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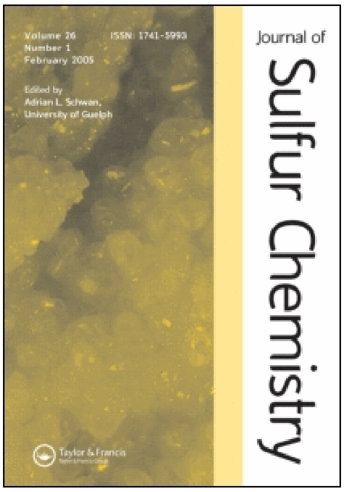

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# ELECTROCHEMICAL ACTIVATION OF SULFUR IN ORGANIC SOLVENTS—NEW SYNTHESES OF THIOORGANIC COMPOUNDS WITH A SACRIFICIAL CARBON-SULFUR ELECTRODE

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*(Received December 25, 1991)*

This review details new methods of preparation for thioorganic compounds derived from the electrogenerated species $S_x^{2}$ and $S_y^{2+}$. Since sulfur has poor solubility in the organic solvents used in electrochemisty it is introduced in the mass of the electrode together with powdered graphite to assure good electric conductivity. When it is used as a cathode at a working potential of about −0.9 V (vs. SCE), the nucleophilic species $S_x^{2-}$ is generated. With a working potential of 2.0 V it is possible to electrogenerate the electrophilic species $S_y^{2+}$. Through reactions with various substrates we could prepare thiophenes, sulfur-containing heterocycles, sulfides, trisulfides, etc. A vicarious nucleophilic substitution has also been observed. High selectivity and regioselectivity are observed in reactions with $S_y^{2+}$.

*Key words*: Electrochemistry of sulfur, organic sulfides, sulfur anions, sulfur cations, thiophenes, trisulfides.

## CONTENTS

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## 1. INTRODUCTION

Various methods have already been described in the chemical literature for the preparation of thioorganic compounds directly from thermally activated elemental sulfur.

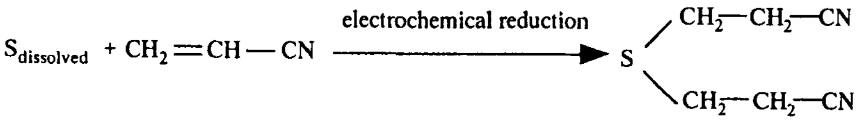
Activation by electrochemisty presents the advantage of working at room temperature; this attractive method, especially for frail molecules, has almost never been used.

For several years, we have been studying the electrochemistry of sulfur and we have at least two good reasons for doing so:

-the electrochemical activation of small molecules must be developed,

-it is very interesting to propose new methods for the preparation of sulfur-containing compounds when one considers the great importance of these products in the chemical industry.

A paper by Tomilov[1] describes the formation of dipropionitrile sulfide **2** in low yield (15%) through reduction of dissolved sulfur in the presence of acrylonitrile **1**. This process has been improved in a recent patent.



**1** **2**

Later on we will discuss another paper by Paris and Plichon[2] describing the preparation of organic polysulfides via nucleophilic substitution of alkyl halides by the sulfur anions $S_6^{2-}$ and $S_8^{2-}$, electrogenerated from dissolved sulfur in *N*, *N*-dimethylacetamide.

$$S_{dissolved} \xrightarrow{\text{electroreduction}} S_6^{2-} \text{ or } S_8^{2-} \xrightarrow{+R-X} R-S_x-R$$

$$x = 3\text{-}8$$

The poor solubility of sulfur in organic solvents currently used in electrochemistry (acetonitrile, *N*,*N*-dimethylformamide, dichloromethane, etc.) may be the reason why this method has almost never been used. It is possible to circumvent this difficulty by introducing the sulfur directly in the mass of the electrode together with graphite powder to assure good electric conduction. Such an electrode can be employed as a cathode or an anode to generate nucleophilic or electrophilic species which can react with a large variety of substrates.

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## 2. THE ELECTROCHEMISTRY OF SULFUR IN NON-AQUEOUS MEDIA

The cyclic structure $S_8$ for sulfur is commonly assumed in solution.[3]

The electroreduction of sulfur in DMF is a well-established process:[4] the first step involves the formation of $S_3^{\cdot-}$, then the formation of $S_4^{2-}$:

First step (at −0·55 V vs. ferrocene-ferrocenium):

$$S_8 + 2e^- \longrightarrow S_8^{2-}$$

$$4\,S_8^{2-} \rightleftharpoons 4\,S_6^{2-} + S_8$$

$$S_6^{2-} \rightleftharpoons 2\,S_3^{\bullet-}$$

Second step (at − 1.32 V V):

$$S_6^{2-} + 2e^- \longrightarrow 2\,S_3^{2-}$$

$$2\,S_3^{2-} + S_6^{2-} \longrightarrow 3\,S_4^{2-}$$

Curiously, electrooxidation of sulfur is only known in molten salts and in fluorosulfuric acid.

In accordance with Fehrmann,[5] the species $S_{16}^{2+}$, $S_8^{2+}$, $S_4^{2+}$, $S_2^{2+}$, $S^{2+}$, and $S^{4+}$ are formed by oxidation of sulfur in molten $AlCl_3$–NaCl at 150°C. The following mechanism has been proposed by Mamantov[6] in this medium at 150–250 °C:

First step

$$S_8 \xrightarrow{1.5\ \text{V (vs Al}^{3+}\text{/Al)}} S_8^{2+} + 2e^-$$

$$S_8^{2+} + S_8 \rightleftharpoons S_{16}^{2+}$$

Second step

$$S_8^{2+} \overset{1.75\ \text{V}}{\rightleftharpoons} 4\,S_2^{2+} + 6\,e^-$$

Third step

$$S_2^{2+} \overset{1.88\ \text{V}}{\rightleftharpoons} 2\,S^{4+} + 6\,e^-$$

The electrochemistry of sulfur in fluorosulfuric acid has been studied by Herlem.[7] Sulfur dissolves only in boiling $HFSO_3$ to give colored solutions. The proposed mechanism assumes $S^+$ and $S_2^+$ as the starting ions:

- in acidic melts

$$S^+ \longrightarrow S^{2+} + e^-$$

$$S^{2+} \longrightarrow S^{4+} + 2\,e^-$$

- in basic melts

$$S_2^+ \longrightarrow 2\,S^{2+} + 3\,e^-$$

$$2\,S^{2+} \longrightarrow 2\,S^{4+} + 4\,e^-$$

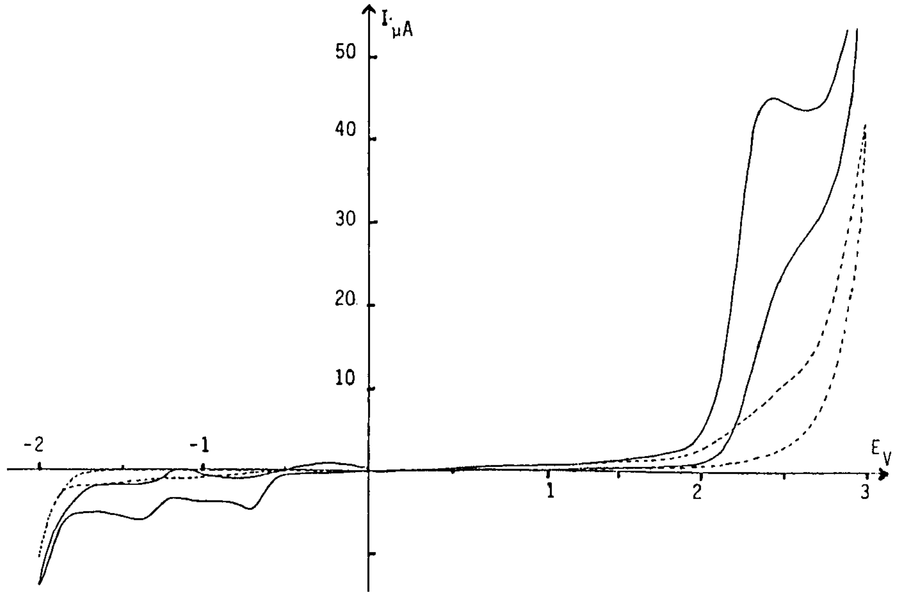

**Figure 1.** Cyclic voltammetry of sulfur at a platinum microelectrode—sweep rate 100 mV $s^{-1}$—reference electrode: SCE (medium: *n*-$Bu_4NBF_4$, 0.1 M in acetonitrile): --- without sulfur —— with sulfur ($C_{S_8}$ = 7.81 × $10^{-4}$ mol $l^{-1}$).

Through cyclic voltammetry (Figure 1), we have observed[8] a high irreversible peak in organic solvents at 2.42 V (vs. SCE) and, by comparison with the height of the peaks observed upon reduction, we propose a sixteen-electron process. The consumption of sixteen Faradays per mole is confirmed by coulometry. The final formation of $S^{2+}$ is assumed and confirmed by the results of macroscale electrolyses,

$$S_8 \longrightarrow 8\,S^{2+} + 16\,e^-$$

but the presence of the intermediary species $S_8^{2+}$, $S_4^{2+}$, and $S_2^{2+}$ is not totally dismissed.

In the presence of Lewis acids ($AlCl_3$, $SnCl_4$) a second irreversible sixteen-electron process is observed at 2.90 V, leading to $S^{4+}$.

## 3. SACRIFICIAL CARBON-SULFUR ELECTRODES

In 1978 Berge[9] had the excellent idea of introducing sulfur in an electrode together with powdered graphite to assure a sufficient electric conductivity of the cathode (1 part graphite for 4 parts sulfur).

We have tested different ways to build a convenient electrode. The best way is schematized in Figure 2. A graphite cloth is introduced in a test tube of suitable size. Then a mixture of powdered sulfur and powdered graphite is introduced. The test tube is heated in an oven at 130 °C. Once the sulfur has melted, a carbon rod is introduced in the pasty mixture. After return to room temperature, the test tube is broken to release

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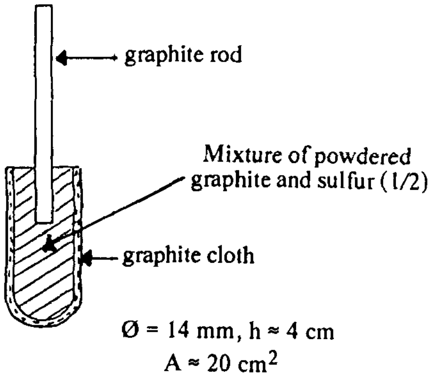

**Figure 2.** Carbon-sulfur electrode.

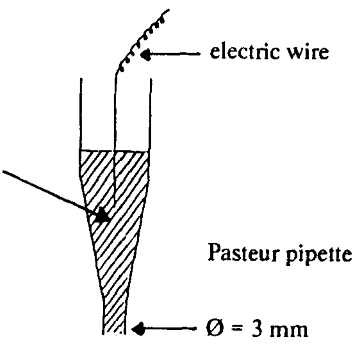

**Figure 3.** Carbon-sulfur microelectrode.

the compact electrode. The graphite cloth holds back the powdered graphite during the destruction of the electrode and obviates filtering of the electrolyte solution.

We have tried different proportions of sulfur and graphite ranging from 4 parts of the former and 1 part of the latter to 1 part/1 part, respectively. Since the yields of thioorganic compounds with a great excess of sulfur in the electrode are not higher, we opted for 2 parts sulfur for 1 part graphite.[10]

Infrared spectroscopy and electron microscopy on the powder obtained by scratching of the carbon–sulfur electrode show no evidence of a chemical bond between sulfur and carbon.

To determine the field of potential, for a voltammetric study a carbon–sulfur microelectrode was produced in a Pasteur pipette[11] (Figure 3). The intensity was zero between $-0.6$ V and 1.6 V (vs. SCE).

If an organic substrate, electroactive in this field, is added to the solution, we can observe its characteristic peak of oxidation or reduction as with any other inert electrode (platinum, glassy carbon, etc.). For example electrolysis of aniline at 1.0 V leads to the normal expected oxidative product, benzidine, without involvement of sulfur.

For potential below $-0.6$ V a high intensity is observed, due to the reduction of the sulfur present in the electrode. Above 1.6 V, the high wave is associated with the oxidation of the sulfur.

If we consider these phenomena in the case of the carbon–sulfur electrode in an electrochemical cell, we can say that if the applied potential is lower than $-0.6/-0.9$ V, the electrode acts as a source of nucleophilic species of the general formula $S_x^{2+}$; if it is above 1.6/1.8 V, electrophilic species $S_y^{2+}$ are formed ($x$ and $y$ can have several values depending on the experimental conditions which will be discussed later). The field of activity of the carbon–sulfur electrode is shown in Figure 4.

Through new methods, the species $S_x^{2-}$ and $S_y^{2+}$ can be made available to react with a variety of substrates to produce thioorganic compounds.

## Experimental conditions

Macroscale electrolyses are generally conducted in an H-type cell with an intermediary compartment. Other types of cells are used for industrial developments.

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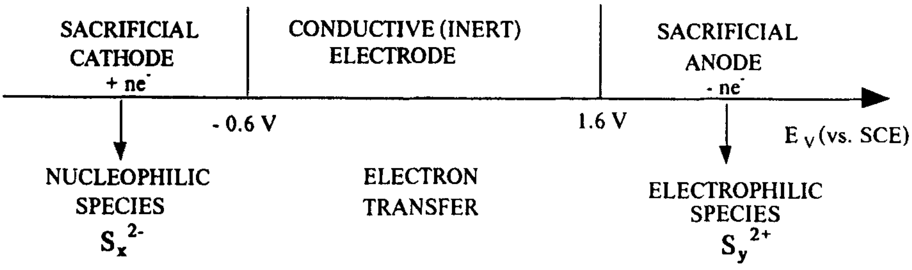

**Figure 4.** Field of activity of the carbon-sulfur electrode.

If the carbon–sulfur electrode is used as a cathode, the substrate is introduced at the beginning of the electrolysis because the working potential is only − 0.9 V (vs. SCE). The solvent commonly used is *N*,*N*-dimethylformamide (DMF), acetonitrile or *N*-methylpyrrolidone (NMP); $NaClO_4$ or $Et_4NClO_4$ (TEAP) is added as a supporting electrolyte ($C = 0.5\,mol\,l^{-1}$).

The electrogeneration of electrophilic species from a carbon–sulfur anode requires a very high positive potential [2.0 V (vs. SCE)], so we have to proceed in two steps:
—first step: generation of $S_y^{2+}$ in a solution of TEAP, 0.2 M in $CH_3CN$. Other solvents can be used (dichloromethane, nitromethane, nitrobenzene, etc.) with supporting electrolytes of the type $R_4NClO_4$ or $R_4NBF_4$. A current corresponding to 2000 to 5000 coulombs is passed through the cell.

For this step we can also work at a constant current (20–50 mA).
—second step: the electrolysis is stopped, the solution containing $S_y^{2+}$ transferred to a flask with a stoichiometric amount of the substrate, and stirred for several hours.

In these two cases the resulting solutions are treated in the usual way and the products purified by liquid chromatography on silica gel.

## 4. THE ELECTROGENERATION OF NUCLEOPHILIC SPECIES

### *4.1. Mechanistic Aspects*

With UV spectroscopy as the method of detection we have tried to identify the reduced forms of sulfur by conducting electrolyses, without substrates, with only a carbon–sulfur cathode in a solution of $NaClO_4$, 0.5 M in DMF, at a working potential of − 0.90 V vs. SCE.

In the beginning we observe[12] absorptions at 618 nm and 505 nm, clearly attributable to $S_3^{\cdot-}$ and $S_8^{2-}$. Between 14 coulombs and 500 coulombs we observe an increase in the 505 nm absorption, and a change in the color of the solution from blue to purple. A third absorption appears at 424 nm; at 900 coulombs it is the only one left. At this point, the species $S_4^{2-}$ dominates in the solution which has now turned deep red.

Thus when the carbon–sulfur electrode is used as a cathode, at a working potential of − 0.9 V (vs. SCE), in the presence of an organic substrate, the species $S_3^{\cdot-}$, $S_8^{2-}$ and $S_4^{2-}$ can react competitively. This can explain the mixtures of products different from those obtained by chemical reaction between elemental sulfur and organic substrates.

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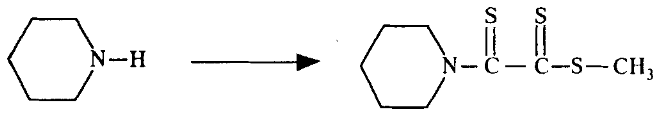
Here are the types of reactions we have observed with a large variety of substrates:

—attack by $S_3^{\cdot -}$ gives dimerization products, observed with alkenes and alkynes,

—attack by $S_x^{2-}$ ($S_8^{2-}$, $S_4^{2-}$, etc.) leads to:

- —addition to double bonds (C=C) or triple bonds (C≡C or C≡N) produces Michael-type adducts which generally are sources of sulfides,
- —substitution of a halogen group in halogenated compounds, chlorovinylic compounds (alkenes with a leaving group), halogenated aromatics,
- —substitution of a hydrogen atom, known as vicarious nucleophilic substitution, observed with α,β-ethylenic ketones. In some cases when reactions are carried out in DMF, incorporation of a solvent molecule in the final product is observed.

Rozas[13] has described reactions where carbon and sulfur are simultaneously introduced in a molecule; this is observed with cyclic amines.

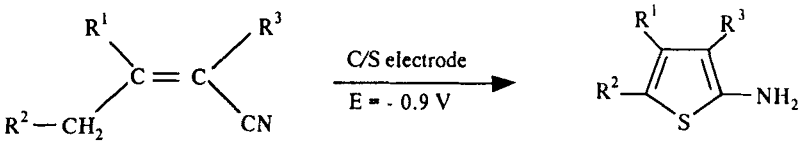


The nature of the solvent or of the supporting electrolyte can also influence the product distribution (see Sections 4.3, 4.4, and 5.1.4).

### *4.2. Reactions with Ylidenenitriles*

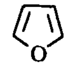
In type 3 ylidenenitriles, where $R^1 = R^2$ = alkyl and $R^3$ = electron-withdrawing groups such as CN, $CO_2C_2H_5$, COPh, one hydrogen atom of the $CH_2$ group is acidic and, by reaction with sulfur in basic media, 2-aminothiophenes **4** are obtained.[14]

Several ylidenenitriles have been tested in an electrochemical cell with a carbon–sulfur electrode as the cathode. They are reducible at a potential close to −0.9 V, the selected working potential; 2-aminothiophenes **4** are sometimes obtained in higher yields than by the Gewald method (Table 1).[10]



**3** **4**

**Table 1.**

| Substrate **3**<br>$R^1$ | $R^2$ | $R^3$ | Yield (%)<br>of 2-aminothiophene |
|---|---|---|---|
| | $(CH_2)_4$ | CN | 90 |
| | $Ch_2)_4$ | $CO_2C_2H_5$ | 61 |
| | $(CH_2)_4$ | COPh | 65 |
|  | $CH_3$ | CN | 91* |
| Ph-$CH_2$ | $CH_3$ | CN | 72 |

*Berge[9] had obtained this product in 58% yield.

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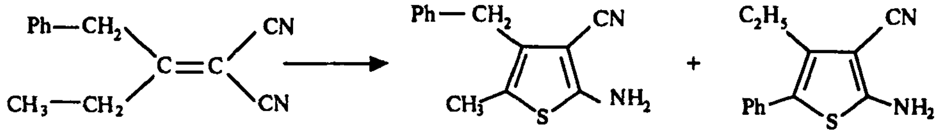
With an ylidenenitrile **5** bearing two activated $CH_2$ groups, two different 2-aminothiophenes are obtained:



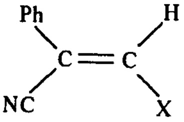
**5** (30 %) (42 %)

If $R^3 = CO_2H$ or $CONH_2$, the electrochemical mixture is very complex and we were unable to isolate 2-aminothiophenes.

In these reactions, polysulfide ions act first as electrogenerated bases to deprotonate the activated $CH_2$ group.[10]

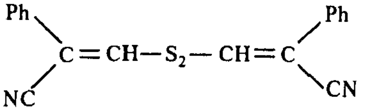
### 4.3. *Reactions with Alkene-bearing Leaving Groups*

In my group, we have intensively studied the reaction of electrogenerated sulfide ions with 2-phenylpropenenitriles bearing a leaving group X, with X = Cl, OCOPh, OTs.[11]

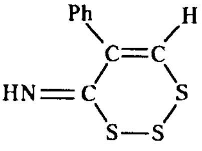


**6**

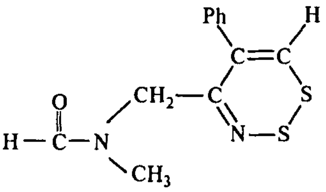
The following products have been characterized: bis(2-cyano-2-phenylvinyl) disulfide **7**, 5-phenyl-4*H*-1,2,3-trithiin-4-imine **8**, *N*-methyl-*N*-[(5-phenyl-1,2,3-dithiazin-4-yl)methyl] formamide **9**, *N*-methyl-*N*-[(6-phenyl-1,2,3,4-trithiazepin-5-yl)-methyl]-formamide **10**, 1-[(5-phenyl-1,2,3-dithiazin-4-yl)methyl]-2 pyrrolidone **11**, and 1-methyl-5-(5-phenyl-1,2,3-dithiazin-4-yl)-2-pyrrolidone **12**.



**7**



**8**



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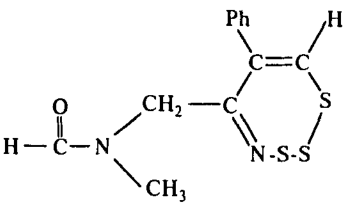

**10**

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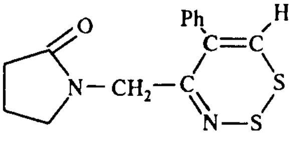
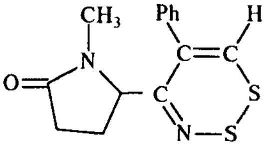


**11**

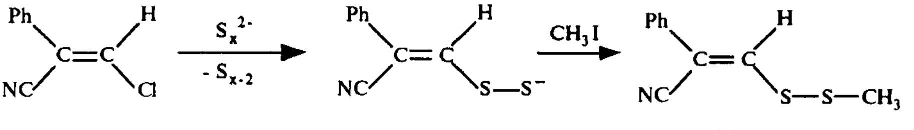


**12**

If the working potential of the cathode is maintained at $-0.9\,V$, a passivation phenomenon is often observed so that the potential must be changed to $-1.9\,V$.

The choice of the solvent is of great importance in these electrolyses. In acetonitrile, we isolate only the disulfide **7** in relatively high yield. In *N*,*N*-dimethylformamide (DMF) or *N*-methylpyrrolidone, the yield of **7** is low and we find sulfur-containing heterocycles. These two solvents take part in the reaction and are introduced in the sulfur-containing heterocycles **9** and **10** with DMF, **11** and **12** with NMP. The mechanism of such an introduction of the solvent has already been discussed[11] (see results in Table 2).

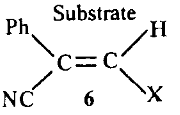
The presence of the intermediary anion **13** is clearly brought to the fore because when methyl iodide is added at the end of the electrolysis of 3-chloro-2-phenylpropenenitrile **6**, methyl (2-cyano-2-phenylvinyl) disulfide **14** is isolated (yield 51%).



**6** **13** **14**

We have compared the results obtained with a carbon–sulfur electrode with those with dissolved sulfur reduced on a platinum or carbon rod cathode. We note several differences: the yields of **7** are higher, the yields of products in which a molecule of DMF is introduced are lower. We have never observed the heterocycle **10** under these conditions.

**Table 2**

| Substrate  | Electrolysis conditions | | | isolated products and yields | | | | |
|---|---|---|---|---|---|---|---|---|
| | cathode | working potential | solvent | **7** | **8** | **9** | **10** | **11** and **12** |
| Cl | C/S | $-0.9\,V$ | DMF | 13 | 11 | 14 | | |
| OCOPh | C/S | $-0.9\,V$ | DMF | 14 | 10 | 16 | | |
| Cl | C/S | $-0.9\,V$ | $CH_3CN$ | 55 | | | | |
| Cl | C/S | $-1.9\,V$ | DMF | 7 | 4 | 20 | 5 | |
| OCOPh | C/S | $-1.9\,V$ | DMF | 11 | 5 | 17 | 6 | |
| OTs | C/S | $-1.9\,V$ | DMF | 20 | 25 | 25 | | |
| Cl | C/S | $-1.9\,V$ | NMP | 15 | 18 | | | 10 |
| Cl | Pt (with dissolved sulfur) | $-1.9$ | DMF | 15 | 4 | 10 | | |
| Cl | graphite rod (with dissolved sulfur) | $-1.9\,V$ | DMF | 47 | 5 | 17 | | |

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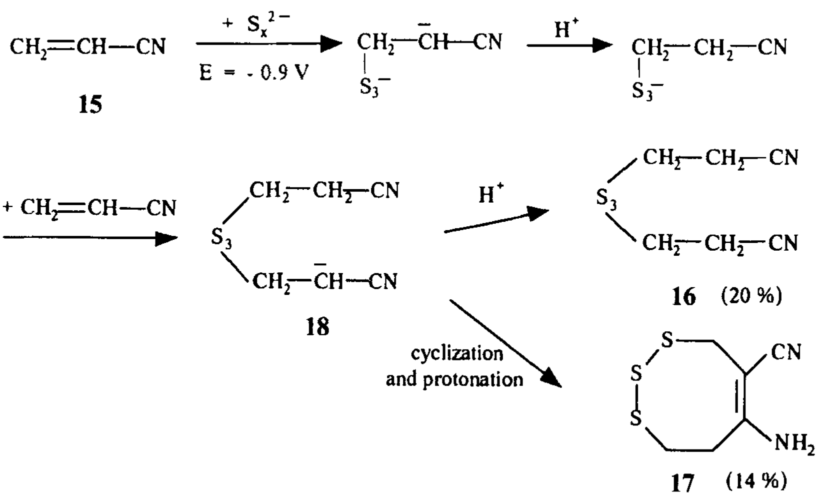
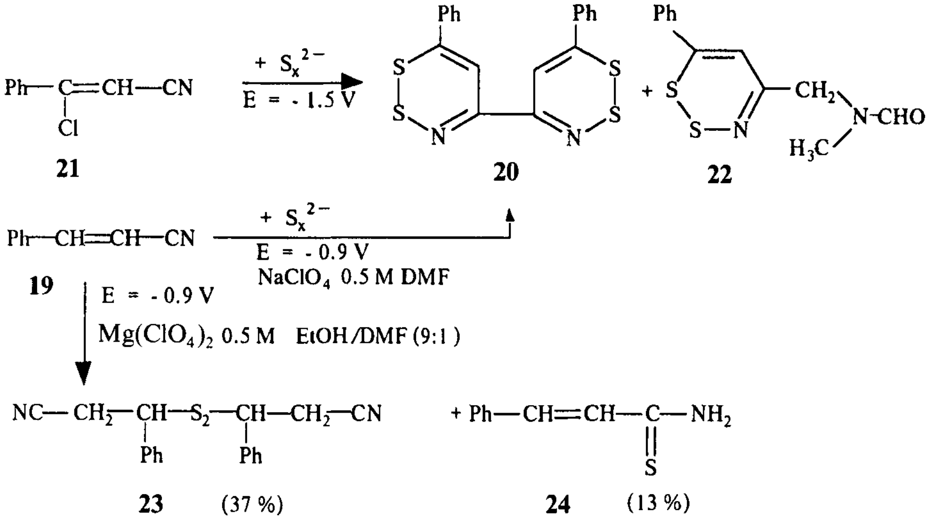
### 4.4. *Reactions with Alkenes*

The reactivity of alkenes, activated by nitrile or keto groups, has been tested in relation to the electrogenerated sulfide ions $S_x^{2-}$. It is impossible to establish general rules as the product differs from one reaction to the next.

From acrylonitrile **15**, bis(2-cyanoethyl) trisulfide **16** is the main product. The intermediary anion **18** can also be cyclized to 6-amino-5-cyano-7,8-dihydro-4*H*-1,2,3-trithiocine **17** in the strong basic reaction medium.[15]



Curiously, cinnamonitrile **19** gives a bicyclic product, 6,6′-diphenyl-4,4′-bis(1,2,3-dithiazine) **20** in high yield (75%) at a working potential of $-0.9\,V$.[14] This product is also obtained (44%) from 3-chloro-3-phenylpropenenitrile **21** at a working potential of $-1.5\,V$, with a small amount (13%) of the dithiazine **22** substituted by one molecule of the solvent DMF.



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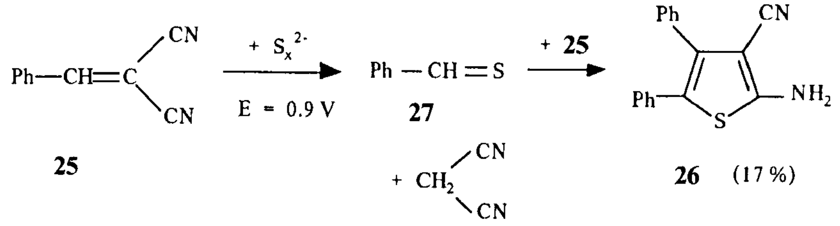
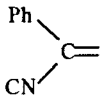
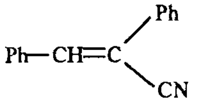
The above reactions are carried out in the presence of $NaClO_4$ as the supporting electrolyte in DMF. If it is replaced by $Mg(ClO_4)_2$ in a mixture of ethanol and DMF (9 : 1), a disulfide **23** and the thiocinnamide **24** are isolated; we do not know why.

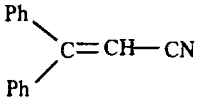
2-Amino-3-cyano-4,5-diphenylthiophene **26** is obtained from benzylidene-malononitrile **25** by a complex mechanism. Thiobenzaldehyde **27**, intermediately formed by cleavage of the C=C double bond of benzylidenemalononitrile, can react with the starting compound to yield the thiophene **26**. Such cleavages in basic media have already been observed in Perkin, Knoevenagel, and Claisen condensations.[16]

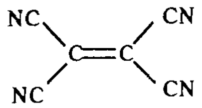


2-Phenylpropenenitile **28** gives only dimeric sulfur-free compounds. 2,3-Diphenylpropenenitrile **29**, 3,3-diphenylpropenenitrile **30** and tetracyanoethylene **31** do not react under these conditions.

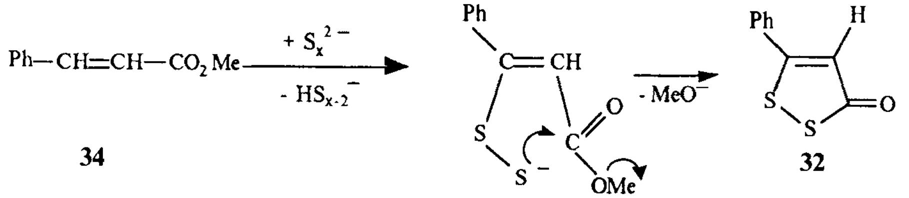

**28**

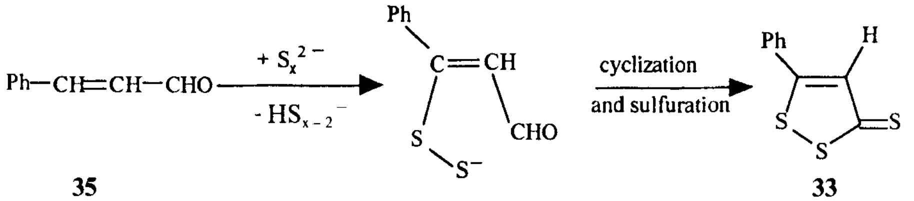

**29**


**30**


**31**

With ethylenic ketones or esters a vicarious nucleophilic substitution (VNS) is observed. This type of substitution has been proposed by Makosza[17] when a hydrogen atom attached to a carbon atom of a C=C double bond is substituted by a carbanion. The experimental conditions are appropriate for VNS: (i) the electrogenerated sulfide ions $S_x^{2-}$ are strongly basic, (ii) in excess, and (iii) cleavage of the S–S bonds leads to a leaving group, $HS_{x-1}^-$ or $HS_{x-2}^-$. More often than not an internal cyclization follows. For example, 5-phenyl-3*H*-1,2-dithiol-3-one **32** and 5-phenyl-3-*H*-1,2-dithiole-3-thione **33** are isolated from methyl cinnamate **34** and cinnamaldehyde **35**, respectively.[10,15]





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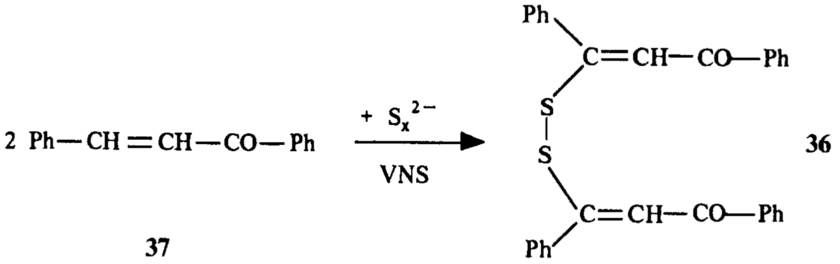
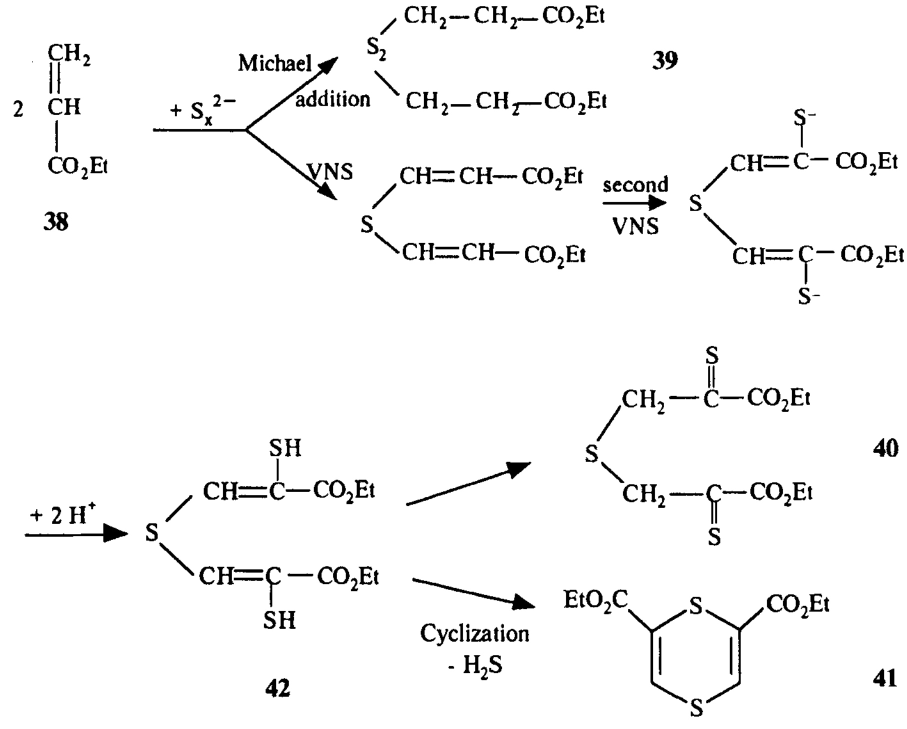
With certain substrates such as benzalacetophenone **37** two molecules of the reagent take part in the vicarious nucleophilic substitution[15] and bis(2-benzoyl-1-phenylvinyl) disulfide **36** is obtained in the following reaction:



In the case of ethyl acrylate **38** competition is observed between Michael addition of $S_x^{2-}$ to the double bond and two successive vicarious nucleophilic substitutions. Bis(2-ethoxycarbonylethyl) disulfide **39** and bis(2-ethoxycarbonyl-2-thioxoethyl) sulfide **40** are isolated in 55% and 35% yields, respectively. A small amount of the dithiine **41**, detected by mass spectroscopy,[10,15] is formed by internal cyclization of the intermediate **42**.



Sometimes addition of the nucleophilic species $S_x^{2-}$ to the double bond is the only observed reaction.[14] For example, bis(2,3-diphenyl-3-oxopropyl) disulfide **44** is isolated

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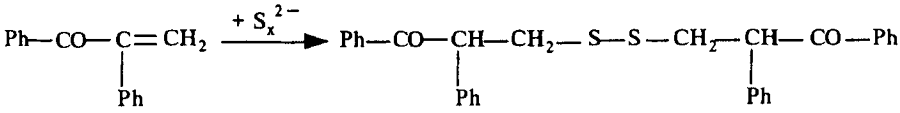
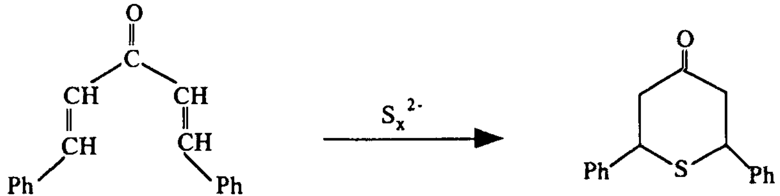
from the reaction with 1,2-diphenylprop-2-en-1-one **43**. Such a reaction has been previously observed with sodium polysulfide[18] with a chemical yield of 2%.



$$\underset{\mathrm{Ph}}{\mathrm{Ph{-}CO{-}C}}{=}\mathrm{CH_2} \xrightarrow{+\,S_x^{2-}} \mathrm{Ph{-}CO{-}}\underset{\mathrm{Ph}}{\mathrm{CH}}\mathrm{{-}CH_2{-}S{-}S{-}CH_2{-}}\underset{\mathrm{Ph}}{\mathrm{CH}}\mathrm{{-}CO{-}Ph}$$

**43** **44** (8 %)

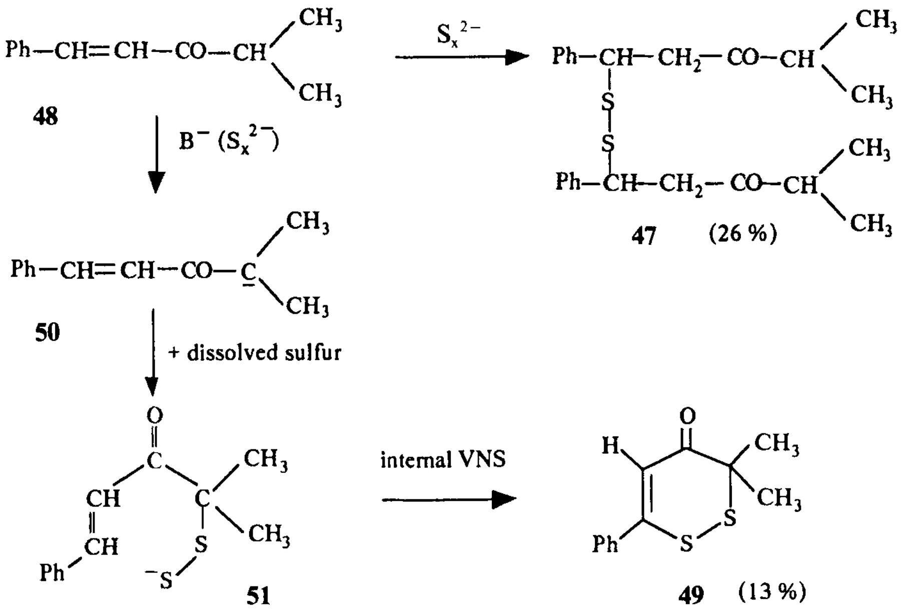
If the substrate contains two C=C double bonds in favored positions such as in 1,5-diphenyl-1,4-pentadiene-3-one **45**, for example, a cyclic sulfide is formed, in this case 2,6-diphenyl-4-oxotetrahydrothiopyran **46**.



(18 %)

**45** **46**

Bis(4-methyl-1-phenyl-3-oxopentyl) disulfide **47** is still the main product formed from 4-methyl-1-phenylpent-1-en-3-one **48**, but the second isolated product, 3,3-dimethyl-4-oxo-6-phenyl-3,4-dihydro-1,2-dithiin **49**, suggests a deprotonation of the starting material by the electrogenerated polysulfide ions (acting as electrogenerated base) leading to the anion **50** which can react with dissolved sulfur; the new anion **51** cyclizes to **49** by internal vicarious nucleophilic substitution.[10,15]



**48** **47** (26 %) **50** **51** **49** (13 %)

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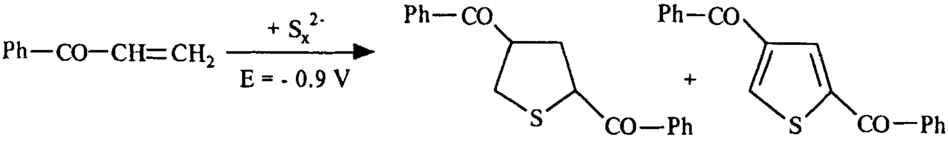
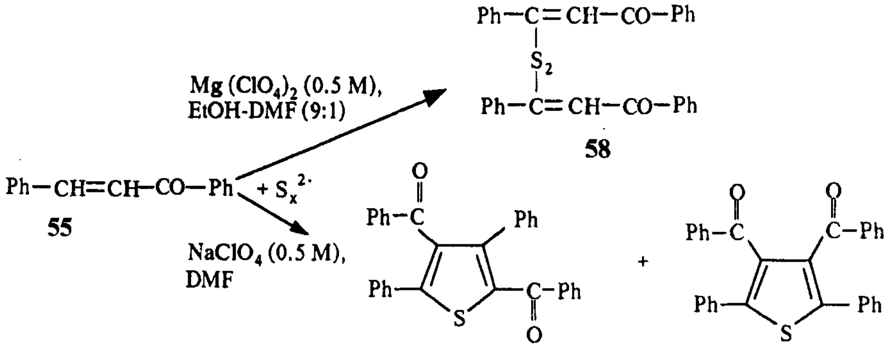
With several α,β-unsaturated ketones it is possible to observe the formation of thiolanes and thiophenes. This complex mechanism has already been discussed in the Do thesis[10] and in another paper.[15]

A mixture of 2,4-dibenzoylthiolane **52** (21%) and 2,4-dibenzoylthiophene **53** (10%) is obtained from 1-phenylprop-2-en-1-one **54**.



**54** **52** **53**

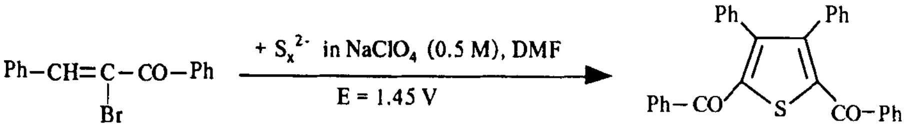
We have especially studied reactions with benzalacetophenone **55** because many data are given in the chemical literature concerning reactions of this compound with sodium sulfide and sodium polysulfides. Electrogenerated sulfide anions at −0.9 V in DMF containing 0.5 M $NaClO_4$, give a mixture of two isomeric thiophenes: 2,4-dibenzoyl-3,5-diphenylthiophene **56** and 3,4-dibenzoyl-2,5-diphenylthiophene **57** in the ratio 2 : 1. If the medium is changed and the electrochemical reaction conducted in 0.5 M $Mg(ClO_4)_2$ in ethanol-DMF (9 : 1), bis(2-benzoyl-1-phenylvinyl) disulfide **58** is the only characterized product (25%).[15] With the bromo derivative **59**, at a working potential of −1.45 V in 0.5 M $NaClO_4$ in DMF, the leaving group Br favors the formation of the thiophene derivative **60**, an isomer of the two compounds mentioned above.[19] The complex problem of structural determination has been resolved by $^{13}C$ NMR spectroscopy.



**58**

**55**

**56** (17 %) **57**



**59** **60**

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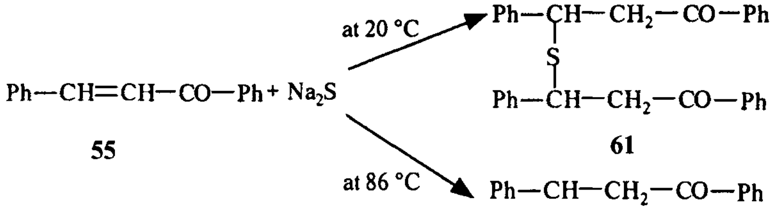
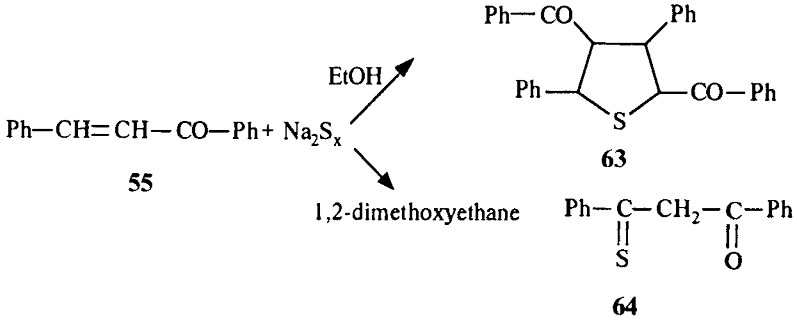
The results of chemical reactions of sodium sulfide or sodium polysulfides with benzalacetophenone are totally different. With sodium sulfide, we have shown[15] that it is possible to obtain either bis(1,3-diphenyl-3-oxopropyl) sulfide **61** (yield 35%) or 1,3-diphenylpropanone **62** (yield 80%), depending on the reaction temperature: 20 °C in the first case, 86 °C in the second.



The nature of the solvent influences the nature of the final product obtained with sodium polysulfides: 2,4-dibenzoyl-3,5-diphenylthiolane **63** in ethanol (74%)[20] and 1,3-diphenylthioxopropan-1-one **64** in 1,2-dimethoxyethane (75%).[21]

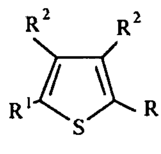


Benzalacetone reacts with $S_x^{2-}$, giving an unidentified dimeric sulfur-containing product $C_{20}H_{12}O_2S_2$.

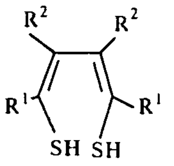
$$Ph{-}CH{=}CH{-}CO{-}CH_3 \xrightarrow{+\ S_x^{2-}} C_{20}H_{12}O_2S_2$$

*4.5. Reactions with Alkynes*

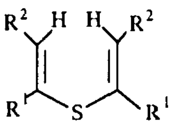
If alkynes $R^1{-}C{\equiv}C{-}R^2$ are introduced in the cathodic compartment of the electrochemical cell, four types of products are observed: a thiophene **65**, a dithiol **66**, a sulfide **67**, and a trimer **68** (only in one experiment). The thiophene is the major product and this reaction is a new method to prepare it.[22]



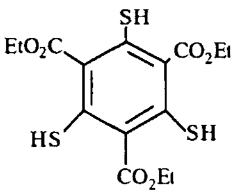
**65**



**66**



**67**



**68**

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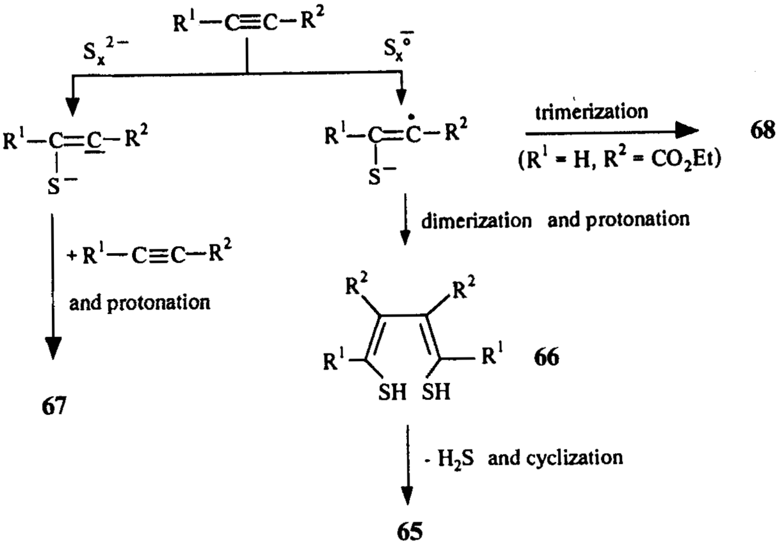
**Table 3.**

| $R^1$-C≡C-$R^2$ | | isolated products and yields (%) | | | |
|---|---|---|---|---|---|
| $R^1$ | $R^2$ | **65** | **66** | **67** | **68** |
| H | Ph | no reaction | | | |
| H | $CO_2Et$ | 10 | | 12 | 6 |
| Ph | CHO | 82 | | | |
| Ph | $CO_2Me$ | 85 | | | |
| Ph | CN | 80 | | | |
| $CO_2Me$ | $CO_2Me$ | 32 | 53 | | |

The product distribution depends on the nature of $R^1$ and $R^2$ (Table 3).

The yields are satisfactory only when the alkynes are strongly activated by electron-withdrawing groups.

The product distribution is explained by initial attack on the alkynes either by $S_x^{2-}$ or $S_x^{\cdot-}$.[10]



The chemical reaction of $Na_2S$ with alkynes ($R^1$ = H, $R^2$ = $CO_2Et$ and $R^1$ = Ph, $R^2$ = CN) gives the sulfides **67** in yields ranging from 60 to 85%.[10,11]

### 4.6. *Reactions with Halogenated Compounds*

Paris and Plichon[2] have described the preparation of polysulfides through reaction of alkyl halides with a solution of electrogenerated polysulfide ions, $S_6^{2-}$ (in equilibrium with $S_3^{\cdot-}$) or $S_8^{2-}$, from dissolved sulfur in *N*,*N*-dimethylacetamide.

$$2\,RX + 2\,S_3^{\cdot-} \longrightarrow R\text{-}S_3\text{-}R + 3/8\,S_8 + 2\,X^-$$

$$2\,RX + S_8^{2-} \longrightarrow R\text{-}S_4\text{-}R + 1/2\,S_8 + 2\,X^-$$

In concentrated solutions they always obtain a mixture containing about a third of trisulfide, a third of tetrasulfide, and a third of higher polysulfides (penta-, hexa-, hepta-, octa-). In dilute solutions the reactions lead to mixtures of dialkyl trisulfides and tetrasulfides as shown by voltammetry coupled with absorption spectroscopy.

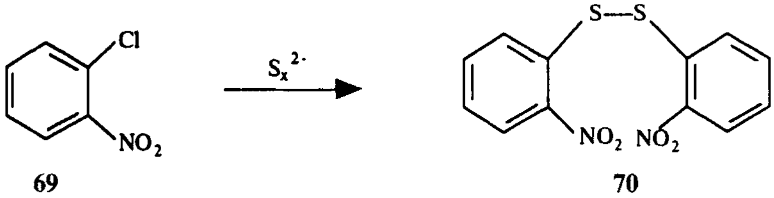
With a carbon/sulfur electrode working at a potential of −0.9 V, as alkyl halides are not easily reducible, they can be introduced at the beginning of the electrolysis. By this method we are able to prepare polysulfides R–$S_x$–R where $x$ equals 2, 3, and 4.

$$\mathrm{RX} \xrightarrow[\mathrm{E} = -0.9]{\text{carbon-sulfur electrode}} \mathrm{R{-}S_x{-}R}$$

The conversion rate is rather high, but the distribution depends on the working potential. Thus at −0.9 V the formation of tri- and tetrasulfide is almost exclusive whereas at −1.5 V we obtained equal quantities of di-, tri-, and tetrasulfide. Tertiary bromides do not react under these conditions.

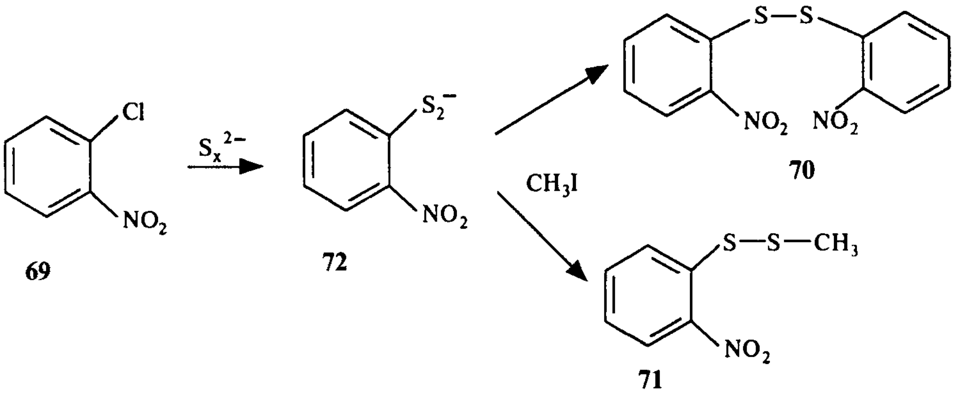
We have observed a more complex reaction upon electrolysis of dissolved sulfur in DMF in the presence of alkyl halides.

Berge[9] was the first to describe the reaction of electrogenerated sulfide ions with a halogenated aromatic compound; the disulfide **70** is obtained from 2-chloronitrobenzene **69**.



Repeating this reaction we also identified the sulfide together with the disulfide **70** as a 2 : 1 mixture.[10]

When methyl iodide is added at the end of the electrolysis to react with the nucleophiles present, the isolation of 2,2′-dinitrodiphenyl disulfide **70** (63%) and methyl (2-nitrophenyl) disulfide **71** (26%) allow us to conclude that the disulfide is formed via the intermediary anion **72**.[18]



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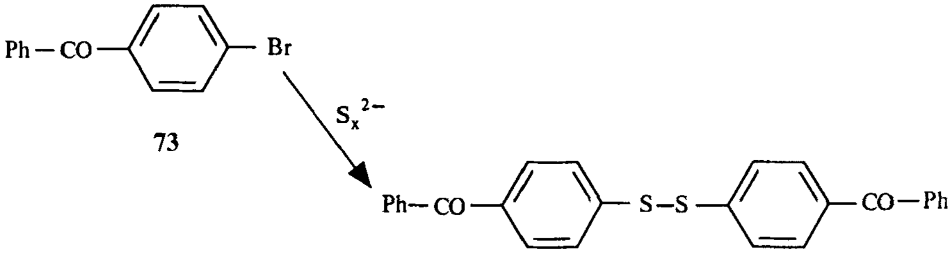
The formation of this aryl disulfide ion **72** is confirmed by an UV-visible spectroscopic study published by Paris[23] in which he shows that polysufide ions $S_3^{-}$ and $S_8^{2-}$, electrogenerated from dissolved sulfur in *N*,*N*-dimethylacetamide, readily react with aromatic halides (Cl, Br, I, F) activated by electron-withdrawing substituents such as $NO_2$. The nucleophilic substitution leads to aryl monosulfide and aryl disulfide.

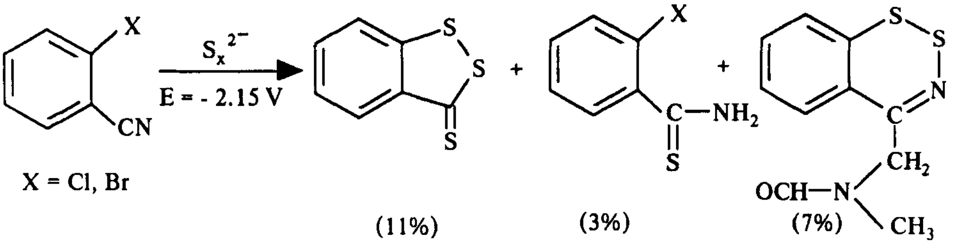
Also with 4-bromobenzophenone **73** a disulfide, **74**, is obtained in a yield of 50%.[10]



**73**

**74**

The reactions are more complex in the case of 2-chloro-(bromo)benzonitrile **75**.[10] The working potenital of the carbon–sulfur electrode must be adjusted to −2.15 V to obtain the product; the nitrile group is attacked to give the cyclic product **76** and the thiomide **77**; one molecule of DMF (solvent) is incorporated in the cyclic sulfur-containing derivative **78**.

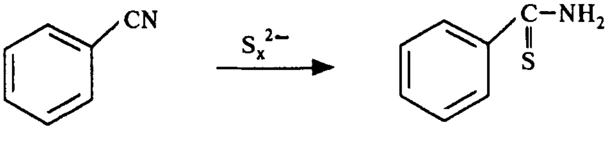


**75** **76** **77** **78**

Reaction with $Na_2S$ produces the disulfide 2-$XC_6H_4$-S-S-$C_6H_4X$-2 (74%), together with a small amount of **77** (11%).

### 4.7. Other Reactions

Berge[8] has patented a method to transform benzonitrile **79** into thiobenzamide **80** in a yield of 40%.



**79** **80**

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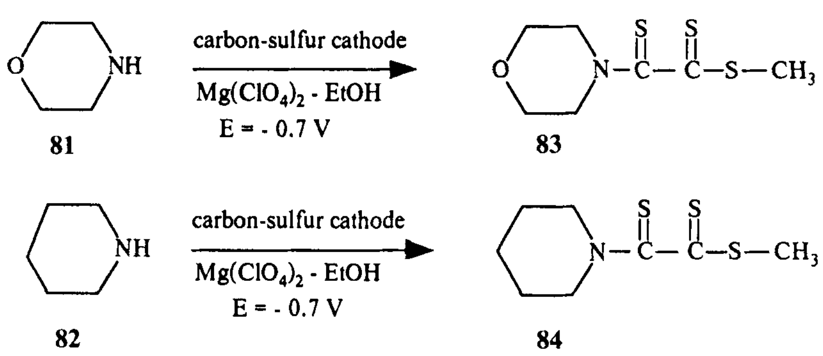
The products obtained by Rozas[13] are original because they are the only examples of the simultaneous introduction of carbon and sulfur in a substrate. Reactions of electrogenerated sulfide ions with morpholine **81** and piperidine **82** lead, respectively, to methyl 4-morpholino-α-thioxoethanedithioate **83** (yield 25–43%) and methyl 1-piperidino-α-thioxoethanedithioate **84** (yield 40–62%) only in the presence of $Mg(ClO_4)_2$ in ethanol; no reaction is observed in the presence of $NaClO_4$ in DMF.



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## 5. THE ELECTROGENERATION OF ELECTROPHILIC SPECIES

If the carbon–sulfur electrode is used as a sacrificial anode, we notice that sulfur cations $S^{2+}$ are generated, essentially $S_2{}^{2+}$ and $S^{2+}$; a high positive potential close to 2.1–2.3 V favors the formation of the most oxidized form of sulfur: $S^{2+}$.

At present our group is the only one to work in this field.

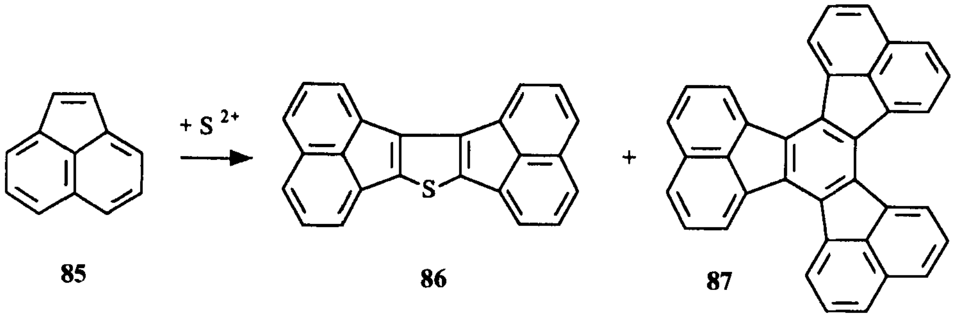
These new types of cations, never before prepared in this way, can react with suitable substrates to initiate electrophilic substitutions (with aromatics, formation of sulfides), reactions with nucleophiles (formation of trisulfides, for example), or oxidation reactions with very easily oxidizable compounds such as thiols, for example.

These electrogenerated cations are stable in solution for several days; thus, it is no problem to prepare them before they react with an organic substrate.

### *5.1. Preparation of Sulfides*

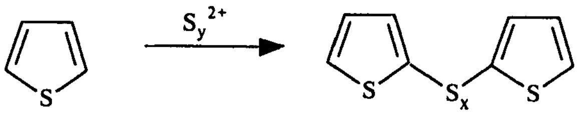
Sulfides are obtained by reaction of electrogenerated sulfur cations with aromatic hydrocarbons or aromatic compounds such as aromatic ethers, phenols, aromatic amines, and heterocycles.

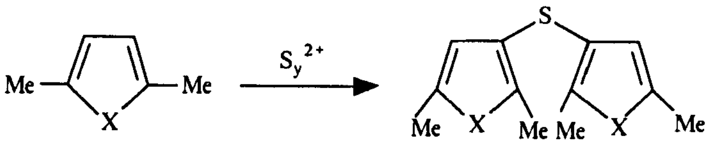
*5.1.1. Reactions with aromatic hydrocarbons* Simple aromatic hydrocarbons such as benzene and toluene do not react with electrogenerated $S_p{}^{2+}$. We have observed[24] a reaction with acenaphthylene **85**, giving essentially a thiophene **86** (70%), in addition to the trimer **87** (20%).


**85** **86** **87**

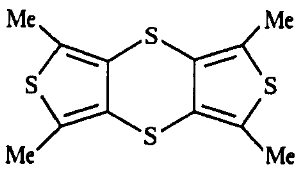
This thiophene has been prepared previously by direct reaction of sulfur with acenaphthylene at high temperatures.[25]

*5.1.2. Reactions with heterocycles* Three experiments have been carried out with thiophene **88**, 2,5-dimethylthiophene **89** (X = S), and 2,5-dimethylfuran **89** (X = O).[27] The yield is small (30%) in the first experiment and mass spectroscopy indicates a mixture of mono-, di-, tri-, and tetrasulfide **90**; a great quantity of polymers is also obtained. The yield of monosulfide **91** is almost quantitative with **89** (X = O) (92%); it is also high with **89** (X = S) (73%) and in this case the product of disubstitution **92** is also isolated (15%).


**88** **90**


X = O,S

**89** **91**


**92**

*5.1.3. Reactions with aromatic ethers* If we add a stoichiometric amount of anisole **93** to a solution of sulfur cations $S_y^{2+}$ we only obtain the sulfide, bis(2-methoxyphenyl) sulfide **95**, in a yield of 50%. The presence of an electron-donating substituent is

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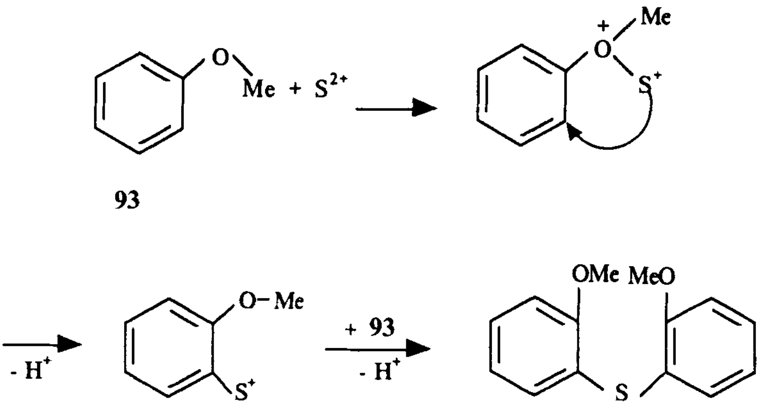
necessary for this reaction and this group appears to direct the substitution into the ortho position. This high regioselectivity is observed in acetonitrile containing tetraethylammonium perchlorate (TEAP) as the supporting electrolyte. We propose the following mechanism with formation of the intermediate cation **94**.[26]



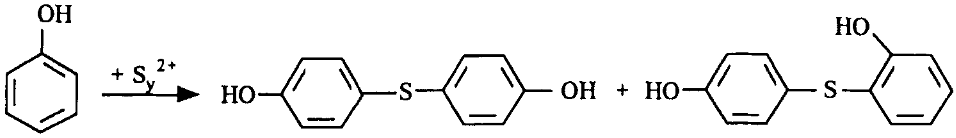
**93** **94** **95**

Additional results are described in Table 4. An internal cyclization to phenoxathiin is possible with diphenyl ether.

From 6-methoxyquinoline we isolated bis(6-methoxy-3-quinolyl) sulfide. Quite unexpectedly, the electrophilic substitution occurs in the pyridine ring.

*5.1.4. Reactions with phenols* With phenols we observe either ortho- or para-substitution.[24,27] Two factors determine this: the structure of the phenol and the composition of the reaction mixture.

Thus with phenol **96**, we have characterized two sulfides: a para-para one **97** and a para-ortho one **98**. In $CH_3CN$ with 0.1 M TEAP, we observe the exclusive formation of the first in a yield of 95%. In $CH_2Cl_2$ containing 1 M $CCl_3CO_2H$ and 0.2 M TEAP, we obtain a mixture of **97** (49%) and **98** (37%).



**96** **97** **98**

If the para-position of phenol **99** is occupied by Cl, Br, or $NO_2$, ortho-substitution is observed exclusively giving the sulfide **100**.

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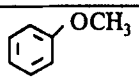
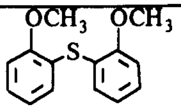
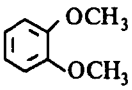
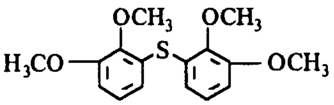
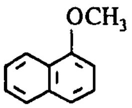
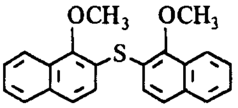
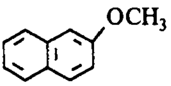
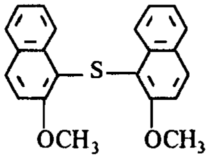
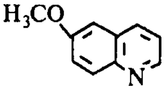
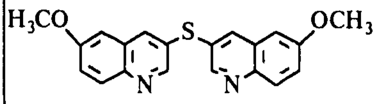
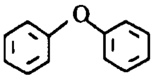
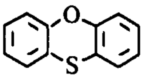
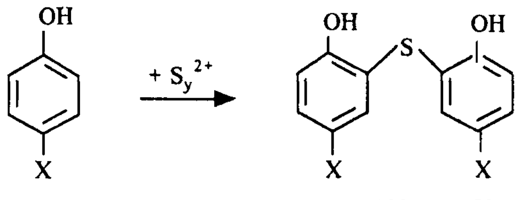
**Table 4. Sulfides from aromatic ethers**

| Substrate | Product | Yield (%) |
|---|---|---|
|  |  | 50 |
|  |  | 80 |
|  |  | 82 |
|  |  | 60 |
|  |  | 70 |
|  |  | 61 |



99

100 X = Cl (40 %)
Br (32 %)
$NO_2$ (30 %)

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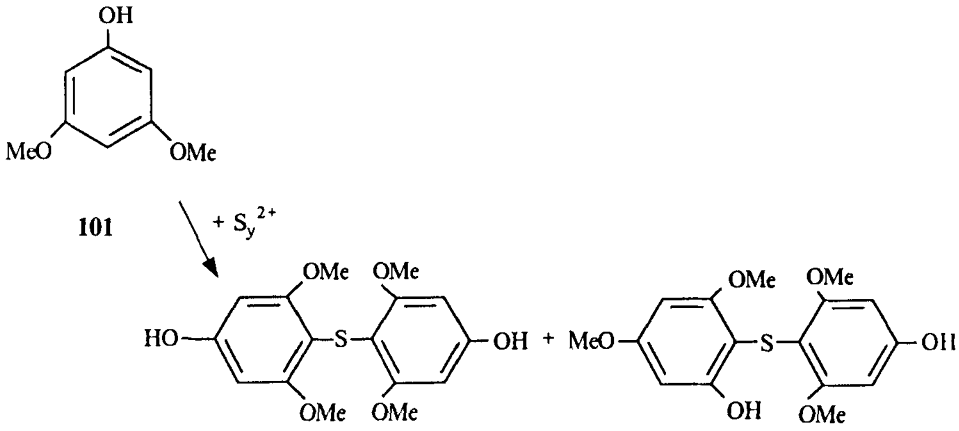
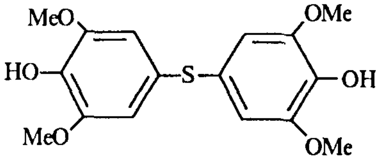
Analogous behavior is observed with 3,5-dimethoxyphenol **101**: in acetonitrile, the symmetric sulfide **102** is the sole product (yield 70%); in dichloromethane and 1 M trichloroacetic acid, we obtain a mixture of **102** (10%) and of the symmetric sulfide **103** (50%).



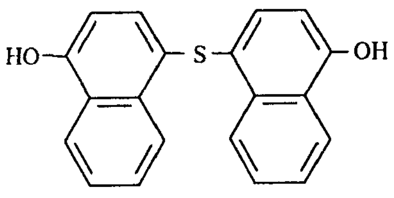
**101**

**103** **102**

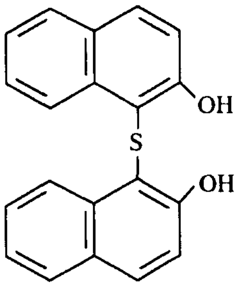
The electrophilic substitution of 2,6-dimethoxyphenol, 1-naphthol, and 2-naphthol with $S_y^{2+}$ cations has only been investigated in acetonitrile; only one sulfide is obtained in each case, bis(3,5-dimethoxy-4-hydroxyphenyl) sulfide **104** (54%), bis-(4-hydroxy-naphthyl) sulfide **105** (30%), and bis(2-hydroxyl-1-naphthyl) sulfide **106** (16%), respectively.



**104**



**105**



**106**

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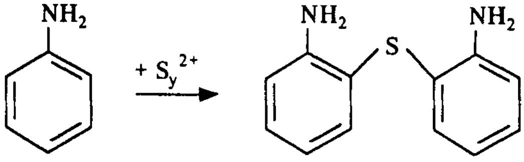
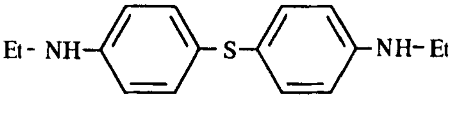
*5.1.5. Reactions with aromatic amines* In the case of primary aromatic electrophilic substitution with electrogenerated sulfur cations $S_y^{2+}$ gives small yields.[24,27] With aniline **107**, the ortho-substituted derivative **108** is observed in 16% yield.

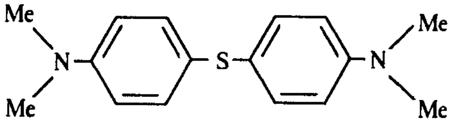


**107** **108**

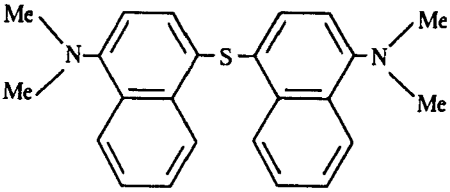
Better yields are obtained with secondary and tertiary amines and the substitution always takes place in the para-position. For example, bis[4-(*N*-ethylamino)phenyl] sulfide **109**, bis-[4-(*N*,*N*-dimethylamino)penyl] sulfide **110**, and bis[4-(*N*,*N*-dimethylamino)-1-naphthyl] sulfide **111** have obtained from *N*-ethylaniline, *N*,*N*-dimethylaniline, and *N*,*N*-dimethyl-1-naphthylamine, respectively.



**109** (70 %)



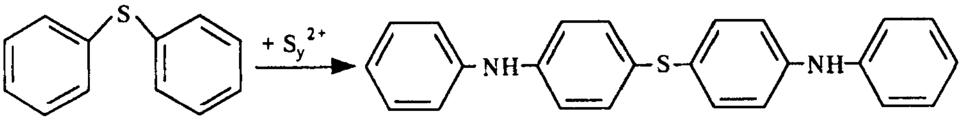
**110** (32 %)



**111** (49 %)

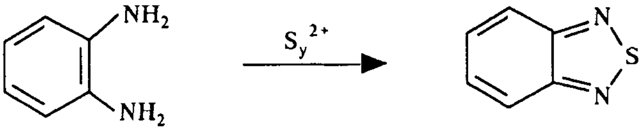
To obtain the indicated yields it is necessary to add Lewis acids ($AlCl_3$, $SnCl_4$, about one equivalent per mole of substrate) or small amounts of Fe or $FeCl_3$ considered as catalysts, during the condensation of $S_y^{2+}$ with the appropriate substrate.[24,27] Other parameters such as choice of solvent or temperature add nothing to the result.

The role of the catalyst or the Lewis acid is not universal; it seems to depend on the nature of the substrate. If the catalyst is active, para-substitution is favored. This perhaps explains why it is impossible to synthesize phenothiazine from diphenylamine **112**, since the para-substituted sulfide **113** is always isolated.



**112** **113**

However, it is possible to prepare a cyclic sulfide, 2,1,3-benzothiadiazole **115**, from *o*-phenylenediamine **114** in 22% yield.



**114**

**115**

### 5.2. *Preparation of trisulfides*

Electrogenerated cations of sulfur in dichloromethane react with thiols to give trisulfides.[28,29] The condensation works better if the thiol is added as a thiolate ion.

$$2\,RS^- + S^{2+} \longrightarrow R{-}S{-}S{-}S{-}R$$

R can be aliphatic or aromatic.

By mass spectroscopy disulfides and tetrasulfides have also been detected and the composition of the mixture can be determined by HPLC. The results are listed in Table 5.

We explain the formation of the tetrasulfide in the medium by the presence of the species $S_2^{2+}$ besides $S^{2+}$. A high working potential (2.3 V) favors the latter, a low working potential (about 1.8 V) favors the former and we observe a rise in the yield of tetrasulfide.

The disulfide results from an oxidation of the thiol or thiolate ion by $S_y^{2+}$. This oxidative role is reinforced in the presence of trichloroacetic acid, for example.

From ethanedithiol, cyclic sulfur-containing products are isolated, 1,2,3-trithiolane being the main product.

## 6. CONCLUSION

I would like to summarize the most important points of this report.

Direct introduction of sulfur via the working electrode by generation of either nucleophilic species $S_x^{2-}$ or electrophilic species $S_y^{2+}$ is a good method for the electrochemical preparation of thioorganic compounds. This method circumvents the poor solubility of sulfur in the usual organic solvents.

The electrogeneration of these species is very easy and opens interesting perspectives, which ought to be developed on an industrial scale when one considers the great importance of sulfur-containing compounds as pharmaceuticals, pesticides, etc.

A new aspect of this method is the generation of $S^{2+}$, never before prepared in this way in organic solvents. This species can react with aromatics to give sulfides by electrophilic substitution or with nucleophiles such as thiols to afford trisulfides. This method presents advantages over the classical sulfur chloride procedures which are dangerous to operate and emit noxious by-products.

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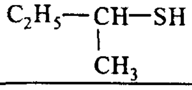
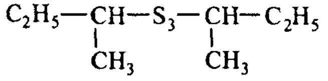
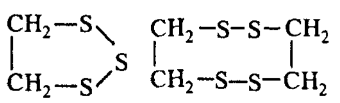
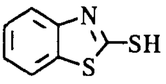
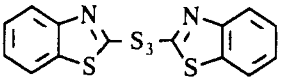
Table 5. Preparation of trisulfides from thiols

| Substrate | Main product | Yield % of trisulfide | Composition of the mixture di- | tri- | tetrasulfide |
|---|---|---|---|---|---|
| $n\text{-}C_3H_7-SH$ | $n\text{-}C_3H_7-S_3-C_3H_7\text{-}n$ | 74 | 0 | 80 | 20 |
| $n\text{-}C_4H_9-SH$ | $n\text{-}C_4H_9-S_3-C_4H_9\text{-}n$ | 56 | 11 | 64 | 25 |
|  $C_2H_5-\underset{CH_3}{CH}-SH$ |  $C_2H_5-\underset{CH_3}{CH}-S_3-\underset{CH_3}{CH}-C_2H_5$ | 53 | 24 | 67 | 9 |
| $Ph-CH_2-SH$ | $Ph-CH_2-S_3-CH_2-Ph$ | 45 | 30 | 56 | 14 |
| $Ph-SH$ | $Ph-S_3-Ph$ | 58 | 15 | 69 | 16 |
| $4\text{-}Me-C_6H_4-SH$ | $4\text{-}Me-C_6H_4-S_3-C_6H_4-Me\text{-}4$ | 68 | 5 | 80 | 15 |
| $4\text{-}MeO-C_6H_4-SH$ | $4\text{-}MeO-C_6H_4-S_3-C_6H_4-OMe\text{-}4$ | 53 | 8 | 67 | 25 |
| $4\text{-}Cl-C_6H_4-SH$ | $4\text{-}Cl-C_6H_4-S_3-C_6H_4-Cl\text{-}4$ | 12 | 60 | 17 | 23 |
| $HS-CH_2-CH_2-SH$ |  | 48 |  | 80 | 20 |
|  |  | 18 | 65 | 19 | 16 |

We have observed a high selectivity and high regioselectivity which can be modified in some cases by the choice of the medium.

The carbon-sulfur electrode is a powerful tool for the preparation of new thioorganic compounds under mild conditions and at room temperature. In our group research concerning additional substrates is in progress.

It is possible to extend this type of sacrificial electrode to other electroactive substrates such as selenium,[30] tellurium,[31] which suffer from poor solubility in organic solvents.

## ACKNOWLEDGMENTS

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