</sup> The results indicate that the more stable (less basic) thiolate anion is displaced; the order of thiophilicity is found to be as follows:



The cyanide ion is regarded as a typical anthioanion, which has a great affinity for sulfur to form a thioanion (the thiocyanate ion).<sup>3)</sup> The first example of desulfurization of disulfides with cyanide ion was reported by Braun and Stechele in 1903.<sup>4)</sup> They found that bis(dialkylthiocarbamoyl) disulfides and bis(alkylarylthiocarbamoyl) disulfides react with potassium cyanide to give the corresponding monosulfides. In 1930, Cambron concluded that these reactions take place in two steps as follows:<sup>5)</sup>



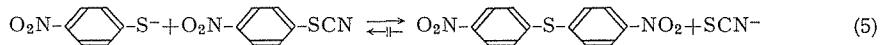
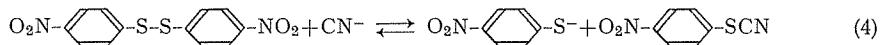
The analogous desulfurization of symmetrical disulfides has been reported for dixanthyl disulfide,<sup>6)</sup> bis(2-benzothiazolyl) disulfide,<sup>7)</sup> dithiodiglycolic acid,<sup>8)</sup> and diallyl disulfide,<sup>9)</sup> however, diphenyl disulfide,<sup>6)</sup> bis(*p*-tolyl) disulfide,<sup>8)</sup> and dibenzyl disulfide<sup>8)</sup> do not react with cyanide ion. The unsymmetrical disulfides with electron-withdrawing substituents on the aromatic nucleus were reported to be cleaved by cyanide ion at room temperature in ethanol.<sup>2)</sup>

In this short review, detailed discussions will be made on the reactions of symmetrical disulfides with cyanide ion in various solvents.<sup>10~12)</sup>

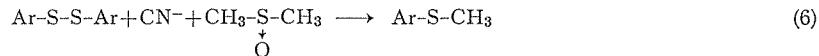
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## II. REACTION OF DISULFIDES WITH CYANIDE ION IN DIPOLAR APROTIC SOLVENTS

Since the nucleophilicity of cyanide ion is enhanced  $\sim 10^5$  times in dipolar aprotic solvents,<sup>13)</sup> it is expected that dialkyl disulfides and diaryl disulfides can react with cyanide ion in dipolar aprotic solvents. Thus, dibenzyl disulfide afforded dibenzyl monosulfide on treatment with cyanide ion in dimethyl sulfoxide. The results are summarized in Table 1. Bis(*p*-nitrophenyl) and bis(*o*-nitrophenyl) disulfides were easily cleaved by cyanide ion and gave the corresponding monosulfides in 60% and 76% yields respectively; while bis(*m*-nitrophenyl), diphenyl, and bis(*p*-tolyl) disulfides were not desulfurized to monosulfides on treatment with cyanide ion in dimethyl sulfoxide. Bis(*p*-nitrophenyl) sulfide did not react with thiocyanate ion in dimethyl sulfoxide at 80°C for 50 hr, and was recovered unchanged. Hence, the reverse reaction in Eq. (5) should be neglected.



As cited above, diaryl disulfides which have electron-donating substituents were not desulfurized at 65°C, however, they afforded aryl methyl sulfide on treatment with cyanide ion in dimethyl sulfoxide at 180°C.



Phenyl thiocyanate and thiophenol, which were formed by the cleavage of diphenyl disulfide with cyanide ion, also reacted with dimethyl sulfoxide in the presence of cyanide ion to afford aryl methyl sulfides in 63% and 65% yields respectively. Reaction conditions

Table 1. Desulfurization of Disulfides with Cyanide Ion.

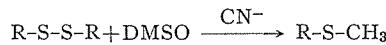


| Disulfide  | Cyanide | Solvent | Reaction      |              | Monosulfide<br>Yield (%)  |
|--|---------|---------|---------------|--------------|---|
|  |         |         | temp.<br>(°C) | time<br>(hr) |   |
| ( <i>n</i> -C <sub>3</sub> H <sub>7</sub> S-) <sub>2</sub>                 | NaCN    | DMSO    | 80            | 15           | ( <i>n</i> -C <sub>3</sub> H <sub>7</sub> -) <sub>2</sub> S 61                                |
| [-(CH <sub>2</sub> ) <sub>4</sub> -] <sub>2</sub> S-S-                     | NaCN    | DMF     | 80            | 2            | [-(CH <sub>2</sub> ) <sub>4</sub> -] <sub>2</sub> S 43  |
| (C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> S-) <sub>2</sub>            | NaCN    | DMSO    | r.t.          | 72           | (C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> -) <sub>2</sub> S 58                           |
| (C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> S-) <sub>2</sub>            | NaCN    | DMF     | 60            | 14           | (C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> -) <sub>2</sub> S 36                           |
| ( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> S-) <sub>2</sub> | NaCN    | DMSO    | 65            | 6            | ( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> S-) <sub>2</sub> (73) <sup>a)</sup> |
| ( <i>o</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> S-) <sub>2</sub> | NaCN    | DMSO    | 60            | 3            | ( <i>o</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -) <sub>2</sub> S 76                |
| ( <i>m</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> S-) <sub>2</sub> | NaCN    | DMSO    | 60            | 3            | ( <i>m</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> S-) <sub>2</sub> (36) <sup>a)</sup> |
| ( <i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> S-) <sub>2</sub> | NaCN    | DMSO    | 60            | 3            | ( <i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -) <sub>2</sub> S 60                |
| (2-NO <sub>2</sub> -4-ClC <sub>6</sub> H <sub>3</sub> S-) <sub>2</sub>     | NaCN    | DMSO    | 80            | 9            | (2-NO <sub>2</sub> -4-ClC <sub>6</sub> H <sub>3</sub> -) <sub>2</sub> S 36                    |

a) Recovered disulfide.

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Table 2. Formation of Alkyl Aryl Sulfide in the Reaction of Disulfide with Cyanide Ion.



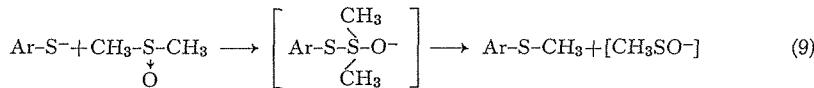
| Disulfide  | Cyanide         | Reaction   |           | Yield of sulfide (%)  |
|--|-----------------|------------|-----------|---|
|  |                 | temp. (°C) | time (hr) |   |
| (C <sub>6</sub> H <sub>5</sub> S-) <sub>2</sub>                            | NaCN (1 equiv.) | reflux     | 6         | C <sub>6</sub> H <sub>5</sub> SCH <sub>3</sub> (52)                           |
| (C <sub>6</sub> H <sub>5</sub> S-) <sub>2</sub>                            | NaCN (2 equiv.) | reflux     | 6         | C <sub>6</sub> H <sub>5</sub> SCH <sub>3</sub> (66)                           |
| ( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> S-) <sub>2</sub> | NaCN (1 equiv.) | reflux     | 6         | <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SCH <sub>3</sub> (63) |

Table 3. Methylation of Thiophenols and Thiocyanates with DMSO in the Presence of Cyanide Ion.

| Starting material  | Cyanide           | Reaction   |           | Product Yield (%)   |
|--|-------------------|------------|-----------|---|
|  |                   | temp. (°C) | time (hr) |   |
| C <sub>6</sub> H <sub>5</sub> SH                             | NaCN (1 equiv.)   | reflux     | 24        | C <sub>6</sub> H <sub>5</sub> SCH <sub>3</sub> (65)   |
| <i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SH   | NaCN (1 equiv.)   | reflux     | 19        | <i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SCH <sub>3</sub> (73)                             |
| <i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SH   | NaCN (1 equiv.)   | reflux     | 14        | <i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SCH <sub>3</sub> (73)                             |
| <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SH   | none              | reflux     | 6         | ( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> S-) <sub>2</sub> (86)                           |
| <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SH   | NaCN (1 equiv.)   | reflux     | 8         | <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SCH <sub>3</sub> (86)                             |
| <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SH   | NaCN (1 equiv.)   | reflux     | 24        | <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SCH <sub>3</sub> (92)                             |
| <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SH   | NaCN (0.2 equiv.) | reflux     | 24        | <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SCH <sub>3</sub> (70)                             |
| <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SH   | NaOH (1 equiv.)   | reflux     | 7         | <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SCH <sub>3</sub> (74)                             |
| <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SHNa | none              | reflux     | 6         | <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SCH <sub>3</sub> (80)                             |
| <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SH   | NaCN (1 equiv.)   | 170        | 6         | <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SC <sub>2</sub> H <sub>5</sub> (46) <sup>a)</sup> |
| C <sub>6</sub> H <sub>5</sub> SCN                            | NaCN (1 equiv.)   | reflux     | 6         | C <sub>6</sub> H <sub>5</sub> SCH <sub>3</sub> (63)   |
| <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SCN  | NaCN (1 equiv.)   | reflux     | 6         | <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SCH <sub>3</sub> (58)                             |

a) Diethyl sulfoxide was used instead of DMSO.

and yield of products are summarized in Table 2 and 3. The mechanistic pathway would be as follows:



Although the detailed mechanism of this novel reaction is not yet clear, the *S*-methylation of thiols with dimethyl sulfoxide is a useful method for preparing aryl methyl sulfides.

### III. REACTION OF DIARYL DISULFIDES WITH CYANIDE ION IN ALCOHOLS

Whitby and Greenberg reported that diaryl disulfides do not react with cyanide ion

Table 4. Formation of Alkyl Aryl Sulfide in the Reaction of Disulfide with Cyanide Ion in Alcohol.



| Disulfide  | Cyanide           | Alcohol                          | Reaction time (hr) | Yield of Sulfide (%)   |
|--|-------------------|----------------------------------|--------------------|--|
| (C <sub>6</sub> H <sub>5</sub> S-) <sub>2</sub>                            | NaCN (2.7 equiv.) | CH <sub>3</sub> OH               | 3                  | C <sub>6</sub> H <sub>5</sub> SCH <sub>3</sub> (66)                                      |
| ( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> S-) <sub>2</sub> | NaCN (2.7 equiv.) | CH <sub>3</sub> OH               | 3                  | <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SCH <sub>3</sub> (67)            |
| ( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> S-) <sub>2</sub>               | NaCN (2.7 equiv.) | CH <sub>3</sub> OH               | 3                  | <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> SCH <sub>3</sub> (60)                          |
| ( <i>o</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> S-) <sub>2</sub> | NaCN (2.7 equiv.) | CH <sub>3</sub> OH               | 3                  | <i>o</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> SCH <sub>3</sub> (81)            |
| ( <i>m</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> S-) <sub>2</sub> | NaCN (2.7 equiv.) | CH <sub>3</sub> OH               | 3                  | <i>m</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> SCH <sub>3</sub> (81)            |
| ( <i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> S-) <sub>2</sub> | NaCN (2.7 equiv.) | CH <sub>3</sub> OH               | 3                  | <i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> SCH <sub>3</sub> (79)            |
| (3-NO <sub>2</sub> -4-ClC <sub>6</sub> H <sub>3</sub> S-) <sub>2</sub>     | NaCN (1.2 equiv.) | CH <sub>3</sub> OH               | 5                  | 3-NO <sub>2</sub> -4-ClC <sub>6</sub> H <sub>3</sub> SCH <sub>3</sub> (55)               |
| (2-Cl-5-NO <sub>2</sub> C <sub>6</sub> H <sub>3</sub> S-) <sub>2</sub>     | KCN (2.5 equiv.)  | CH <sub>3</sub> OH               | 4                  | 2-Cl-5-NO <sub>2</sub> C <sub>6</sub> H <sub>3</sub> SCH <sub>3</sub> (78)               |
| (2-Cl-5-NO <sub>2</sub> C <sub>6</sub> H <sub>3</sub> S-) <sub>2</sub>     | NaCN (1.7 equiv.) | C <sub>2</sub> H <sub>5</sub> OH | 4                  | 2-Cl-5-NO <sub>2</sub> C <sub>6</sub> H <sub>3</sub> SC <sub>2</sub> H <sub>5</sub> (48) |
| (2-Br-5-NO <sub>2</sub> C <sub>6</sub> H <sub>3</sub> S-) <sub>2</sub>     | NaCN (1.4 equiv.) | CH <sub>3</sub> OH               | 2                  | 2-Br-5-NO <sub>2</sub> C <sub>6</sub> H <sub>3</sub> SCH <sub>3</sub> (55)               |

a) Refluxing in alcohol.

in alcohol.<sup>6)</sup> We have found that symmetrical diaryl disulfides react with alcohols to give alkyl aryl sulfides in high yields in the presence of cyanide ion. The results of this novel reaction are summarized in Table 4.

It is expected that alkyl aryl sulfides would be derived from aryl thiocyanates. Thus, aryl thiocyanates were found to react with alcohols in the presence of cyanide ion to give alkyl aryl sulfides. The reaction conditions and the yields of alkyl aryl sulfides are listed in Table 5. In order to examine the general application of this novel reaction, we attempted to prepare benzyl and *n*-butyl aryl sulfides by the same procedure. However, sodium cyanide and potassium cyanide were only slightly soluble in these alcohols. This was overcome by using dimethyl sulfoxide as a solvent or by using tetraethylammonium cyanide as a cyanide in acetonitrile. Thus, benzyl *p*-tolyl sulfide was obtained in a 68% yield in the reaction of *p*-tolyl thiocyanate with benzyl alcohol in the presence of sodium cyanide in dimethyl sulfoxide, and *n*-butyl *p*-tolyl sulfide was obtained in a 59% yield by using tetraethylammonium cyanide in a mixture of *n*-butyl alcohol and acetonitrile.

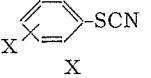
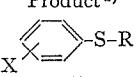
When *p*-tolyl thiocyanate was treated with cyanide ion in methanol at 0°C, *O*-methyl *S*-*p*-tolyl thioiminocarbonate was obtained. *O*-Alkyl *S*-aryl thioiminocarbonates, which were synthesized independently, were treated with base in alcohol. In all the cases studied, alkyl aryl sulfides were isolated in fairly good yields. The results are summarized in Table 6 and 7.

The reaction of *O*-methyl *S*-*p*-tolyl thioiminocarbonate with cyanide ion in ethanol afforded methyl *p*-tolyl sulfide exclusively, while the reaction of *O*-ethyl *S*-*p*-tolyl thioiminocarbonate with cyanide ion in methanol gave a mixture of ethyl *p*-tolyl sulfide (64%) and methyl *p*-tolyl sulfide (7%). These results show that the alkyl moieties of sulfides were derived from that of thioiminocarbonates, not from the alcohol used as a solvent. The mixture of *O*-methyl *S*-*p*-tolyl thioiminocarbonate and *O*-ethyl *S*-*p*-chlorophenyl thioiminocarbon-

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Table 5. Formation of Alkyl Aryl Sulfides in the Reaction of Aryl Thiocyanates with Alcohols in the Presence of Cyanide Ion.



| Aryl thiocyanate<br> | Alcohol <sup>a)</sup><br>ROH<br>R | Cyanide  | Reaction            |                      | Product <sup>b)</sup><br><br>(%) |
|---|-----------------------------------|--|---------------------|----------------------|--|
|   |                                   |  | temp.<br>(°C)       | time<br>(hr)         |  |
| <i>p</i> -Me <sub>2</sub> N   | Me                                | NaCN   | 60                  | 3                    | 50   |
| <i>o</i> -Me  | Me                                | NaCN   | 50                  | 3                    | 59   |
| <i>m</i> -Me  | Me                                | NaCN   | 50                  | 3                    | 50   |
| <i>p</i> -Me  | Me                                | NaCN   | 50                  | 3                    | 55   |
| <i>p</i> -Me  | Me                                | NaCN (2 eq. excess)  | 50                  | 3                    | 58   |
| <i>p</i> -Me  | Me                                | NaCN   | 0, 50 <sup>c)</sup> | 0.5, 3 <sup>c)</sup> | 66   |
| <i>p</i> -Me  | <i>n</i> -Bu                      | Et <sub>4</sub> N CN (in CH <sub>3</sub> CN) <sup>d)</sup> | r.t.                | 21                   | 59   |
| <i>p</i> -Me  | <i>n</i> -Bu                      | NaCN (in DMSO) <sup>d)</sup>                               | r.t.                | 22                   | 60   |
| <i>p</i> -Me  | Me                                | NaCN   | 50                  | 24                   | 78   |
| <i>p</i> -Me  | Bz <sup>e)</sup>                  | NaCN (in DMSO) <sup>d)</sup>                               | 50                  | 20                   | 68   |
| H   | Me                                | NaCN   | r.t.                | 3                    | 51   |
| <i>o</i> -Cl  | Et                                | NaCN   | r.t.                | 5                    | 47   |
| <i>o</i> -Cl  | <i>n</i> -Pr                      | NaCN   | 50                  | 4                    | 29   |
| <i>o</i> -Cl  | <i>n</i> -Pr                      | NaCN (in DMSO) <sup>d)</sup>                               | 50                  | 5                    | 50   |
| <i>o</i> -Cl  | <i>t</i> -Pr                      | NaCN (in DMSO) <sup>d)</sup>                               | 50                  | 5                    | 34   |
| <i>m</i> -Cl  | Me                                | NaCN   | r.t.                | 3                    | 61   |
| <i>p</i> -Cl  | Me                                | NaCN   | 50                  | 1                    | 59   |
| <i>p</i> -Br  | Me                                | NaCN   | r.t.                | 5                    | 59   |
| <i>p</i> -SCN   | Me                                | NaCN (2 eq. excess)  | 50                  | 4                    | 37   |
| <i>o</i> -NO <sub>2</sub>   | Me                                | NaCN   | 45                  | 1                    | 70   |
| <i>o</i> -NO <sub>2</sub>   | Et                                | NaCN   | 50                  | 2                    | 36   |
| <i>m</i> -NO <sub>2</sub>   | Me                                | NaCN   | r.t.                | 0.5                  | 66   |
| <i>m</i> -NO <sub>2</sub>   | Et                                | NaCN   | r.t.                | 1                    | 50   |
| <i>p</i> -NO <sub>2</sub>   | Me                                | NaCN   | 50                  | 2                    | 70   |
| 2-Cl-5-NO <sub>2</sub>  | Me                                | KCN  | reflux              | 4                    | 48   |
| 2-NO <sub>2</sub> -4-Cl   | Et                                | NaCN   | 50                  | 4                    | 27   |

a) Alcohol was used as solvent

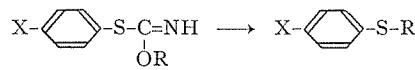
b) Isolated yield

c) 0.5 hr at 0°C, then 3 hr at 50°C

d) Mixture of alcohol and DMSO or CH<sub>3</sub>CN

e) Benzyl

carbonate was treated with cyanide ion in ethanol, all four sulfides, *i.e.*, methyl *p*-tolyl sulfide, ethyl *p*-tolyl sulfide, methyl *p*-chlorophenyl sulfide, and ethyl *p*-chlorophenyl sulfide were obtained. As previously discussed, *O*-methyl *S*-*p*-tolyl thioiminocarbonate underwent no ester exchange with ethanol used as the solvent, and the following is considered to be a quite reasonable mechanism.

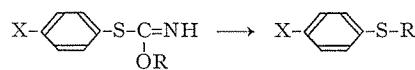
Table 6. Formation of Alkyl Aryl Sulfides in the Reaction of *O*-Alkyl *S*-Aryl Thioiminocarbonates with Bases.

| Thioiminocarbonate |    | Solvent | Base                | Reaction   |           | Yield of Sulfide (%)                             |
|--------------------|----|---------|---------------------|------------|-----------|--|
| X                  | R  |         |                     | temp. (°C) | time (hr) |  |
| Me                 | Me | MeOH    | NaCN                | 50         | 3         | <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SMe 55 |
| Me                 | Me | DMSO    | NaCN                | r.t.       | 5         | <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SMe 81 |
| Me                 | Et | EtOH    | IR-45 <sup>a)</sup> | 60         | 12        | <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SEt 53 |
| Me                 | Et | EtOH    | b                   | reflux     | 7.5       | c  |

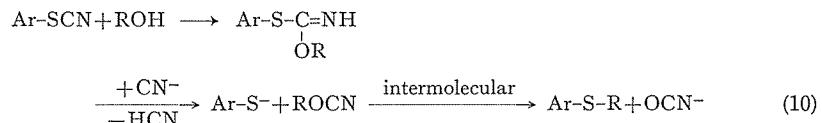
a) Weak basic ion-exchange resin Amberlite IR-45 (OH-form).

b) Without base.

c) 87% of starting material was recovered unchanged.

Table 7. Formation of Alkyl Aryl Sulfides in the Reaction of *O*-Alkyl *S*-Aryl Thioiminocarbonates with Cyanide Ion.

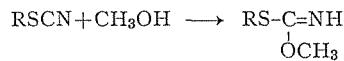
| Thioiminocarbonate |    | Solvent | Cyanide | Reaction   |           | Product Yield (%)                                   |
|--------------------|----|---------|---------|------------|-----------|---|
| X                  | R  |         |         | temp. (°C) | time (hr) |   |
| Me                 | Me | EtOH    | NaCN    | 50         | 3         | <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SMe (67%) |
| Me                 | Et | MeOH    | NaCN    | 50         | 3         | <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SMe (7%)  |
|                    |    |         |         |            |           | <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SEt (64%) |



Direct evidence for the existence of aryl mercaptide ion was obtained by the reaction of *O*-methyl *S*-*p*-tolyl thioiminocarbonate with cyanide ion in the presence of 2,4-dinitrochlorobenzene, which is known to be a good mercaptide ion scavenger. Thus, when *O*-methyl *S*-*p*-tolyl thioiminocarbonate was treated with cyanide ion in the presence of 2,4-dinitrochlorobenzene in methanol, 2,4-dinitrophenyl *p*-tolyl sulfide was isolated in a 24% yield. Furthermore, it was found that thiocyanates reacted with alcohol in the presence of a catalytic amount of cyanide ion to give thioiminocarbonates. Of the various catalysts examined, it was found that sodium azide and sodium methoxide were effective, while triethylamine, sodium thiocyanate, potassium iodide, triphenylphosphine, sodium acetate, and mercuric cyanide were ineffective in the formation of thioiminocarbonates.

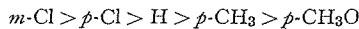
## Cyanide-Ion Cleavage of Organic Disulfides

Table 8. Preparation of Thioiminocarbonates.

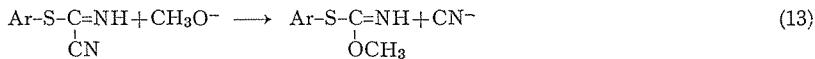
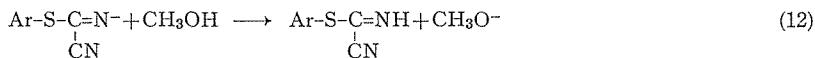


| R-SCN<br>R   | Catalyst           | R-SCN:<br>Catalyst<br>(mol ratio) | Reaction      |              | Yield of<br>thioiminocarbonate<br>(%) |
|--|--------------------|-----------------------------------|---------------|--------------|---------------------------------------|
|  |                    |                                   | temp.<br>(°C) | time<br>(hr) |                                       |
| C <sub>6</sub> H <sub>5</sub> -                    | NaCN               | 7 : 1                             | 0             | 6            | 72                                    |
| C <sub>6</sub> H <sub>5</sub> -                    | NaOCH <sub>3</sub> | 9 : 1                             | 0             | 6            | 77                                    |
| C <sub>6</sub> H <sub>5</sub> -                    | NaN <sub>3</sub>   | 7 : 1                             | 0             | 7            | 73                                    |
| p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> - | NaCN               | 8 : 1                             | 0             | 17           | 84                                    |
| p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -  | NaN <sub>3</sub>   | 5 : 1                             | 0             | 1            | 70                                    |
| p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -  | NaOCH <sub>3</sub> | 5 : 1                             | 0             | 1            | 64                                    |
| p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -  | NaCN               | 5 : 1                             | 0             | 1            | 70                                    |
| p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -  | NaCN               | 8 : 1                             | 0             | 8.5          | 74                                    |
| m-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -  | NaCN               | 11 : 1                            | 0             | 17           | 84                                    |
| p-ClC <sub>6</sub> H <sub>4</sub> -                | NaCN               | 7 : 1                             | 0             | 6            | 74                                    |
| C <sub>2</sub> H <sub>5</sub> -                    | NaCN               | 8 : 1                             | 0             | 24           | 60                                    |

Thioiminocarbonate formation was enhanced by the presence of electron-withdrawing groups on the aryl thiocyanates:



The reaction scheme of the addition of methanol to thiocyanates in the presence of cyanide-ion catalyst may be postulated to be as follows:



## IV. SUMMARY AND CONCLUSION

1. Dialkyl disulfides and *ortho*- and *para*-nitro-substituted diaryl disulfides give the corresponding monosulfides in the reaction with cyanide ion in dipolar aprotic solvents.
2. Diaryl disulfides with electron-donating substituents react with dimethyl sulfoxide to afford aryl methyl sulfides.
3. Diaryl disulfides react with cyanide ion in alcohol to give alkyl aryl sulfides.
4. Thiocyanates react with alcohol in the presence of a catalytic amount of cyanide ion to afford thioiminocarbonates.

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## REFERENCES

- (1) A. J. Parker and N. Kharasch, *Chem. Rev.*, **59**, 583 (1959).
- (2) A. J. Parker and N. Kharasch, *J. Amer. Chem. Soc.*, **82**, 3071 (1960).
- (3) R. E. Davis, "Survey of Progress in Chemistry," Vol. 2, ed. by A. Scott, Academic Press, New York, 1964, p. 189.
- (4) J. von Braun and F. Stechele, *Ber.*, **36**, 2275 (1903).
- (5) A. Cambron *Canad. J. Res.*, **2**, 341 (1930).
- (6) G. S. Whitby and H. Greenberg, *Trans. Roy. Soc. Can.*, **III**, **23**, 21 (1929); *Chem. Abstr.*, **24**, 593 (1930).
- (7) K. D. Petrow, Russ. Pat., 40564 (1934); *Chem. Zentr.*, **II**, 3589 (1935).
- (8) Y. Minoura, *Nippon Gomu Kyokai Shi*, **23**, 213 (1950).
- (9) C. G. Moore and B. R. Trego, *J. Chem. Soc.*, **1962**, 4205.
- (10) K. Tanaka, J. Hayami, and A. Kaji, *Bull. Chem. Soc. Japan*, **45**, 536 (1972).
- (11) K. Tanaka, J. Hayami, and A. Kaji, *ibid.*, **44**, 2815 (1971).
- (12) K. Tanaka, *ibid.*, **45**, 834 (1972).
- (13) A. J. Parker, "Advances in Organic Chemistry *Methods and Results*," Vol. 5, ed. by R. A. Raphael, E. C. Taylor, and H. Wynberg, Interscience Publishers, New York, N. Y., 1965, p. 1.