Communications

Arylation of Arenethiolate Ions by the $S_{RN}1$ Mechanism. A Convenient Synthesis of Diaryl Sulfides.

Summary: Aryl iodides react with arenethiolate ions in liquid ammonia under irradiation by Pyrex-filtered light to form diaryl sulfides in good yields, probably by the $S_{RN}1$ mechanism.

Sir: The recently recognized $S_{RN}1$ mechanism of aromatic substitution[1] involves radical and radical anion intermediates and electron-transfer steps. Heretofore it has been observed with nitranion (NH_2^-, $PhNH^-$)[1,2b] and several kinds of carbanion nucleophiles.[2a,c–e,3] Arenethiolate ion nucleophiles are, however, known to participate in $S_{RN}1$ reactions at saturated carbon sites[4] and in the 4 position of the isoquinoline system.[5] We now report conditions in which arenethiolate ions react very satisfactorily at benzene ring sites, probably by the $S_{RN}1$ mechanism.

When solutions of an aryl iodide and an arenethiolate ion in refluxing liquid ammonia (−33°) under nitrogen are irradiated with Pyrex-filtered light, reaction occurs to form a diaryl sulfide, according to Chart I. The arenethiolate ion can be supplied with sodium or potassium gegenion or, more conveniently, by dissolving the arenethiol in ammonia with which it undergoes an acid–base reaction. Several reactions of this type are summarized in Table I.

Chart I

$$\mathrm{ArI} + \mathrm{Ar'S^-} \xrightarrow[\mathrm{NH_3}]{h\nu} \mathrm{ArSAr'} + \mathrm{I^-}$$

Preparatively, this procedure is attractive for preparation of diaryl sulfides on about a 10-g scale. The procedure is simple and conditions are mild. The aryl iodide is simply mixed with thiophenol and ammonia is condensed. Photostimulation in a 350-nm photochemical reactor leads to a facile substitution reaction. Despite the low solubility of certain aryl iodides in liquid ammonia, reaction still occurs. Upon completion of the reaction, the ammonia is allowed to evaporate. An aqueous work-up followed by simple distillation or recrystallization affords the diaryl sulfide in high purity. Other methods for the preparation of diaryl sulfides mostly involve long periods of heating at temperatures of 175° or higher, or explosive intermediates, or other unwelcome features.[6]

Aryl bromides also react, but much more slowly than aryl iodides.

The presumed mechanism is sketched in Chart II. This is the standard $S_{RN}1$ mechanism[1] adapted to the immediate case. Photons probably stimulate electron transfer from thiolate ion to aryl iodide (eq 1), and thus are involved in initiation of a chain mechanism.

Chart II

$$\mathrm{Ar'S^-} + \mathrm{ArI} \xrightarrow{h\nu} \mathrm{Ar'S\cdot} + [\mathrm{ArI}]\cdot^- \qquad (1)$$

$$[\mathrm{ArI}]\cdot^- \longrightarrow \mathrm{Ar\cdot} + \mathrm{I^-} \qquad (2)$$

$$\mathrm{Ar\cdot} + \mathrm{Ar'S^-} \longrightarrow [\mathrm{ArSAr'}]\cdot^- \qquad (3)$$

$$[\mathrm{ArSAr'}]\cdot^- + \mathrm{ArI} \longrightarrow \mathrm{ArSAr'} + [\mathrm{ArI}]\cdot^- \qquad (4)$$

$$\text{termination steps} \qquad (5)$$

The low yield of sulfide from 2-iodo-*m*-xylene is due in part to a substantial fraction of the 2,6-dimethylphenyl radicals being diverted to *m*-xylene. Combination of thiophenoxide ion with that radical is apparently hindered significantly by the ortho methyl groups. In contrast, a pair of

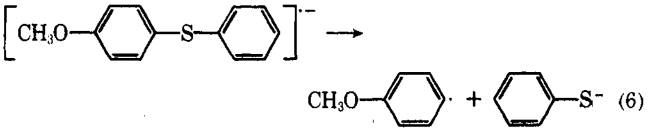
Table I
Photoinitiated Reaction of Aryl Iodides with Thiophenoxide in Liquid Ammonia

Run no.	Substrate	Reaction time, min	Sulfide product	% yield[a]	Other products[b]
1	PhI	70	PhSPh	94[c]	
2	1-Iodonaphthalene	75	1-$PhSC_{10}H_7$	85[d]	Naphthalene
3	*o*-$CH_3OC_6H_4I$	90	*o*-$MeOC_6H_4SPh$	91[d]	Anisole
4	*m*-$MeOC_6H_4I$	90	*m*-$MeOC_6H_4SPh$	88[d]	Anisole
5	*p*-$MeOC_6H_4I$	30	*p*-$MeOC_6H_4SPh$	76[e]	Anisole
6	*o*-$CH_3C_6H_4I$	165	*o*-$CH_3C_6H_4SPh$	68[f]	Toluene, PhSSPh
7	*m*-$CH_3C_6H_4I$	135	*m*-$CH_3C_6H_4SPh$	81[e]	Toluene
8	*p*-$CH_3C_6H_4I$	360	*p*-$CH_3C_6H_4SPh$	72[g]	Toluene, PhSSPh
9	2-iodo-*m*-xylene	140	2-PhS-*m*-xylene	19[c,h]	*m*-xylene (28%)[c] PhSSPh (36%)[i]
10	*m*-FC_6H_4I	100	*m*-FC_6H_4SPh	96	
11	*p*-IC_6H_4OPh	120	*p*-$PhSC_6H_4OPh$	92	PhOPh, PhSPh
12	*m*-$IC_6H_4CF_3$	170	*m*-$PhSC_6H_4CF_3$	71[d]	*m*-$PhSC_6H_4CF_2SPh$ (16%)
13	PhBr	120	PhSPh	23[j]	
14	$C_5H_5FeC_5H_4I$	60			$C_5H_5FeC_5H_5$ (15%)[c] PhSSPh (17%)[c]

[a] Isolated yield unless otherwise indicated. [b] Trace amounts unless otherwise indicated. [c] Yield by gc. [d] Trace of unreacted starting material remaining. [e] Approximately 10% unreacted aryl iodide remaining. [f] 18% unreacted *o*-iodotoluene. [g] 14% unreacted *p*-iodotoluene. [h] 39% unreacted 2-iodo-*m*-xylene.[c] [i] Yield based on 2-iodo-*m*-xylene. [j] Based on bromide titration; mostly unreacted bromobenzene recovered.

ortho methyl groups does not appear to affect combination of an aryl radical with the amide ion[2b] or with picolyl anions.[3b] Formation of *m*-xylene from its 2-iodo derivative represents reduction; the concomitant product of oxidation is diphenyl disulfide.

A companion experiment to run 5, Table I, was reaction of iodobenzene with *p*-methoxybenzenethiolate ion (120 min) to form phenyl *p*-methoxyphenyl sulfide in 71% yield. It is significant that no trace of bis(*p*-methoxyphenyl) sulfide was found as a product. Alkali metal cleavage of phenyl *p*-methoxyphenyl sulfide in ammonia or methylamine affords thiophenol and anisole,[7] indicating that its radical anion undergoes fission as shown in eq 6.[2e] If *p*-methoxyphenyl radical were formed in the presence of *p*-methoxybenzenethiolate ion, some bis(*p*-methoxyphenyl) sulfide should be formed. We conclude that in this system the phenyl *p*-methoxyphenyl sulfide radical anion transfers an electron to iodobenzene (eq 4) faster than it splits as in eq 6.


(6)

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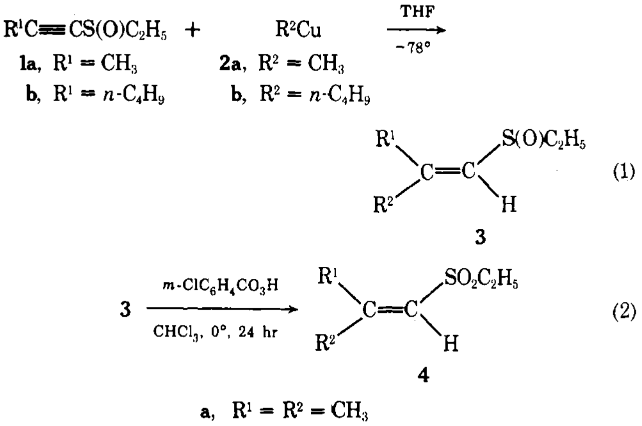
The Addition of Organocopper(I) Reagents to α,β-Acetylenic Sulfoxides[1,2]

Summary: Monoalkylcopper(I) reagents (2) add to α,β-acetylenic sulfoxides (1) with almost exclusive cis stereoselectivity to form β-alkylated α,β-ethylenic sulfoxides (3) in high yield.

Sir: Organocopper(I) reagents add to a variety of α,β-unsaturated compounds,[3] including α,β-ethylenic sulfones[4] and α,β-acetylenic esters[5] and acids.[5c,6] Our continuing interest in nucleophilic additions to activated acetylenes,[7] and in the ability of organosulfur functionalities to activate the triple bond toward conjugate addition, prompted an investigation of the reaction of organocopper(I) reagents with α,β-acetylenic sulfur compounds.

We have found that α,β-acetylenic sulfoxides (1)[8] react readily with monoalkylcopper(I) reagents (2) to produce, after work-up, high yields of the corresponding β-alkylated α,β-ethylenic sulfoxides (3). Furthermore, the addition reaction was shown to be highly stereoselective, producing the product of cis addition to the triple bond almost exclusively.



1a, $R^1 = CH_3$
b, $R^1 = n\text{-}C_4H_9$

2a, $R^2 = CH_3$
b, $R^2 = n\text{-}C_4H_9$

3 (1)

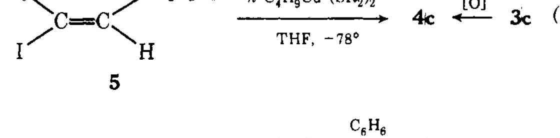
4 (2)

a, $R^1 = R^2 = CH_3$
b, $R^1 = R^2 = n\text{-}C_4H_9$
c, $R^1 = CH_3$; $R^2 = n\text{-}C_4H_9$
d, $R^1 = n\text{-}C_4H_9$; $R^2 = CH_3$

The following procedures are representative. Into a 50-ml flask, equipped with a stopple-covered side arm, an adapter tube with stopcock connected to a mercury bubbler, and a magnetic stirring bar, is weighed 0.727 g (3.82 mmol, 2% in excess of the alkyllithium reagent to be used) of cuprous iodide. After oven drying, the flask is cooled while flushing with nitrogen, 12.9 ml of dry THF is injected, and to the resulting suspension at 0° is added 2.1 ml (3.74 mmol) of a 1.78 *M* solution of methyllithium in diethyl ether over a 2-min period. The resulting suspension of methylcopper(I) (25% excess) is cooled to −78° for 15 min and a solution of 0.473 g (2.99 mmol) of ethyl 1-hexynyl sulfoxide (**1b**) in 12.0 ml (~0.25 *M*) of dry THF, precooled to −78°, is injected rapidly. After stirring for 1.5 hr at −78° the reaction mixture is quenched by injecting 5 ml of methanol precooled to −78° and then pouring into 25 ml of saturated aqueous ammonium chloride solution. Extraction with dichloromethane (3 × 25 ml), drying over $MgSO_4$, and evaporation *in vacuo* gives 0.549 g (>100%) of **3d.** In a similar manner the reaction of 3.87 mmol (25% excess) of *n*-butylcopper(I) in THF (~0.25 *M*) with 0.360 g (3.1 mmol) of ethyl 1-propynyl sulfoxide (**1a**) in 12.4 ml of dry THF for 2 hr at −78° followed by quenching with precooled methanol and work-up gives 0.531 g (98%) of the other geometrical isomer, **3c.**

It was also shown that the α,β-ethylenic sulfoxides **3** can be oxidized almost quantitatively to the corresponding sulfones **4** (with no evidence of isomerization about the double bond) by treatment with 1 equiv of *m*-chloroperbenzoic acid in chloroform at 0° for 24 hr.[10]

The cis stereoselectivity of the organocopper(I) addition to α,β-acetylenic sulfoxides was established unambiguously[11] by an alternate stereospecific synthesis of sulfone **4c.** The reaction of the iodovinyl sulfone **5** with 2.5 equiv of *n*-butylcopper–bis(diisopropyl sulfide) complex[12,13] in dry



5 (3)

$$CH_3C{\equiv}CH + C_2H_5SO_2I \xrightarrow[h\nu]{C_6H_6} \mathbf{5} \qquad (4)$$