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Electrochemical transformation of diazonium salts into diaryl disulfides

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ABSTRACT

Electrolyses of aryldiazonium tetrafluoroborates in CS_2/EtOH and Bu_4NClO_4, as the solvent-supporting electrolyte system, led to the corresponding diaryl disulfides in good yields.

Diaryl disulfides are important intermediates in various organic transformations.[1,2] These compounds can be employed in the preparation of 4-arylthio-5-pyrazolone magenta photographic couplers.[3] Diphenyl disulfide as a devulcanization agent increases the effectivity during thermochemical devulcanization.[4] Hydrothiolation of terminal alkynes with diaryl disulfides has been developed.[5]

The anodic oxidation of diphenyl disulfides allows the formation of PhS^+ capable of in situ reaction with a large palette of nucleophiles.[6]

There are many reports involving the synthesis of diaryl disulfides;[7–9] however, most of these methods require unusual substrates and relatively harsh reaction conditions. More recently, a selective reduction of arenesulfonyl chlorides promoted by samarium metal in DMF to the corresponding disulfides has been published.[10]

The conversion of arylthiols to diaryl disulfides has been performed by different oxidative procedures, from electrochemistry[11] to the oxidation with 1,3-dibromo-5,5-dimethylhydantoin[12] or using *n*-butyltriphenylphosphonium dichromate.[13]

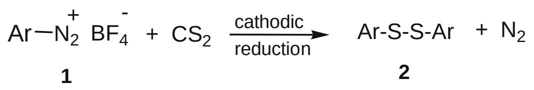
In the literature, there are two papers concerning the conversion of aryldiazonium fluoroborates to diaryl disulfides. In the first case, the diazonium salts were treated with sodium iodide in acetone/carbon disulfide, [14] but the obtained yields were poor. In the second case, the diazonium salts react with benzyltriethylammonium tetrathiomolybdate.[15]

In this Letter we present a very easy, clean, and good-yielded synthesis of diaryl disulfides **2** by cathodic reduction of aryldiazonium fluoroborates **1**(**a**–**k**) at the potential of their first reduction wave (−0.5 V vs Ag/Ag^+). The reaction proceeds in good yield, as summarized in Table 1.

In previous papers, we have demonstrated that the aryldiazonium salts are easily reduced to the corresponding aryl radicals that can react with the solvent, acetonitrile, DMF, or 1,2-dichloroethane to produce the dimethylaminocarbonyl, cyanomethyl, or 1,2-dichloroethyl radicals, respectively.[27] Now, the electrogenerated aryl radicals react with carbon disulfide as indicated in Scheme 1.

It is well known that the attack of a radical on a substrate should be favored when the substrate has vacant p or d orbitals

Table 1
Obtained yields of diaryl disulfides **2**



$$\text{Ar}-\overset{+}{N_2}\ \overset{-}{BF_4} + CS_2 \xrightarrow[\text{reduction}]{\text{cathodic}} \text{Ar-S-S-Ar} + N_2$$

1 **2**

Ar:	Yield of **2** (%)	Mp (°C)
a: C_6H_5	61	61–63 [lit[16]: 61–62]
b: 4-MeO–C_6H_4	65	44–45 [lit[17]: 44–45]
c: 4-Et–C_6H_4	73	22–24 [lit[18]: 23.4–24.3]
d: 2-Me–C_6H_4	82	36–38 [lit[19]: 36]
e: 3-Me–C_6H_4	72	43–45 [lt[20]: 44–45]
f: 4-Cl–C_6H_4	78	72–73 [lit[21]: 72]
g: 4-Br–C_6H_4	96	94–95 [lit[22]: 94–95]
h: 4-MeCO–C_6H_4	60	96–98 [lit[23]: 97–98]
i: 4-MeOOC–C_6H_4	72	126–127 [lit[24]: 127]
j: 2-MeS–C_6H_4	70	83–85 [lit[25]: 85]
k: 2,6-DiMe–C_6H_3	65	**bp (°C) (3 Torr)**: 173 [lit[26]: 173–174]

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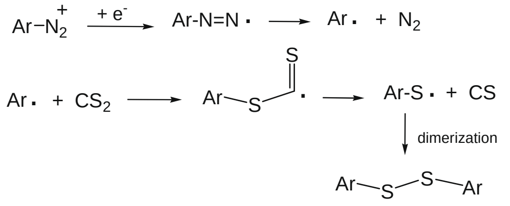
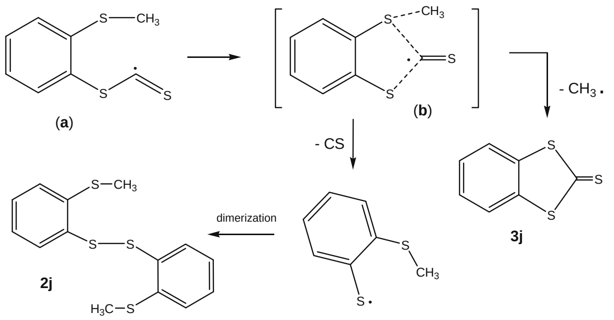
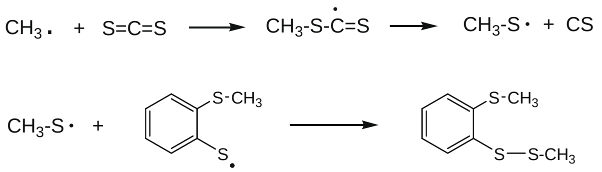


Scheme 1. Proposed pathway formation of diaryl disulfides.



Scheme 2. Common intermediate (**b**) in the formation of **2j** and 1,3-benzodithiole-2-thione (**3j**).



Scheme 3. Radical coupling formation of methyl 2-(methyl thio)phenyl disulfide.

available for coordination with the radical, since a bond between the radical and the substrate can then be formed before any bonds are broken.[28]

When the diazonium salt of 2-methylthioaniline (**1j**) was reduced, together with the corresponding disulfide **2j** (70% yield), 1,3-benzodithiole-2-thione[29] (**3j**) (15%) was obtained. The formation of this product can be explained as follows: the reaction starts, as described above, with the formation of the radical **a**. But this radical is able to intramolecularly attack the sulfur atom of the methylthio group (again the vacant d orbitals at the sulfur are available for coordination) giving the intermediate **b**, which evolves to **2j** after dimerization or to **3j** through a methyl radical evolution (see Scheme 2).

The methyl radical reacts with CS_2 (solvent) to afford a methylthio radical which can be coupled with any of the radicals present in the solution to give, for instance, methyl 2-(methylthio)phenyl disulfide (Scheme 3) detected by GC–MS.[30]

The presented methodology[31] is clearly a convenient and useful alternative that can be generalized to the obtention of diaryl disulfides from anilines.

Acknowledgment

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29. Mp: 164–166 °C [lit. 164–165 °C (Nakayama, J. *Chem. Lett.* **1977**, 127–130)].
30. GC–MS (EI): m/z (%) = 204 (M^++2, 5), 202 (M^+, 36), 187 (M^+−15, 17), 172 (M^+−15−15, 10), 156 (M^+−CH_2S (McLafferty), 93), 153(78), 141 (M^+−CH_2S-15, 10), 91(100).
31. The electroactive diazonium tetrafluoroborates were prepared according to conventional methods (*Organic Reactions*; Krieger, R.E., Ed.; Publishing Company: Huntington, NY, 1977; Vol. V, pp 198–228).The electrochemical reductions were performed under potentiostatic conditions in a concentric cell with two compartments separated by a low porosity (D4) glass frit diaphragm and equipped with a magnetic stirrer. The temperature was maintained constant at 0 °C with a cryostat. A graphite electrode was used as the cathode, a platinum plate as the anode, and a saturated Ag/Ag^+ electrode as the reference. The SSE (solvent-supporting-electrolyte) was CS_2/EtOH (20:50) containing 0.1 M tetrabutylammonium perchlorate.The aryldiazonium tetrafluoroborate (2.0 mmol) was added, in small solid portions for 4 h, to the cathodic compartment, to be electrolyzed at a constant potential of −0.5 V (vs Ag/Ag^+). The slow addition of the substrate was made in order to avoid the dimerization of the aryl radical.The substrate can be reduced faster at a mercury cathode; however, the electrogenerated aryl radicals evolve in the presence of mercury to undesired organomercury compounds.Once the reaction was finished the cathodic solution was removed under reduced pressure. The residue was then extracted with ether/H_2O. The organic phase was dried over $MgSO_4$ and concentrated by evaporation. The resulting disulfides were purified by flash chromatography on Silica Gel 60 (35–70 mesh) in a (12 × 2.5 cm) column, using mixtures Tol/Hex (1:20) (**2a**–**g**, **2j** and **2k**) and CH_2Cl_2/EtOH (100:1) (**2h**, **2i**) as eluents. The physical and spectroscopical properties of the obtained diaryl disulfides were coincident with those already described in the literature. However, IR or NMR is not very resolutive in this case, and the experimental MS spectra of **2** are given:MS (EI): m/z (%) (**2a**): 219 (M^++1, 12), 218 (M^+, 84), 185(14), 154(16), 140(6), 109(100), 65(29). (**2b**): 278 (M^+, 11), 260(5), 200(33), 172(18), 171(28), 140(49), 139(100), 125(26), 108(35), 97(21), 95(26). (**2c**): 275 (M^++1, 23), 274 (M^+, 100), 260(19), 210(23), 195(23), 181(24), 137(81), 135(38), 123(35), 91(44). (**2d**): 247 (M^++1, 12), 246 (M^+, 64), 213(6), 211(8), 123(100), 121(41), 91(88). (**2e**): 247 (M^++1, 19), 246 (M^+, 100), 213(36), 198(23), 182(69), 167(42), 123(37), 121(14), 91(75). (**2f**): 290 (M^++4, 11), 288 (M^++2, 50), 286 (M^+, 64), 145(40), 143(100), 108(60). (**2g**): 378 (M^++4, 16), 376 (M^++2, 28), 374 (M^+, 13), 297(9), 295(9), 216(17), 189(44), 187(44), 108(100), 82(16). (**2h**): 303 (M^++1, 20), 302 (M^+, 100), 287(70), 136(74), 108(17). (**2i**): 335 (M^++1, 12), 334 (M^+, 57), 303(16), 270(5), 239(8), 198(8), 184(18), 167(37), 139(63), 136(100), 108(38), 82(19). (**2j**): 311 (M^++1, 12), 310 (M^+, 62), 155(32), 121(9), 91(100). (**2k**): 274 (M^+, 91), 241 (4), 168(9), 138(75), 137(90), 105(100), 91(53).