Displacement of aromatic nitro groups by anionic sulfur nucleophiles: reactivity of aryl disulfide † and thiolate ions towards dinitrobenzenes in *N*,*N*-dimethylacetamide

Julie Robert,[a] Meriem Anouti,[a] Gérard Bosser,[a] Jean-Luc Parrain[b] and Jacky Paris *,[a]
[a] *Laboratoire de Physicochimie des Interfaces et des Milieux Réactionnels, UFR Sciences et Techniques, Parc de Grandmont, 37200 Tours, France*
[b] *Laboratoire de Synthèse Organique (CNRS), Faculté des Sciences et Techniques, 2 rue de la Houssinière, 44072 Nantes, France*

Nucleophilic substitutions of 1,2- and 1,4-dinitrobenzenes (*o*DNB and *p*DNB) by thiolates ArS^- (**a**) and aryl disulfide ions ArS_2^- (**b**) [Ar = 4-methylphenyl (**1**), 4-fluorophenyl (**2**)] have been studied in dilute solutions by spectroelectrochemistry in *N*,*N*-dimethylacetamide. Compounds **1b**–**2b** are the predominant reactive species in ArS_x^- ($\bar{x} = 2$) solutions when sulfur is added to electrogenerated thiolates **1a**–**2a**. In all cases the addition of dinitrobenzenes led to the fast displacement of one of the NO_2 groups at room temperature. With thiolate ions, the stoichiometric formation of the expected unsymmetrical diaryl monosulfides $NO_2C_6H_4SAr$ was observed. Aryl disulfide ions reacted in two successive steps: (*i*) SNAr substitution affording $NO_2C_6H_4S_2Ar$; (*ii*) displacement of $NO_2C_6H_4S_x^-$ ions ($x = 1,2$) by *S*-nucleophilic attack of the S–S bond or a concurrent redox process. Reactions between $4\text{-}CH_3C_6H_4S_x^-$ ($\bar{x} = 2$) ions and *o*DNB or *p*DNB which were performed on the preparative scale confirmed the formation of mixtures of Ar_2S_2 and Ar_2S_3 symmetrical polysulfides.

In protic or dipolar aprotic solvents, nucleophilic displacement of a nitro group from nitro-activated aromatic compounds by thiolate ions has been described in several instances.[1–9] With anionic sulfur nucleophiles, the enhanced mobility of NO_2 with respect to fluorine, which is the best nucleofuge of the halogens,[10] was attributed to its high polarizability favouring its departure in the presence of highly polarizable reagents.[5,10] Substitutions (SNAr) leading to alkyl aryl sulfides, ArSR, by nitro displacement occur in rather mild conditions.[7,10] However, the synthesis of unsymmetrical diaryl monosulfides has been more limited, requiring strong activation of aromatics by several electron-withdrawing groups,[1,5] high reaction times at 25 °C,[4] or phase transfer catalysis.[11] These species, with benzene rings bearing, respectively, electron-donating and -accepting groups, were investigated as being representative of organic crystals with non-linear optical properties.[12] With regard to the preparation of unsymmetrical diaryl disulfides, only a few methods with low yields were reported, generally based on the reactions of sulfenyl reagents with arylthiolates.[13–15] In a previous paper,[16] we discussed the substitution of *ortho*- or *para*-dinitroaromatics by polysulfide ions S_6^{2-} ($\rightleftharpoons S_3^{\bullet -}$) in *N*,*N*-dimethylacetamide (DMA). The fast displacement of one of the NO_2 groups at 20 °C led to nitroaryl mono- and di-sulfide ions in equilibrium. 2-Nitrophenyl disulfide ions slowly reacted in turn with *o*-dinitrobenzene, producing bis(2-nitrophenyl) disulfide. Stable aryl disulfide ions, ArS_2^-, were obtained directly as main products from the reaction in DMA of sulfur on arylthiolates ArS^-.[17] One might expect that their substitution on dinitroaromatics would provide access to unsymmetrical nitrophenyl aryl disulfides.

We report here on the reactivities of ArS^- (**a**) and ArS_2^- (**b**) ions [Ar = 4-methylphenyl (**1**) and 4-fluorophenyl (**2**)] towards 1,4- and 1,2-dinitrobenzenes (*p*DNB and *o*DNB), studied in dilute solutions in DMA by UV–VIS absorption spectrophotometry coupled with classic voltammetry. The processes were confirmed at the preparative scale on the example Ar = 4-methylphenyl.

Results and discussion

Generation and characteristics of ArS^- and ArS_x^- ($\bar{x} = 2$) ions in DMA

Thiolate ions, ArS^- (**1a**, **2a**), were generated in low concentrations ($[ArS^-]_0 < 3.5 \times 10^{-3}$ mol dm^{-3}) by electrolysis at controlled potential on a gold electrode of thiols which are reduced according to the totally irreversible process (1) in the absence of hydrogen.[18]

$$ArSH + e^- \longrightarrow ArS^- + \tfrac{1}{2}H_2 \qquad (1)$$

The electrochemical and spectrophotomeric characteristics of ArS^- and Ar_2S_2 (**c**) species (Table 1) were determined from the evolutions of voltammograms and spectra during the electrooxidation of thiolate ions on their well defined oxidation wave [eqn. (2)].

$$2ArS^- - 2e^- \rightleftharpoons Ar_2S_2 \qquad (2)$$

We previously reported on the coloured 2-nitro- and 4-nitrophenyl disulfide ions in DMA stemming from the reaction (3) of sulfur on $NO_2C_6H_4S^-$ ions.[19]

$$ArS^- + \tfrac{1}{8}S_8 \rightleftharpoons ArS_2^- \qquad (3)$$

$$K_1 = [ArS_2^-][ArS^-]^{-1}[S_8]^{-1/8} \qquad (4)$$

$$K_1(oNO_2) = 14.0\ (\text{mol dm}^{-3})^{-1/8}$$

$$K_1(pNO_2) = 0.53\ (\text{mol dm}^{-3})^{-1/8}$$

These species [parameters in Table 1, constant $K_1(oNO_2)$, $K_1(pNO_2)$] will be involved in the reactions described below.

When arylthiolates like **1a** and **2a** lack an electron-

---

† Aryl disulfide ion = aryldisulfanide.

Table 1 Electrochemical and spectrophotometric characteristics of thiolate ions, disulfide ions and diaryl disulfides in *N*,*N*-dimethylacetamide. $E_{1/2}$ at a rotating gold-disc electrode *vs.* reference Ag/AgCl, KCl sat. in DMA/N(Et)$_4$ClO$_4$ 0.1 mol dm^{-3}

	ArS^-			ArS_2^-			Ar_2S_2		
Ar	λ_{max}/nm	ε_{max}/dm^3 mol^{-1} cm^{-1}	$E_{1/2}$(O)/V	λ_{max}/nm	ε_{max}/dm^3 mol^{-1} cm^{-1}	$E_{1/2}$(O)/V	λ_{max}/nm	ε_{max}/dm^3 mol^{-1} cm^{-1}	$E_{1/2}$(R)/V
4-$CH_3C_6H_4$	308	21 200	+0.10	≈318	—	−0.10	260	6 500	−1.25
4-FC_6H_4	304	15 600	+0.13	≈330	—	−0.08	260	5 000	−1.20
2-$NO_2C_6H_4$[a,b]	502	1 860	+0.55	681	5 200	+0.05	362	8 500	−0.67
4-$NO_2C_6H_4$[a]	507	30 000	+0.67	600[c]	11 000	+0.27	322	21 400	−0.62

[a] Values previously determined.[17] [b] At 502 nm, $\varepsilon(2\text{-}NO_2C_6H_4S_2^-) = 500$; this value was used for calculations of $NO_2C_6H_4S^-/NO_2C_6H_4S_2^-$ concentrations. [c] Shoulder.

Table 2 Composition (mol%) of $[ArS^-]_0 + [S_8]_0 = \frac{1}{8}[ArS^-]_0$ solutions calculated with K_1(Ar) and K_2(Ar) constants

Ar	ArS^- (%)	ArS_2^- (%)	ArS_3^- (%)
4-FC_6H_4	19.1	61.8	19.1
4-$CH_3C_6H_4$	28.4	43.2	28.4

withdrawing group on the aromatic ring, ArS_2^- ions whose formation is more quantitative, react in turn with sulfur, affording ArS_3^- ions[17] [eqn. (5)].

$$ArS_2^- + \tfrac{1}{8}S_8 \rightleftharpoons ArS_3^- \quad (5)$$

$$K_2 = [ArS_3^-][ArS_2^-]^{-1}[S_8]^{-1/8} \quad (6)$$

ArS_x^- ions further oxidize into Ar_2S_2 and $S_5^{\bullet -}$ ions[17] which are detected by their absorption at 617 nm and their oxidation wave ($E_{1/2} = -0.20$ V *vs.* ref.) [eqn. (7)].

$$2ArS_3^- + \tfrac{1}{4}S_8 \longrightarrow Ar_2S_2 + 2S_3^{\bullet -} \quad (7)$$

The values of the constants K_1 and K_2 are essential in order to know an accurate composition for the **1b** and **2b** solutions noted ArS_x^- ($\bar{x} = 2$). They were obtained by addition of sulfur to coloured solutions of ArS^- ions in the presence of 2-$NO_2C_6H_4S^-$ ions ($\lambda_{max} = 502$ nm), from the evolution of VIS spectra as shown in the example of Fig. 1 (Ar = 4-$CH_3C_6H_4$). The competing formation of ArS_2^- and ArS_3^- ions with that of *o*-$NO_2C_6H_4S_2^-$ species only ($\lambda_{max} = 681$ nm) lead to equilibria (8) and (9).

$$NO_2C_6H_4S^- + ArS_2^- \rightleftharpoons NO_2C_6H_4S_2^- + ArS^- \quad (8)$$

$$NO_2C_6H_4S^- + ArS_3^- \rightleftharpoons NO_2C_6H_4S_2^- + ArS_2^- \quad (9)$$

Constants K_1(Ar) and K_2(Ar) were calculated (±15%) from conservation equations in ArS^- and $NO_2C_6H_4S^-$, K_1(*o*NO$_2$) and experimental values of A_{681} giving $[NO_2C_6H_4S_2^-]$ at equilibrium.

$$K_1(F) = 42\ (mol\ dm^{-3})^{-1/8};\ K_2(F) = 4\ (mol\ dm^{-3})^{-1/8}$$

$$K_1(CH_3) = 60\ (mol\ dm^{-3})^{-1/8};\ K_2(CH_3) = 26\ (mol\ dm^{-3})^{-1/8}$$

The affinity of ArS^- and ArS_2^- ions for sulfur is analogous to that of a number of anions (CN^-, SO_3^{2-}, *etc.*); this was termed '*S*-nucleophilicity' or 'thiophilicity' by Karasch and Parker.[20] The sequence $K_1(CH_3) > K_1(F) > K_1(oNO_2) > K_1(pNO_2)$ is in agreement with the expected reactivities of the thiolate ions from the electronic effects as a function of the nature of Ar. The ratios K_1/K_2 imply a rather large disproportionation of ArS_2^- ions [eqn. (10)].

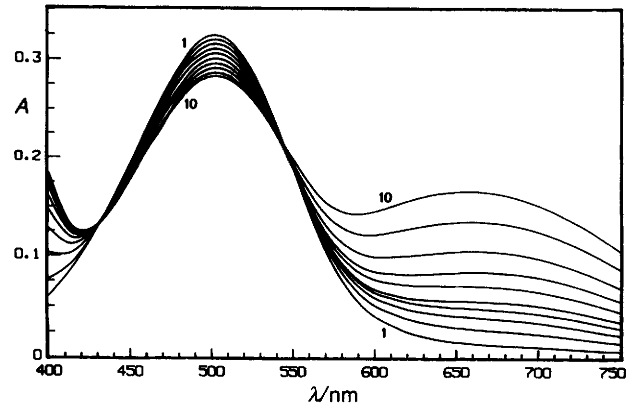

Fig. 1 Evolution of VIS absorption spectra during the addition of sulfur to a solution $c_0 = [CH_3C_6H_4S^-]_0 + [o\text{-}NO_2C_6H_4S^-]_0 = 2.45 \times 10^{-3} + 1.63 \times 10^{-3}$ mol dm^{-3}. $8[S_8]/c_0$ = 0 (1); 0.07 (2); 0.18 (3); 0.29 (4); 0.39 (5); 0.50 (6); 0.60 (7); 0.74 (8); 0.88 (9); 1.0 (10). Thickness of the cell 0.1 cm.

$$2ArS_2^- \rightleftharpoons + ArS^- + ArS_3^- \quad (10)$$

The compositions (mol%) of the solutions $[ArS^-]_0$ added with sulfur $[S_8]_0 = \frac{1}{8}[ArS^-]_0$ are reported in Table 2.

Reactivity of arylthiolate ions with 1,2- and 1,4-dinitrobenzenes

The reactions between *o*DNB and **1a**, *p*DNB and **1a**, **2a** or benzenethiolate ions, PhS$^-$ [$\lambda_{max} = 310$ nm, ε_{max} = 21 800 dm^3 mol^{-1} cm^{-1}; $E_{1/2}$(O) = +0.16 V *vs.* ref.], were fast and quantitative under our experimental conditions (T = 18–20 °C), according to eqn. (11).

$$C_6H_4(NO_2)_2 + ArS^- \xrightarrow{k_1} NO_2C_6H_4SAr + NO_2^- \quad (11)$$

As an example, Figs. 2 and 3 show the evolution of the UV–VIS spectra and voltammograms when a concentrated solution of *p*DNB was progressively added to a solution $[PhS^-]_0 = 1.15 \times 10^{-3}$ mol dm^{-3}. The maximal absorbance, A_{310}, of PhS$^-$ ions decreased while the band of $NO_2C_6H_4SPh$ increased ($\lambda_{max} = 340$ nm) with the occurrence of an isosbestic point at 324 nm. At the same time, the oxidation wave of PhS$^-$ ions ($E_{1/2} = +0.16$ V) decreased to the benefit of the monoelectronic reduction wave[21] of the nitrophenyl aryl sulfide ($E_{1/2} = -0.76$ V). The absorbance and the reduction currents of this product were the same as those of commercial samples of 4-nitrophenyl phenyl sulfide at equal concentrations.

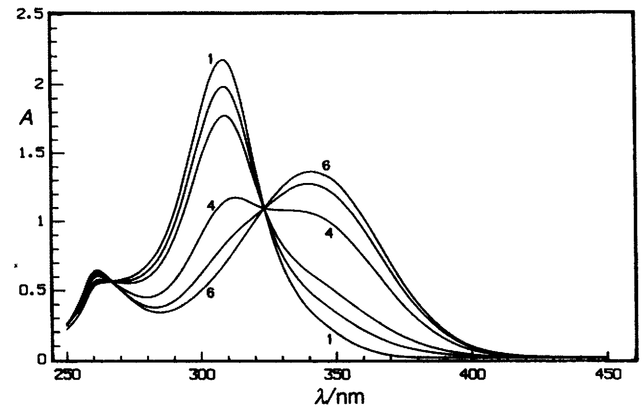

Fig. 2 Evolution of UV–VIS spectra during the addition of *p*DNB to a solution of benzenethiolate ions $[PhS^-]_0 = 1.15 \times 10^{-3}$ mol dm^{-3}. $[DNB]/[PhS^-]_0$ = 0 (1); 0.12 (2); 0.25 (3); 0.45 (4); 0.62 (5); 0.87 (6); 1.0 (7).

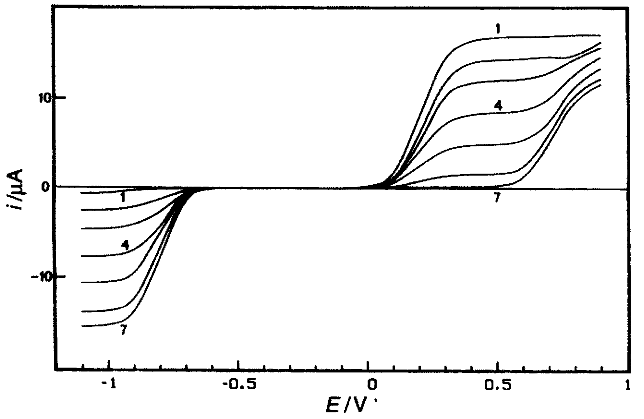

Fig. 3 Evolution of voltammograms during the reaction of *p*DNB with benzenethiolate ions. Same conditions as for Fig. 2. Rotating gold-disc electrode Ω = 1000 rev min^{-1}, diameter = 2 mm; *E vs.* reference Ag/AgCl, KCl sat. in DMA/$N(Et)_4ClO_4$ 0.1 mol dm^{-3}.

As in other aprotic solvents,[22] NO_2^- ions coming from the substitutions were detected by the growth of their oxidation wave ($E_{1/2} \approx 0.65$ V) [eqn. (12)].

$$2NO_2^- - e^- \longrightarrow NO_3^- + NO \qquad (12)$$

NO_2^- concentrations can be estimated after calibrating with a solution of $NaNO_2$ in DMA. At the end of reaction (11), dinitrobenzenes in excess were observed by their first monoelectronic reduction wave[23] and by the addition of their own absorptions on spectra[16] [*p*DNB = $E_{1/2}(R) = -0.45$ V; $\lambda_{max} = 262$ nm; $\varepsilon_{max} = 12\,700$ dm^3 mol^{-1} cm^{-1}; *o*DNB = $E_{1/2}(R) = -0.62$ V; $\lambda_{max} = 262$ nm; $\varepsilon_{max} = 5900$ dm^3 mol^{-1} cm^{-1}]. The experimental characteristics of nitrophenyl aryl monosulfides are reported in Table 3. These results were confirmed by typical synthesis of 4-nitrophenyl and 2-nitrophenyl 4-methylphenyl sulfides $NO_2C_6H_4SC_6H_4CH_3$ (see Experimental section). The reactions were performed between thiolate ions **1a** which were electrogenerated from thiocresol ($\approx$1 g) and *p*DNB or *o*DNB. Nucleophilic displacements of the NO_2 group gave the nitrophenyl sulfides at room temperature in good crude yields ($\geqslant$85%).

Reactivity of ArS_x^- (x = 2, Ar = 1, 2) solutions with 1,2- and 1,4-dinitrobenzenes

Aryl disulfide ions **1b** and **2b** are predominant in ArS_x^-($\bar{x}$ = 2) solutions (Table 2). According to the Edwards–Davis[24] approach, the nucleophilicity of ArS_x^- anions correlates with their reducing and basic properties. For polysulfide ions S_x^{2-} (x = 4, 6, 8), these characteristics decrease upon lengthening the sulfur chain.[25] However, ArS_2^- is a better nucleophilic agent towards alkyl halides than the corresponding thiolates.[26] This enhanced reactivity was usually explained by the 'α-effect' observed when unshared electron pairs lie on an atom adjacent to the nucleophilic centre[27] (ClO^-, RO_2^-, *etc.*). In that connection it should be noticed that ArS_2^- ions oxidize into Ar_2S_2 faster than ArS^- species,[17] according to the electrocatalytic process (3) + (13) [see $E_{1/2}$(O) in Table 1].

$$ArS^- + \tfrac{1}{8}S_8 \longrightarrow ArS_2^- \qquad (3)$$

$$ArS_2^- - e^- \longrightarrow \tfrac{1}{2}Ar_2S_2 + \tfrac{1}{8}S_8 \qquad (13)$$

Consequently, high proportions of unsymmetrical disulfides $NO_2C_6H_4S_2Ar$ could be expected in mixtures resulting from substitutions of ArS_x^-($\bar{x}$ = 2) species on dinitrobenzenes. Surprisingly, the additions of *o*DNB or *p*DNB to these solutions immediately lead to the appearance of the red colours of $NO_2C_6H_4S^-/NO_2C_6H_4S_2^-$ ions which are generated in great quantities, as will be shown below on the spectra.

A mechanism consistent with this observation implies the initial SNAr attack (14) of ArS_2^- ions on DNB.

$$C_6H_4(NO_2)_2 + ArS_2^- \xrightarrow{k_2} NO_2C_6H_4S_2Ar + NO_2^- \qquad (14)$$

Reactions involving ionic scission of the sulfur–sulfur bond of unsymmetrical disulfides RSSR′ by many nucleophilic species Y^- [reaction (15)] have been extensively reviewed.[28]

$$RSSR' + Y^- \rightleftharpoons RSY + R'S^- \qquad (15)$$

With $Y^- = R''S^-$, disulfide interchanges [reaction (16)] may occur, the more stabilized thiolate ions $R'S^-$ being displaced. Eqn. (16) is analogous to a redox reaction. The reactivity of

$$RSSR' + R''S^- \longrightarrow RSSR'' + R'S^- \qquad (16)$$

ArS_2^- ions on $NO_2C_6H_4S_2Ar$ can be conceived from two competing pathways: (i) thiophilic substitution (17) of ArS_2 ions releasing the thiolate $NO_2C_6H_4S^-$;

$$NO_2C_6H_4S_2Ar + ArS_2^- \rightleftharpoons NO_2C_6H_4S^- + Ar_2S_3 \quad (17)$$

(ii) redox reaction between the two systems (13) and (18).

$$2ArS_2^- - 2e^- \rightleftharpoons Ar_2S_2 + \tfrac{1}{4}S_8 \qquad (13)$$

$$NO_2C_6H_4S_2Ar + 2e^- \rightleftharpoons NO_2C_6H_4S^- + ArS^- \quad (18)$$

Sulfur coming from (13) leads to $NO_2C_6H_4S_2^-$ and ArS_3^- ions in equilibrium, with a redox process thus summarized by eqns. (19) + (9).

$$NO_2C_6H_4S_2Ar + ArS_2^- \rightleftharpoons NO_2C_6H_4S_2^- + Ar_2S_2 \quad (19)$$

$$NO_2C_6H_4S_2^- + ArS_2^- \underset{b}{\overset{f}{\rightleftharpoons}} NO_2C_6H_4S^- + ArS_3^- \quad (9)$$

Side reactions of ArS_3^- ions present in ArS_x^- solutions can be neglected because of their weaker reactivity compared to those of ArS^- and ArS_2^- species: as an example, *p*DNB was

Table 3 Spectrophotometric and electrochemical characteristics of nitrophenyl aryl monosulfides in *N*,*N*-dimethylacetamide

	Ar	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}	$E_{1/2}$(R)/V	i_R/C^a/μA dm^3 mol^{-1}
p-$NO_2C_6H_4$	4-FC_6H_4	340	13 000	−0.88	14.5
	4-$CH_3C_6H_4$	345	14 700	−0.80	15.0
	Ph	340	12 500	−0.76	14.5
o-$NO_2C_6H_4$	4-$CH_3C_6H_4$	372	3 700	−0.90	13.5

[a] $i_R/C = a$; this experimental parameter will be used below.

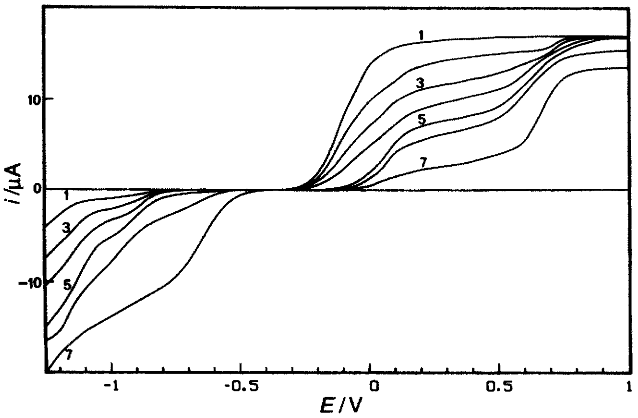

Fig. 4 Evolution of voltammograms during the addition of *o*DNB to a solution $[FC_6H_4S^-]_0 = 1.30 \times 10^{-3}$ mol dm^{-3} + $8[S_8]_0 = 1.32 \times 10^{-3}$ mol dm^{-3}. *o*DNB/$[ArS^-]_0$ = 0 (1); 0.14 (2); 0.28 (3); 0.42 (4); 0.56 (5); 0.66 (6); 0.89 (7).

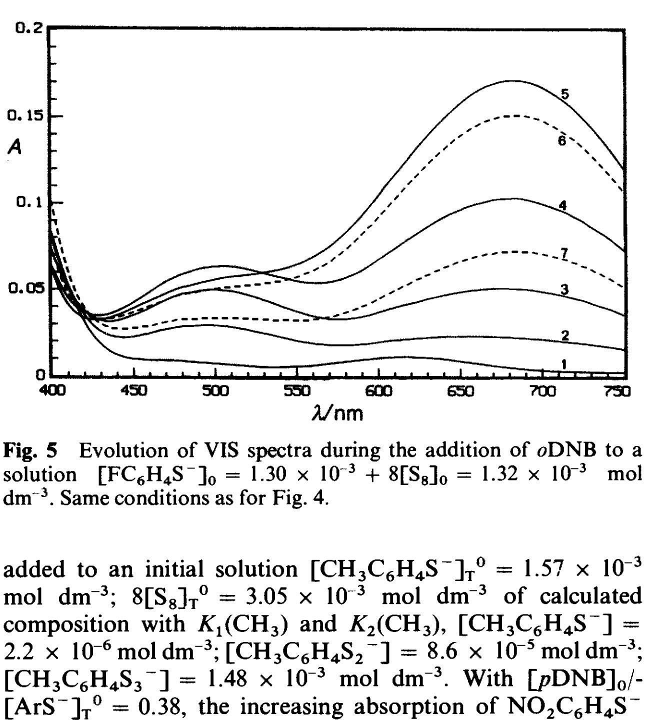

Fig. 5 Evolution of VIS spectra during the addition of *o*DNB to a solution $[FC_6H_4S^-]_0 = 1.30 \times 10^{-3}$ + $8[S_8]_0 = 1.32 \times 10^{-3}$ mol dm^{-3}. Same conditions as for Fig. 4.

added to an initial solution $[CH_3C_6H_4S^-]_T{}^0 = 1.57 \times 10^{-3}$ mol dm^{-3}; $8[S_8]_T{}^0 = 3.05 \times 10^{-3}$ mol dm^{-3} of calculated composition with $K_1(CH_3)$ and $K_2(CH_3)$, $[CH_3C_6H_4S^-] = 2.2 \times 10^{-6}$ mol dm^{-3}; $[CH_3C_6H_4S_2^-] = 8.6 \times 10^{-5}$ mol dm^{-3}; $[CH_3C_6H_4S_3^-] = 1.48 \times 10^{-3}$ mol dm^{-3}. With $[p\mathrm{DNB}]_0/[ArS^-]_T{}^0 = 0.38$, the increasing absorption of $NO_2C_6H_4S^-$ ions at 507 nm reached equilibrium after about 15 min. So reaction (14) of residual ArS_2^- ions rather than that of ArS_3^- species probably points to the determining step of the substitution, the rate of which is lowered in the presence of excess sulfur.

The changes in voltammograms and spectra agree with the initial SNAr reaction (14) of ArS_2^- ions on DNB and the subsequent displacements (17) and (19) of $NO_2C_6H_4S_x^-$ ions (x = 1, 2) as shown for the example *o*DNB + 4-$FC_6H_4S_x^-$ (Figs. 4 and 5): the oxidation current of ArS_x^- ions [$E_{1/2}$(O) = −0.08 V] decreased with the appearance of the oxidation waves for both $NO_2C_6H_4S^-/NO_2C_6H_4S_2^-$ species ($E_{1/2}$ = +0.05 V) and NO_2^- ions ($E_{1/2} \approx +0.65$ V); at the same time (curves 2–5, Fig. 4) the current increased at potentials where the S–S bond of Ar_2S_2—and probably that of Ar_2S_3—reduce ($E_{1/2} \approx -1.20$ V). The cathodic wave of $NO_2C_6H_4SAr$ ($E_{1/2}$ = −0.88 V) also developed. However the electrolysis of the solution at controlled potential ($E_{1/2} \approx -1.0$ V) exhibits a poor electric yield because of the fast reoxidation of the unstable radical-anion $NO_2C_6H_4SAr^{\bullet -}$,[21] and the visible absorption of $NO_2C_6H_4S^-$ (λ_{max} = 502 nm) increased; a part of the limiting current can thus be assigned to the two electron reduction of $NO_2C_6H_4S_2Ar$ at intermediate potentials of $(NO_2C_6H_4S)_2$ ($E_{1/2}$ = −0.67 V) and Ar_2S_2 ($E_{1/2}$ = −1.20 V) (Table 1). In spectra, the advancement of reactions (17) and (19) on the product of substitution (14) is shown by the increase of maximal absorptions of $NO_2C_6H_4S^-$ (λ_{max} = 502 nm) and $NO_2C_6H_4S_2^-$ ions (λ_{max} = 681 nm). When the consumption of ArS_2^- ions approaches completion (curve 5, Fig. 5) an enhanced formation of $NO_2C_6H_4S_2^-$ is observed at the expense of $NO_2C_6H_4S^-$, corresponding to the backward displacement of equilibrium (9). This evolution was all the more noticeable as formation of ArS_3^- ions (K_2) was favoured with respect to that of $NO_2C_6H_4S_2^-$ (K_1) in agreement with the relative values of constants $K_1(o\mathrm{NO_2}) \gg K_1(p\mathrm{NO_2})$; $K_2(CH_3) > K_1(o\mathrm{NO_2}) > K_2(F)$.

Contrary to p-$NO_2C_6H_4S_x^-$ (x = 1, 2) ions, o-$NO_2C_6H_4S^-$ and o-$NO_2C_6H_4S_2^-$ ions can react with *o*DNB according to second-order reactions (20) and (21), as was reported in a

$$C_6H_4(NO_2)_2 + o\text{-}NO_2C_6H_4S^- \xrightarrow{k_3} (o\text{-}NO_2C_6H_4)_2S + NO_2^- \quad (20)$$

$$C_6H_4(NO_2)_2 + o\text{-}NO_2C_6H_4S_2^- \xrightarrow{k_4} (o\text{-}NO_2C_6H_4S)_2 + NO_2^- \quad (21)$$

previous paper,[16] with k_3 = 0.83 and k_4 = 22 dm^3 mol^{-1} s^{-1} In this way, with further addition of *o*DNB after the consumption of ArS_x^- ions, the characteristic absorptions of $NO_2C_6H_4S^-$ (λ_{max} = 502 nm) and especially that of $NO_2C_6H_4S_2^-$ (λ_{max} = 681 nm) decreased, $(o\text{-}NO_2C_6H_4S)_2$ now being detected on the voltammograms by its reduction wave ($E_{1/2}$ = −0.67 V: curves 6–7 on Figs. 4 and 5).

In the course of the reaction *o*DNB + $CH_3C_6H_4S_x^-$ no unsymmetrical $NO_2C_6H_4S_xAr$ (x = 1, 2) compounds were detected on $i = f(E)$ recordings and all the concentrations of anionic species were easily calculated from spectrophotometric parameters (Table 1, 2-$NO_2C_6H_4S^-$, 2-$NO_2C_6H_4S_2^-$) and oxidation currents (ArS_x^-, NO_2^-). Fig. 6 illustrates their evolution as a function of y = [*o*DNB]/$[ArS_x^-]_0$: (*i*) as long as y remains lower than ≈1/3, the nearly quantitative reaction (19) and reaction (9f) entail the observed balance (22) (increasing $[NO_2C_6H_4S^-]$); (*ii*) for $0.5 > y > 0.33$, ArS_3^- ions release reactive ArS_2^- species by reaction (9b) (increasing $[NO_2C_6H_4S_2^-]$ at the expense of $[NO_2C_6H_4S^-]$); (*iii*) for the values $y > 0.5$, o-$NO_2C_6H_4S_x^-$ (x = 1, 2) slowly displace

$$C_6H_4(NO_2)_2 + 3ArS_2^- \longrightarrow o\text{-}NO_2C_6H_4S^- + ArS_3^- + Ar_2S_2 + NO_2^- \quad (22)$$

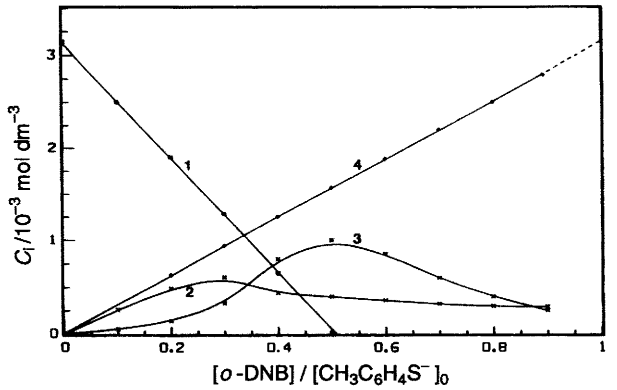

Fig. 6 Evolution of $CH_3C_6H_4S_x^-$ ($\bar{x} = 2$) (1), $NO_2C_6H_4S^-$ (2), $NO_2C_6H_4S_2^-$ (3), NO_2^- (4) concentrations during the addition of *o*DNB to a solution $[CH_3C_6H_4S^-]_0 = 3.14 \times 10^{-3} + 8[S_8]_0 = 3.17 \times 10^{-3}$ mol dm^{-3}

NO_2^- ions from *o*DNB according to eqns. (20) and (21). The reaction of *o*DNB with $CH_3C_6H_4S_2^-$ ions thus agrees with the prevailing balance (23) of eqns. [(14) + (19) + (21)].

$$2C_6H_4(NO_2)_2 + 2ArS_2^- \longrightarrow (o\text{-}NO_2C_6H_4S)_2 + Ar_2S_2 + 2NO_2^- \quad (23)$$

The proportions of molecular products $NO_2C_6H_4SAr$, $NO_2C_6H_4S_2Ar$, Ar_2S_y ($y = 2, 3$) resulting from reactions DNB + ArS_x^- ($\bar{x} = 2$, Ar = **1**, **2**) when $NO_2C_6H_4S_x^-$ concentrations reached a maximal value were calculated by solving the set of eqns. (24)–(26), i_R is the total limiting current of the

$$i_R = a[NO_2C_6H_4SAr] + 2a[NO_2C_6H_4S_2Ar] \quad (24)$$

$$[DNB]_T = [NO_2C_6H_4SAr] + [NO_2C_6H_4S_2Ar] + \sum_y [Ar_2S_y] \quad (25)$$

$$\sum_y [Ar_2S_y] = [NO_2C_6H_4S^-] + [NO_2C_6H_4S_2^-] \quad (26)$$

reductions of $NO_2C_6H_4SAr$ (monoelectronic process, $\bar{a} = i/C$ parameter ≈ 14.5 µA dm^3 mol^{-1} from average experimental values in Table 3) and $NO_2C_6H_4S_2Ar$ (two electron process, $2\bar{a}$ coefficient). The maximal absorbances of $NO_2C_6H_4S^-$ (λ_o = 502 nm, λ_p = 507 nm), and of $NO_2C_6H_4S_2^-$ (λ_o = 681 nm, λ_p = 600 nm) give $[Ar_2S_2] + [Ar_2S_3]$. $[NO_2C_6H_4S^-]$ and $[NO_2C_6H_4S_2^-]_T$ cannot be ranked respectively with $[Ar_2S_3]$ and $[Ar_2S_2]$ as expected from eqns. (17) and (19) because, except for the base *o*DNB + $CH_3C_6H_4S^-$, the simultaneous formation of $NO_2C_6H_4SAr$ and $NO_2C_6H_4S_2Ar$ observed and reaction (27) of ArS^- with $NO_2C_6H_4S_2Ar$ could also be assumed.

$$NO_2C_6H_4S_2Ar + ArS^- \longrightarrow NO_2C_6H_4S^- + Ar_2S_2 \quad (27)$$

Table 4 summarizes the compositions of the molecular mixtures linked to initial concentrations in $[ArS_x^-]_0$ and $y = [DNB]_0/[ArS^-]_T{}^0$.

*o*DNB and *p*DNB were added to $CH_3C_6H_4S_x^-$ solutions on a preparative scale at *y* values close to those of Table 4 (see Experimental section). The proportions in mixtures of products which are reported in Table 5 are in rather good agreement with those calculated in dilute solutions.

The ratios k_2/k_1 pointing out the comparative rates for SNAr reactions of ArS_2^- and ArS^- ions are probably more important with *o*DNB than *p*DNB because amounts of $NO_2C_6H_4SAr$ species remain low (Ar = FC_6H_4) or undetected (Ar = $CH_3C_6H_4$) in the first case. *S*-Nucleophilic and reductive properties of ArS_2^-/ArS^- ions ($CH_3C_6H_4$ > FC_6H_4) depicted by the compared proportions of products of reactions (17) and (19) agree with the greater basicity of 4-methylbenzenethiolate with respect to those of 4-halobenzenethiolates in water and DMSO.[29]

To conclude, a NO_2 group is readily displaced at room temperature by aryl disulfide ions and monosulfide ions from 1,2- and 1,4-dinitrobenzenes in a dipolar aprotic medium such as *N*,*N*-dimethylacetamide. Thiolates afford nitrophenyl aryl sulfides in almost quantitative yields. With aryl disulfide ions, unsymmetrical diaryl disulfides which are formed in the initial substitution further partly react with ArS_2^- species by *S*-nucleophilic and redox processes giving appreciable amounts of symmetrical diaryl di- and tri-sulfides.

Other displacements of NO_2 groups involving substitutions of aryl and alkyl disulfide ions on mononitroaromatic compounds are presently in progress in our laboratory.

Experimental

Materials and equipment

1,2- and 1,4-dinitrobenzenes, benzenethiol, 4-fluoro- and 4-methyl-benzenethiol and 4-nitrophenyl phenyl sulfide of commercial origin (purity > 98%) were used as received. The purification of *N*,*N*-dimethylacetamide and its storage after addition of $N(Et)_4ClO_4$ (0.1 mol dm^{-3}) as supporting electrolyte have been reported elsewhere.[30] Electrochemical and spectrophotometric equipment, the flow-through cell and the two-compartment preparative cell were the same as previously described.[30] All the potentials were referenced to Ag/AgCl, KCl saturated in DMA–$N(Et)_4ClO_4$ (0.1 mol dm^{-3}). The synthesized products and mixtures were analysed by ^1H (200.132 MHz) and ^{13}C NMR spectroscopy (50.323 MHz) (Brucker AC 200 spectrometer, $CDCl_3$ as solvent, chemical shifts in ppm relative to Me_4Si as internal standard, *J* values in Hz) and mass spectrometry (Hewlett-Packard 5989 A, EI 70 eV).

Synthesis

The reactions of 4-methylbenzenethiolate ions, alone or in the presence of sulfur, with *p*DNB or *o*DNB were carried out according to the same procedure at the preparative scale: 1–2 g (see later) of *p*-thiocresol ($4\text{-}MeC_6H_4SH$) were dissolved in 120 cm^3 of the catholyte $N(Et)_4ClO_4$ (0.5 mol dm^{-3} in DMA). The electroreductions of ArSH into ArS^- ions at controlled potential ($-0.9 > E > -1.3$ V) at a large gold grid electrode were performed within 2 h. When used, ArS_x^- ($\bar{x} = 2$) ions were obtained by addition of known quantities of solid sulfur into the cathode compartment at the end of the electrolysis. Sulfur dissolved by heating at 40 °C during 10 min. *o*DNB or *p*DNB were also added in the solid state in slight deficit with respect to ArS^- concentrations, or *y* values for ArS_2^- solutions (see Table 4). In the latter case the red colour of $NO_2C_6H_4S_x^-$ ($x = 1, 2$) ions immediately appeared. After heating (10 min, 40 °C), the mixtures were diluted wih 4 vol. of 3% aq. NaOH before extraction with diethyl ether in order to eliminate the residual ArSH, ionic species $[NO_2PhS_x^-$ and NO_2^- ions, $N(Et)_4ClO_4]$ and DMA which is partially soluble in ether. The organic phase was washed with water and dried (Na_2SO_4).

The crude compounds, *o*- and *p*-$NO_2C_6H_4SC_6H_4CH_3$, were recrystallized from methanol. The resulting mixtures of the reactions, $CH_3C_6H_4S_2^-$ + *o*- or *p*-DNB, were passed through a silica gel column with hexane–methylene chloride, 85:15 as eluent. In this way, for *p*DNB two fractions (A, B) of products were separated before analysis.

Reaction of 4-methylbenzenethiolate (1a) and *p*DNB. *p*-Thiocresol: 0.974 g (7.68 mmol); *p*DNB: 1.05 g, (6.25 mmol). Product: *p*-nitrophenyl *p*-tolyl sulfide (1.19 g, 77%), mp 79–80 °C (lit.,[31] 78–80 °C); δ_H 2.41 (3 H, s, Me), 7.1–7.5 (6 H, m) and 8.04 (2 H, br d, *J* 6.5); δ_C 21.2, 123.8 (2 C), 125.9 (2 C),

Table 4 Composition (mol% ± 10) of the products of reactions DNB + ArS_x^- ions ($\bar{x} = 2$) from spectroelectrochemical studies

Ar/DNB	$4\text{-}FC_6H_4/o$DNB	$4\text{-}CH_3C_6H_4/o$DNB	$4\text{-}CH_3C_6H_4/p$DNB	$4\text{-}FC_6H_4/p$DNB
$[ArS^-]_0{}^T$/mmol dm^{-3}	1.30	3.14	1.25	1.37
$8[S_8]_0$/mmol dm^{-3}	1.32	3.17	1.18	1.28
y^a	0.6(2)	0.5(0)	0.7(2)	0.8(0)
$NO_2C_6H_4SAr$ (%)	5	—	35	20
$NO_2C_6H_4S_2Ar$ (%)	20	—	15	40
ΣAr_2S_y (%)	75	100^b	50	40

^{a} y Values at maximum in absorption of $NO_2C_6H_4S_x^-$ ions. ^{b} % $Ar_2S_2 \approx 70$; % $Ar_2S_3 \approx 30$.

Table 5 Composition (mol% ± 5) of the products of reactions $4\text{-}CH_3C_6H_4S_x^-$ ($\bar{x} = 2$) + *o*- or *p*-DNB at the preparative scale

Ar/DNB	$NO_2C_6H_4SAr$ (%)	$NO_2C_6H_4S_2Ar$ (%)	Ar_2S_2 (%)	Ar_2S_3 (%)
$4\text{-}CH_3C_6H_4/o$DNB	—	—	76	23
$4\text{-}CH_3C_6H_4/p$DNB	36	9	22	33

126.7, 130.7 (2 C), 134.9 (2 C), 140.1, 145.3 and 149.3 (δ_H and δ_C in agreement with ref. 32); *m*/*z* 245 (M^+, 100%).

Reaction of 1a and *o*DNB. *p*-Thiocresol: 0.950 g (7.5 mmol); *o*DNB: 1.07 g (6.36 mmol). Product: *o*-nitrophenyl *p*-tolyl sulfide (1.03 g, 66%), mp 88–89 °C; δ_H 2.43 (3 H, s), 6.83 (1 H, dd, *J* 8, 1), 7.18 (1 H, m), 7.28 (2 H, br d, *J* 8), 7.3 (1 H, m), 7.46 (2 H, br d, *J* 8) and 8.22 (1 H, dd, *J* 8, 1.2); δ_C 21.4, 124.8, 125.7, 127.2, 128.1, 131.0 (2 C), 133.5, 136.0 (2 C), 140.1, 140.5 and 144.7; *m*/*z* 245 (M^+, 22%), 197 (13), 184 (12), 180 (100), 166 (10), 152 (11), 139 (13) and 91 (12).

Reaction of 4-methylbenzenedisulfanide (1b) ($\bar{x} = 2$) and *o*DNB. *p*-Thiocresol: 1.90 g (15.0 mmol); S_8: 0.44 g (13.7 mmol S); *o*DNB: 1.00 g (5.95 mmol). Products: from δ_H (6 H, s, Me) di-*p*-tolyl disulfide (76%); di-*p*-tolyl trisulfide (23%). Di-*p*-tolyl disulfide: δ_H 2.29 (6 H, s, Me), 7.07 (4 H, br d, *J* 8) and 7.34 (4 H, br d, *J* 8); δ_C 20.9 (2 C), 128.3 (4 C), 129.6 (4 C), 133.7 (2 C) and 137.2 (2 C); *m*/*z* 246 (M^+, 51%), 123 (100), 91 (18), 79 (39), 77 (42), 69 (16), 65 (13), 63 (14), 51 (14), 45 (76) and 39 (27). Di-*p*-tolyl trisulfide: δ_H 2.32 (6 H, s, Me), 7.07 (4 H, br d, *J* 8) and 7.38 (4 H, br d, *J* 8); δ_C 21.0 (2 C), 129.8 (4 C), 130.9 (4 C), 132.8 (2 C) and 138.5 (2 C); *m*/*z* 278 (M^+, 84%), 214 (28), 180 (11), 155 (13), 121 (10), 91 (100), 77 (20), 65 (20) and 45 (22).

Reaction of 1b ($\bar{x} = 2$) and *p*DNB. *p*-Thiocresol: 1.84 g (14.5 mmol); S_8: 0.44 g (13.7 mmol S); *p*DNB: 1.58 g (9.4 mmol). Products: fraction A 450 mg, R_f (hexane–methylene chloride: 85:15) 0.55; from δ_H (6 H, s, CH_3) di-*p*-tolyl disulfide (40%); di-*p*-tolyl trisulfide (59%). Fraction B 349 mg, R_f 0.24; from MS and δ_H (3 H, s), *p*-nitrophenyl *p*-tolyl sulfide (77%), *p*-nitrophenyl *p*-tolyl disulfide (≈20%). Preceding ^1H NMR, ^{13}C NMR and MS characteristics, and for *p*-nitrophenyl *p*-tolyl disulfide, δ_H 2.32 (3 H, s, CH_3); *m*/*z* 277 (M^+, 32%) and 123 (100).

References

1 J. F. Bunnett and W. D. Merritt, *J. Am. Chem. Soc.*, 1957, **79**, 5967.
2 J. B. Baumann, *J. Org. Chem.*, 1971, **36**, 396.
3 (*a*) J. R. Beck, *J. Org. Chem.*, 1972, **37**, 3224; (*b*) J. R. Beck, R. L. Sobczak, R. G. Suhr and J. A. Yahner, *J. Org. Chem.*, 1974, **39**, 1839.
4 N. Kornblum, L. Cheng, R. C. Kerber, M. M. Kestner, B. N. Newton, H. W. Pinnick, R. G. Smith and P. A. Wade, *J. Org. Chem.*, 1976, **41**, 1560.
5 G. Bartoli and P. E. Todesco, *Acc. Chem. Res.*, 1977, **10**, 125.
6 (*a*) J. R. Beck and J. A. Yahner, *J. Org. Chem.*, 1978, **43**, 2048; (*b*) 2052.
7 J. R. Beck, *Tetrahedron*, 1978, **34**, 2057.
8 P. Cogoli, L. Testaferri, M. Tingoli and M. Tiecco, *J. Org. Chem.*, 1979, **44**, 2636.
9 F. Benedetti, D. R. Marshall, C. J. M. Stirling and J. L. Leng, *J. Chem. Soc., Chem. Commun.*, 1982, 918.
10 F. Terrier, *Nucleophilic Aromatic Displacement* (*XI*), *series: Organic Nitro Chemistry*, VCH, Weinheim, 1991, p. 1–36 and refs. cited therein.
11 (*a*) J. T. B. Ferreira, F. Simonelli and J. V. Comasseto, *Synth. Commun.*, 1986, **16**, 1335; (*b*) W. P. Reeves, T. C. Bothwell, J. A. Rudis and J. McClusky, *Synth. Commun.*, 1982, **12**, 1071.
12 (*a*) D. W. Robinson, M. Abdel-Halim, M. Inoue, M. Kimura and D. O. Cowan, *J. Chem. Phys.*, 1989, **90**, 3427; (*b*) M. Barzoukas, D. Josse, J. Zyss, P. Gordon and J. O. Morley, *Chem. Phys.*, 1989, **139**, 359.
13 E. Campaigne, J. Tsurugi and W. W. Meyer, *J. Org. Chem.*, 1961, **26**, 2486.
14 R. Sato, S. Chiba, N. Saito, M. Sato and M. Saito, *Phosphorus Sulfur*, 1984, **19**, 205.
15 L. Benati, P. C. Montevecchi and P. Spagnolo, *Tetrahedron Lett.*, 1986, **27**, 1739.
16 G. Bosser, M. Benaïchouche, R. Coudert and J. Paris, *New J. Chem.*, 1994, **18**, 511.
17 M. Benaïchouche, G. Bosser, J. Paris, J. Auger and V. Plichon, *J. Chem. Soc., Perkin Trans. 2*, 1990, 31.
18 (*a*) F. Magno, G. Bontempelli and G. Pilloni, *J. Electroanal. Chem.*, 1971, **30**, 375; (*b*) J. R. Bradbury, A. F. Masters, A. C. McDonell, A. A. Brunette, A. M. Bond and A. G. Wedd, *J. Am. Chem. Soc.*, 1981, **103**, 1959.
19 G. Bosser, J. Paris and V. Plichon, *J. Chem. Soc., Chem. Commun.*, 1988, 720.
20 (*a*) A. J. Parker and N. Kharasch, *Chem. Rev.*, 1959, **59**, 583; (*b*) A. J. Parker and N. Kharash, *J. Am. Chem. Soc.*, 1960, **82**, 3071.
21 G. Capobianco, G. Farnia, M. G. Severin and E. Vianello, *J. Electroanal. Chem.*, 1984, **165**, 251 and refs. cited therein.
22 (*a*) G. Bontempelli, G. A. Mazochin and F. Magno, *J. Electroanal. Chem.*, 1974, **55**, 101; (*b*) A. Boughriet, J. C. Fisher, G. Leman and M. Wartel, *Bull. Soc. Chim. Fr.*, 1985, **1**, 8.
23 H. Bock and V. Lechner-Knoblauch, *Z. Naturforsch, Teil B*, 1985, **40**, 1463 and refs. cited therein.
24 (*a*) J. O. Edwards, *J. Am. Chem. Soc.*, 1956, **78**, 1819; (*b*) R. E. Davis, *Survey of Progress in Chemistry*, ed. A. Scott, vol. 2, Academic Press, New York, 1964, p. 189.
25 J. Paris and V. Plichon, *Electrochim. Acta*, 1982, **10**, 1501.
26 M. Benaïchouche, G. Bosser, J. Paris and V. Plichon, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1421.
27 J. E. Dixon and T. C. Bruice, *J. Am. Chem. Soc.*, 1972, **94**, 2052.
28 S. Oae, *Organic Chemistry of Sulfur: Structure and Mechanism*, CRC Press, Ann Arbor, 1991, pp. 119–134 and refs. cited therein.
29 F. G. Bordwell and D. L. Hughes, *J. Org. Chem.*, 1982, **47**, 3224.
30 (*a*) J. Paris and V. Plichon, *Electrochim. Acta*, 1981, **26**, 1823; (*b*) G. Bosser and J. Paris, *J. Chem. Soc., Perkin Trans. 2*, 1992, 2057.
31 K. A. Durkin, R. F. Langler and N. A. Morrison, *Can. J. Chem.*, 1988, **66**, 3070.
32 R. Chandrasekaran, S. Perumal and D. A. Wilson, *Magn. Reson. Chem.*, 1987, **25**, 1001.

Paper 5/00887E
Received 14*th February* 1995
Accepted 22*nd March* 1995