201. Electrochemical Oxidation of Bis(methylthio)benzenes

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Dedicated to Professor *Edgardo Giovannini* on the occasion of his 70th birthday

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Summary

The bis(methylthio)benzenes **3a**-**3c** are oxidized to the methylsulfinyl-methylthiobenzenes **4a**-**4c** on a Pt-anode in good yields.

In preceding publications [1] [2] we had discussed the electrochemical oxidation of some dialkoxybenzenes, *e.g.* the conversion **1**→**2**. Although the voltammetric behaviour of the analogous disulfur compounds has been reported in detail [3] [4], possible subsequent chemical reactions have not received a great deal of attention. The anodic oxidation of some simple sulfides has been investigated [5], *e.g.* thioanisole has been reported to give 74% methylsulfinylbenzene on Pt [6], but for these examples the conventional oxidation of sulfides to sulfoxides by sodium metaperiodate [7] is superior, giving better yields and being easier to handle. We now report on the electrochemical oxidation of the bis(methylthio)benzenes **3a**-**3c**.

Electrolysis of these compounds in MeOH/THF 5:1, the latter being added for solubility reasons, or in CH_3CN/H_2O 99:1 on Pt-electrodes with tetraethylammoniumperchlorate (TEAP) as electrolyte leads to the formation of the methylsulfinyl-methylthiobenzenes **4a**-**4c** in good yields, the oxidation of the second methylthio group or of the sulfoxide to the sulfone beginning to compete after a much higher degree of conversion **3**→**4** than with any chemical oxidizing agent. For illustration, **4a** had only been obtained from **3a** in a four-step reaction [8], while compounds as **4b** and **4c** had not been isolated at all, only the bis(methylsulfonyl)benzenes being known. The electrochemical oxidation of **3a**-**3c** to **4a**-**4c** being much more selective than any chemical oxidation is therefore a synthetic useful reaction. NMR.- and mass-spectral data of **4a**-**4c** are summarized in the *Table*.

In contrast to compounds like **1**, no anodic addition [9] has been observed with **3a**-**3c**. In methanolic KOH no conversion **3**→**4** takes place, presumably due to reduction of the radical cation by the nucleophile CH_3O^-. Acetate or pyridine also did not add to the aromatic ring. No benzylic substitution was observed with either **3c** or the monothiomethyl compound **3d**. Less than 5% of **2** were detected after oxidation of **3e** in MeOH, arising most probably from an anodic substitution/anodic addition sequence. All these results indicate that the positive

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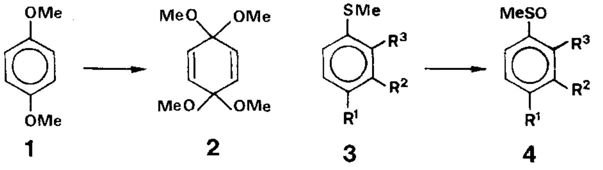
Table. *^{1}H-NMR.- and mass-spectral data of* **4a**–**4c**

Compound	^{1}H-NMR. ($CDCl_3$)	MS.
4a	2.55 (*s*, 3 H); 2.75 (*s*, 3 H); 7.45 and 7.65 (*AA'XX'*, 4 H, *J*=8.5 Hz)	186, *171*
4b	2.52 (*s*, 3 H); 2.75 (*s*, 3 H); 7.50–7.70 (*m*, 4 H)	186, *171*
4c	2.42 (*s*, 3 H); 2.53 (*s*, 3 H); 2.80 (*s*, 3 H); 7.26–7.93 (*m*, 3 H)	200, *185*



1 **2** **3** **4**

a R^1=SMe; R^2=R^3=H
b R^2=SMe; R^1=R^3=H
c R^3=SMe; R^1=Me; R^2=H
d R^1=Me; R^2=R^3=H
e R^1=OMe; R^2=R^3=H

charge in the radical cation is localized on the sulfur atom [6] so that nucleophilic addition to the benzene ring or substitution on the benzylic methyl groups do not become competitive.

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Experimental Part

The electrolysis apparatus consisted of a 200 ml cell, a cylindrical Pt-anode (6 cm^2) and a Pt-foil as cathode (4 cm^2) with a distance of 0.5 cm between the electrodes. The power supply was a d.c. adjustable source. For a constant current intensity of 0.150 A the tension varied between 9–10.5 V.

Materials. The bis(methylthio)benzenes **3a** [8] and **3b** [10] and the thiomethylbenzenes **3d** [11] and **3e** [12] were synthesized following the literature. **3c** was obtained by methylation of 3,4-dimercaptotoluene *(Prolabo SA)* with dimethylsulfate in 87% yield (m.p. 39–40°; ^{1}H-NMR. ($CDCl_3$): 2.35 (*s*, 3 H); 2.46 (*s*, 3 H); 2.48 (*s*, 3 H); 7.10–7.28 (*m*, 3 H)).

Preparation of methylsulfinylmethylthiobenzenes **4**. – **4a** *and* **4c**. A solution of 10^{-2} mol **3a** or **3c** and 1.5 g TEAP in 150 ml MeOH/THF 5:1 was electrolyzed with 120% of the theoretical current amount. After evaporation of the solvent the residue was extracted 3 times with 100 ml boiling hexane; **4a** crystallizes on cooling and is obtained in 83% yield after recrystallization from hexane, m.p. 101–102° (lit. [8]: 102°), **4c** is obtained as a colorless oil after evaporation of the hexane and column chromatography (SiO_2, C_6H_6/MeOH 6:1) in 74% yield.

4b. As the reaction in MeOH proceeds very slowly, CH_3CN/H_2O 99:1 was used as solvent. Thus 10^{-2} mol **3b** (1.5 g TEAP) were electrolyzed with 90–95% of the theoretical current amount. After evaporation of the solvent, extraction with boiling hexane and reevaporation, column chromatography of the residue (50% **3b** and 50% **4b**) on SiO_2 (CH_2Cl_2/MeOH 11:1) gave **4b** as a colorless oil in 45% yield. On increasing the current amount, the sulfoxide is oxidized to the sulfone and the overall yield of **4b** is lowered.

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