# Electrochemical Evidence for an Unusual Base-Catalysed Chain Mechanism in an Intramolecular Homolytic Arylation

**Marino Novi,* Giacomo Garbarino, Carlo Dell'Erba, and Giovanni Petrillo**

*Istituto di Chimica Organica dell'Università, CNR Centro di Studio sui Diariloidi e loro Applicazioni, Corso Europa, Palazzo delle Scienze, 16132, Italy*

Cyclic voltammetry and controlled-potential electrolysis of the disulphone (**1a**) in dimethyl sulphoxide show that its transformation into the dibenzothiophene dioxide (**2a**), in the presence of a base, is an efficient electrocatalytic process.

The photo-induced single-electron transfer from arenethiolate anions to the *o*-bis(phenylsulphonyl)benzene derivatives (**1a**,**b**) in dimethyl sulphoxide (DMSO) leads to the formation of the dibenzothiophene dioxides (**2a**,**b**) together with smaller amounts of the uncyclised monosulphones (**3a**,**b**).[1,2] A chain process for the formation of (**2a**,**b**) (Scheme 1) has been advanced.[2]

However, in electrochemically induced electron-transfer experiments,[3] we found that the controlled-potential electrolysis of (**1a**) in DMSO (at a potential corresponding to the plateau of the first polarographic wave) caused a charge consumption of 1 F $\text{mol}^{-1}$, leading to good yields of (**2a**) and (**3a**) and minor amounts of the dihydro derivative (**6**), clearly excluding a chain mechanism.

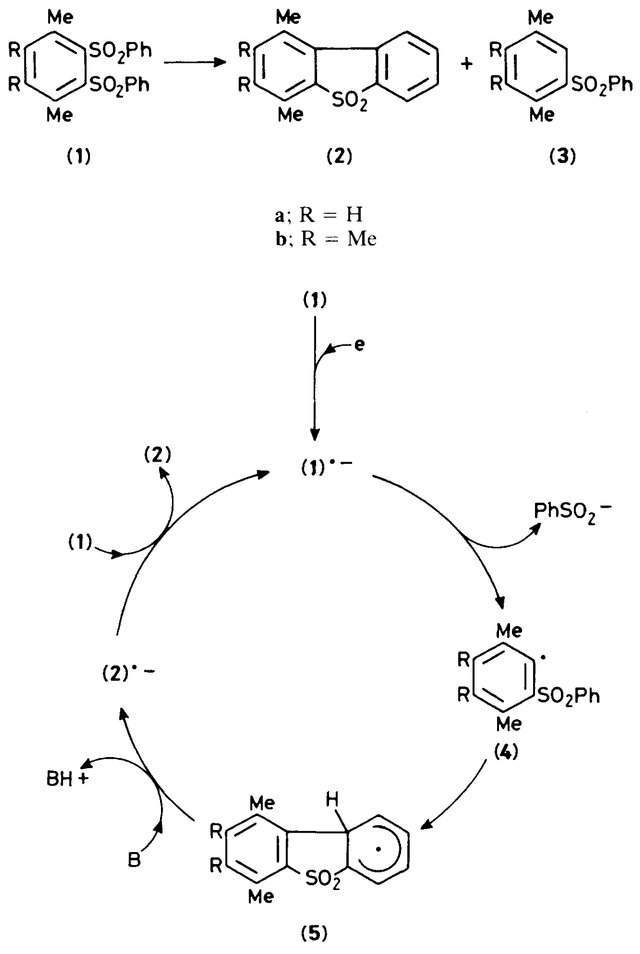
The main difference between the above processes is that in the photo-induced reactions (besides the fact that excited states could be involved) the arenethiolate anion, a strong base in DMSO,[4] is present as an electron donor.

Assuming that proton abstraction from the cyclohexadienyl intermediates (**5a**,**b**) by the base is a key step in the propagation cycle, we have undertaken an electrochemical investigation on the cathodic reduction of (**1a**) in DMSO, on

**Table 1.** Results of the controlled-potential electrolyses of (**1a**) in DMSO at a mercury pool cathode.[a]

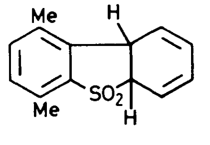
| Run no. | Base | Base/substrate molar ratio | $pK_{BH(BH^+)}$ (DMSO) | F mol$^{-1}$[b,c] | Relative yields (%)[c,d] (**2a**) | (**3a**) | (**6**) | (**7**) |
|---|---|---|---|---|---|---|---|---|
| 1 | None | | | 0.98 | 68.2 | 10.0 | 21.8 | |
| 2 | pyridine | 2.0 | 3.4[e] | 0.96 | 68.0 | 10.4 | 21.0 | |
| 3 | $Et_3N$ | 2.0 | 9.0[e] | 0.55 | 80.1 | 3.5 | 16.3 | |
| 4 | $PhS^-$[f] | 2.0 | 10.3[g] | 0.22 | 86.3 | 10.0 | | 3.7 |
| 5 | $AcO^-$[h] | 2.0 | 12.6[e] | 0.14 | 95.7 | 4.3 | | |
| 6 | $AcO^-$[h] | 1.0 | 12.6[e] | 0.24 | 90.5 | 4.2 | 5.3 | |
| 7 | $AcO^-$[h] | 0.5 | 12.6[e] | 0.54 | 81.5 | 4.5 | 14.0 | |

[a] [Substrate] = 2 × $10^{-3}$ M, electrolysis potential = −1.65 V *vs.* $Ag/Ag^+$ 0.01 M in DMSO, supporting electrolyte: 0.1 M $Bu_4NBF_4$. The overall yields, estimated by $^1H$ n.m.r. spectroscopy with 1,4-bis(chloromethyl)benzene as an internal standard, were almost quantitative in every case. For more experimental details see ref. 3. [b] Faradays per mole of reacted starting material. Average error ± 0.02 F mol$^{-1}$. [c] Average values of at least three independent determinations. [d] Determined by h.p.l.c. on a 0.39 × 30 cm μ-Porasil column [$CH_2Cl_2$ or $CH_2Cl_2$-hexane (4 : 1) (run 4) as eluants]. The average errors from the mean values listed are ±2%. [e] Ref. 6. [f] As sodium salt. [g] Ref. 4. [h] $AsBu_4N^+$ salt.

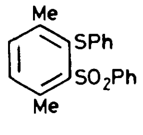


a; R = H
b; R = Me
B = PhS$^-$

Scheme 1



(6)



(7)

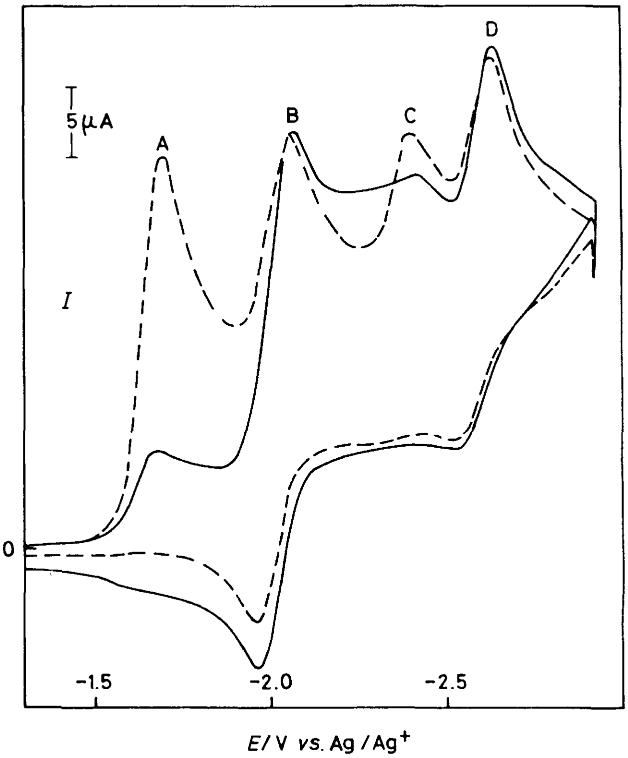


**Figure 1.** Cyclic voltammetry of 2,3-bis(phenylsulphonyl)-1,4-dimethylbenzene (**1a**) in DMSO and 0.1 M $Bu_4NBF_4$ [working electrode: platinum sphere (surface area *ca.* 7 mm$^2$); reference electrode: $Ag/AgNO_3$ 0.01 M in DMSO; sweep rate: 100 mV s$^{-1}$]. Dashed line: (**1a**) (2 × $10^{-3}$ M) alone. Continuous line: after addition of one molar equivalent of $AcOBu_4N$.

the premise that, if the mechanistic hypothesis outlined in Scheme 1 is tenable the addition of an efficient base to the catholyte would reduce the charge consumption.

The electrocatalytic nature of the process leading to (**2a**) was investigated by cyclic voltammetry (Figure 1). By addition of increasing amounts of base (acetate) we observed a significant lowering of the reduction wave of the substrate (wave A) coupled with a decrease in peak C [due to the side products (**3a**) and/or (**6**)]† while peaks B and D [due to (**2a**)] remained almost unaffected. These findings are indicative of an efficient electrocatalytic process[5] where the number of Faradays required to drive the reaction to completion tends toward zero.

Controlled-potential electrolyses and coulometric measurements were carried out on a mercury pool working electrode, the potential of which was set at the level of the first reduction wave of the substrate. The preliminary results obtained from the cathodic reduction of (**1a**) in the presence of some bases are given in Table 1.‡

From examination of the data the following points emerge: The addition of bases causes the number of Faradays consumed per mole of starting material to drop to low values. This increase in the current yield approximately parallels the increase in strength (runs 2—5) and in concentration (runs 5—7) of the base employed. Thus, while pyridine ($pK_{BH^+}$ 3.4; run 2) has no effect at all, the current efficiency jumps to *ca.* 700% with the same concentration of acetate ($pK_{BH}$ 12.6; run 5). In other words, under these conditions each 'hole' generated by electron transfer from the cathode produces an average transformation of seven molecules of substrate. That this transformation does not take place spontaneously under the conditions employed (h.p.l.c.) is strong evidence for the chain reaction.

On going from run 2 to run 5 the yield of (**2a**) increases as that of (**6**) decreases. On the assumption that (**6**) arises from disproportionation of the intermediate (**5a**), this result is explained if the base acts as a catalyst for the aromatisation of (**5a**) to (**2a**).

The yield of (**3a**) decreases on going from run 1 (or 2) to run 3 and then remains practically constant (*ca.* 4%) through runs 5—7. This last figure probably reflects the percentage of (**3a**) which is formed *via* H-atom abstraction from the solvent by the intermediate σ radical (**4a**). The additional yield of (**3a**) is most likely due to an H-atom transfer from another source, *e.g.* the radical (**5a**) itself. It is possible that the more the rate of aromatisation of (**5a**) is increased by addition of base the less probable will be the H-atom transfer to (**4a**).

Runs 3 and 7 show, within experimental error, that the product distribution is the same when the concentration of different bases is adjusted so as to have the same charge consumption.

Run 4 deserves some more comments. The formation of small amounts of the substitution product (**7**) [*via* trapping of the intermediate σ radical (**4a**) by the nucleophile ($S_{RN}1$ pathway)] was expected in view of our previous results[1,2] and of the large affinity of $PhS^-$ for radicals.[7] Furthermore, within the proposed mechanism, a larger yield of (**3a**) (with respect to that obtained with other bases) was expected as benzenethiol, formed along the propagation cycle, has been shown[2] to favour the formation of (**3a**) by acting as an efficient H-atom donor for the intermediate (**4a**).

This substantial evidence in support of an unusual base-catalysed chain mechanism in an intramolecular homolytic arylation could have interesting synthetic implications.

*Received, 11th June 1984; Com. 804*

## References

1 M. Novi, C. Dell'Erba, G. Garbarino, and F. Sancassan, *J. Org. Chem.*, 1982, **47**, 2292.

2 M. Novi, G. Garbarino, and C. Dell'Erba, *J. Org. Chem.*, in the press.

3 M. Novi, C. Dell'Erba, G. Garbarino, G. Scarponi, and G. Capodaglio, *J. Chem. Soc., Perkin Trans. 2*, 1984, 951.

4 F. G. Bordwell and D. L. Hughes, *J. Org. Chem.*, 1982, **47**, 3224.

5 J. M. Saveant, *Acc. Chem. Res.*, 1980, **13**, 323.

6 I. M. Kolthoff, M. K. Chantooni, and S. Bhownik, *J. Am. Chem. Soc.*, 1968, **90**, 23.

7 J. F. Bunnett, *Acc. Chem. Res.*, 1978, **11**, 413.

---

† An investigation on the electrochemical reduction of (**6**) showed that its reduction wave is very close to that of (**3a**).

‡ The product distribution given for run 1 is somewhat different from that previously reported.[3] This difference can be ascribed mainly to the instability of (**6**).