

Electrochemically Induced Rearrangement of *S,S*-Diaryl Benzene-1,2-dicarbothioates*

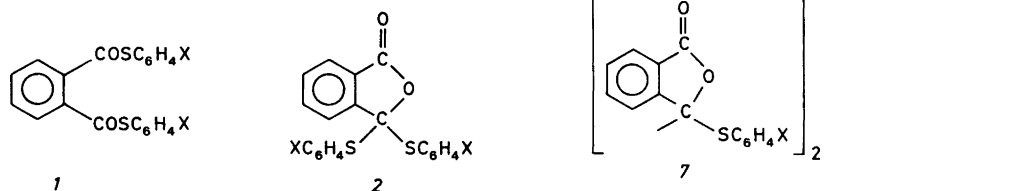
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The electrochemical reduction of some *S,S*-diaryl benzene-1,2-dicarbothioates (*1*) in aprotic medium leads to 3,3-bis-(aryltio)phthalides (*2*) in almost quantitative yield. The reaction is an example of an electrochemically induced chemical reaction, $S_{RN}1$, in which no external nucleophile is needed and for which the required amount of charge is less than $0.1 F \text{ mol}^{-1}$.

Different types of electrochemically induced reactions are known; electropolymerization² has been widely studied, Baizer *et al.*³ have investigated reactions catalyzed by electrogenerated bases, and the electrochemical initiation of $S_{RN}1$ reactions have been studied by Savéant *et al.*,^{4–7} who also treated such reactions theoretically in the case where the nucleophile is present in excess relative to the substrate.⁴ A cathodically induced sigmatropic rearrangement⁸ and an anodically promoted $2\pi + 2\pi$ -cycloaddition⁹ have been reported. A substitution of fluorine by acetoxy through anodic oxidation has been shown¹⁰ to be anodically induced.

This investigation concerns an electrochemically induced rearrangement of *S,S*-diaryl benzene-1,2-dicarbothioates (*1*) to the isomeric 3,3-bis-(*p*-X-phenylthio)phthalides (*2*).



Scheme 1. 1a, X=H; 1b, X=4-CH₃; 1c, X=4-Cl; 2a, X=H; 2b, X=4-CH₃; 2c, X=4-Cl; 6, diphenyl-disulfide.

* Organic Sulfur Compounds XLV. For Part XLIV, see Ref. 1.

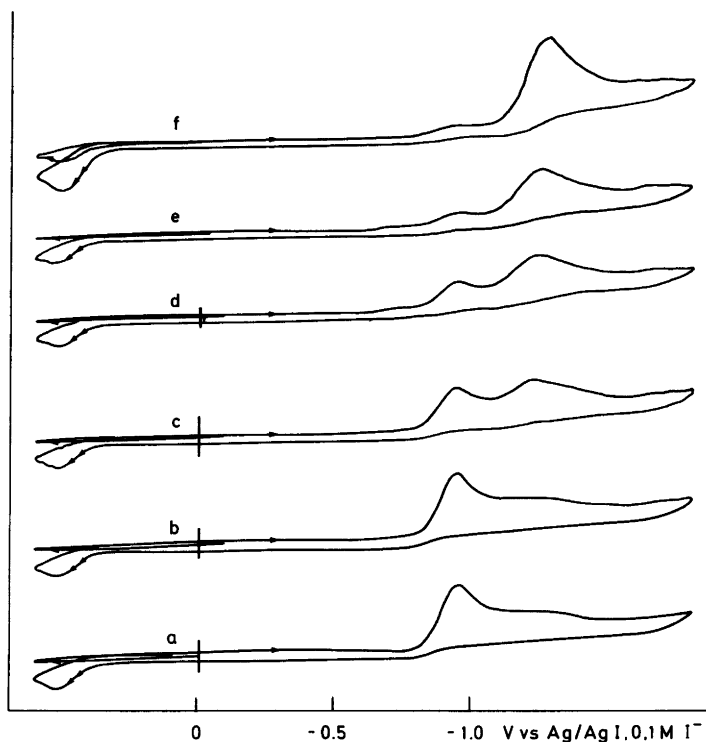
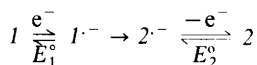


Fig. 1. CV of *S,S*-diphenyl benzene-1,2-dicarbothioate (0.01 M in DMF/0.1 M TBABF₄) at a Pt-electrode before and after a short electrolysis (20 mA for 3 min, $n=0.05$), $v=0.4$ V s⁻¹. *a* before electrolysis, *b* immediately after. *c* after 30 min, *d* after 1 h, *e* after 2 h, *f* solution *e* to which 2*a* is added.

RESULTS AND DISCUSSION

The rearrangement $1 \rightarrow 2$ is akin to the S_{RN}1 reaction and can be described in the following way (cf. Scheme 1):



The sequence can be a catalytic reaction, if $E_1^{\ominus} > E_2^{\ominus}$.

The S_{RN}1 reaction is preferentially studied in liquid ammonia in order to minimize hydrogen atom abstraction, but the rearrangement described below proceeds in *N,N*-dimethylformamide (DMF) in almost quantitative yield so this medium was used for both preparative and cyclic voltammetric experiments.

Cyclic voltammetry (CV) of *1a-c* in DMF at a hanging mercury drop (HMD) electrode shows one peak at about -1.0 V vs. Ag/AgI which is irreversible at all scan rates ($v < 1000$ Vs⁻¹). The current (i)

function ($i_p v^{-1/2}$) varies less than 20% for 0.04 Vs⁻¹ $< v < 1000$ Vs⁻¹. The cyclic voltammetric behaviour resembles that of monofunctional aromatic carbothioic *S*-esters.¹¹ Alumina could not be used for the removal of impurities as it somehow promoted the transformation of *1* to *2*.

The reaction might be followed by CV as shown in Fig. 1. Curve *a* is a CV of a 10⁻² M solution of *1a* in DMF/0.1 M TBABF₄; this scan (as well as the later scans) starts in the anodic direction before sweeping cathodic as indicated by arrows; the double arrows indicate the second anodic sweep. The solution is then electrolyzed for a short time (20 mA for 3 min., $n=0.05$ F mol⁻¹) and the electrolysis discontinued. CV was then recorded (curve *b*) and again recorded at the time intervals indicated.

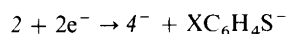
From Fig. 1 is seen how the wave of *1a* disappears and another wave at a potential 0.3 V more negative than that of *1a* appears. The last curve (*f*) is

a CV of the solution (*e*) to which is added authentic 2*a*; it is seen that the peak height of the new peak increases.

It should also be noticed that there is no anodic peak corresponding to the oxidation of the benzenethiolate anion on the first anodic sweep of any of the CV, but a peak on the second one. This means that there is no appreciable bulk concentration of benzenethiolate ion at any time.

During the reaction the catholyte is greenish but the colour fades at the end of the reaction.

Constant potential electrolysis (CPE) of 2 gives a deep green product, the carbanion (*4*⁻) in a 2-electron reaction;



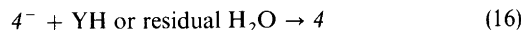
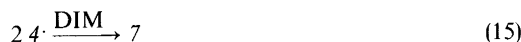
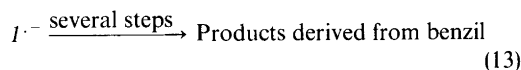
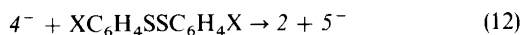
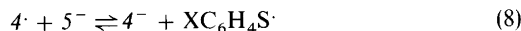
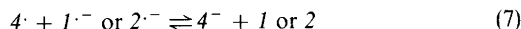
4⁻ is stable for several hours. An EPR spectrum of the catholyte after exhaustive electrolysis shows no signals even at the highest sensitivity. The isolated yield of *4* is rather low; *4* is reducible at the applied potential so a protonation of *4*⁻ to *4* during electrolysis would lead to a diminishing of the yield.

No anodic wave of *4*⁻ was observed at a Pt-electrode which is surprising in view of its very easy oxidation; *4*⁻, prepared from authentic *4* by addition of freeze-dried tetrabutylammonium hydroxide in DMF, gave no anodic wave; probably a film formation causes this behaviour.

As a treatment of *1* with the corresponding benzenethiolate in DMF causes a slow conversion of *1* to *2*, there might be both a chemical and an electrochemical reaction.

The mechanism of the "chemical" reaction could be described as a nucleophilic attack by the benzenethiolate ion on one of the carbothioate groups; the oxygen atom acquires thereby a negative charge and can thus attack the other carbothioate group; the reaction is finished by elimination of the catalyst, the benzenethiolate ion. Other strong nucleophiles should be able to initiate the reaction but the catalytic circle would rely on the benzenethiolate (*5*⁻).

For the electrochemical transformation the eqns. (1)–(16) might apply.



The reaction sequence (1)–(5) accounts for the catalytic conversion. No excess of nucleophile is needed because even if eqn. (4) is not able to compete with eqns. (6), (7), and/or (8), the radical *4*^{·-} is not "lost" but is reduced to the stable carbanion *4*⁻ from which it can be regenerated by loss of an electron. This is a significant difference between this reaction and the previously described systems,^{4–7} because the analogue of *4*⁻ in those systems is a very strong base; the difference in basicity explains why this reaction can be performed in DMF.

The termination steps (13)–(16) play only a minor role. Trace amounts of *4* are found together with the disulfide, both probably formed during work up. On irradiation, however, both *1* and *2* give *trans*-3-(3-oxo-1(3H)-isobenzofuranylidene)-1(3H)-isobenzofuranone (8) (biphthalylidene) *via* 7 (the dimer of *4*) which could be isolated in two cases.¹²

The corresponding anion radicals of the *S*-phenyl benzenecarbothioate decompose with a rate con-

stant higher than 10^4 s^{-1} .⁷ k_2 must, therefore, be significantly higher because no benzil-type compounds are detected from the preparative scale electrolysis of *1*.

Electron transfer in solution from the benzenthioate ions cannot be ruled out; such a reaction would start a catalytic circle which would give the same products. The importance of this pathway depends on the standard potential of the couple $1/1^-$ and $4/4^-$ relative to the standard potential of the couple $\text{XC}_6\text{H}_4\text{S}^{\cdot-}/\text{XC}_6\text{H}_4\text{S}^-$; none of these potentials could be determined by CV. However, addition of the corresponding disulfide to a solution of 4^- immediately decolorized the solution, and after work up, *2* was isolated in good yield, indicating that eqn. (12) can play a role. Addition of phenol to a solution containing 4^- results in a slow reaction from which a moderate yield of *4* could be isolated.

The reaction of $4a^-$ with diphenyldisulfide (*6*) is in accordance with the observation¹³ that $4a^-$ is able to transfer electrons to compounds, such as nitrobenzene, fluorenone, and *p*-diacetylbenzene which are reversibly reduced at potentials less negative than $-1.0 \text{ V vs. Ag/AgI, 0.1 M I}^-$. This means that $4a^-$ also would be able to transfer electrons to *1a* and *6*.

A similar estimation¹³ of the oxidation potential of 5^- to about $-0.5 \text{ V vs. Ag/AgI, 0.1 M I}^-$ shows that an electron transfer from *5* to *1* would be much slower than from 4^- to *1*, but probably not impossible. A more definite statement must await a knowledge of k_2 and the relevant potentials. It is thus not possible to say whether there exists two competing pathways or whether the chemical and electrochemical reactions go through the same steps.

In the ground state *1* and *2* are different; previously it has been shown that they behave comparably when they are excited, either in the mass spectrometer¹⁴ or photochemically;¹² here is found that also their electrochemical behaviour is comparable.

EXPERIMENTAL

Materials. Compounds *1a–1c* and *2a–2b* were synthesized according to literature methods.^{15,16} *S,S*-di(4-chlorophenyl)benzene-1,2-dicarbothioate (*1c*) has not been prepared previously: m.p. $155–157^\circ\text{C}$. IR (Beckman, CHCl_3): $\text{CO–S } 1685 \text{ cm}^{-1}$. Mass spectrum¹⁵ (m/e): 275 ($\text{M–C}_6\text{H}_4\text{ClS}$) 100%. Anal.: $\text{C}_{20}\text{H}_{12}\text{Cl}_2\text{O}_2\text{S}_2$: C, H. Purity of the com-

pounds was checked by GLC and HPLC analysis. For preparative purposes *N,N*-dimethylformamide (DMF) was used as received after storage over 4 Å molecular sieves, whereas freshly distilled DMF was used for CV. Tetrabutylammonium iodide (TBAI) was used as received.

Apparatus. The electroanalytical equipment^{17,18} and the equipment for preparative electrolysis²⁰ have been described elsewhere.

General procedure for reduction of 1, 2 and disulfides. The substrate (1 g) was dissolved in dry DMF (150 ml) containing TBAI (7.5 g) and reduced under nitrogen at a mercury pool (area 25 cm^2) at the peak potential. For *1* the electrolysis was stopped when $n=0.05 \text{ F mol}^{-1}$ and allowed to stand with stirring for 1 h. It was worked up by dilution of the catholyte with water and extraction of the products with diethyl ether, from which DMF and basic impurities were removed by washing with dilute acid and water. The organic phase was dried over MgSO_4 and after evaporation of the solvent, the crude product was, if necessary, separated by means of column chromatography on silica, gradually changing the eluent from light petroleum to diethyl ether. For *2* and disulfide exhaustive electrolysis was performed. The reduced compounds were used directly for further reactions (see below) which were worked up as described above.

Reduction of 1a. One g of *1a* was reduced at $-1.05 \text{ V vs. Ag/AgI}$. Isolated was *2a*^{12,21} (0.87 g, 87%), m.p. 101°C . Mass spectrum¹⁴ (m/e): (M–SPh), IR (KBr): 1760 cm^{-1} . Trace amounts of diphenyl disulfide and 3-thiophenoxyphthalide were also identified.

Reduction of 1b. One g of *1b* was reduced at $-1.15 \text{ V vs. Ag/AgI}$. Isolated was *2b*¹⁵ (0.89 g, 89%), m.p. 149°C . IR (KBr): 1780 cm^{-1} . Mass spectrum¹⁴ (m/e): 254.

Reduction of 1c. One g of *1c* was reduced at $-1.00 \text{ V vs. Ag/AgI}$. Isolated was 3,3'-bis(*p*-chlorophenylthio)phthalide (*2c*) (0.86 g, 86%), m.p. 161.8°C , mixed m.p. with *1c* $140–145^\circ\text{C}$. IR (KBr): 1760 cm^{-1} . Mass spectrum¹⁴ (m/e): 275, identical with that of *1c*. Anal.: $\text{C}_{20}\text{H}_{12}\text{Cl}_2\text{O}_2\text{S}_2$: C, H.

Reduction of 2a. One g of *2a* was reduced at $-1.50 \text{ V vs. Ag/AgI}$. $n=1.95 \text{ F mol}^{-1}$. (a) Addition of 1 g of diphenyl disulfide to the catholyte decolorized immediately the catholyte. Isolated was *2a* (0.82 g, 82%). (b) Addition of 0.5 g phenol, stirring for 2 h gave *4a*¹⁹ (0.18 g, 26%), m.p. 103°C . ¹H NMR spectrum (CDCl_3): δ 6.7 (1 H, s), 7.1–7.8 (9 H, m). IR (KBr): 1765 cm^{-1} . Mass spectrum (m/e): 242 (M^+).

Reaction of 1a with phenylthiolate. (a) One g of diphenyl disulfide was reduced at $-0.8 \text{ V vs. Ag/AgI}$. $n=2 \text{ F mol}^{-1}$. After exhaustive electrolysis 1 g of *1a* was added to the catholyte. The reaction

was followed by CV. The first CV at 0.4 Vs^{-1} was performed after 3 h, the peak of *1a* was still observable. Immediately after the CV of the catholyte it was diluted with water and worked up according to the procedure described above. Isolated as a mixture of *2a* and *1a*. (b) 2 ml of a solution, containing benzenethiolate ions, was added to a solution of 1 g of *1a* in 100 ml of deaerated DMF. The reaction vessel was sealed. The reaction was allowed to run for 16 h. Less than 10% was converted to the isomer *2a*.

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