Electrochemical Reduction of Some *o*-Bis(phenylsulphonyl)benzene Derivatives. Effect of the Substrate Structure and of the Addition of Bases on the Product Distribution.

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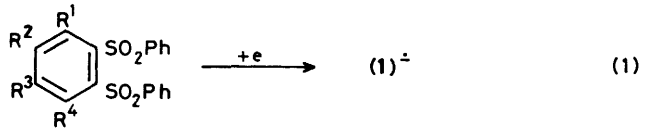
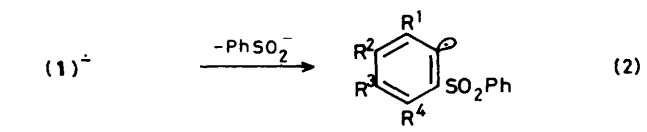
A study of the electrochemical behaviour of the *o*-bis(phenylsulphonyl)benzene derivatives (**1a**—**e**) in dimethyl sulphoxide containing 0.1 M-tetrabutylammonium tetrafluoroborate has been undertaken. The results from cyclic voltammetry, controlled-potential electrolysis, and coulometry strongly argue in support of a mechanism involving initial formation of the radical anion $(\mathbf{1})^{-\cdot}$ which fragments into the σ radical (**2**) and $PhSO_2^-$. Competing pathways for (**2**) are: (*a*) intramolecular homolytic arylation eventually leading to dibenzothiophene (**4**) together with dihydrodibenzothiophene (**5**) derivatives and (*b*) hydrogen-atom transfer leading to monosulphones (**6**). The fact that compounds (**1a, b**) undergo mainly cyclization, whereas the hydrogen-atom transfer predominates in the case of compounds (**1c, d**), indicates that the structure of the starting substrate is a major governing factor for the above competition. An explanation, based on a concomitance of steric effects of the methyl groups *ortho* to the phenylsulphonyl substituents, is given. Experiments carried out in the presence of different bases show that the intramolecular arylation leading to the cyclized product can occur also through an unprecedented chain mechanism whose efficiency, which increases as the strength and the concentration of the base is increased, is found in turn to be dependent on the substrate structure. Finally, when arenethiolates are used as bases, a third pathway (the nucleophile–radical coupling step of the $S_{RN}1$ process) is found to compete for the intermediate σ radical (**2**) eventually leading to sulphides resulting from the overall substitution of an arylthio for a phenylsulphonyl moiety in (**1**). When the intramolecular cyclization does not compete efficiently almost quantitative yields of sulphides are obtained *via* an $S_{RN}1$ route.

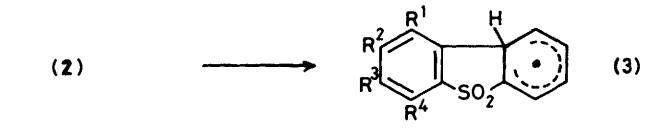
The photo- or electro-chemically induced electron-transfer to the bis(sulphone) (**1a**) in dimethyl sulphoxide (DMSO) was shown in our earlier papers[1,2] to proceed *via* the anion radical $(\mathbf{1a})^{-\cdot}$, which rapidly cleaves to the benzenesulphinate anion and the σ radical (**2a**) [equations (1) and (2)]. The radical (**2a**) can then participate in several competing processes: (*a*) intramolecular homolytic arylation (S_Hi) eventually leading to (**4a**) with (**5a**) as a by-product [equations (3), (4), and (5)], (*b*) abstraction of a hydrogen atom [equation (6)] from a suitable donor [the solvent, the supporting electrolyte in the electrochemical experiments, or the cyclohexadienyl radical (**3a**)], and (*c*) trapping by a nucleophile such as PhS^-, when present, which triggers an $S_{RN}1$ chain process[3] [equations (7), (8), and (2) in a cycle].



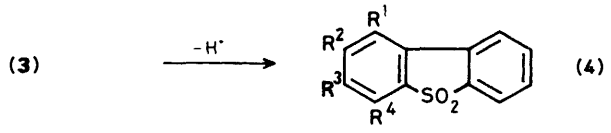
(1) $\longrightarrow$ $(\mathbf{1})^{-\cdot}$ (1)



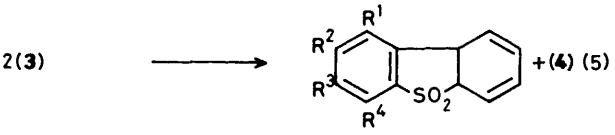
$(\mathbf{1})^{-\cdot}$ $\longrightarrow$ (2) (2)



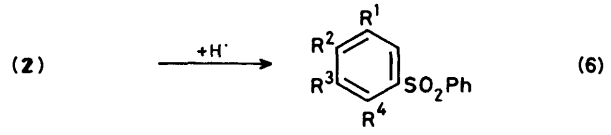
(2) $\longrightarrow$ (3) (3)



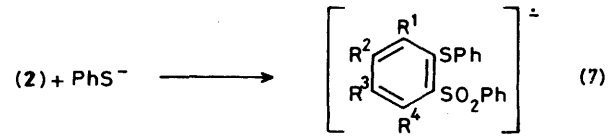
(3) $\longrightarrow$ (4) (4)



2(3) $\longrightarrow$ +(4) (5)



(2) $\longrightarrow$ (6) (6)



(2) + PhS^- $\longrightarrow$ (7) (7)

$(\mathbf{7})^{-\cdot}$ + (1) $\longrightarrow$ (7) + $(\mathbf{1})^{-\cdot}$ (8)

a; $R^1 = R^4 = Me$, $R^2 = R^3 = H$
b; $R^1 = R^2 = R^3 = R^4 = Me$
c; $R^1 = R^2 = R^3 = R^4 = H$
d; $R^1 = R^4 = H$, $R^2 = R^3 = Me$
e; $R^1 = R^3 = Me$, $R^2 = R^4 = H$
e′; $R^1 = R^3 = H$, $R^2 = R^4 = Me$

In a preliminary communication[2] we reported that in the electrochemical reduction of (**1a**), in the presence of an efficient base, steps (5) and (6) become less important and the re-aromatization of the cyclohexadienyl radical (**3a**) involves abstraction of a proton by the base with formation of the radical anion $(\mathbf{4a})^{-\bullet}$, which is eventually oxidized to (**4a**) by electron transfer to a substrate molecule [equations (9) and (10)]. The

$$(\mathbf{3}) + B \rightleftharpoons (\mathbf{4})^{\bullet-} + BH^{+} \quad (9)$$

$$(\mathbf{4})^{\bullet-} + (\mathbf{1}) \rightleftharpoons (\mathbf{4}) + (\mathbf{1})^{\bullet-} \quad (10)$$

sequence of steps (2), (3), (9), and (10) constitutes an electrocatalytic process[3b] of which (5) and (6) represent possible terminations.

Here, we describe the results obtained from an extension of these electrochemical studies to the bis(sulphones) (**1b—e**) (carried out with the aim of elucidating the inter-relation between structural features in the substrate and the scope of the cyclization process) and to discuss their mechanistic implications.

Results and Discussion

Voltammetric Behaviour of the Bis(sulphones) (**1a—e**).—Cyclic voltammetry (c.v.) of the bis(sulphones) (**1a—e**) was carried out in DMSO containing 0.1M-tetrabutylammonium tetrafluoroborate (TBAT) at a platinum bead electrode. Some typical voltammograms, recorded at a 100 mV s^{-1} sweep rate, are shown in the Figure and experimental reductive peak potentials (E_{pc}), *vs.* an Ag–$AgNO_3$ (0.01M in DMSO) reference electrode, are given in Table 1. Curve A depicts the voltammogram for a 2mM-solution of (**1a**). The reduction wave of the C–SO_2Ph bond (E^1_{pc}) is followed by three waves attributable to the reduction of the products formed in the fast follow-up chemical reactions (see curve C), *i.e.* (**4a**), (**5a**), and (**6a**):* while E^2_{pc} and E^4_{pc} correspond to the two reduction waves of (**4a**), E^3_{pc} results from an overlapping of the (**5a**) and (**6a**) reduction processes (ΔE_{pc} = 10 mV).

The voltammetric behaviour of (**1b**) and (**1e**) bears a close resemblance to that of (**1a**). In the case of (**1b**) E^2_{pc} and E^4_{pc} could likewise be attributed to reduction of the cyclized product (**4b**), whereas E^3_{pc} corresponded to reduction of (**6b**). A low peak corresponding to the reduction of (**5b**) (E_{pc} = −2.58 V)* was masked by the raising portion of the wave at E^4_{pc} and could be detected by derivative cyclic voltammetry. As far as (**1e**) is concerned, the cyclic voltammogram, when compared to those relative to (**1a, b**), showed a slight increase in the E^3_{pc} peak height with respect to E^2_{pc} and E^4_{pc}, suggesting an increased role of the steps leading to the monosulphones (**6**). The isomeric cyclization products [(**4e**) and (**4e′**)] as well as sulphones [(**6e**) and (**6e′**)], expected on the basis of the outlined mechanistic paths, were independently synthesized and analysed by c.v. under the same conditions as those used for (**1e**). Unfortunately the E_{pc} values shown by (**4e**) (−2.09 and −2.69 V), (**4e′**) (−2.12 and −2.72 V), (**6e**) (−2.42 and −2.78 V), and (**6e′**) (−2.44 V) were so close that no unambiguous information about the product distribution could be obtained by this technique.

Curve D of the Figure shows the voltammetric behaviour of the bis(sulphone) (**1d**) whose pattern is similar to that of (**1c**). It is evident in these cases that, unlike (**1a, b, e**), after the reduction wave of the substrate the main peak corresponds to E^3_{pc} indicating that, as independently ascertained, the main products of the follow-up chemical reactions are (**6d**) and (**6c**) respectively. The reduction wave at E^2_{pc}, due to the cyclized products (**4d**) or (**4c**), appeared as shoulder or low peak, suggesting a very low yield of these products. The low wave at E^4_{pc} could be attributed either to the second wave of (**6d**) or (**6c**), or to the lack of resolution of this with the second wave of the

* Isolated from large-scale constant-potential electrolyses.

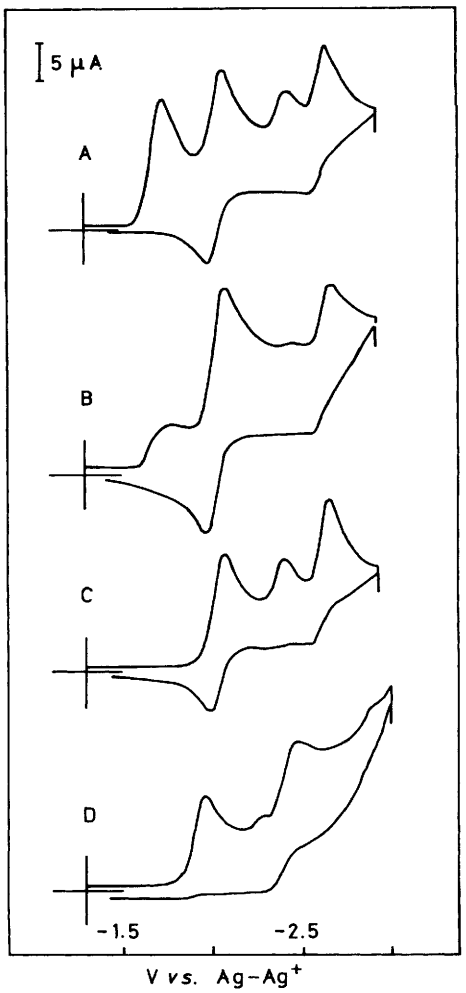


Figure. Cyclic voltammetry of (A) 2mM-bis-sulphone (**1a**), (B) 2mM-bis-sulphone (**1a**) in the presence of 2mM-$AcOBu_4N$, (C) the mixture of products after exhaustive electrolysis at −1.65 V of 2mM-bis-sulphone (**1a**), (D) 2mM-bis-sulphone (**1d**). Platinum bead electrode; DMSO with 0.1M-Bu_4NBF_4; reference electrode Ag–0.01M-$AgNO_3$ in DMSO; sweep rate 100 mV s^{-1}.

Table 1. Reduction peak potentials by cyclic voltammetry of the bis-sulphones (**1a—e**)[a]

Substrate	$-E^1_{pc}$ [b]	$-E^2_{pc}$ [c]	$-E^3_{pc}$	$-E^4_{pc}$
(**1a**)	1.73	2.05	2.41	2.65
(**1b**)	1.79	2.14	2.45	2.69
(**1c**)	1.86[d]	2.28[e]	2.40	2.89[f]
(**1d**)	1.97[d]	2.25[e]	2.49	2.92[f]
(**1e**)	1.86	2.08	2.40	2.65

[a] V *vs.* Ag–0.01M-$AgNO_3$ in DMSO, Pt bead cathode, 0.1 V s^{-1}, DMSO–Bu_4NBF_4 (0.1M), [Substrate] *ca.* 10^{-3}M. No *iR* compensation was applied. [b] Unless otherwise stated peaks are irreversible at up to 100 V s^{-1} when carrying a sweep ranging ±250 mV around the E_{pc} value. [c] Reversible peak in every case. [d] In the reverse anodic sweep the reoxidation peak was clearly detectable at a sweep rate of 0.05 V s^{-1} for (**1c**) and of 0.2 V s^{-1} for (**1d**). [e] Shoulder. [f] Partly masked by the catholyte discharge.

Table 2. Coulometric data and product distributions for electrolytic reduction of the bis-sulphones (**1a**—**e**) in DMSO at a mercury pool cathode[a]

Run	Substrate	Base[b] (mol equiv.)	n[c,d]	Product distribution (%)[c,e] (6)	(4)	(5)	Sulphides	Cyclized: Uncyclized[f]
1	(**1a**)	None	0.98[g]	10.0	68.2	21.8		9.0
2	(**1a**)	Pyridine (2.0)	0.96[g]	10.4	68.0	21.6		8.6
3	(**1a**)	Et_3N (2.0)	0.55[g]	3.5	80.2	16.3		27.6
4	(**1a**)	PhS^-[h] (0.5)	0.60	16.5	80.8	2.7		5.1
5	(**1a**)	PhS^-[h] (1.0)	0.31	13.1	85.6		(**7a**): 1.3	
6	(**1a**)	PhS^-[h] (2.0)	0.22[g]	10.0	86.3		(**7a**): 3.7	
7	(**1a**)	PhS^-[i] (20.0)	0.18	6.0	58.0		(**7a**): 36.0	
8	(**1a**)	PhS^-[i] (50.0)	0.15	2.0	41.0		(**7a**): 56.0	
9	(**1a**)	3-$ClC_6H_4S^-$[i] (50.0)	0.16	2.0	54.0		(**9a**): 44.0	
10	(**1a**)	4-$MeOC_6H_4S^-$[i] (50.0)	0.12	tr.	41.7		(**10a**): 58.3	
11	(**1a**)	AcO^-[i] (0.5)	0.54[g]	4.5	81.5	14.0		21.2
12	(**1a**)	AcO^-[i] (1.0)	0.24[g]	4.2	90.5	5.3		22.8
13	(**1a**)	AcO^-[i] (2.0)	0.14[g]	4.3	95.7			22.2
14	(**1b**)	None	1.00	10.3	74.6	15.1		8.7
15	(**1b**)	AcO^-[i] (1.0)	0.39	8.4	85.6	6.0		10.9
16	(**1b**)	AcO^-[i] (2.0)	0.25	5.5	91.8	2.7		17.2
17	(**1c**)	None	1.15	92.0	8.0			0.09
18	(**1c**)	AcO^-[i] (2.0)	1.08	90.5	9.5			0.10
19	(**1c**)	PhS^-[i] (50.0)	0.24	10.7			(**7c**): 89.3	
20	(**1d**)	None	1.23	97.5	2.5			0.03
21	(**1d**)	AcO^-[i] (2.0)	1.23	98.0	2.0			0.02
22	(**1d**)	PhS^-[i] (50.0)	0.24	10.0			(**7d**): 90.0	
23	(**1e**)	None	1.01	(**6e**): 33.4	(**4e**): 12.1	*j*		0.36
				(**6e'**): 16.7	(**4e'**): 37.8			2.26
24	(**1e**)	AcO^-[i] (2.0)	0.81	(**6e**): 29.1	(**4e**): 17.3			0.59
				(**6e'**): 14.6	(**4e'**): 39.0			2.67

[a] [Substrate] = 2×10^{-3}M, supporting electrolyte: 0.1M-Bu_4NBF_4, reference electrode: Ag–0.01M-$AgNO_3$ in DMSO. Cathode potentials (V): −1.65 for (**1a**), −1.81 for (**1b**), −1.84 for (**1c**), −1.97 for (**1d**), and −1.88 for (**1e**). The overall yields, estimated by n.m.r. spectroscopy and/or h.p.l.c., range between 90—95%. [b] pK_a of the conjugate acids in DMSO: pyridine 3.4,[7] Et_3N 9.0,[7] PhS^- 10.3,[8] 3-$ClC_6H_4S^-$ 8.6,[8] 4-$MeOC_6H_4S^-$ 11.2,[8] and AcO^- 11.6.[9] [c] Average values of at least three independent determinations. [d] Average error ±0.02 F mol^{-1}. [e] Determined by h.p.l.c. The average errors from the mean values listed are ±2%. [f] Ratio between the sum of the yields of cyclized products (**4**) and (**5**) and the yield of sulphone (**6**). [g] Data from the preliminary communication.[2] [h] As sodium salt. [i] As tetrabutylammonium salt. [j] Trace amounts of (**5e**, **e'**) are probably formed (see Experimental section).

cyclized products. Another difference between the voltammetric behaviour of compounds (**1a, b, e**) and (**1c, d**) is that in the latter cases, when the cyclic voltammetry was carried out between (E^1_{pc} + 0.25 V) and (E^1_{pc} − 0.25 V), an anodic current due to the partial recovery of the bis(sulphone) radical anion was clearly seen at a sweep rate of 50 mV s^{-1} for (**1c**) and of 200 mV s^{-1} for (**1d**). The substantial increase in the radical anion lifetime on going from (**1a, b, e**) to (**1c, d**) is in good agreement with the expectation[3d,4] that *ortho*-substitution destabilizes an aromatic radical anion (steric acceleration of radical anion decomposition)[5] and matches the voltammetric results found for simple monosulphones.[4,6]

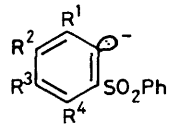
As expected[2] the addition of increasing amounts of a base such as triethylamine (pK_a 9.0),[7] benzenethiolate (pK_a 10.3),[8] and acetate (pK_a 11.6)[9] caused a significant lowering of the reduction wave of (**1a**) (see curve B of the Figure), while the addition of pyridine (pK_a 3.4)[7] had no effect at all. The peak decrease at E^1_{pc}, which parallels the increase in concentration and strength of the added base, was observed to be coupled with a peak decrease at E^3_{pc}; the E^2_{pc} and E^4_{pc} waves remaining apparently unaffected. These findings are indicative of an efficient electrocatalytic process[3b] where the number of Faradays required to drive the reaction to completion tends towards zero. Further evidence from coulometry (see later) led us to confirm[2] that a propagation cycle including equations (2), (3), (9), and (10) is operative in the formation of the cyclized product (**4a**). As far as the substrates (**1b**—**e**) are concerned, the effect of acetate addition, the most efficient base used, was similar for substrates (**1a**) and (**1b**), less sizeable for (**1e**), and negligible for (**1c**) and (**1d**). This is consistent with the mechanism proposed since (**1c**) and (**1d**) give only small yields of cyclized products.

Controlled-potential Electrolysis of the Bis-sulphones (**1a**—**e**) *and Coulometry.*—Listed in Table 2 are the coulometric results and product distributions for the controlled-potential electrolysis (c.p.e.) of the bis-sulphones (**1a**—**e**) at a mercury pool cathode in DMSO containing 0.1M-TBAT and, for some runs, variable concentrations of different bases. The working potential was usually set positive (70—100 mV) with respect to E^1_{pc} and normal exponential current–time curves were observed in all experiments. Data for runs 1—3, 6, and 11—13 are those reported in our earlier work.[2] It has been carefully checked by h.p.l.c. that in any case the transformation of (**1a**—**e**) into the final products does not take place spontaneously under the conditions used. The various products were isolated from preparative-scale experiments, and identified either by ^1H n.m.r. spectroscopy and microanalytical data, or by comparison with authentic samples independently prepared (see Experimental section). ^1H N.m.r. and/or h.p.l.c. were employed to determine both the overall yield (which is satisfactory in every case) and the product distributions given in Table 2.

In the absence of added bases (*runs* 1, 14, 17, 20, *and* 23). Both the current consumption and the product distribution indicate a very similar behaviour between (**1a**) and (**1b**) and between (**1c**) and (**1d**). At the potential employed for the electrolysis of (**1a, b**) there is no significant deviation from a coulometric n value of unity, indicating that the net process is the single-electron reduction of the C–SO_2Ph bond. Taking into account both the nature of the electrolysis products and the

experimental n value, the simplest reduction mechanism for the (**1a, b**) pair is represented by a stepwise process with formation of (**1a,b**)$^{-\bullet}$ and (**2a,b**) as intermediates [equations (1) and (2)], followed by a fast $S_{RN}1$ process [equations (3) and (4) together with (5) as a secondary route]. For these substrates the hydrogen-atom abstraction reaction (6) competes only to a minor extent.

In sharp contrast with the (**1a, b**) pair, the cathodic reduction of (**1c, d**) gave almost exclusive formation of the uncyclized products (**6c, d**) with a current consumption slightly higher than one faraday per mole (*ca.* 1.2 F mol^{-1}). As other experimental results (see runs 19 and 22 below) bear evidence that steps (1) and (2) are also operative in the case of (**1c, d**), this last result is a sign of the intervention, to the extent of *ca.* 20%, of another single-electron process leading to (**6c, d**) from (**2c, d**) in competition with the hydrogen-atom abstraction step (6). As to

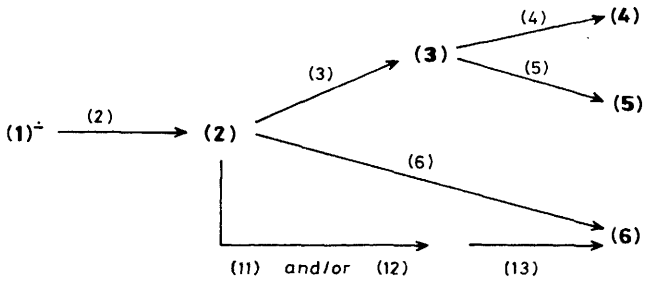
(2) + e $\xrightarrow{\text{cathode}}$  (11)

(8)

(1)$^{\bullet-}$ + (2) $\longrightarrow$ (1) + (8) (12)

(8) + SH $\longrightarrow$ (6) + S$^-$ (13)

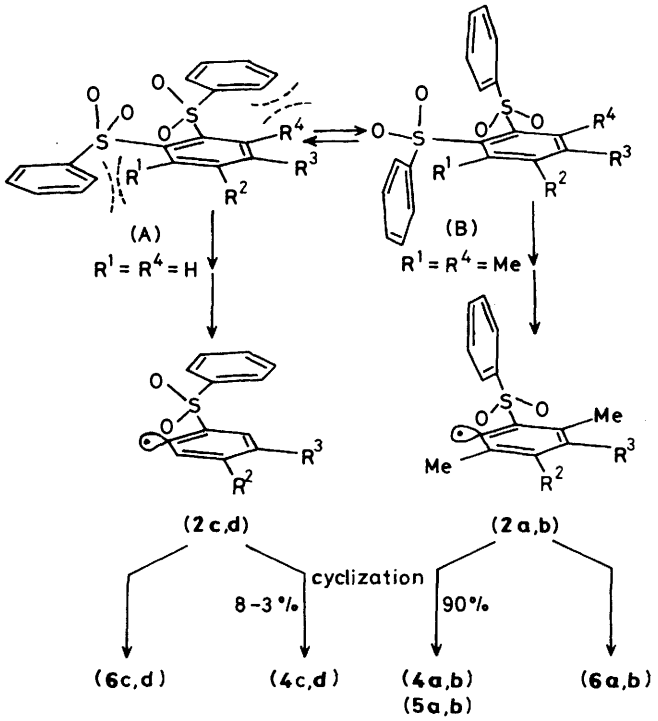
the nature of this process, by analogy with what is known about the extensively studied cathodic reductions of aryl halides,[10,11] the possibilities shown in equations (11)—(13) come to mind.[3b,11,12] The σ radicals (**2c, d**) do not undergo, unlike (**2a, b**), a fast $S_{RN}1$ process and can be further reduced either at the electrode [equation (11)] or in solution [equation (12)]. The resulting strongly basic aryl anions (**8c, d**) are then protonated by either the solvent-supporting electrolyte system or the unavoidable residual water in the catholyte [equation (13)] to give eventually monosulphones (**6c, d**) *via* an overall two-electron process. The most interesting difference between runs 1, 14 and runs 17, 20, however, stands out from the marked increase (at least one-hundred fold) in the yield ratio between [(**4**) + (**5**)] and (**6**), on going from (**1c, d**) to (**1a, b**). This result can be well interpreted when considering that such ratio tightly depends on how effectively step (3) can compete with the electron-transfer reactions (11) and (12) or hydrogen-atom abstraction reaction (6) (Scheme 1). The results obtained by c.v. and c.p.e. indicate that in the case of (**1a, b**), though k_2 is large the reduction of (**2a, b**) produced at the electrode is negligible



Scheme 1.

and k_3 is large enough to make reaction (6) compete but to a minor extent only. In contrast, for (**1c, d**) k_3 is so small relatively speaking that the reduction to the monosulphone (**6**) can, to a large extent, overcome the process leading to the cyclization products. In our opinion, steric and conformational features both in (**1**) [and consequently also in (**1**)$^{-\bullet}$] and in (**2**) are the most likely governing factors in these competitions. It is well known, in fact, that in intramolecular arylation processes,[13] conformational factors can be of considerable importance:[13,14] an efficient intramolecular trapping of the forming aryl radical is observed when the substrate (for steric, electronic, or geometrical reasons) can adopt predominantly a conformation suitable for cyclization. In unfavourable cases the intramolecular arylation is superseded by alternative processes[14,15] such as hydrogen-atom transfer or dimerization.

An examination of molecular models shows that on going from (**1c**) to (**1a**) [or likewise from (**1d**) to (**1b**)] the substitution



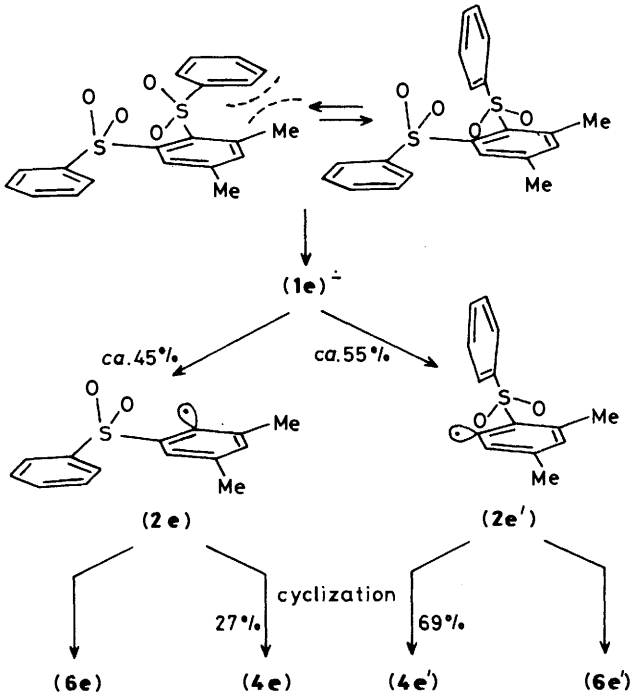
Scheme 2.

of the hydrogens *ortho* to the phenylsulphonyl moieties with methyl groups results in an extremely congested molecule in which free rotation around the C–S bonds is hindered.* In particular, steric hindrance due to the presence of the *o*-methyl substituents (see A in Scheme 2, where, as in Scheme 3, the molecular geometries are shown, for clarity, only schematically) favours conformers of (**1a, b**) in which the phenyl ring of a $PhSO_2$ group and the carbon atom bearing the adjacent leaving $PhSO_2$ group are nearer to each other in space (see B in Scheme 2). Thus, in consequence of the ejection of a benzene-

* It is well known[5,16] that in the case of an irreversible chemical reaction subsequent to a single-electron transfer, the E_p value is shifted anodically by 30 mV, at constant sweep rate, for every ten-fold increase in the rate constant. The 130 and 180 mV anodic shift of E_p observed on going from (**1c**) to (**1a**) and from (**1d**) to (**1b**) [in spite of the electronic effect of the two extra methyl groups which should act in the opposite direction, see *e.g.* the cathodic shift of 110 mV observed in going from (**1c**) to (**1d**)] is, in our opinion, a consequence of the increased overcrowding of the molecule. In fact, as evidenced by c.v., these anodic shifts are associated with a decrease in the radical anion lifetime and it is conceivable that additional driving force for reaction (**2**) could be provided by the steric relief [greater for the (**1a, b**) than for the (**1c, d**) couple] attendant upon ejection of a benzenesulphinate anion.

sulphinate anion from (**1a, b**)$^{-\bullet}$, the geometry of the forming σ radicals (**2a, b**) is suitable for a fast cyclization process. It is evident that in the case of (**1c, d**) such stereopopulation control cannot operate and that, therefore, the σ radicals (**2c, d**) are consumed mainly by the alternative pathways (6), (12), and perhaps (11).

The results obtained with (**1e**) not only confirm the above hypothesis but also emphasize that the presence in compound (**2**) of a methyl group *ortho* to the carbon atom bearing the odd



Scheme 3.

electron is another important factor governing the cyclized to uncyclized product ratio in the reactions studied. As sketched in Scheme 3, analysis of the product distribution in experiment 23 suggests that (*a*) there is no preferential fragmentation for (**1e**)$^{-\bullet}$, the yield of (**4e**) + (**6e**) being almost the same as that of (**4e'**) + (**6e'**), and (*b*) in agreement with the assumptions previously made, the steric effect of the methyl *ortho* to the remaining $PhSO_2$ group favours cyclization in (**2e'**) whilst, in contrast, (**2e**) mainly undergoes hydrogen-atom transfer. However, the results also show that on going from (**2c, d**) to (**2e**) and likewise from (**2e'**) to (**2a, b**) the presence of an additional methyl group *ortho* to the radical centre results in an approximately 4-fold increase in the cyclized to uncyclized product ratio. A possible explanation for this effect is that such a methyl group sterically hinders the intermolecular hydrogen-atom transfer reaction.

In conclusion when both R^1 and R^4 are methyl groups, as in (**1a, b**), because of the synergic effect of the two groups, cyclization represents the main route for the chemical transformation of (**1a, b**)$^{-\bullet}$. Conversely, when both R^1 and R^4 are hydrogen atoms, as in (**1c, d**), the cyclization process is negligible as there is no steric or conformational factor to favour it. Compound (**1e**) represents a system which is intermediate between the two limiting cases above.

In the presence of added bases. The results obtained from the c.p.e. of (**1a**), carried out in the presence of different bases, together with previous experimental results,[1c] led us[2] to propose that the transformation of (**1a**) into (**4a**) is a base-catalysed chain process [steps (2), (3), (9), and (10) in a propagation cycle]. The most interesting point is represented by step (9) where the aromatization of the cyclohexadienyl radical intermediate (**3a**) occurs through the base-assisted formation of its conjugate base (**4a**)$^{-\bullet}$ at a rate competitive with the disproportionation (5) and with the hydrogen-atom transfer process (4). Evidence[17] for proton abstraction at benzylic positions of neutral radicals has previously been obtained in the anthracene series. Moreover, in the case of (**3a**), the acidity of the benzylic protons is likely to be further enhanced by the *ortho* electron-withdrawing sulphonyl group. The successive step (10), which initiates another propagation cycle, involves electron transfer from (**4a**)$^{-\bullet}$ to (**1a**). As c.v. experiments show that the oxidation of (**4a**)$^{-\bullet}$ occurs at a potential more negative than does the reduction of (**1a**), it is conceivable that this electron transfer is thermodynamically favourable[3b,c,11,18] and hence presumably very fast.

In agreement with the hypotheses advanced, the coulometric results showed that, by addition of different bases, the *n* value decreases as the strength (*cf.* runs 2, 3, 6, and 13) and the concentration (runs 4—6 and 11—13) of the base are increased. Thus, while pyridine (pK_a 3.4)[7] has a negligible effect the current yield jumps to *ca.* 700% with the same concentration of acetate (pK_a 11.6).[9] Moreover, a significant change in the product distribution is associated with the increase in the current yield: the yield of (**4a**) increases as that of (**5a**) and (**6a**) decreases. Finally, when the concentration of different bases is adjusted so as to have comparable current consumptions (*cf.* runs 3 and 11) the product distribution is identical, within experimental error. The case of benzenethiolate (see *e.g.* run 4) is particular and will be discussed later.

Experiments 16, 18, 21, and 24 show that, on going from (**1c, d**) to (**1e**) and also to (**1b**), the more effectively the cyclization of (**2**) competes with the steps leading to (**6**) the more evident is the catalytic effect of the base. Thus while with (**1c, d**) there is no appreciable effect, addition of acetate on the c.p.e. of (**1e**) results in a small decrease in the coulometric *n* value associated with a similar small increase in the cyclized to uncyclized product ratio. Both effects are more evident in the case of (**1b**). However, comparison of the current yields obtained in runs 15 and 16 respectively with those of runs 12 and 13 shows that the catalytic effect of the base is greater with (**1a**) than with (**1b**). An explanation of this lies in the different stability of the conjugate bases of (**3a**) and (**3b**). Actually the electronic effect of the two extra methyl groups in (**4b**)$^{-\bullet}$ renders this radical anion less stable than the analogue (**4a**)$^{-\bullet}$ so that step (9) is less favoured with (**3b**) than with (**3a**).

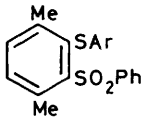
It must be pointed out that the present results on the effect of bases, while fulfilling theoretical expectation,[19] open new perspectives in the field of aromatic homolytic arylations. In fact, besides the hitherto recognized pathways, the base-assisted deprotonation of cyclohexadienyl radical intermediates represents, in our opinion, a potentially powerful route for re-aromatization to which due attention has so far not been paid: its occurrence, subject to the fulfilment of appropriate requirements, surely contributes to higher yields, by avoiding undesired by-products, and furthermore can trigger, in particularly favourable cases as those described therein, an efficient propagation cycle.

The results obtained from the experiments carried out in the presence of benzenethiolate deserve further comment. The larger yield of (**6a**) (with respect to that obtained with other bases, *cf.* run 4 with runs 3 and 11) can be attributed to the formation, along the propagation cycle, of benzenethiol, which has been shown[1c] to be a good hydrogen-atom donor[11d,20] for the intermediate (**2a**): *i.e.* the propagation cycle generates a species leading to deactivation of the cycle itself. For this reason it is possible that the catalytic efficiency of the benzenethiolate, if

deduced only from the decrease in the coulometric *n* value, could be underestimated. A strong indication that it could well be so comes from the observation that, for similar experimental *n* values, the decrease in the yield of (**5a**) with respect to run 1 is higher for benzenethiolate (run 4) than for triethylamine or acetate (runs 3 and 11 respectively): this points to a greater efficiency of benzenethiolate in favouring a process (step 9) competing for (**3**) with the disproportionation leading to (**5a**) (step 5).

However, the most remarkable difference between benzenethiolate and the other bases used lies in the fact that the former is a reagent able to participate also in $S_{RN}1$ processes.[1a,c,3,11b,d,20b,21,22] Accordingly, runs 5—8 show that increasing concentrations of benzenethiolate anion make the $S_{RN}1$ propagation cycle compete more and more favourably with the S_Hi process *via* trapping of the σ radical intermediate (**2a**) by the nucleophile. Moreover, the substantial formation of the sulphides (**7c**) and (**7d**) (runs 19 and 22) accompanied by a remarkable decrease in current consumption proves that, as previously advanced, (**2c, d**) are also intermediates in the electrolytic reduction of (**1c**) and (**1d**). Runs 19 and 22 represent, to our knowledge, the cleanest examples so far[3] of an $S_{RN}1$ displacement of a phenylsulphonyl group in the aromatic series.

Finally, examination of the results obtained in runs 8, 9, and 10 shows that the competition between the $S_{RN}1$ and the S_Hi processes is sensitive to the nucleophilicity of the sulphur reagent. In fact, on going from the 3-chlorobenzenethiolate to the unsubstituted and to the 4-methoxybenzenethiolate, *i.e.* on increasing nucleophilicity of the anion,[8] the yield of the



(**7a**) Ar = Ph
(**9a**) Ar = 3-ClC_6H_4
(**10a**) Ar = 4-$MeOC_6H_4$

sulphides (**7a**), (**9a**), and (**10a**) increases, the sulphide to cyclized product ratios increasing from 0.8 to 1.1 and to 1.4.

Experimental

M.p.s were taken on an Electrothermal melting point apparatus and are uncorrected. ^1H N.m.r. spectra were recorded on a Varian FT 80 spectrometer (Me_4Si as an internal standard). H.p.l.c. was performed on a Waters Model ALC-202 chromatograph equipped with a model 440 u.v. detector, monitoring at 254 nm, and using a 0.39 × 30 cm μ-Porasil column. Preparative experiments carried out under argon were deaerated using five freeze-pump-thaw cycles and stoppered either with a rubber septum or left under a positive gas pressure (*ca.* 30 mmHg regulated with a mercury bubbler). Both the electrolyses and the syntheses performed in DMSO were routinely worked up by dilution with brine (5—6 vol), 3-fold extraction with Et_2O, followed by washing of the combined extracts with brine. The ether extract was dried (Na_2SO_4) and the solvent removed with a reduced-pressure rotary evaporator (bath temperature *ca.* 30 °C).

Materials. The following substrates or authentic samples were prepared as reported in literature: 1,4-dimethyl-2,3-bis(phenylsulphonyl)benzene (**1a**),[1a] 3,4,5,6-tetramethyl-1,2-bis(phenylsulphonyl)benzene (**1b**),[1a] 1,4-dimethyl-2-(phenylsulphonyl)-3-(phenylthio)benzene (**7a**),[1a] 1,4-dimethyl- (**4a**),[1a] 1,2,3,4-tetramethyl- (**4b**),[1a] and the unsubstituted dibenzothiophene 5,5-dioxide (**4c**),[23] 5a,9a-dihydro-1,4-dimethyldibenzothiophene 5,5-dioxide (**5a**),[1b] 1,4-dimethyl-2-(phenylsulphonyl)benzene (**6a**),[24] 2,3,4,5-tetramethyl-1-(phenylsulphonyl)benzene (**6b**),[1c] diphenyl sulphone (**6c**),[24] 2,4-dimethyl- (**4e'**),[24] and 3,5-dimethyl-1-(phenylsulphonyl)benzene (**4e**).[24]

The supporting electrolyte, tetrabutylammonium (TBA) tetrafluoroborate, as well as TBA acetate and TBA hydroxide (40% in water) were Fluka AG reagents and were used without further purification. Sodium[25] and TBA[11d] arenethiolates were prepared as reported. Spectroscopic grade DMSO, distilled under reduced pressure over calcium hydride, was stored over molecular sieves (type 4 Å). All other commercial solvents and reagents were purified according to literature methods to match reported physical constants.

1,2-*Bis*(*phenylthio*)-, 4,5-*Dimethyl*-1,2-*bis*(*phenylthio*)-, *and* 3,5-*Dimethyl*-1,2-*bis*(*phenylthio*)*benzene*.—A solution of the appropriate 1,2-dihalogenobenzene derivative (see below) (30 mmol) and sodium benzenethiolate (66 mmol) in DMSO (100 ml), made under argon in a 250 ml round bottom flask, was irradiated, with stirring, with a 300W Osram Vitalux sunlamp placed *ca.* 8 cm from the flask. The reaction temperature was maintained at *ca.* 45 °C by means of a cooling fan placed beside the flask and the irradiation continued until t.l.c. showed the complete disappearance of the starting substrate (1.5—2.5 h). After the usual work up, the residue of the ether extract, dissolved in hexane, was chromatographed on a silica gel column by first eluting with hexane to remove diphenyl disulphide, benzenethiol, and traces of by-products which were not investigated, then the main component was eluted using hexane–dichloromethane (3:1). The yields of the 1,2-bis(phenylthio) derivatives were in the range 40—50%. 1,2-Bis(phenylthio)benzene (prepared from 2-chloroiodobenzene[26]) was obtained as an oil, b.p. 183 °C/0.5 mmHg (lit.,[27] b.p. 187 °C/1 mmHg); δ_H (CD_3COCD_3) 7.36 (10 H, m) and 7.18 (4 H, m).

4,5-*Dimethyl*-1,2-*bis*(*phenylthio*)*benzene* (prepared from 1-bromo-2-iodo-4,5-dimethylbenzene[28]) had m.p. 100—101 °C (from light petroleum b.p. 30—50 °C) (Found: C, 74.5; H, 5.7. $C_{20}H_{18}S_2$ requires C, 74.5; H, 5.6%); δ_H($CDCl_3$) 7.24 (10 H, m), 7.02 (2 H, s), and 2.09 (6 H, s).

1,2-*Bis*(*phenylthio*)-3,5-*dimethylbenzene* (prepared from 1-bromo-2-iodo-3,5-dimethylbenzene) was a colourless oil, b.p. 186—188 °C/0.05 mmHg (Found: C, 74.4; H, 5.7. $C_{20}H_{18}S_2$ requires C, 74.5; H, 5.6%); δ_H($CDCl_3$) 7.23 (10 H, m), 6.90 (1 H, br s), 6.54 (1 H, br s), 2.33 (3 H, s), and 2.15 (3 H, s).

1-*Bromo*-2-*iodo*-3,5-*dimethylbenzene* (synthesized in 60% yield by the Gattermann reaction[29] on 2-amino-1-bromo-3,5-dimethylbenzene[30]) was purified by column chromatography (silica gel–hexane) followed by distillation, b.p. 140—142 °C/10 mmHg (Found: C, 30.9; H, 2.6. C_8H_8BrI requires C, 30.9; H, 2.6%); δ_H($CDCl_3$) 7.25 (1 H, br s), 6.94 (1 H, br s), 2.48 (3 H, s), and 2.21 (3 H, s).

1,2-*Bis*(*phenylsulphonyl*)- (**1c**), 4,5-*Dimethyl*-1,2-*bis*(*phenylsulphonyl*)- (**1d**), *and* 3,5-*Dimethyl*-1,2-*bis*(*phenylsulphonyl*)-*benzene* (**1e**).—The bis(sulphides) described above were oxidized with an excess of 34% hydrogen peroxide in glacial acetic acid at 100 °C. The following bis(sulphones) were obtained in almost quantitative yield: 1,2-bis(phenylsulphonyl)benzene (**1c**), m.p. 165—166 °C (from EtOH–dioxane) (lit.,[27] m.p. 165—166 °C); δ_H($CDCl_3$) 8.45 (2 H, m), 7.88 (6 H, m), and 7.53 (6 H, m); 4,5-*dimethyl*-1,2-*bis*(*phenylsulphonyl*)*benzene* (**1d**), m.p. 202 °C (from EtOH) (Found: C, 62.2; H, 4.7. $C_{20}H_{18}O_4S_2$ requires C, 62.2; H, 4.7%); δ_H($CDCl_3$) 8.20 (2 H, s), 7.92 (4 H, m), 7.48 (6 H, m), and 2.38 (6 H, s); 3,5-*dimethyl*-1,2-*bis*(*phenylsulphonyl*)-*benzene* (**1e**), m.p. 226—227 °C (from EtOH–dioxane) (Found: C, 62.0; H, 4.7. $C_{20}H_{18}O_4S_2$ requires C, 62.2; H, 4.7%);

$\delta_H(CDCl_3)$ 8.52 (1 H, br s), 8.07 (2 H, m), 7.80 (2 H, m), 7.50 (6 H, m), 7.35 (1 H, br s), 2.51 (3 H, s), and 2.47 (3 H, s).

Preparation of Authentic Samples of 2,3- (**4d**), 1,3- (**4e**), *and* 2,4-*Dimethyldibenzothiophene 5,5-Dioxide* (**4e'**).—(*a*) *Dimethylphenyl 2-nitrophenyl sulphides.* 3,4-, 2,4-, or 3,5-Dimethylbenzenethiol[31] (15.9 g, 0.115 mol) was dissolved in 1M-sodium methoxide in methanol (108 ml) and this was added to a solution of commercial (Fluka) 2-chloronitrobenzene (17.1 g, 0.108 mol) in the same solvent (140 ml). The mixture was deaerated with argon gas, heated under reflux overnight, and then cooled in an ice-bath. The nitro sulphide which precipitated was filtered off, washed with water to remove sodium chloride, and was then crystallized from methanol. 2-(3,4-*Dimethylphenylthio*)*nitrobenzene* (**11**) was obtained in 75% yield, m.p. 93—94 °C (Found: C, 64.8; H, 5.1; N, 5.4. $C_{14}H_{13}NO_2S$ requires C, 64.9; H, 5.0; N, 5.4%); $\delta_H(CDCl_3)$ 8.20 (1 H, m), 7.30 (5 H, m), 6.90 (1 H, m), and 2.35 and 2.31 (6 H in all, overlapping s).

2-(2,4-*Dimethylphenylthio*)*nitrobenzene* (**12**) was obtained in 50% yield, m.p. 97 °C (Found: C, 64.9; H, 5.1; N, 5.4. $C_{14}H_{13}NO_2S$ requires C, 64.9; H, 5.0; N, 5.4%); $\delta_H(CDCl_3)$ 8.22 (1 H, m), 7.25 (5 H, m), 6.69 (1 H, m), 2.38 (3 H, s), and 2.29 (3 H, s).

2-(3,5-*Dimethylphenylthio*)*nitrobenzene* (**13**) was obtained in 65% yield, m.p. 95 °C (Found: C, 64.8; H, 5.0; N, 5.4. $C_{14}H_{13}NO_2S$ requires C, 64.9; H, 5.0; N, 5.4%); $\delta_H(CDCl_3)$ 8.20 (1 H, m), 7.20 (5 H, m), 6.88 (1 H, m), and 2.33 (6 H, s).

(*b*) *Reduction of the nitro sulphides* (**11**)—(**13**). The above nitrosulphides (5 g) were reduced with hydrogen over palladium (10% on activated carbon) in dichloromethane (100 ml). Filtration, evaporation, and distillation or crystallization gave the corresponding amino sulphides in 85—95% yield.

2-(3,4-*Dimethylphenylthio*)*aminobenzene* (**14**) had m.p. 67 °C (from hexane) (Found: C, 73.4; H, 6.6; N, 6.2. $C_{14}H_{15}NS$ requires C, 73.4; H, 6.6; N, 6.1%); $\delta_H(CDCl_3)$ 7.00 (7 H, m), 4.24 (2 H, NH_2), and 2.17 (6 H, s).

2-(2,4-*Dimethylphenylthio*)*aminobenzene* (**15**) was obtained as an oil, b.p. 139 °C/0.08 mmHg (Found: C, 73.5; H, 6.6; N, 6.3. $C_{14}H_{15}NS$ requires C, 73.4; H, 6.6; N, 6.1%); $\delta_H(CDCl_3)$ 7.39 (1 H, m), 7.18 (1 H, m), 6.99 (1 H, m), 6.78 (4 H, m), 4.22 (2 H, NH_2), 2.43 (3 H, s), and 2.29 (3 H, s).

2-(3,5-*Dimethylphenylthio*)*aminobenzene* (**16**) was an oil, b.p. 122—124 °C/0.03 mmHg (Found: C, 73.5; H, 6.7; N, 6.0. $C_{14}H_{15}NS$ requires C, 73.4; H, 6.6; N, 6.1%); $\delta_H(CDCl_3)$ 7.26 (2 H, m), 6.71 (5 H, m), 4.20 (2 H, NH_2), and 2.19 (6 H, s).

(*c*) *Aprotic diazotization of the amino sulphides* (**14**)—(**16**) *and oxidation of the crude mixture of reaction products.* A mixture of the amino sulphide (**14**), (**15**), or (**16**) (2.3 g, 10 mmol), freshly distilled isopentyl nitrite (17.4 ml, 13 mmol), and ethyl acetate (50 ml) was kept at 50 °C for 5 h. The solvent was removed and the residue, dissolved in hexane–dichloromethane (3:1), was filtered through a short silica gel column (eluting with the same solvent mixture) in order to remove unwanted coloured material which remained on the top of the column. The solvent was removed under reduced pressure and the residue was dissolved in glacial acetic acid and oxidized with an excess of 34% hydrogen peroxide at 100 °C. After the usual work-up, the crude mixture of oxidized products was flash-chromatographed on a silica gel column.

Starting from the amino sulphide (**14**) the column chromatography [ether–hexane (6:1) as the eluant] gave: (*i*) 3,4-dimethyl-1-(phenylsulphonyl)benzene (**6d**) (28%), identified by comparison of its ^1H n.m.r. spectrum and mixed m.p. with those of an authentic sample (see below); (*ii*) 2,3-*dimethyldibenzothiophene 5,5-dioxide* (**4d**) (17%), m.p. 209 °C (from EtOH) (Found: C, 68.8; H, 5.0. $C_{14}H_{12}O_2S$ requires C, 68.8; H, 4.9%); $\delta_H(CDCl_3)$ 7.71 (2 H, m), 7.55 (3 H, m), 7.23 (1 H, s), and 2.35 (6 H, s); (*iii*) 1,2-*dimethyldibenzothiophene 5,5-dioxide* (26%), m.p. 248—249 °C (from EtOH–dioxane) (Found: C, 68.9; H, 5.0. $C_{14}H_{12}O_2S$ requires C, 68.85; H, 4.9%); $\delta_H(CDCl_3)$ 8.02 (1 H, m), 7.82 (1 H, m), 7.54 (3 H, m), 7.32 (1 H, d, *J* 7.9 Hz), 2.62 (3 H, s), and 2.43 (3 H, s).

From the amino sulphide (**15**) the following oxidation products were separated by column chromatography using hexane–ether (2:1) as the eluant: (*i*) 2,4-dimethyl-1-(phenylsulphonyl)benzene (**6e'**) (6%), identified by comparison of its ^1H n.m.r. spectrum and mixed m.p. with those of an authentic sample;[24] (*ii*) 2,4-*dimethyldibenzothiophene 5,5-dioxide* (**4e'**) (5%), m.p. 212—213 °C (from EtOH) (Found: C, 68.7; H, 4.9. $C_{14}H_{12}O_2S$ requires C, 68.8; H, 4.9%); $\delta_H(CDCl_3)$ 7.64 (4 H, m), 7.38 (1 H, br s), 7.05 (1 H, br s), 2.65 (3 H, s), and 2.41 (3 H, s).

Column chromatography of the mixture obtained from the amino sulphide (**16**) [eluant hexane–ether (1:2)] gave: (*i*) 3,5-dimethyl-1-(phenylsulphonyl)benzene (**6e**) (16%), identified by comparison (^1H n.m.r. spectrum and mixed m.p.) with an authentic sample;[24] (*ii*) 1,3-*dimethyldibenzothiophene* 5,5-*dioxide* (**4e**) (60%), m.p. 216 °C (from EtOH–dioxane) (Found: C, 68.6; H, 4.9. $C_{14}H_{12}O_2S$ requires C, 68.8; H, 4.9%); $\delta_H(CDCl_3)$ 7.71 (5 H, m), 7.20 (1 H, br s), 2.65 (3 H, s), and 2.40 (3 H, s).

3,4-*Dimethyl*-1-(*phenylsulphonyl*)*benzene* (**6d**).—A solution of 1-iodo-3,4-dimethylbenzene[32] (2.32 g, 10 mmol) and sodium benzenethiolate (1.45 g, 11 mmol) in DMSO (40 ml) was irradiated for 2 h with a sunlamp as described for the preparation of 1,2-bis(phenylthio)benzene derivatives. Usual work-up gave a residue which was chromatographed on a silica gel column using hexane as the eluant. The main component of the mixture was a colourless oil (1.2 g) which was dissolved in acetic acid and oxidized with an excess of 34% hydrogen peroxide to give 1.1 g (45% as based on the starting iodo derivative) of the *title sulphone* (**6d**), m.p. 130 °C (from EtOH) (Found: C, 68.2; H, 5.7. $C_{14}H_{14}O_2S$ requires C, 68.3; H, 5.7%); $\delta_H(CDCl_3)$ 7.93 (2 H, m), 7.56 (5 H, m), 7.10 (1 H, d, *J* 8.7 Hz), and 2.28 (6 H, s).

Preparation of the Sulphides (**7c**), (**7d**), (**9a**), *and* (**10a**).—Authentic samples of these sulphides were prepared from the corresponding bis(phenylsulphonyl)benzene derivatives [(**1c**), (**1d**), and (**1a**) respectively] by reaction with the appropriate sodium arenethiolate in DMSO as described in a previous paper.[1a] The various sulphides synthesized, reaction temperature, reaction time, yield, and physical, analytical, and ^1H n.m.r. spectroscopic data are as follows.

1-(*Phenylsulphonyl*)-2-(*phenylthio*)*benzene* (**7c**), 120 °C, 1.5 h, 97%, m.p. 96.5—97.5 °C (from EtOH) (Found: C, 66.2; H, 4.3. $C_{18}H_{14}O_2S_2$ requires C, 66.3; H, 4.3%); $\delta_H(CDCl_3)$ 8.25 (1 H, m), 8.03 (2 H, m), and 7.25 (11 H, m).

4,5-*Dimethyl*-1-(*phenylsulphonyl*)-2-(*phenylthio*)*benzene* (**7d**), 120 °C, 9 h, 72% [20% of unchanged (**1d**) recovered], m.p. 153 °C (from EtOH) (Found: C, 67.6; H, 5.1. $C_{20}H_{18}O_2S_2$ requires C, 67.8; H, 5.1%); $\delta_H(CDCl_3)$ 8.03 (3 H, m), 7.46 (3 H, m), 7.14 (5 H, m), 6.82 (1 H, s), 2.30 (3 H, s), and 2.11 (3 H, s).

2-(3-*Chlorophenylthio*)-1,4-*dimethyl*-3-(*phenylsulphonyl*)-*benzene* (**9a**), 120 °C, 40 min, 95%, m.p. 126 °C (from EtOH) (Found: C, 61.7; H, 4.3. $C_{20}H_{17}ClO_2S_2$ requires C, 61.8; H, 4.4%); $\delta_H(CDCl_3)$ 7.83 (2 H, m), 7.36 (2 H, br s), 7.22 (3 H, m), 6.90 (2 H, m), 6.44 (1 H, m), 6.20 (1 H, m), 2.96 (3 H, s), and 2.17 (3 H, s).

2-(4-*Methoxyphenylthio*)-1,4-*dimethyl*-3-(*phenylsulphonyl*)-*benzene* (**10a**), 20 °C, 52 h, 70%, m.p. 146 °C (from EtOH) (Found: C, 65.7; H, 5.2. $C_{21}H_{20}O_3S_2$ requires C, 65.6; H, 5.2%); $\delta_H(CDCl_3)$ 7.91 (2 H, m), 7.29 (5 H, m), 6.50 (4 H, m), 3.69 (3 H, s), 2.94 (3 H, s), and 2.10 (3 H, s).

Cyclic Voltammetry and Controlled-potential Electrolysis.—Cyclic voltammetry and controlled-potential electrolysis of 10^{-3}M solutions of the bis-sulphones (**1a**—**e**) in 0.1M-DMSO–TBAT were conducted using an Amel model 551 potentiostat equipped with the following Amel units: a model 563 multipurpose unit, a model 566 function generator, and a model 863 x–y recorder. Coulometry was conducted by integration of current–time curves. In order to correct for the background current, the quantity of electricity given by the reduction of the various substrates was determined by the method of plotting the charge as a function of time and extrapolating the linear portion back to zero time. Standard, three-compartment cells were used for all electrochemical experiments. Cells were flushed with and kept under a positive pressure of high purity argon which was previously passed through columns of granular silica gel. Cyclic voltammograms were recorded on a platinum bead working electrode (surface area *ca.* 6 mm^2). Silver–0.01M-silver nitrate in DMSO was used as a reference electrode, and all potentials are quoted with respect to this reference. A platinum wire served as a counter electrode. Further experimental details have been reported elsewhere.[1b]

Identification and determination of products. Most electrolysis products were isolated from preparative-scale experiments and identified by either ^{1}H n.m.r. spectroscopic and microanalytical data, or by comparison (^{1}H n.m.r., t.l.c., h.p.l.c., and mixed m.p.s) with authentic samples prepared as reported above. The overall yields, determined by ^{1}H n.m.r. spectroscopy and/or h.p.l.c. using proper internal standards, ranged from 90 to 95%. The relative yields reported in Table 2 were determined by h.p.l.c. The peak areas were measured with the aid of a Spectra-Physics Minigrator and were corrected for molar response as determined from standard solutions of the products. The formation of trace amounts of the dihydro derivatives (**5e**) and (**5e′**) in experiment 23 is supposed on the basis of ^{1}H n.m.r. spectroscopic evidence and of the similarity of their h.p.l.c. retention times with those of the analogues (**5a, b**). No attempt at separation of (**5e** and **e′**) was made owing to their low yield. The dihydrodibenzothiophene derivatives (**5a, b**) proved to be quite stable when in pure, crystalline form. However, in solution, compounds (**5a, b**) undergo decomposition which is sufficiently slow to allow h.p.l.c. runs to be carried out without any appreciable loss of product. In order to obtain reproducible results, special care was taken in the isolation and to the treatment of the reaction mixtures, *e.g.* evaporation of the ether extract was carried out below room temperature, the dry crude residue was stored at −20 °C, and the mixtures were purified by rapid flash-chromatography.

A pure sample of 5a,9a-*dihydro*-1,2,3,4-*tetramethyldibenzothiophene* 5,5-*dioxide* (**5b**) could be obtained in 10% yield of the crystallized product from two preparative-scale electrolyses, m.p. 209 °C (from EtOH) (Found: C, 70.2; H, 6.7; S, 11.7. $C_{16}H_{18}O_2S$ requires C, 70.1; H, 6.6; S, 11.7%); $\delta_H(CDCl_3)$ 6.43 (1 H, dd, *J* 5.3 and 9.7 Hz), 5.98 (2 H, m), 5.59 (1 H, d, *J* 10.1 Hz), 4.46 (1 H, d, *J* 11.0 Hz), 4.16 (1 H, dd, *J* 5.8 and 11.0 Hz), 2.58 (3 H, s), and 2.29 and 2.24 (9 H in all, two overlapping s); $\delta_C(CDCl_3)$ 141.69, 136.47, 135.54, 134.37, 131.39, 130.80, 129.78, 125.05, 122.89, 115.57, 60.59, 36.49, 16.94, 15.63, 15.03, and 14.86.

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