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Electrophilic substitutions with the electrogenerated sulfenium cation R^1-S^+

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Abstract: The sulfenium cation R^1-S^+ electrogenerated by oxidation of organic disulfides, reacts with phenols, aromatic ethers and ketones bearing an hydrogen atom in α position, to give alkyl (aryl) sulfanyl compounds. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Arenes, Disulfides, Electrochemistry, Sulfur compounds.

We have recently reported that electrochemical oxidation of organic disulfides, at a platinum electrode in dichoromethane, affords the transient electrophilic cation R^1-S^+ from the cleavage of the S-S bond, according to a two-electron process[1].

$$R^1\text{-S-S-}R^1 \xrightarrow{-2\ e^-} 2\ R^1\text{-}S^+$$

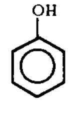
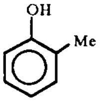
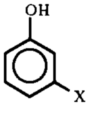
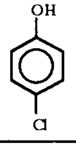
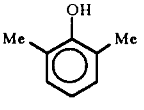
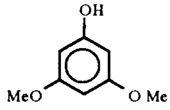
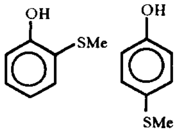
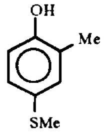
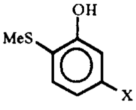
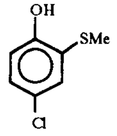
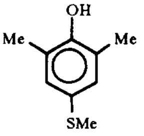
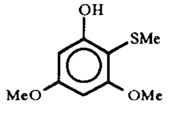
It was shown that unsymmetrical disulfides can be prepared by reaction of R^1-S^+ with thiols[2].

As methylsulfanylarenes have found use as pesticidal and pharmaceutical intermediates and as anti-oxidants, we propose a new method to prepare them by electrophilic substitution of phenols and aromatic ethers with R^1-S^+ prepared from electrooxidation of dimethyl disulfide.

A selective reaction has been observed with phenols. One product was formed with introduction of only one Me-S group (Table I), except for phenol itself for which ortho and para derivatives have been isolated. Yields are equivalent to those observed for the direct reaction of dimethyl disulfide with a phenol in the presence of a catalyst : phosphoric acid[3], aluminium phenoxide[4], alumino silicate[5], except if a Lewis acid is used in large excess[6]. Here regioselectivity is interesting and will be discuss later on.

As formed products are also electroactive in almost the same range of potential, the reaction was carried out in two steps. - First step - The suitable organic disulfide (C = 76 mM) was oxidized for about fifteen hours (electric consumption of 800 C), in an H-type cell in 70 mL of the medium CH_2Cl_2-n-Bu_4NBF_4 0.2 M on a platinum foil (initial intensity 1.25 mA/cm^2 -working potential vs SCE : 1.5 V with CH_3-S-S-CH_3, 1.7 V with

Table I - Preparation of methylsulfanylphenols.

Substrate						
Product						
Isolated Yield (%)	8 18	64	X = Br 20 Cl 32	31	65	77

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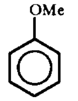
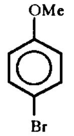
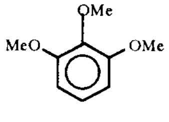
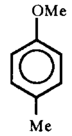
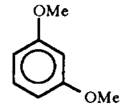
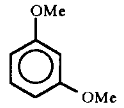
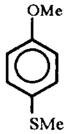
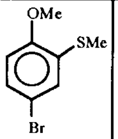
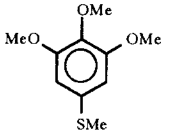
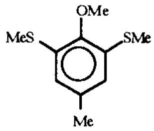
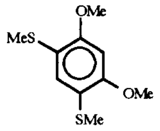
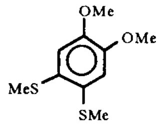
Ph-S-S-Ph). - Second step - After electrolysis was stopped, solution of the sulfenium cation was transferred into a flask containing a substrate (C = 140 mM) and stirred for several hours. Yields are better if dimethyl disulfide is in slight excess in connection with the stoichiometry of the reaction. n-Bu_4NBF_4 was selectively adsorbed by a fast chromatography on a small amount of silica gel with CH_2Cl_2 as eluent. Then residue was chromatographied on a silical gel column using the mixture cyclohexane/ethyl acetate (9:1, v : v) as eluent. Yields are determined after this separation. Products were characterized by microanalysis, IR, ^{1}H-NMR and mass spectroscopy.

The subtitution was not so selective with aromatic ethers and a disubstitution product was often observed (Table II). Only one attempt was made with Ph-S^+ and anisole; 4-phenylsulfanylanisole was isolated in 67% yield.

Table II - Preparation of methylsulfanyl aromatic ethers

	Monosubstitution			Disubstitution		
Substrate						
Product						
Isolated yield (%)	29	35	28	11	26	14

This reaction is also working with ketones bearing an hydrogen atom in α position and here two types of sulfenium cation R^1-S^+ (R^1 = Ph, CH_3) were tested. The selectivity is good and yields turn around 50-55 %, except for the reaction with ethyl acetoacetate (Table III).

Table III - Preparation of α-alkyl (aryl) sulfanyl ketones

Substrate $R^2\text{-CO-}CH_2\text{-}R^3$		R^1-S^+	Product $R^2\text{-CO-}\overset{R^3}{\overset{\vert}{C}}H\text{-S-}R^1$ and isolated yield (%)
R^2	R^3	R^1	
C_3H_7	C_2H_5	Ph	26
CH_3	$CO_2C_2H_5$	Ph	10
Ph	CH_3	Ph	55
Ph	CH_3	CH_3	54
Ph	C_2H_5	CH_3	53
Ph	C_3H_7	CH_3	50

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