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# The Electrochemical Reduction and a Novel Base-Catalyzed Rearrangement of 2,5-Diaryl-1,4-dithiins

Mogens Larsen Andersen,† Merete Folmer Nielsen and Ole Hammerich*

Department of Chemistry, University of Copenhagen, Symbion Science Park, Fruebjergvej 3, DK-2100 Copenhagen, Denmark

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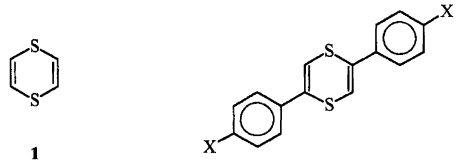
The electrochemical reduction of 2,5-diphenyl-1,4-dithiin (DPD) and three derivatives carrying chloro (BCD), bromo (BBD) or nitro (BND) substituents in the *p*-position of both phenyl rings is reported.

The results obtained by cyclic voltammetry in MeCN indicated that DPD is reduced in a two-electron process to a dihydro derivative. However, analysis by constant current coulometry in the presence of acetic acid showed that the apparent number of electrons transferred increased with increasing concentration of the acid with only little consumption of substrate, most likely due to catalytic reduction of the acid (protons). The two halogen derivatives, BCD and BBD, initially underwent cleavage of the C–X bonds (X = Cl or Br) resulting in the formation of DPD. The nitro derivative, BND, was reduced to a dianion stable on the voltammetric timescale in two one-electron transfers separated by 55–60 mV.

During constant current coulometry in the absence of acid DPD, BCD and BBD rearranged to the corresponding 2,6-diaryl-1,4-dithiafulvenes in 0.1–0.2 *F* processes. Evidence is presented that these rearrangements do not involve the radical anions of the 1,4-dithiins, but, rather, are catalyzed by base generated during the electrolysis. The rearrangements were shown to take place also by addition of $Bu_4NOH$ to MeCN solutions of the dithiins with yields ranging from 38% (DPD) to 93% (BBD). For DPD, BCD and BBD a mechanism including deprotonation of the 1,4-dithiin followed by ring opening to yield the thiolate intermediate, $Ar-C\equiv C-S-C(Ar)=CH-S^-$, as the first part is proposed. The second part involves ring closure by intramolecular nucleophilic attack of the thiolate at the triple bond to yield the 1,4-dithiafulvene anion followed by protonation and thus regeneration of the base catalyst. In the case of BND the thiolate ion is further cleaved to $p\text{-}O_2N-C_6H_4-C\equiv C-S^-$, which upon protonation dimerizes and undergoes ring closure to the 1,4-dithiafulvene.

Compounds derived from the 1,4-dithiin ring system (**1**) (Scheme 1), and its benzo- and dibenzo-derivatives are electron rich species that are easily converted into the corresponding radical cations by voltammetric[1–4] or conventional chemical oxidation.[5–9] The radical cations have been characterized by ESR spectroscopy[10–13] and their reactivity has been studied, in particular that of the dibenzo-1,4-dithiin (thianthrene) radical cation, which served as a model compound in earlier work on the kinetics and mechanisms of radical cation reactions.[14,15]

On the other hand, the sulfur atom in many respects resembles the –CH = CH– linkage and for that reason the 1,4-dithiin ring system is expected to have properties similar to those of cyclooctatetraene, a well-known electron accepting compound that can be reduced successively to the radical anion and the dianion, for example electrochemically.[16–19] With this in mind it would be expected that 1,4-dithiins may also be reduced electrochemically and a number of compounds that are formally 1,4-dithiin derivatives have indeed been demonstrated to



**1**

DPD X = H
BCD X = Cl
BBD X = Br
BND X = $NO_2$

*Scheme 1.*

† Present address: Steacie Institute for Molecular Sciences, National Research Council Canada, Ottawa, Ontario, Canada K1A 0R6

* To whom correspondence should be addressed.

possess electron accepting properties.[20–27] However, common to all these compounds is that they have strongly electron withdrawing groups, i.e., carbonyl and/or cyano, attached directly to the 1,4-dithiin ring and this structural feature dominates the behavior of the molecules to the extent that information concerning the electrochemical reduction of the 1,4-dithiin system itself cannot be extracted from voltammetric studies of such compounds.

Since information about the electrochemical reduction of more simple 1,4-dithiins is apparently not available, we have undertaken a study of 2,5-diphenyl-1,4-dithiin and three *p*-substituted derivatives (Scheme 1).

## Results and discussion

*Electrochemical reduction of 2,5-diphenyl-1,4-dithiin (DPD) in MeCN.* Current–voltage curves for DPD obtained by cyclic voltammetry (CV) at an Hg working electrode in MeCN containing $Bu_4NPF_6$ (0.1 M) are shown in Fig. 1 as $i/v^{1/2}$ vs. $E$, where $E$ is the potential, $i$ is the current and $v$ is the voltage scan rate. Two reduction waves are observed at relatively low scan rates as illustrated in Fig. 1A for $v = 1$ V s$^{-1}$; at this scan rate the corresponding peak potentials, $E_p$, are $-2.62$ V and $-3.01$ V vs. ferrocene/ferricenium[28] ($Fc/Fc^+$), respectively. Anodic current corresponding to the oxidation of products formed during these two reduction processes was not observed. A gradual increase of the scan rate to 100 V s$^{-1}$ resulted in several major changes as seen in Fig. 1B and Table 1.

Inspection of the data in column 4 reveals that $i_p/v^{1/2}$, where $i_p$ is the peak current related to $R^1$, decreases with increasing scan rate. The value obtained at $v = 0.1$ V s$^{-1}$ is approximately twice that obtained at $v = 100$ V s$^{-1}$, or, in other words, the overall number of electrons transferred, $n$, at $v = 0.1$ V s$^{-1}$ is twice that at $v = 100$ V s$^{-1}$. The value of $i_p/v^{1/2}$ obtained at $v = 100$ V s$^{-1}$ is close to that obtained at the same working electrode for anthracene, which has a diffusion coefficient similar to that of DPD[4] and is known to be reduced reversibly in a 1 $F$ process to anthracene radical anion. This indicates that the reduction of DPD is a 1 $F$ process at high scan rates, producing $DPD^{-\cdot}$, and consequently, a 2 $F$ process at low scan rates. The oxidation peak, $O^1$, observed in Fig. 1B, which was apparent only when $v$ exceeded approximately 20 V s$^{-1}$, then reflects the reoxidation of $DPD^{-\cdot}$.

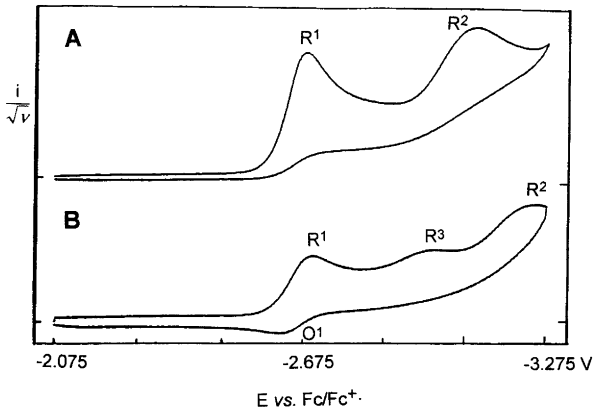



*Fig. 1.* Cyclic voltammograms ($i/v^{1/2}$ vs. $E$) recorded at an Hg working electrode for the reduction of DPD (0.88 mM) in MeCN containing $Bu_4NPF_6$ (0.1 M) as supporting electrolyte at $v = 1$ V s$^{-1}$ (A) and $v = 100$ V s$^{-1}$ (B); $t = 20$ °C.

It was observed also in passing from $v = 1$ V s$^{-1}$ to $v = 100$ V s$^{-1}$ that the second reduction peak, $R^2$, moved in the negative direction by approximately 0.2 V and a new peak, $R^3$, appeared between $R^1$ and $R^2$. The height of $R^3$ followed closely the height of $O^1$ indicating that the process taking place at $R^3$ is the further reduction of $DPD^{-\cdot}$ to the dianion, $DPD^{2-}$, and that the peak, $R^2$, is due to the further reduction of the product formed at $R^1$. Addition of neutral alumina to the voltammetric cell[29] caused $O^1$ and $R^3$ to grow at the expense of $R^2$ indicating that the follow-up reaction is protonation of $DPD^{-\cdot}$ by residual water leading eventually to the formation of a dihydro derivative, $DPDH_2$, possibly in an $ECE_h$-type process. The dihydro derivative is then the product being reduced at $R^2$.

The suggestion that the process taking place at $R^1$ is of $ECE_h$ type at low scan rates is supported by values of the half-peak widths, $E_{p/2} - E_p$, that are smaller than that, 56.5 mV,[30] for a reversible one-electron couple (Table 1). On the other hand, the values of $E_{p/2} - E_p$ obtained at $v \geq 10$ V s$^{-1}$ are larger than 56.5 mV indicating that the heterogeneous electron transfer process is quasi-reversible at scan rates where the chemical follow-up reaction is of only minor importance. However, the deviation from 'Nernstian' behavior is not sufficient to affect the conclusion arrived at concerning the number of electrons transferred.

The transition from a 2 $F$ $ECE_h$ process at low scan rates to a 1 $F$ process at high scan rates is also in agreement with the results obtained by derivative cyclic voltammetry.[31] The derivative current peak ratio, $R_I'$, which serves as a quantitative measure of the anodic-to-cathodic current ratio, increased from 0.25 at $v = 1$ V s$^{-1}$, indicating a fast follow-up reaction, to 0.85 at $v = 100$ V s$^{-1}$, showing that the reoxidation of $DPD^{-\cdot}$ competes favorably with the chemical follow-up reaction at this scan rate.

Attempts to prepare the proposed product, $DPDH_2$, by electrochemical reduction of DPD at the 1 mmol scale failed owing to isomerization of DPD catalyzed by the base formed in the cathode chamber during the experiment. This reaction is described in detail later in a separate section. Instead an attempt was made to carry out the reduction in the presence of small amounts of acetic acid (AcOH).

*Electrochemical reduction of DPD in MeCN in the presence of AcOH.* Initially it was observed by CV that the lifetime of $DPD^{-\cdot}$ was notably reduced in the presence of AcOH

*Table 1.* Voltammetric results for the reduction of 2,5-diphenyl-1,4-dithiin (DPD).[a]

| | Reduction wave, $R^1$ | | | | | Reduction wave, $R^2$ |
|---|---|---|---|---|---|---|
| $v/V\ s^{-1}$ | $E_p/V$[b] | $(E_{p/2}-E_p)/mV$ | $i_p/C^\circ v^{1/2}$[c] | $i_p/C^\circ v^{1/2}$[d] | $R_I'$[e] | $E_p/V$[b] |
| 0.1 | −2.593 | 50.9 | 992 | 1082 | — | — |
| 1 | −2.624 | 53.4 | 847 | 926 | 0.25 | −3.01 |
| 10 | −2.649 | 62.1 | 651 | 856 | 0.48 | −3.09 |
| 100 | −2.653 | 65.1 | 449 | 785 | 0.85 | −3.19 |

[a] In MeCN containing $Bu_4NPF_6$ (0.1 M) using an Hg working electrode; $C^\circ_{DPD}=0.88$ mM, $t=21°C$. [b] Peak potential given relative to $Fc/Fc^+$. [c] In arbitrary units; $C^\circ=C^\circ_{DPD}$. [d] In the presence of AcOH (3.5 mM); same units as in the previous column. [e] Ratio of derivative current peaks measured at $E^{\circ\prime}-E_{sw}=150$ mV; conditions as in footnote *a* except that $C^\circ=0.45$ mM.

and no trace of the reoxidation of $DPD^{-\cdot}$ (peak $O^1$) was observed even at $v = 100\ V\ s^{-1}$ at AcOH concentrations as low as 3.5 mM (Fig. 2A and 2B). In fact, the values of $i_p/v^{1/2}$ (Table 1, column 5) approached that obtained in the absence of acid at $v = 0.1\ V\ s^{-1}$ showing that $n$ is now close to two at all but the highest scan rate and at the same time the peak, $R^3$, corresponding to the further reduction of $DPD^{-\cdot}$ had completely vanished.

However, it is also seen by comparison of the voltammograms in Figs. 1 and 2 that the current observed after the first reduction peak, $R^1$, in the presence of AcOH does not decay as rapidly as expected for a simple $ECE_h$ process. Instead the current between $R^1$ and $R^2$ tends to approach a constant value pointing towards a catalytic process.[32] This was supported by a series of constant current coulometry experiments showing that the apparent value of $n$ increased with increasing concentrations of AcOH from 2.5, at an AcOH/DPD concentration ratio of 1.1, to 5.4, at a concentration ratio of 9.5. In addition, it was found that DPD could be recovered in 86% yield when the electrolysis of a solution containing 0.75 mmol DPD and 2.25 mmol AcOH was stopped after an amount of charge corresponding to two electrons per molecule of DPD had passed through the cell. Thus,

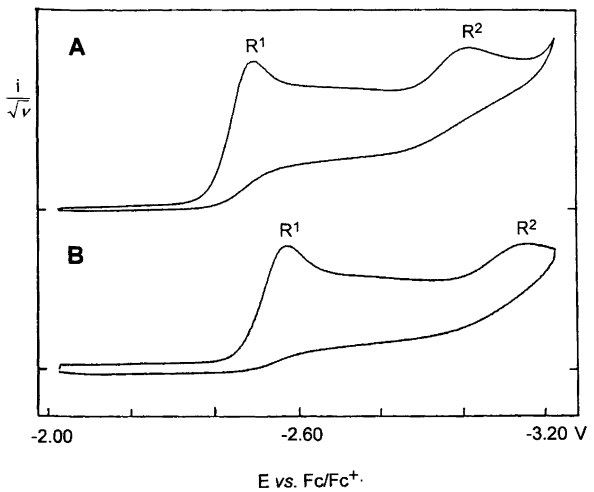



*Fig. 2.* The effect of addition of AcOH (3.5 mM) to the solution used for Fig. 1. The conditions are otherwise as given in the legend to Fig. 1.

the electrochemical reduction of DPD in the presence of AcOH most likely involves the competition between protonation of $DPD^{-\cdot}$ by AcOH (predominant at low acid concentrations) and catalytic reduction of AcOH, i.e., protons (predominant at high acid concentrations).[33] For comparison, the $E^\circ$ value for reduction of protons in MeCN has recently been estimated to be −1.77 V vs. NHE,[34–36] which translates to −2.32 V vs. $Fc/Fc^+$. This is approximately 0.3 V positive of $E^{\circ\prime}$ for DPD, which was estimated from Fig. 1B to be −2.61 V and shows that the reduction of protons in the potential region for reduction of DPD is indeed a thermodynamically favorable process.

Similar results have been obtained for other substrates, which in the presence of suitable proton donors are capable of forming weakly bonded associates.[37] Thus, in the present case the catalytic process probably involves the reduction of DPD/AcOH, where the slash indicates a weak hydrogen-bond like interaction, rather than electron transfer between $DPD^{-\cdot}$ and AcOH.[37]

*Electrochemical reduction of 2,5-bis(p-chlorophenyl)-1,4-dithiin (BCD) and 2,5-bis(p-bromophenyl)-1,4-dithiin (BBD).* Cyclic voltammograms for BCD and BBD recorded at $v = 1$ and $100\ V\ s^{-1}$ are shown in Figs. 3 and 4, respectively, and the voltammetric data are summarized in Table 2. The voltammograms are, as expected, very similar and include an irreversible reduction peak, $R^X$, which at $v = 1\ V\ s^{-1}$ was observed at −2.49 V (BCD) or −2.35 V (BBD), followed by three other peaks, $R^1$, $R^2$ and $R^3$, the potentials of which match those observed for DPD (Table 1) indicating that DPD is the product formed at $R^X$. Oxidation current corresponding to $R^X$ could not be observed for either of the compounds at scan rates up to $1000\ V\ s^{-1}$ in experiments in which the direction of the scan was reversed before $R^1$.

Reliable values of $i_p$ for $R^X$, and thus $i_p/v^{1/2}$ could not be obtained for BCD due to the overlap of the first two reduction waves. For BBD, however, the first wave is well separated from the second and the values of $i_p/v^{1/2}$ for $R^X$, obtained from measurements of $i_p$ using the same working electrode as for DPD, were found to be approximately twice that for the DPD two-electron peak, $R^1$, obtained at $v = 0.1\ V\ s^{-1}$ (see Table 1). This indicates that $R^X$ in this case (and obviously for BCD also) cor-

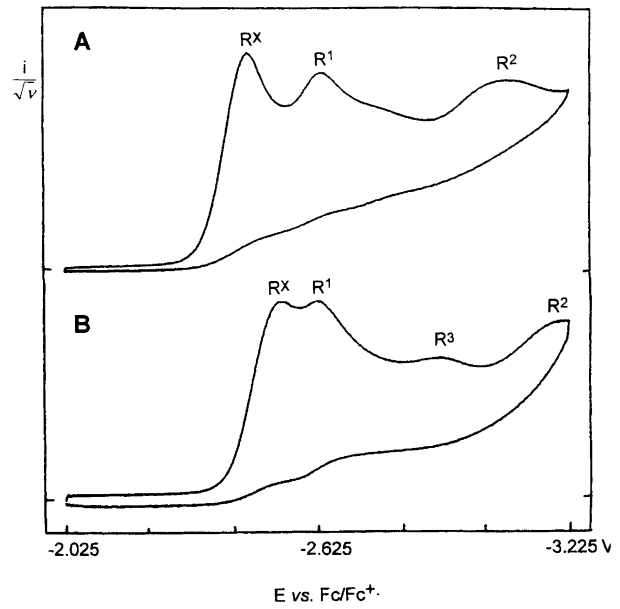



*Fig. 3.* Cyclic voltammograms ($i/v^{1/2}$ vs. $E$) recorded at an Hg working electrode for the reduction of BCD (0.75 mM) in MeCN containing $Bu_4NPF_6$ (0.1 M) as supporting electrolyte at $v = 1$ V $s^{-1}$ (A) and $v = 100$ V $s^{-1}$ (B); $t = 20$ °C.

responds to an overall four-electron reduction as summarized in eqn. (1), where BXD is either BCD or BBD and HB is a proton donor, presumably residual water. The observation that BBD is easier to reduce than BCD is in agreement with results obtained for other aromatic halogen compounds.[38–41]

$$BXD + 4\,e^- + 2\,HB \rightarrow DPD + 2\,X^- + 2\,B^- \qquad (1)$$

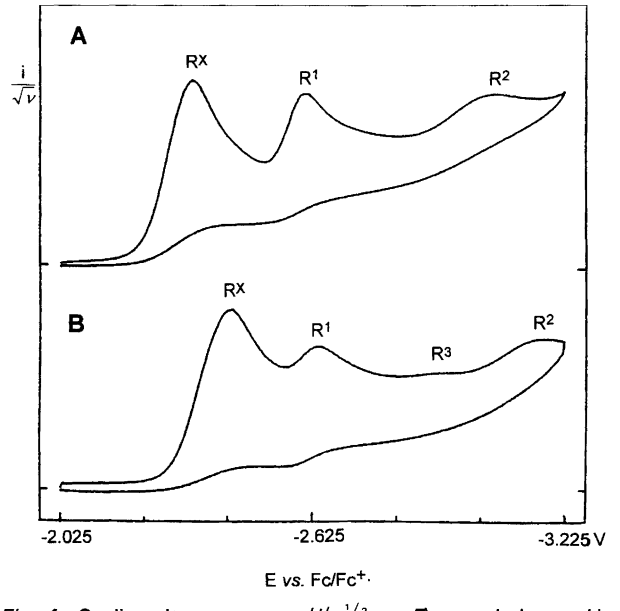



*Fig. 4.* Cyclic voltammograms ($i/v^{1/2}$ vs. $E$) recorded at an Hg working electrode for the reduction of BBD (0.86 mM) in MeCN containing $Bu_4NPF_6$ (0.1 M) as supporting electrolyte at $v = 1$ V $s^{-1}$ (A) and $v = 100$ V $s^{-1}$ (B); $t = 20$ °C.

The stoichiometry of reaction (1) was supported by results obtained for BBD by constant current coulometry and preparative electrolysis. As for DPD, it was also necessary in this case to carry out the experiments under slightly acidic conditions in order to avoid rearrangement of substrate. The results given in Table 2 show that the reduction of BBD at the voltammetric time scale is not significantly affected by the presence of small amounts of AcOH.

The decrease of the BBD concentration during constant current coulometry, as measured by the voltammetric peak height of $R^X$, is shown in Fig. 5 for experiments carried out with 1.5 mM BBD and 2.1 mM or 3.8 mM AcOH, respectively. At 2.1 mM AcOH it is clearly seen that the decay of substrate is linear in time and that the consumption of charge is in agreement with a 4 $F$ process. However, the apparent number of electrons also increased with increasing acid concentration in this case as seen in Fig. 5 where data points obtained at 3.8 mM AcOH are included as well. It is clearly seen that the consumption of substrate is less effective under these conditions with the regression line (not shown) corresponding to approximately 5 $F$. Work-up of the latter solution after 4.1 $F$ based on BBD resulted in the isolation of 68% DPD and 18% of unchanged BBD in good agreement with the coulometric result. (See the Experimental section for details). The isolation of an appreciable amount of starting material after 4.1 $F$ again indicates that a catalytic reaction takes place in parallel to the dehalogenation and again most likely involving the reduction of an associate, here BBD/AcOH, rather than electron transfer between $BBD^{-\cdot}$ and AcOH. This is even more so in this case since the results from fast scan voltammetry have demonstrated that the unimolecular cleavage of the C–Br bond leading eventually to DPD is an extremely fast process leaving little chance for a bimolecular reaction to compete.

It is also of interest to note that the monobromo derivative, 2-phenyl-5-(*p*-bromophenyl)-1,4-dithiin (PBD), was not observed. In spite of this BBD is without doubt first reduced in a two-electron process to PBD, which is further reduced to DPD in a subsequent two-electron process at nearly the same potential. The observation that the half-peak widths observed for $R^X$ at low scan rates are approximately 18 mV larger than that for an ECE-type process with a fast chemical step[30] may reflect two overlapping waves illustrating that the intermediate PBD is slightly more difficult to reduce than BBD.

Dehalogenation of aromatic halides by voltammetric reduction is well known and the mechanism, which has been studied in detail,[42–44] includes the initial formation of the radical anion followed by rate-determining cleavage of the carbon–halogen bond. Usually, disubstituted halogen derivatives are observed to undergo reduction more easily than the corresponding mono-halogen derivatives.[38,45] The observation that PBD and BBD are reduced at nearly the same potential indicates that there is little electronic interaction between two aryl groups at-

*Table 2.* Voltammetric results for the reduction of 2,5-bis(*p*-chlorophenyl)-1,4-dithiin (BCD) and 2,5-bis(*p*-bromophenyl)-1,4-dithiin (BBD).[a]

| | Reduction wave, $R^X$ | | | | | | | Reduction wave, $R^1$ |
|---|---|---|---|---|---|---|---|---|
| Compound | $v$/V $s^{-1}$ | $E_p$/V[b] | $E_p$/V[b,c] | $(E_{p/2}-E_p)$/mV | $(E_{p/2}-E_p)$/mV[c] | $i_p/C^\circ v^{1/2}$[d] | $i_p/C^\circ v^{1/2}$[d,e] | $E_p$/V[b] |
| BCD | 1 | −2.491 | | | | | | −2.657 |
| BCD | 100 | −2.571 | | | | | | −2.658 |
| BBD | 0.1 | −2.315 | −2.319 | 65.3 | 69.5 | 1931 | 1956 | — |
| BBD | 1 | −2.346 | −2.349 | 65.9 | 69.4 | 1792 | 1788 | −2.644 |
| BBD | 10 | −2.388 | −2.388 | 71.0 | 73.5 | 1701 | 1671 | −2.654 |
| BBD | 100 | −2.437 | −2.426 | 82.5 | 79.1 | 1585 | 1626 | −2.655 |

[a] In MeCN containing $Bu_4NPF_6$ (0.1 M) using the same Hg working electrode as referred to in Table 1; $C^\circ_{BCD}=1.16$ mM, $C^\circ_{BBD}=0.65$ mM, $t=20°C$. [b] Peak potential given relative to $Fc/Fc^+$. [c] In the presence of AcOH (3.5 mM). [d] In arbitrary units; $C^\circ=C^\circ_{BBD}$. [e] In the presence of AcOH (3.5 mM); same units as in the previous column.

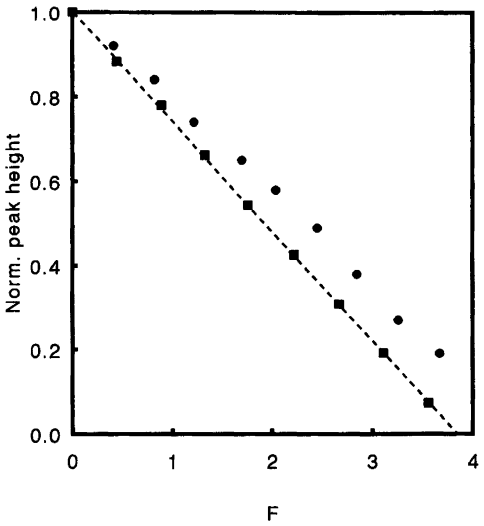



*Fig. 5.* Analysis by constant current coulometry of a 50 ml MeCN–$Bu_4NPF_6$ (0.1 M) solution containing 1.5 mM BBD and 2.1 mM (■) or 3.8 mM (●) AcOH using an Hg pool cathode; $i=50$ mA and $t=20°C$. The substrate concentrations are given as the CV peak heights divided by the height corresponding to the initial concentration. The regression line (----) defined by the filled squares corresponds to 3.8 F.

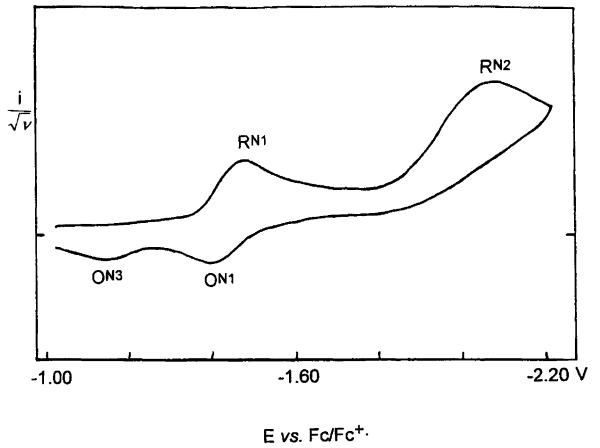



*Fig. 6.* Cyclic voltammograms ($i/v^{1/2}$ vs. $E$) recorded at a Pt working electrode for the reduction of BND (0.65 mM) in MeCN containing $Bu_4NPF_6$ (0.1 M) as supporting electrolyte at $v=1$ V $s^{-1}$; $t=20°C$.

tached to each of the two SCCS halves of 1,4-dithiin. This feature of the ring system was demonstrated more clearly by results obtained for the 2,5-bis(*p*-nitrophenyl) derivative.

*Electrochemical reduction of 2,5-bis(p-nitrophenyl)-1,4-dithiin (BND).* The reproducibility of the results obtained by voltammetric reduction of BND at Hg working electrodes was not satisfactory, presumably owing to adsorption of substrate and/or electrode products. However, it was found that reliable results could be obtained at Pt electrodes.

A voltammogram recorded in MeCN is depicted in Fig. 6. The first reduction peak, $R^{N1}$, is located at −1.45 V vs. $Fc/Fc^+$ showing that BND is reduced approximately 1.17 V more easily than DPD. A second peak, $R^{N2}$, is observed at −2.05 V. Reverse current is observed for $R^{N1}$, but not for $R^{N2}$. Instead an oxidation peak, $O^{N3}$, is observed at approximately −1.15 V vs. $Fc/Fc^+$. This peak is observed only when the negative scan encompasses $R^{N2}$ and reflects therefore most likely the oxidation of a species produced at $R^{N2}$.

The voltammetric data related to $R^{N1}$ are summarized in Table 3 and it is seen that the value of $i_p/v^{1/2}$ for BND at $v=1$ V $s^{-1}$ is approximately 1.5 times that observed for a typical one-electron couple such as the oxidation of ferrocene and this together with the observation that the values of $E_{p/2}-E_p$ increases from approximately 75 at $v=0.1$ V $s^{-1}$ to approximately 90 mV at $v=10$ V $s^{-1}$ indicates that the first reduction wave is composed of two overlapping one-electron waves analogously to what has been observed for other aromatic dinitro compounds with separated nitroaryl units.[46,47] Results obtained by digital simulation (see the Experimental for details) showed that the data in Table 3 are compatible with an $E^\circ$ difference of 55–60 mV. This value of $\Delta E^\circ$ is only 20–25 mV larger than that expected for a hypothetical compound in which the two nitro groups do not interact. In that case $\Delta E^\circ$, which is of purely statistical origin, is equal to 35.0 mV

*Table 3.* Voltammetric results for the reduction of 2,5-bis(*p*-nitrophenyl)-1,4-dithiin (BND).[a]

| | Reduction wave, $R^{N1}$ | | |
|---|---|---|---|
| $v$/V s$^{-1}$ | $E_p$/V[b] | $(E_{p/2}-E_p)$/mV | $i_p/C^\circ v^{1/2}$[c] |
| 0.1 | −1.440 | 76.5 | 608 |
| 1 | −1.445 | 79.6 | 553 |
| 10 | −1.461 | 87.3 | 532 |
| 1[d] | 0[d] | 58.3[d] | 383[d] |

[a] In MeCN containing $Bu_4NPF_6$ (0.1 M) using a Pt working electrode; $C^\circ_{BND}$=0.65 mM, $t$=20°C. [b] Peak potential given relative to $Fc/Fc^+$. [c] In arbitrary units; $C^\circ = C^\circ_{BND}$. [d] Results obtained for the oxidation of Fc at the same working electrode; $C^\circ = C^\circ_{Fc}$ = 1.20 mM.

at 20°C.[46] Thus, also for BND we arrive at the conclusion that the electronic interaction between two aryl groups through the 1,4-dithiin system is indeed very small. Otherwise, the voltammetric results obtained for BND are, as for most aromatic nitro compounds, completely dominated by the nitro substituent and further voltammetric work was abandoned.

*Studies of DPD, BCD and BBD by constant current coulometry in the absence of added acid.* In general the decrease in substrate concentration during constant current coulometry is observed to be linear in time as illustrated for example by Fig. 5 for the reduction of BBD (1.5 mM) in the presence of AcOH (2.1 mM). However, the results obtained for DPD, BCD and BBD by constant current coulometry in the absence of acid were unusual as seen in Fig. 7A. The decrease in substrate concentration with time is clearly non-linear and, in addition, the amount of charge consumed for total conversion of the substrate was less than 1 *F* for BCD and BBD. It is also seen that the conversion obtained for a given amount of charge depends on the nature of the *p*-substituent and increases in the order H < Cl < Br. Inspection of the figure further reveals that the substrate concentration initially decreases rather slowly, but after a short induction period corresponding to approximately 0.1 *F* a rapid decrease is observed. Finally, it was found that the amount of charge necessary for the complete conversion of substrate decreased with increasing concentration of starting material as seen in Fig. 7B for DPD at $C^\circ_{DPD}$ = 1.94, 3.88 and 7.04 mM, respectively.

The products of the reaction, which separated during coulometry and could be isolated by filtration, were identified to be 2,6-diaryl-1,4-dithiafulvene (Scheme 2), an isomer of the starting material. Preparative electrolysis on the 1 mmol scale demonstrated that 2,6-diphenyl-1,4-dithiafulvene could be isolated in 45% yield from DPD after reduction corresponding to 0.2 *F* (see the Experimental section for details). Similarly, 2,6-bis(*p*-chlorophenyl)-1,4-dithiafulvene was obtained in 71% yield from BCD in a 0.2 *F* process. The fulvenes are slightly more

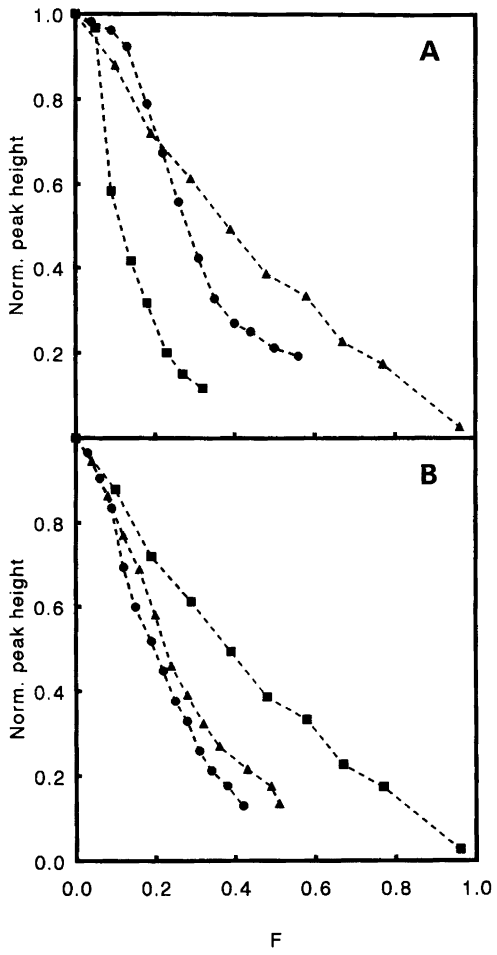
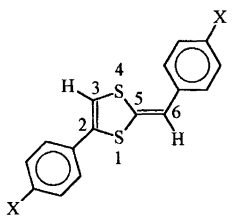



*Fig. 7.* Analysis by constant current coulometry of 2,5-diaryl-1,4-dithiins in 50 ml MeCN, $Bu_4NPF_6$ (0.1 M) using an Hg pool cathode; $i$=30 mA and $t$=20°C. (A): 1.93 mM DPD (▲), 2.20 mM BCD (●) and 2.04 mM BBD (■). (B): 1.94 mM (■), 3.88 mM (▲) and 7.04 mM (●) DPD. The substrate concentrations are given as the CV peak heights divided by the height corresponding to the initial concentration.

difficult to reduce than the corresponding dithiins and therefore not converted further under the conditions of the experiment. (Peak potentials are given in the Experimental section). Thus, it appears that electrochemical reduction of 2,5-diaryl-1,4-dithiins in the absence of acid initiates a chain process resulting in rearrangement of the starting material.

This conclusion was supported by results obtained from a coulometric experiment carried out in a slightly




*Scheme 2.*

different fashion. Usually, constant current coulometry requires that electrolysis and stirring is interrupted, for example every minute, while a slow scan cyclic voltammogram is recorded to monitor the (decrease in) substrate concentration. This takes typically 15–20 s after which electrolysis and stirring are resumed. In the modified procedure the current source and the stirring motor remained disconnected after the voltammogram had been recorded and a second voltammogram was recorded after a total of 1.5 min. After this electrolysis and stirring were resumed. The results obtained for DPD and BCD are shown in Fig. 8 and it is clearly seen that the consumption of substrate also continued in the periods where no current was flowing through the cell.

Electrochemically induced rearrangements of organic sulfur compounds have been reported in several other cases. For example, cathodic reduction of 2,2,4,4-tetraalkylcyclobutane-1,3-dithiones was found to result in the formation of the isomeric β-dithiolactones[48] and reduction of *S,S*-diaryl benzene-1,2-dicarbothioates gave the corresponding 3,3-bis(arylthio)phthalides.[49] Definitive conclusions regarding the mechanism of the rearrangement were not reached in either of the two cases. The products may arise through $S_{RN}1$-type electron transfer chain mechanisms, in which the radical anions of the starting materials are key intermediates, or via catalysis by electrochemically generated bases. In both cases the amount of charge required for the total conversion is predicted to be low and the rearrangement of the *S,S*-diaryl benzene-1,2-dicarbothioates was indeed observed to involve less than 0.1 *F*.[49]

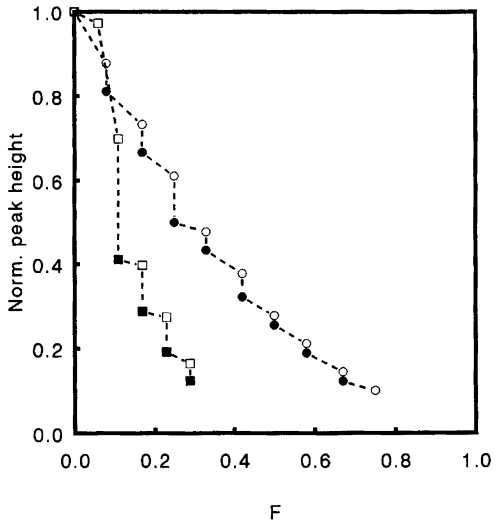



*Fig. 8.* Analysis by constant current coulometry of 2.20 mM DPD (○) and 2.18 mM BCD (□) in 50 ml MeCN, $Bu_4NPF_6$ (0.1 M) using an Hg pool cathode; $i=30$ mA and $t=20°C$. The points illustrated by filled symbols were measured after the current had been interrupted for 1.5 min (see the text). The substrate concentrations are given as the CV peak heights divided by the height corresponding to the initial concentration.

However, in the present case an $S_{RN}1$-type mechanism appears to be unlikely since the results obtained by fast scan CV for BCD and BBD showed that the corresponding radical anions undergo very rapid cleavage of a C–X and not a C–S bond. When at the same time it is considered that the halogen atoms are totally preserved in the 2,6-diaryl-1,4-dithiafulvenes resulting from coulometric reduction of BCD and BBD it appears inconceivable that the corresponding radical anions are involved in the mechanism of the (slow) rearrangement. Thus, at least for BCD and BBD the most likely mechanism involves catalysis by base formed during the electrolysis. This would also account for the induction period observed (Fig. 7A), since the basicity of the solution obviously has to reach a certain level before the catalysis is effective. The nature of the base is unknown, but a good candidate is hydroxide ion resulting from protonation by residual water of the negatively charged species inevitably formed during cathodic reduction.

That the rearrangements do indeed proceed by hydroxide ion catalysis was demonstrated independently in a series of experiments in which $Bu_4NOH$ (40% aqueous solution) was added to MeCN solutions of the 2,5-diaryl-1,4-dithiins.

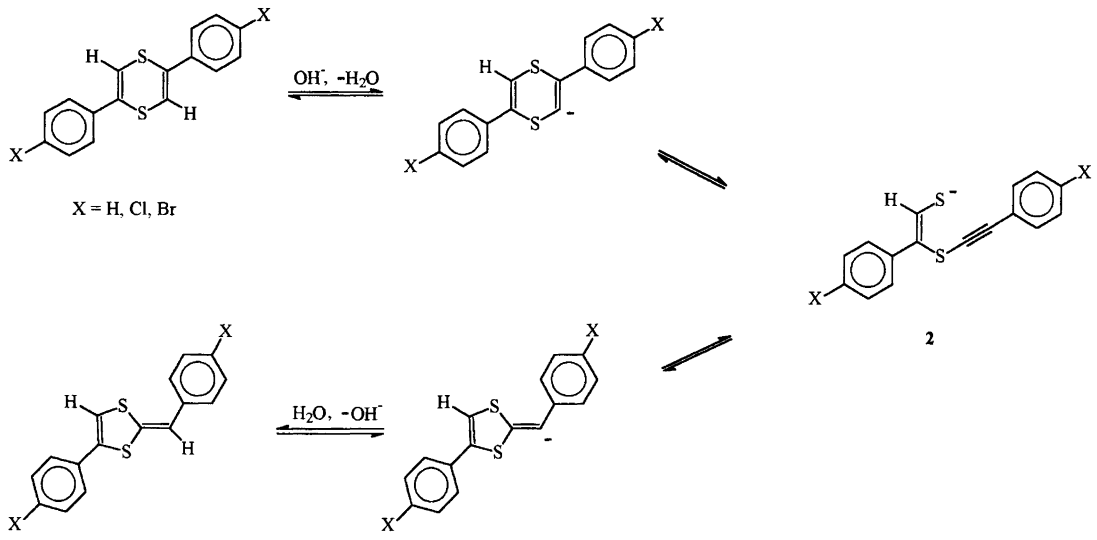
*Hydroxide ion catalyzed rearrangement of 2,5-diaryl-1,4-dithiins.* The results from a series of experiments in which the 2,5-diaryl-1,4-dithiins were treated with $Bu_4NOH$ (40% aqueous solution) in MeCN are summarized in Table 4. It is seen that, except for DPD, good yields of the corresponding 2,6-diaryl-1,4-dithiafulvenes were obtained.

The first part of the mechanism proposed for the rearrangement (Scheme 3) involves the abstraction of a C-3 or C-6 proton and ring opening resulting in formation of the intermediate anion, $Ar-C\equiv C-S-C(Ar)=CH-S^-$ (**2**), reminiscent of the formation of acetylenes from the reaction of vinyl sulfides with base.[50] Similar ring openings have been reported for unsubstituted 1,4-dithiin upon treatment with BuLi[51] and for the 1-alkyl-1,4-dithiinium cation with BuLi,[52,53] NaH[54] or even aqueous phosphate buffer.[55] The second part involves ring closure by intramolecular nucleophilic addition of the thiolate group in **2** to the triple bond[56] and protonation resulting in formation of the 1,4-dithiafulvene and regeneration of the basic catalyst. (Scheme 3 has deliberately been shown in

*Table 4.* Yields of 2,6-diaryl-1,4-dithiafulvenes from the $Bu_4NOH$ catalyzed rearrangement of 2,5-diaryl-1,4-dithiins.[a]

| Dithiin | $t_{react}$/h | Yield (%) |
|---|---|---|
| DPD | 24 | 38 |
| BBD | 2 | 93 |
| BCD | 3 | 90 |
| BND | 2 | 72[b] |

[a] In MeCN at 20°C; details are given in the Experimental section. [b] After addition of water to the reaction mixture. See the Experimental section.




*Scheme 3.*

terms of the E1cB notation owing to the anion stabilizing effect of the sulfur atoms).

The reaction between BND and $Bu_4NOH$ took a slightly different course as indicated by a dark purple color formed immediately upon addition of $Bu_4NOH$ to the MeCN solution. Initially, the color was believed to be due to the thiolate anion, $p$-$O_2N$-$C_6H_4$-C≡C-S-C($p$-$O_2N$-$C_6H_4$)=CH-$S^-$ (**3**), but an attempt to trap **3** by reaction with MeI resulted in formation of methylthio($p$-nitrophenyl)acetylene (**4**) in 64% yield (Scheme 4). This indicates that **3** is further cleaved to $p$-$O_2N$-$C_6H_4$-C≡C-$S^-$ (**5**) in analogy with the formation of alkynylthiolates from cleavage of 1,3-oxathiol-2-ones by BuLi.[57] In the presence of a suitable proton donor **5** exists in equilibrium with the tautomeric aldothioketene (**6**) – alkynethiol (**7**) system and the fact that addition of water to the reaction mixture resulted in a considerable improvement of the yield of the dithiafulvene (see Table 4 and the Experimental section) indicates that the reaction between **6** and **7** formed by protonation may indeed be the origin of the dithiafulvene in this case.[58] Thus, the purple color observed upon addition of $Bu_4NOH$ to the MeCN solution of BND is more likely caused by the equilibrium system, **5**–**7**.[58] The difference in mechanism between BND and the three other 2,5-diaryl-1,4-dithiins is believed to reflect that the nucleophilicity of the thiolate group in **3** is strongly reduced owing to the electron-withdrawing properties of the nitro group and for this reason further cleavage to **5**, which is stabilized by the presence of the nitro group, competes favorably with nucleophilic attack at the triple bond.

*The driving force.* Comparison of the structures of the 2,5-diaryl-1,4-dithiins and the 2,6-diaryl-1,4-dithiafulvenes shows that the observed rearrangements formally involve only a 90° in-plane rotation of one C=C–Ar unit accompanied by the shift of a hydrogen atom. Thus, the structural features of the two isomers are very similar and for this reason the rearrangements would be expected to be accompanied only by a small enthalpy change, $\Delta H_{rearr}$. The energetics of the rearrangement were examined in more detail by force-field (MMX) and semiempirical (AM1 and PM3) calculations.

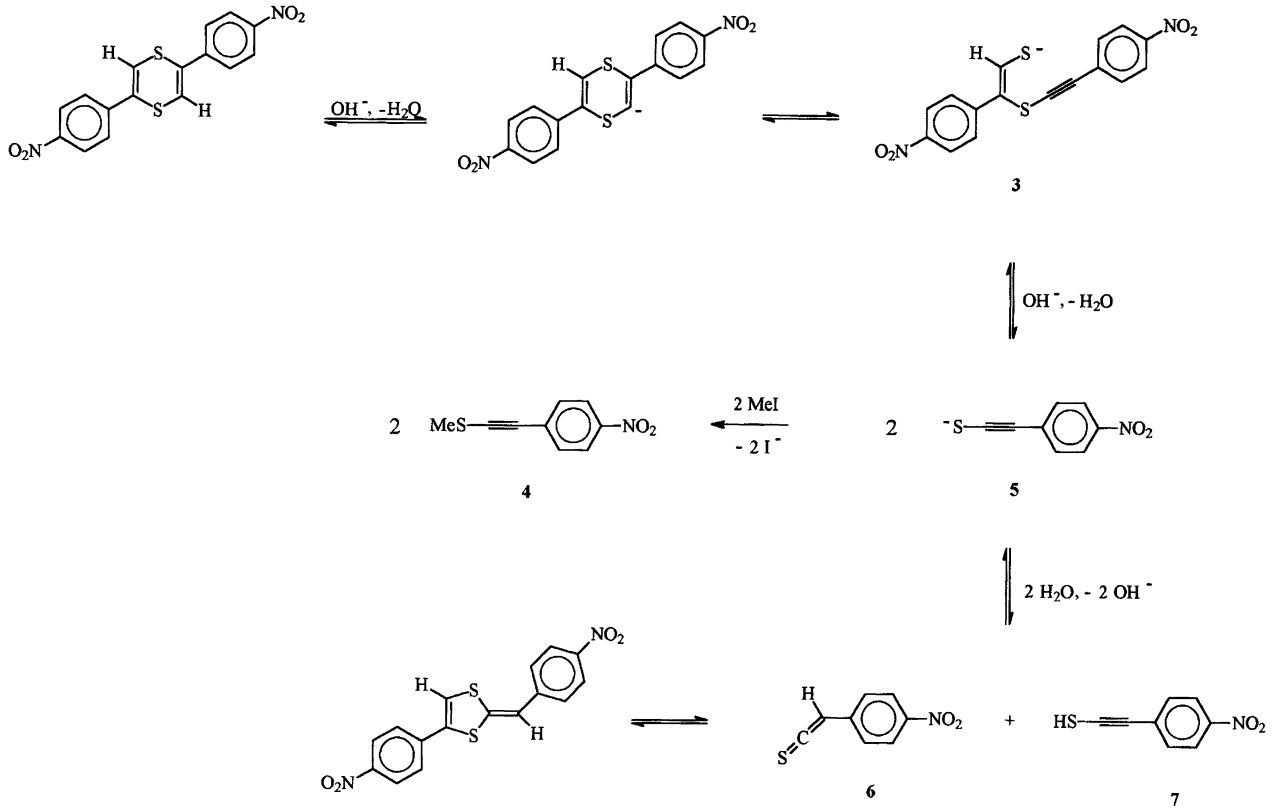
The semiempirical methods predicted, not unexpectedly,[27,59,60] that the conformers of lowest energy for both **1** and DPD include a co-planar arrangement of the two SCCS planes, whereas the force-field method in both cases predicted the angle between the two planes to be close to 120°, not far from the angles, 137° for **1**[61–63] and 133° for DPD,[64,65] observed experimentally. The problems encountered by the semiempirical methods, in contrast with *ab initio* methods,[59,66–69] in reproducing the correct conformation for simple 1,4-dithiin derivatives have been attributed to an overestimation of the π-bonding contribution of the sulfur atoms.[27]

Values of $\Delta H_f$ for **1** and DPD calculated by the MMX method as well as the AM1 and PM3 methods are summarized in Table 5 for both 120° and 180° angles between the SCCS planes and it is seen for DPD, for ex-

*Table 5.* Heats of formation, $\Delta H_f$, calculated by MMX, AM1 and PM3.[a]

| | MMX | AM1 | PM3 |
|---|---|---|---|
| 1,4-Dithiin[b] | — | 31.7 | 38.8 |
| 1,4-Dithiin[c] | 36.2 | 39.2 | 45.5 |
| 2,5-Diphenyl-1,4-dithiin[b] | — | 87.4 | 96.9 |
| 2,5-Diphenyl-1,4-dithiin[c] | 90.0 | 96.9 | 101.3 |
| 1,4-Dithiafulvene | 42.0 | 36.6 | 43.0 |
| 2,6-Diphenyl-1,4-dithiafulvene | 92.9 | 85.3 | 96.2 |

[a] In kcal $mol^{-1}$. [b] Values for the lowest-energy conformation including coplanar SCCS units. [c] Values for the conformation including a 120° angle between the SCCS units as predicted by force-field calculations.



*Scheme 4.*

ample, that a change of the angle from 180° to 120° results in an increase in $\Delta H_f$ by 4.4 (PM3) or 9.5 (AM1) kcal $mol^{-1}$. A similar trend is seen for **1**. The values of $\Delta H_{rearr}$ based on the minimum values of $\Delta H_f$ for DPD predicted by the method in question are +2.9 (MMX), −2.1 (AM1) and −0.7 (PM3) kcal $mol^{-1}$.

Thus, it seems impossible to draw definitive conclusions regarding the relative stability of the 2,5-diaryl-1,4-dithiins and the corresponding 2,6-diaryl-1,4-dithiafulvenes from these calculations, but the data in Table 5 do indicate, at least, that it is unlikely that $\Delta H_{rearr}$ takes large positive or negative values and therefore that the good to high yields obtained for the rearrangement of 2,5-diaryl-1,4-dithiins to 2,6-diaryl-1,4-dithiafulvenes do not reflect that the latter as a rule are thermodynamically more stable than their 2,5-diaryl-1,4-dithiin precursors. We suggest that the driving force is instead the low solubility of the 2,6-diaryl-1,4-dithiafulvenes,[70] which causes them to separate from the reaction mixtures. This also forces the conclusion that the rearrangement is reversible (Scheme 3).[†] The fact that the fulvenes as a rule are much less soluble in organic solvents than the corresponding dithiins indicates that the intermolecular forces in the crystalline phase are much larger for the fulvenes as also reflected by their much higher melting points.

[†] We thank the Editor for directing our attention to this consequence of the solubility argument.

## Experimental

*Chemicals.* The 2,5-diaryl-1,4-dithiins were prepared according to literature methods.[71,72] The supporting electrolyte, $Bu_4NPF_6$,[73] was added to MeCN (Rathburn, HPLC-grade) corresponding to a concentration of 0.1 M and the resulting solution was passed through a column of neutral alumina (ICN, Super I). Tetrabutylammonium hydroxide (40% solution in water, Fluka, *purum*) was used as received. All other chemicals were reagent grade and used without further purification.

*Voltammetric measurements.* The electrochemical equipment and measurement procedures were essentially as earlier described.[74] The Pt electrodes ($d = 0.6$ mm) were polished frequently using silicon carbide paper #4000 and a Struers DAP-V polishing machine.

*Constant current coulometry.* A known amount of the 1,4-dithiin (0.1–0.2 mmol) was dissolved in MeCN (50 ml) containing $Bu_4NPF_6$ (0.1 M). Dissolved oxygen was removed by being bubbled with nitrogen. The cathode was an Hg pool. The anolyte was separated from the catholyte by a sintered glass disk containing a layer (3–5 mm) of neutral alumina. The reduction process was monitored by CV through measurements of the reduction peak height. The current was 50 mA unless otherwise stated.

*The product from constant current electrolysis of BBD in the presence of AcOH.* BBD (32.5 mg, 0.0765 mmol) was dissolved in 50 ml MeCN containing $Bu_4NPF_6$ (0.1 M) after which AcOH (11 µl, 0.19 mmol) was added. The solution was then bubbled with nitrogen in order to remove oxygen. The cathode was an Hg pool. The anolyte was separated from the catholyte by a sintered glass disk containing a layer (3–5 mm) of neutral alumina. The electrolysis ($i = 50$ mA) was stopped when an amount of charge corresponding to 4.1 $F$ had passed through the solution. The solvent was evaporated off and the resulting solid was extracted three times with 15 ml diethyl ether. The combined ether extracts were concentrated to a solid, which was then chromatographed on silica gel, using tetrachloromethane as the eluent. The products were BBD (18%) and DPD (68%).

*Preparative constant current electrolysis of DPD and BCD.* The equipment and procedures were the same as used above, except that larger amounts of the 2,5-diaryl-1,4-dithiins (DPD, 1.2 mmol and BCD, 1.5 mmol) were used. In both cases a yellow material separated during the electrolysis. The current was stopped when 0.2 $F$ had passed through the solution. The product was isolated by filtration and recrystallized from tetrachloromethane (DPD) or 1,4-dioxane (BCD). This gave the corresponding 2,6-diaryl-1,4-dithiafulvenes in 45% and 71% yield, respectively.

*Base-catalyzed isomerization of DPD, BCD and BBD.* The 2,5-diaryl-1,4-dithiin (0.1 mmol) was dissolved in 50 ml MeCN under $N_2$ after which $Bu_4NOH$ (100 µl of a 40% aqueous solution) was added. The resulting 2,6-diaryl-1,4-dithiafulvene was isolated by filtration after the reaction time given in Table 4 and then washed with MeCN and several portions of diethyl ether. Owing to the very low solubility of the dithiafulvenes in common solvents it was impossible to obtain NMR spectra. Yields are given in Table 4.

*2,6-Diphenyl-1,4-dithiafulvene:* IR (KBr) $cm^{-1}$: 1596w, 1582s, 1565s, 1490s, 1442s, 1343w, 1189w, 925m, 897w, 812s, 737s, 686s; MS (EI+): 268, 134, 121. M.p. 203°C (203–204°C).[75] CV ($v = 1$ V $s^{-1}$): $E_p(R^1) = -2.77$ V vs. $Fc/Fc^+$.

*2,6-Bis(*p*-chlorophenyl)-1,4-dithiafulvene:* IR (KBr) $cm^{-1}$: 3025w, 3003w, 1578s, 1556m, 1538m, 1489s, 1399m, 1211m, 1096s, 1010m, 923m, 841s, 832s, 763s; MS (EI+): 336, 168. UV–VIS (1,4-dioxane): $\lambda_{max} = 347$ (shoulder), 361 nm (347 (shoulder), 363 nm).[76] M.p. decomp. 234°C (239–241°C).[75] CV ($v = 1$ V $s^{-1}$): $E_p(R^{X1}) = -2.55$ V, $E_p(R^{X2}) = -2.64$ V, $E_p(R^1) = -2.74$ V vs. $Fc/Fc^+$.

*2,6-Bis(*p*-bromophenyl)-1,4-dithiafulvene:* IR (KBr) $cm^{-1}$: 1577s, 1553m, 1537m, 1484s, 1396s, 1210m, 1118w, 1076s, 1007s, 924w, 840s, 825s, 763s, 703w; MS (EI+): 426, 346 ($M$ – Br), 266 ($M$ – 2 Br), 214. M.p. 246°C (decomp.) (251–253°C).[75] CV ($v = 1$ V $s^{-1}$): $E_p(R^{X1}) = -2.42$ V, $E_p(R^{X2}) = -2.59$ V, $E_p(R^1) = -2.79$ V vs. $Fc/Fc^+$.

*Base-catalyzed isomerization of BND.* BND (0.1 mmol) was dissolved in 50 ml MeCN under $N_2$ after which $Bu_4NOH$ (100 µl of a 40% aqueous solution) was added. The color of the solution immediately turned dark purple. After two hours 9 mg (24%) of 2,6-bis(*p*-nitrophenyl)-1,4-dithiafulvene was isolated by filtration. Addition of 30 ml water and 50 ml diethyl ether to the filtrate resulted in precipitation of an additional 18 mg (48%) of the dithiafulvene. This was collected by filtration and was washed with MeCN and several portions of diethyl ether.

*2,6-Bis(*p*-nitrophenyl)-1,4-dithiafulvene:* IR (KBr) $cm^{-1}$ 1589s, 1564s, 1537m, 1515s, 1409v, 1333s(broad), 1108s, 851m, 745m. MS (EI+): 358, 312 ($M - NO_2$), 282 ($M - 2\ NO_2$), 165. M.p. 283°C decomp. UV–VIS (MeCN): $\lambda_{max} = 273$, 439 nm.

*Trapping of the intermediate in the reaction of BND with $Bu_4NOH$.* BND (44.4 mg, 0.12 mmol) was dissolved in 50 ml MeCN under $N_2$ after which $Bu_4NOH$ (200 µl of a 40% aqueous solution) was added. The color of the solution immediately turned dark purple. After 2.5 h $CH_3I$ (250 µl, 4 mmol) was added. The color of the solution changed to dark grey. Diethyl ether (30 ml) and water (30 ml) was then added. The ether phase was seperated, washed with water, dried over $MgSO_4$, and evaporated. The oily solid was purified on a column [Silica gel 60, (Merck), eluent: $CH_2Cl_2$] resulting in a yellow compound (31 mg), which was recrystallized from MeOH and identified as *methylthio(*p*-nitrophenyl)acetylene:* NMR ($^1H$, $CDCl_3$): δ 2.53 (s, 3 H), 7.50 (d, 2 H), 8.17 (d, 2 H); IR (KBr) $cm^{-1}$ 2166s, 1592s, 1515s, 1510s, 1338s, 1106m, 856m, 843m, 751m; MS (EI+): 193, 163, 148, 132. M.p. 91–92°C. (92°C).[77]

*Digital simulation.* Simulations related to the reduction of BND were carried out using the implicit method reported by Rudolph[78] assuming identical heterogeneous electron transfer rate constants, $k_s$, for the $BND/BND^{-\cdot}$ and the $BND^{-\cdot}/BND^{2-}$ redox couples and taking into account the disproportionation equilibrium $2\ BND^{-\cdot} \rightleftharpoons BND + BND^{2-}$. The best fit of the theoretical data to the experimental values of $E_p$, $\Delta E_p$ and $E_{p/2} - E_p$ recorded at different scan rates was obtained for $\Delta E° = 55$–$60$ mV and, assuming a diffusion coefficient, $D$, of to $10^{-5}$ $cm^2$ $s^{-1}$, $k_s = 0.08$ cm $s^{-1}$. The program was written in PASCAL and executed on a 386SX personal computer equipped with a numerical coprocessor. The parameter, β, which determines the degree of exponential expansion, was 0.75 in all cases and the dimensionless diffusion constant, $D^*$, was 100. Steps of 2 mV were used throughout.

*Force-field and semiempirical calculations.* Force-field calculations (MMX) were carried out on a 386SX personal computer using PCMODEL (version 88.500) from Serena Software. The AM1 and PM3 programs were both

part of a MOPAC package (version 6.0) installed on a local CONVEX computer.

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