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-(arylthiophthalides) (2) in almost quantitative yield. The reaction is an example of an electrochemically induced chemical reaction, \( S_{R,N,1} \), in which no external nucleophile is needed and for which the required amount of charge is less than 0.1 F mol\(^{-1}\).

Different types of electrochemically induced reactions are known; electropolymerization\( ^2 \) has been widely studied, Baizer et al.\( ^3 \) have investigated reactions catalyzed by electrogenerated bases, and the electrochemical initiation of \( S_{R,N,1} \) 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 rearrangement\( ^8 \) and an anodically promoted \( 2\pi + 2\pi \)-cycloaddition\( ^9 \) have been reported. A substitution of fluorine by acetoxy through anodic oxidation has been shown\( ^10 \) 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-\( \text{(p-X-phenylthio)} \)phthalides (2).

\[ \text{Scheme 1. 1a, X=H; 1b, X=4-CH}_3; 1c, X=4-Cl; 2a, X=H; 2b, X=4-CH}_3; 2c, X=4-Cl; 6, diphenyl-disulfide. \]

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

0302-4369/80/060403-05$02.50
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Fig. 1. CV of S,S-diphenyl benzene-1,2-dicarboxylate (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 2a is added.

RESULTS AND DISCUSSION

The rearrangement 1 → 2 is akin to the S₅N₁ reaction and can be described in the following way (cf. Scheme 1):

\[ \text{L} \stackrel{E_1^-}{\rightarrow} \text{L}^- \stackrel{E_2^-}{\rightarrow} 2 \]

The sequence can be a catalytic reaction, if \( E_1^- > E_2^- \).

The S₅N₁ 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) (v < 1000 V s⁻¹). The current (i) function (i,v⁻¹) varies less than 20 % for 0.04 V s⁻¹ < v < 1000 V s⁻¹. The cyclic voltammetric behaviour resembles that of monofunctional aromatic carboxylic S-esters. 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
2a; 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 benzene-
thiolate 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 concentra-
tion 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:

$$2 + 2e^- \rightarrow 4^- + XC_6H_4S^-$$

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 addi-
tion 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 benzene-
thiolate (5⁻).

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

$$I + e^- \rightarrow I^-$$  \hspace{1cm} (1)

$$I^- \rightarrow k_2 3^-$$  \hspace{1cm} (2)


Rearrangement of Dithiolphthalates

$$3^- \rightarrow k_2 4^+ + 5^-$$  \hspace{1cm} (3)

$$4^+ + 5^- \rightarrow 2^-$$  \hspace{1cm} (4)

$$2^- + 1 \rightarrow 2 + 1^-$$  \hspace{1cm} (5)

$$4^+ + e^- \rightarrow 4^-$$  \hspace{1cm} (6)

$$4^+ + 1^- \rightarrow 2^-$$  \hspace{1cm} (7)

$$4^+ + 5^- \rightarrow 4^- + XC_6H_4S^-$$  \hspace{1cm} (8)

$$4^- + XC_6H_4S^- \rightarrow 2^-$$  \hspace{1cm} (9)

$$2 XC_6H_4S^- \rightarrow XC_6H_4SCSC_6H_4X$$  \hspace{1cm} (10)

$$4^+ + XC_6H_4S^- \rightarrow 2$$  \hspace{1cm} (11)

$$4^- + XC_6H_4SCSC_6H_4X \rightarrow 2 + 5^-$$  \hspace{1cm} (12)

$$\xrightarrow{\text{several steps}} \text{Products derived from benzil}$$

$$4^+ + YH \rightarrow 6$$  \hspace{1cm} (13)

$$\xrightarrow{\text{DIM}} 7$$  \hspace{1cm} (14)

$$4^- + YH \rightarrow \text{residual } H_2O \rightarrow 4$$  \hspace{1cm} (16)

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⁻⁻⁻⁻ 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 \textit{trans}-3-(3-oxo-1(3H)-isobenzofuranyliden)-
1(3H)-isobenzofuranone (8) (biphtalhydridine) 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 10⁴ s⁻¹, k₂ 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 benzene- thiolate 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 XC₅H₄S/ XC₅H₄S⁻: none of these potentials could be determined by CV. However, addition of the corresponding disulfide to a solution of 4⁻ immediately decolourized 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 diphenyl disulfide (6) is in accordance with the observation that 4a⁻ is able to transfer electrons to compounds, such as nitrobenzene, fluorenone, and p-diacylbenzene which are reversibly reduced at potentials less negative than −1.0 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 estimation of the oxidative potential of 5⁻ to about −0.5 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 k₂ 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 spectrometer or photochemically; here is found that also their electrochemical behaviour is comparable.

**EXPERIMENTAL**

**Materials.** Compounds 1a–1c and 2a–2b were synthesized according to literature methods. S,S-dil(4-chlorophenyl)benzene-1,2-dicarbothioate (1c) has not been prepared previously: m.p. 155–157 °C. IR (Beckman, CHCl₃): CO⁻S 1685 cm⁻¹. Mass spectrum (m/e): 275 (M−C₆H₄ClIS) 100 %. Anal.: C₂₀H₁₂Cl₂O₂S₂: C, H. Purity of the compounds 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 and the equipment for preparative electrolysis 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 cm²) at the peak potential. For 1 the electrolysis was stopped when n=0.05 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 diethylether, from which DMF and basic impurities were removed by washing with dilute acid and water. The organic phase was dried over MgSO₄ 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 diethylether. 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 V vs. Ag/AgI. Isolated was 2a (0.87 g, 87 %), m.p. 101 °C. Mass spectrum (m/e): 275 (M−SPh), IR (KBr): 1760 cm⁻¹. Trace amounts of diphenyl disulfide and 3-thiophenoxyphthaldial were also identified.

**Reduction of 1b.** One g of 1b was reduced at −1.15 V vs. Ag/AgI. Isolated was 2b (0.98 g, 89 %), m.p. 149 °C. IR (KBr): 1780 cm⁻¹. Mass spectrum (m/e): 275, identical with that of 1c.

**Reduction of 1c.** One g of 1c was reduced at −1.00 V vs. Ag/AgI. Isolated was 3,3′-bis(p-chlorophenyl)-thio)phthalide (2c) (0.86 g, 86 %), m.p. 161.8 °C, mixed m.p. with 1c 140–145 °C. IR (KBr): 1760 cm⁻¹. Mass spectrum (m/e): 275, identical with that of 1c.

**Reduction of 2a.** One g of 2a was reduced at −1.50 V vs. Ag/AgI, n=1.95 F mol⁻¹. (a) Addition of 1 g of diphenyl disulfide to the catholyte decolourized immediately the catholyte. Isolated was 2a (0.82 g, 82 %). (b) Addition of 0.5 g phenol, stirring for 2 h gave 4a (0.19 g, 26 %), m.p. 103 °C. ¹H NMR spectrum (CDCl₃): 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 V vs. Ag/AgI, n=2 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 V s⁻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.

Acknowledgements. We thank Professor J.-M. Savéant, Paris, for the equipment he has placed at our disposal. This work was supported by a grant from the Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg, Germany, the Gesellschaft von Freunden der Technischen Universität Berlin, Germany, and from Det naturvidenskabelige Fakultet, Aarhus Universitet, Denmark. K. P. thanks the University of Aarhus, Denmark, for the award of a visiting lectureship at its Department of Chemistry during September 1978 when the work was started.

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Received December 19, 1979.