

Electrogenerated Electrophilic Reagents from Sulphur: a New Access to Bis-methoxyaryl Sulphides

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The oxidation of a sulphur/carbon anode may produce electrophilic species derived from sulphur, and addition of aromatic ethers to the solution allows the two-stage formation of the corresponding diaryl sulphides.

The technique of mixed electrolysis^{1,2} appears to be a growing trend in organic electrosynthesis. Sometimes, it can be of interest when the 'pro-reagent' is incorporated into the mass of the electrode and therefore slowly dissolves by electron transfer during the electrolysis. With such cathodes made of carbon-sulphur,^{3,4} carbon-selenium,⁵ and carbon-tellurium,⁶ sulphur, selenium, and tellurium may be incorporated into the final product (special case of a concomitant reduction of a soluble organic compound at that type of electrode). However the way in which such a sacrificial cathode functions is for the moment difficult to establish,⁷ even if it appears obvious that nucleophiles are formed from the progressive reduction and dissolution of the element contained in the electrode matrix. Similarly it would be expected that oxidation of the sulphur (here incorporated into a carbon anode) may produce electrophilic species able to react with aromatic ethers and then make functionalization reactions possible. We have used acetonitrile for this work, but other solvents need to be studied in order to optimise yields.

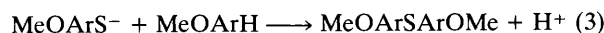
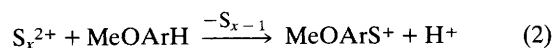
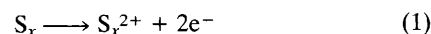
At a polished platinum electrode, the oxidation of dissolved sulphur occurs within the range 1.7–2.0 V (vs. standard calomel electrode, SCE). From molten solutions (AlCl₃/NaCl, 63:37 mol%), the oxidation of sulphur S₈ was reported^{8,9} and interpreted in terms of the successive formation of the entities S₁₆²⁺, S₈²⁺, and S₂²⁺. Similar behaviour would be expected in a non- (or poor) nucleophilic solvent at

room temperature. The main step observable in acetonitrile takes place in the potential range 1.7–2.0 V.

The basic oxidation of the solid sulphur of the electrode may be written as in reaction (1), and the reactivity of the expected bi-electrophilic species is tested towards aromatic systems MeOArH [reactions (2) and (3)].

If an easily oxidisable organic substrate is present in solution (e.g. anisole, oxidation potential 1.76 V) the electrolysis leads to the normal expected oxidative product 4,4'-dimethoxybiphenyl, and the sulphur electrode does not lead to any specificity. However, if current is then passed through the cell in the absence of organic substrate at a working potential *E*_w of +2.0 V until an equivalent of 2 Faradays per mole based on the reactive organic substrate added afterward is passed, a diaryl sulphide is obtained as main product (Scheme 1).

Consequently, from the new two-stage procedure [(i): oxidation of the sulphur electrode considered as a sacrificial

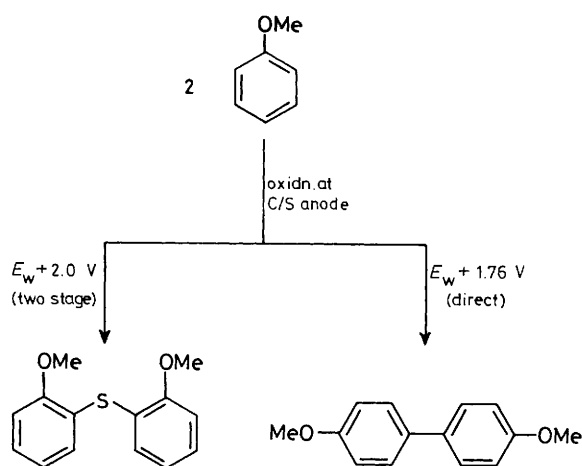


Scheme 1

Table 1. Anodic synthesis of aromatic sulphides.

Entry	Substrate ^a	<i>E</i> _p /V vs. SCE ^b	Product ^c (% Yield)
1	Anisole	1.77	Bis-2-methoxyphenyl sulphide (37%)
2	Veratrole	1.42	Bis-2,3-dimethoxyphenyl sulphide (42%)
3	1-Methoxynaphthalene	1.25	Bis-1-methoxy-2-naphthyl sulphide (41%)
4	2-Methoxynaphthalene	1.48	Bis-2-methoxy-1-naphthyl sulphide (30%)
5	6-Methoxyquinoline	1.65	Bis-6-methoxy-3-quinolyl sulphide (70%)
6	Toluene	2.32	No reaction
7	2-Methoxypyridine	2.02	No reaction
8	Diphenyl ether	1.88	No reaction

^a Substrates are commercially available from Janssen Chimica and Aldrich. ^b Peak potential observed by cyclic voltammetry on a platinum microanode in MeCN-Et₄NClO₄ (0.1 M), sweep rate: 100 mV s⁻¹. ^c Electrolysis conditions: the working anode was prepared by plunging a metal wire into a pasty mixture of 1 part carbon powder and 2 parts of sulphur heated and melted at 130 °C in a test tube. After cooling, the test tube was broken to release the compact electrode (*A* = 20 cm²). Electrolyses were carried out in a three-compartment H-cell. Supporting electrolyte: Et₄NClO₄ (0.1 M) in acetonitrile. About 2000 C are passed through the cell with a working potential of 2.0 V (vs. SCE), current is cut off and 10 mmol of substrate is added: the mixture is stirred during 24 h in order to complete the reaction. At the end of the run carbon powder in suspension in the reaction mixture is then filtered off and acetonitrile evaporated; the water-washed residue is extracted with ether. Products are separated by chromatography on a silica-gel column eluted with the appropriate miscible solvent and well characterized by IR, NMR, and mass spectroscopy.



anode, (ii) addition of the organic compound in a stoichiometric amount at the end of the electrolysis] aromatic ethers may be converted into sulphides in moderate to good yields (see Table 1).

Substrates less easily oxidized than sulphur (entries 6, 7 and 8) do not react at all. The presence of an electron donating substituent (apparently an essential condition), necessary on the one hand to increase the ease of oxidation, also appears to orientate the substitution into the *ortho* position. The regioselectivity of the reaction seems to be due to the presence

of an electron rich group. Note also that the linkage between the two aromatic rings remains limited to monosulphide (disulphides and polysulphides are experimentally excluded).

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