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A MILD AND EFFICIENT $S_{RN}1$ APPROACH TO DIARYL SULFIDES FROM ARENEDIAZONIUM TETRAFLUOROBORATES

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Abstract. - The reaction between arenediazonium tetrafluoroborates and sodium arenethiolates in Me_2SO at 25 °C represents an efficient access to diaryl sulfides. A number of evidences suggest the occurrence of a radical, radical-anion $S_{RN}1$ mechanism, the arenethiolate acting both as electron donor and as aryl-radical trapping nucleophile. Valuable improvements with respect to recent $S_{RN}1$ syntheses of diaryl sulfides from haloarenes are represented, inter alia, by the compatibility of both electron-withdrawing and releasing substituents as well as by the insensitivity to steric hindrance in the diazonium salt. When the arenediazonium ion bears another $S_{RN}1$ leaving group (such as Cl, Br, or I) disubstitution products are predominantly formed.

Arenediazonium salts have always proved to be powerful intermediates to a number of aromatic derivatives, due both to their ready availability and to their wide reactivity.[1] In particular, within the field of dediazoniation reactions, the heating of an aqueous solution of a diazonium salt in the presence of an arenethiolate represents one of the most ancient accesses to diaryl sulfides (Ziegler reaction).[2] The method has experienced until recently a widespred use,[3] but, as a major drawback, has proved occasionally hazardous because of the thermal lability of the postulated intermediate diazosulfides 1.[4]

Actually the thermal decomposition of diazosulfides 1 (R = alkyl or aryl) is a reaction known since 1884,[5] and, at least in aprotic solvents, the intermediacy of aryl and thiyl radicals has found numerous substantiations: variable amounts of products typically originating from such radicals are this way obtained (Scheme 1).[6]

Scheme 1

$$\underset{\underset{\sim}{1}}{Ar\text{-}N{=}N\text{-}SR} \xrightarrow[-N_2]{\Delta} Ar^{\cdot} + RS^{\cdot} \longrightarrow ArSR,\ ArH,\ RSH,\ RSSR,\ \text{solvent derived products}$$

It is on the other hand known that aryl radicals, which can be obtained also by reduction of diazonium salts[1,7] and, possibly, of the diazosulfides themselves[8] in milder conditions, couple with negatively charged nucleophiles (Nu^-), arenethiolates included,[9] to give, when proper conditions are met, ArNu derivatives through an $S_{RN}1$ chain mechanism.[9,10] Finally, it is well

established that arenethiolates can act as reducing agents, as they do transfer electrons to a number of substrates, with or without photostimulation.[9a-i,10,11,12]

Therefore, as finalised to the synthesis of diaryl sulfides, we have undertaken a study of the reaction of diazonium salts with arenethiolates in Me_2SO, a reportedly suitable solvent for electron-transfer processes.[9f,13] It was hoped that a system could be attained where the same arenethiolate exerted the double action of a) mildly generating aryl radicals from an efficient precursor (the diazonium ion itself or the intermediate diazosulfide), and b) coupling with such radicals to trigger a chain pathway to the final desired substitution product.

Accordingly, we have preliminarily reported[14] that arenediazonium tetrafluoroborates smoothly react with excess arenethiolates in Me_2SO at room temperature to give high yields of diaryl sulfides (eq 1), although both the synthetic scope and limitations of the reaction and its mechan

$$ArN_2^+ + Ar'S^- \xrightarrow[Me_2SO]{r.t.} \underset{\underset{\sim}{2}}{ArSAr'} + N_2 \qquad (1)$$

istic details needed further developments. The work hereafter covers these aspects, firmly placing, in our opinion, the present system within the growing field of $S_{RN}1$ processes.

Results and Discussion

The results of the present investigation are collected in the Table. Some data have been already reported in the preliminary communication[14] and are herein recalled for clarity sake. It must be stressed that reaction times in the Table refer to reaction pushed to completion, unless otherwise stated, but are to be regarded as gross indications of reactivity given the tests adopted herein in order to determine the reaction endpoint (ceasing of nitrogen evolution and/or TLC disappearance of diazosulfide; see Experimental section).

A first glance to the Table immediately reveals that, together with several valuable examples of excellent yields of the straightforward substitution products $\underset{\sim}{2}$, some systems lead to overwhelming amounts of different derivatives, generally represented by bis(arylthio)benzenes ($\underset{\sim}{4u}$—$\underset{\sim}{w}$ and $\underset{\sim}{10}$). As such "limits" of the studied reaction as to the synthesis of simple diaryl sulfides strictly depend on the nature of its mechanism, we judge useful to premise the discussion of mechanistic details to the analysis of the synthetic aspects themselves.

Mechanistic aspects. - In principle, the overall formation of diaryl sulfides $\underset{\sim}{2}$ through reaction (1) could fall within a rather wide spectrum of mechanistic possibilities. Nevertheless, the discussion hereafter will make evident that classical ionic pathways such as S_NAr, S_N1, or EA *via* aryne intermediates can be confidently rejected at least as main routes. Furthermore, commonly accepted[10,11] diagnostic tests (see *infra*) strongly support, in keeping with the premises to this work, both the occurrence of radical and radical-anions intermediates and the involvement of a chain process through such intermediates.

Accordingly, as a basis for a detailed analysis, reasonably conceivable steps are outlined in Scheme 2, which also takes into account the possibility that either the diazosulfide $\underset{\sim}{1}$ or the parent diazonium cation (or both) could act as electron acceptors. Thus, the step sequences M3 + M5 + M6 and M5 + M7 represent propagation cycles of $S_{RN}1$ processes[9,10] involving the (phenylthio)azo or the diazonio as leaving groups, triggered respectively by the initiation steps M1 + M2 or M4. In this respect we should point out that, in agreement with the expected high rate of the cation-anion combination,[15] the first chemical event is indeed represented, as evidenced by

Table. Reaction times and yields for the reaction between $ArN_2^+BF_4^-$ and Ar'SNa in Me_2SO at 25 °C.[a]

Expt	Ar	Ar'	Time (min)	Yield (%)[b] monosubstitution ArSAr'	disubstitution Bis(arylthio)arenes	others[c]
1	C_6H_5	C_6H_5	210	2a: 97[d]; 78[e]		
2a	4-$O_2NC_6H_4$	"	15	2b: 79		
2b[f]	"	"	50	": 45		$PhNO_2$[g]: 29
2c	[h]	"	15	": 93		
2d	[i]			": 59[j]		$PhNO_2$[g]: 26
3	3-$O_2NC_6H_4$	C_6H_5	30	2c: 80		
4	4-$MeOC_6H_4$	"	210	2d: 72		
5a	4-MeC_6H_4	"	450	2e: 79		
5b[k]	"	"	50	": 43		
5c[k]	"	" 1	50	": 24		
6	2-MeC_6H_4	"	330	2f: 82		
7	2,6-$Me_2C_6H_3$	"	120	2g: 76		
8	4-FC_6H_4	"	240	2h: 75	4u: <3	
9	4-ClC_6H_4	"	180	2i: 12	": 66	
10	4-BrC_6H_4	"	320	2j: 8	": 69	
11	4-IC_6H_4	"	390	2k: 13	": 63	
12	3-FC_6H_4	"	180	2l: 86		
13	3-ClC_6H_4	"	210	2m: 15	4v: 63	
14	2-FC_6H_4	"	180	2n: 80		
15	2-ClC_6H_4	"	320	2o: 13	4w: 48	2a: traces 5 : 4[j]
16	2-IC_6H_4[m]	"	360	2p: 8	4w: 28	2a: traces 5 : 4[j]
17	2-Cl-4-MeC_6H_3	"	320	2q: 9	10: 34	2e: traces 6 : 3
18	C_6H_5	4-MeC_6H_4	210	2e: 82		
19	"	2,4,6-$Me_3C_6H_2$	330	2r: 67[n]		
20	"	4-ClC_6H_4	180	2i: 34	4u: traces	11: 24 12: 9
21	1-naphthyl	C_6H_5	210	2s: 82		
22a	2-naphthyl	"	330	2t: 78		
22b	"	"	240[o]	": 69		
22c[p]	"	"	240[o]	": 23		
22d[q]	"	"	240[o]	": 46		

[a]Substrate concentrations typically in the range 0.11—0.17 M; $Ar'S^-/ArN_2^+$ molar ratio 3.0 unless otherwise stated. Expts 1, 2a, 4, 5a, 6, 7, 18, 19, 21, 22a-c are those reported in our preliminary communication.[14] [b]Yields refer to isolated products unless otherwise stated. See Experimental section for product identification. [c]By-products from the arenethiolate, viz. $(Ar'S)_2$ and Ar'SH were always observed but not quantified; substrate reduction products (ArH) were generally observed (TLC) in traces (<5%) unless reported; unreacted diazosulfides (in traces unless the reaction was not pushed to completion) were not quantified due to their instability. [d]Crude product, slightly contaminated by PhSH and PhSSPh. [e]After distillation. [f]PhSH (10 mol. equiv. with respect to ArN_2^+) also present. [g]Identified and quantified by HPLC. [h]Reaction was performed with [(4-nitrophenyl)diazothio]benzene in the presence of 2 mol. equiv. of PhSNa. [i]Controlled-potential electrolysis of [(4-nitrophenyl)diazothio]benzene 2.8 mM in Me_2SO—0.01 M TBAF on a Pt flag cathode at -0.9 V vs. $Ag/AgNO_3$ 0.01 M; current consumption 0.4 F/mol. [j]Determined by HPLC. [k]Under irradiation (see Experimental section). [l]$Ar'S^-/ArN_2^+$ molar ratio 1.0. [m]Slight decomposition (gas evolution) of the Me_2SO arenediazonium solution was observed. [n]Determined by ^1H NMR (α,α'-dichloro-p-xilene as internal standard). [o]Reaction not pushed to completion. [p]m-Dinitrobenzene (0.3 mol. equiv. with respect to ArN_2^+) also present. [q]Galvinoxyl (0.2 mol. equiv. with respect to ArN_2^+) also present.

Scheme 2

$$ArN_2^+ + Ar'S^- \rightleftharpoons Ar\text{-}N{=}N\text{-}SAr' \quad (\underset{\sim}{1}) \qquad M1$$

$$\underset{\sim}{1} + Ar'S^- \rightleftharpoons \underset{\sim}{1}^{\cdot-} + Ar'S^{\cdot} \qquad M2$$

$$\underset{\sim}{1}^{\cdot-} \longrightarrow Ar^{\cdot} + N_2 + Ar'S^- \qquad M3$$

$$ArN_2^+ + Ar'S^- \longrightarrow Ar^{\cdot} + N_2 + Ar'S^{\cdot} \qquad M4$$

$$Ar^{\cdot} + Ar'S^- \rightleftharpoons [ArSAr']^{\cdot-} \quad (\underset{\sim}{2}^{\cdot-}) \qquad M5$$

$$\underset{\sim}{2}^{\cdot-} + \underset{\sim}{1} \longrightarrow \underset{\sim}{2} + \underset{\sim}{1}^{\cdot-} \qquad M6$$

$$\underset{\sim}{2}^{\cdot-} + ArN_2^+ \longrightarrow \underset{\sim}{2} + Ar^{\cdot} + N_2 \qquad M7$$

TLC, by the coupling of the diazonium cation with thiolate (step M1). On the grounds of a presumably very high equilibrium constant for such coupling,[15] we believe that the diazonium cation be an unlikely electron-acceptor candidate as compared to the covalent diazosulfide. Furthermore, the actual lying of adduct $\underset{\sim}{1}$ along the reaction coordinate to the final product finds strong, though non definitive, support in the comparison between the reactivities, in analogous conditions, of 4-nitrobenzenediazonium tetrafluoroborate (expt 2a) and of the corresponding independently synthesized diazosulfide (expt 2c), the latter giving higher yields of the substitution product in comparable reaction times.

Effect of inhibitors and electrochemical inducement. - Comparison of expts 22b and 22c shows that m-dinitrobenzene (DNB), a good electron acceptor,[10,11,16] has a markedly negative effect on the reaction rate. This result is clearly diagnostic for the involvement of radical anions, DNB either inhibiting their formation (competing for the arenethiolate in steps M2 or M5) or terminating the propagation cycle (competing for the radical anions themselves in steps M6 or M7).

As far as it concerns experimental evidence for the involvement of aryl radicals as chain-carrying species, both the absence of appreciable amounts of dimerisation products (ArAr), typically originating from them, and the relatively meagre effect of the radical scavenger galvinoxyl[11c,17] (cf. expts 22b and 22d) could be due, in principle, to an intrinsically high efficiency of the chain process. An alternative explanation could be represented, though, by a substantial occurrence of step M5 within a solvent cage, further support coming from the constant-potential electrolysis of [(4-nitrophenyl)diazothio]benzene (expt 2d). In fact, notwithstanding the absence (at least initially) of free PhS^- and the availability of electrons from the cathode, further reduction of the 4-nitrophenyl radical with eventual formation of nitrobenzene is still a minor pathway, a 60% yield of 4-nitrophenyl phenyl sulfide being obtained. It should be pointed out that, although the latter experimental outcome could be rationalised also on the grounds of step M8

$$Ar^{\cdot} + \underset{\sim}{1} \longrightarrow \underset{\sim}{2} + N_2 + Ar^{\cdot} \qquad M8$$

(induced diazosulfide decomposition[6a]), such propagation mode would leave no role to the radical anion $\underset{\sim}{2}^{\cdot-}$, whose intermediacy is definitively supported by the behaviour of haloarenediazonium salts to be discussed in a following section.

Herein, aryl-radical intermediates can be more effectively evidenced by trapping through

H-atom abstraction from a suitable donor. In this respect the reaction medium itself, in agreement with literature reports[13] and positively enough as to the synthetic usefulness of the present reaction, is not effective, as only traces of reduction derivatives (ArH) are at most observed. The yield of nitrobenzene definitely increases, though, when a good H-atom donor such as free thiophenol[9b,j,18] is also present in the reaction between 4-nitrobenzenediazonium and benzenethiolate (expt 2b). Furthermore a negative effect of PhSH on the reaction rate is also at play, what can be taken as an indication that aryl radicals participate to a propagation cycle: their trapping thus represents a termination of the cycle itself.

As far as the involvement of a chain is concerned, the strongest piece of evidence[10b] is undoubtedly represented by the low current consumption (0.4 F mol^{-1}) observed in the aforementioned electrochemically induced experiment 2d, the electrocatalytic nature of the process supporting the intervention of step M6 (or M7).

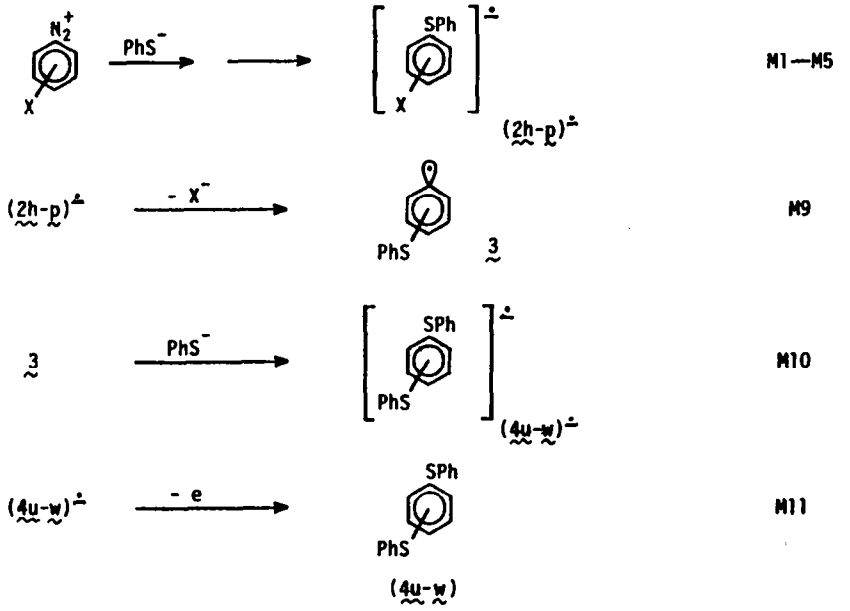
Unfortunately, a further diagnostic test for the $S_{RN}1$ mechanism, that is photostimulation,[10,11] while positive as to the rate of disappearance of the diazosulfide (cf. expts 5a and 5b), proved ambiguous as to the yield of the expected sulfide. Irradiation of the corresponding diazosulfide alone (as obtained in the reaction test-tube from equimolar amounts of diazonium salt and benzenethiolate) gives, within the same reaction time, disappearance of substrate with only a 24% yield of sulfide (expt 5c).

Electronic effects of substituents in the substrate. - It is known[10] that $S_{RN}1$ reactivity is unaffected by those electron releasing substituents which hamper the S_NAr pathway. The expectation is fulfilled herein when comparing the reactivity of the unsubstituted benzenediazonium salt (expt 1) with that of the 4-methoxyderivative (expt 4). On the other hand the nitrogroup, both meta and para with respect to the reaction centre, displays a markedly accelerating effect (expts 2a and 3 respectively) while its strong stabilising effect on radical anions could have a negative influence[19] on the overall reaction rate. In the case of [(4-nitrophenyl)diazothio]benzene, however, cyclic voltammetry analyses (carried out in Me_2SO—0.01 M tetrabutylammonium tetrafluoroborate at a platinum bead electrode and in a 500 mV range around the first reduction peak, E_{pc} = 0.97 V vs. Ag/$AgNO_3$ 0.01 M) showed that there was no tendency toward chemical reversibility when raising the sweep rate up to the maximum (1 V s^{-1}) allowed by the pen-to-chart recording mode. These results are clearly indicative of a high rate of fragmentation for the diazosulfide radical anion. Furthermore the available literature does offer other examples of acceleration of $S_{RN}1$ displacement of the diazonio group induced by nitro substituents,[20] an outcome which has been regarded as definitely excluding the possibility of the S_N1 pathway through aryl-cation intermediates.[20a] Finally, although the increased yield of the reduction product in the presence of free thiophenol (expt 2b) and the electrochemical results evidentiate a fundamental $S_{RN}1$ component, we cannot exclude a minor competitive S_NAr pathway for the 4-nitroderivative, given the electronic effect of the nitrogroup itself.

Behaviour of haloarenediazonium salts. - Inspection of the Table throughout expts 8 to 16 reveals that, with the exclusion of fluoroderivatives, the main reaction product from haloderivatives is invariably represented by a bis(sulfide), resulting from displacement of both the diazonio and the halogen by thiolate.

According to literature data,[9c,d,g,10,21] the formation of such products within the framework of the $S_{RN}1$ process is most easily rationalised on the grounds of Schemes 2 and 3, the crucial point being the partitioning of the intermediate radical anion $\underset{\sim}{2}^{\cdot}$ between electron transfer to $\underset{\sim}{1}$

Scheme 3



4u: PhS at C-4
4v: PhS at C-3
4w: PhS at C-2

or ArN_2^+ (steps M6 and M7 respectively) and expulsion of X^- (step M9), which eventually leads to disubstitution. When such competition occurs in similar systems, the yield in the disubstitution product always parallels the fragmentation-rate order of $ArX^{\cdot-}$, viz. F < Cl < Br < I,[10,22] step M9 being forbidden in practice to fluoroderivatives.[9c,d,g,10,21]

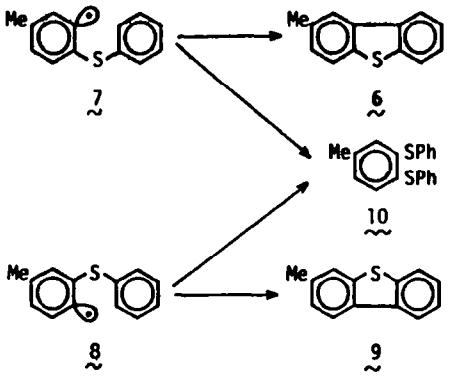
Herein, while differential overall reactivities or product ratios for both ortho and para halobenzenediazonium ions are, as far as Cl, Br, and I are concerned, scarcely significative, the negligible disubstitution observed for all three isomeric fluoroderivatives (expts 8, 12, and 14) constitutes strong substantiation for the proposed Scheme.

Moreover, the intermediacy of radical 3 is evidenced in the reactions of the 2-chloro- and 2-iodobenzenediazonium salts (expts 15 and 16 respectively), which lead to quantifiable amounts of dibenzothiophene 5. Herein a further competition is most likely set up, the corresponding radical 3 undergoing either coupling with thiolate (step M10) or cyclisation to 5 through an intramolecular homolytic arylation.[23]

The intramolecular cyclisation above offers a further compelling mechanistic test when starting from an appropriately substituted substrate. The isolated 2-methyldibenzothiophene 6 (Scheme 4) from 2-chloro-4-methylbenzenediazonium tetrafluoroborate (expt 17) implies the initial replacement of the diazonio group, followed by halide expulsion and cyclisation of 7 to 6, while is in disagreement with a hypothetical initial S_NAr replacement of halogen (activated by either the strongly electronwithdrawing $-N_2^+$ group or the -N=N-SAr' group), which would necessarily be followed by cyclisation of 8 to 9.

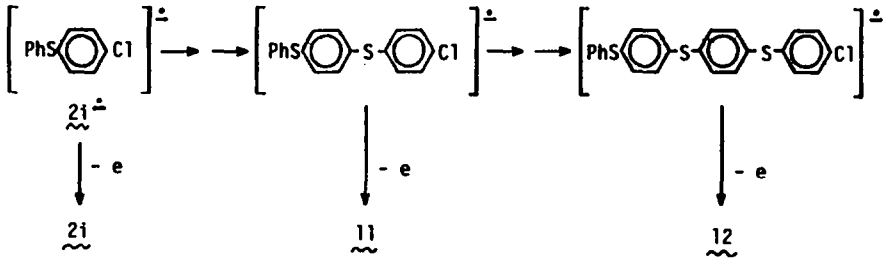
Finally, yet one more test for the correctness of our hypotheses is represented by the possibility of obtaining the same diaryl sulfide radical anion, and hence products originating from the competitive pathways open to it, starting from either 4-chlorobenzenediazonium tetrafluoroborate and benzethiolate or benzenediazonium tetrafluoroborate and 4-chlorobenzenethiolate. Accordingly,

Scheme 4



in the latter case (expt 20), besides the straightforward substitution product, appreciable quantities of 11 and 12 have been isolated, easily rationalisable[9c,d,g,10,21] through Scheme 5.

Scheme 5



Synthetic scope and limitations. - A through inspection of the Table shows that the reaction between arenediazonium tetrafluoroborates and arenethiolates in Me_2SO at 25 °C (eq. 1) represents indeed a powerful route to both symmetrical and unsymmetrical diarylsulfides, to the synthesis of which much effort has been devoted, with different degrees of success, in the last few years. In particular, besides miscellaneous methods[24] and the employment of electrophilic sulfur reagents,[25] chemists have been looking for substantial improvements to the classical nucleophilic replacement of suitable leaving groups in aromatic derivatives by thiolates. In this respect mainly metal[26] or electron-transfer catalysis[9] have been employed, the replaceable groups of choice being halogens in both cases.

A few points seem herein deserving of particular attention. (a) Advantage is taken of readily available starting materials, viz. diazonium tetrafluoroborates. (b) The mild conditions employed overcome any hazard related to the thermal lability of diazosulfides reported[4] in connection with the Ziegler method,[2] although accumulation of such intermediates is evident. Of course, care should be taken in the work-up procedure (see Experimental section) in order to avoid heating of any unreacted diazosulfide. (c) Substituents in the diazonium salt allow good yields in reasonably short times irrespectively to their electronic effects. (d) Steric hindrance by ortho methyl groups has been reported[9c] to hamper the photostimulated $S_{RN}1$ reaction between aryliodides and benzenethiolate in liquid ammonia, although reports referring to different nucleophiles[27,19a] make such an experimental outcome rather unexpected. Herein this factor seems to be somewhat disfavouring

only from the arenethiolate side (expt 19). Conversely, ortho methyl substituents in the diazonium salt appear to play some sort of steric acceleration (cf. expts 5a, 6, and 7). (e) As outlined in the discussion of the mechanistic aspects, the nature itself of the process represents a limitation as to the obtainment of straightforward diaryl sulfides when other good $S_{RN}1$ leaving groups, such as chlorine, bromine, or iodine, are present in the substrate. Of course, looking at this from a different viewpoint, the same haloarenediazonium salts represent suitable substrates for a convenient synthesis of bis(arylthio)arenes, although yields of 1,2-disubstituted isomers seem somewhat less satisfactory.

Experimental

M.p.s were taken on an Electrothermal melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Varian FT 80 instrument (solvent $CDCl_3$; internal standard Me_4Si). HPLC was performed on a Waters model ALC-202 chromatograph equipped with a Model 440 UV detector,monitoring at 254 nm, and using a 0.39 x 30 cm μ-Porasyl column. In quantitative analyses, utilising proper internal standards, the peak areas were measured with the aid of a Spectra-Physics Minigrator and were corrected for molar response as determined from standard solutions. Photostimulated experiments were performed in a Rayonet reactor fitted with eight 350 nm lamps.

Materials.— Arenediazonium tetrafluoroborates[28] were prepared according to reported procedures, parent arylamines being commercial products used without further purification. Crude diazonium salts were purified by insolubilisation with diethyl ether from methanolic solutions and stored at 0°C. The [(4-nitrophenyl)diazothio]benzene[29] was purified by column chromatography [silica gel; dichloromethane—hexane (1:1) as eluant] and stored at 0°C. Sodium arenethiolates were prepared as reported[30] and stored under vacuum. Thiophenol (Fluka AG) was distilled under reduced pressure before use. Tetrabutylammonium tetrafluoroborate, the supporting electrolyte in the electrochemical run (expt 2d in the Table), was a Fluka AG reagent, used without further purification. Dimethylsulfoxide (Fluka AG, reagent grade for the preparative runs, spectroscopic grade for electrochemical and photochemical experiments) was used as received after storage over molecular sieves (type 4Å) under argon. Galvinoxyl and m-dinitrobenzene were commercial samples, crystallised to match reported physical constants.

General synthetic procedure.— Preparative experiments, always carried out under argon, were deaerated using five freeze-pump-thaw cycles and left under a positive pressure (ca. 30 mmHg regulated with a mercury bubbler). The reactions were started by dropping the Me_2SO solution of the arenediazonium salt (1 g in 10 ml) into a double volume of a magnetically stirred solution of arenethiolate (3 mol. equiv.), kept in a water bath at 25°C and wrapped in an aluminum foil. Both gas evolution and darkening of the solution were always immediately observed. The progress of the reactions was followed by TLC (aliquots being diluted with brine and extracted with diethyl ether) and their completion was judged by both ceasing of nitrogen evolution and TLC disappearance of diazosulfide. CAUTION: although no explosions were encountered in the present work, nevertheless caution should be taken in handling the reaction mixture.[4,14]

Both syntheses and electrochemical or photochemical experiments were routinely worked up by dilution with brine (5—6 vol.) and 4-fold extraction with diethyl ether, followed by washing of the combined extracts with 10% NaOH and brine. The organic layer was dried (Na_2SO_4) and the solvent removed under reduced pressure at room temperature. Column chromatography on silica gel (hexane or proper hexane—dichloromethane mixtures as eluant) yielded pure compounds or mixtures further analysed by HPLC and/or ^{1}H NMR.

Sulfides 2a, 2d—o, and 2r, and bis(sulfides) 4v and 4w were oils and were identified by ^{1}H NMR spectroscopy and/or through m.p. and ^{1}H NMR analysis of the corresponding sulfones 2a', 2d'—o', and 2r', or bis(sulfones) 4v' and 4w'. The oxidation to sulfones was performed at 100°C in glacial acetic acid with an excess of 34% hydrogen peroxide.

The m.p.s of the following known compounds matched those reported in literature, the ^{1}H NMR spectra being in agreement with the proposed structure: 2a',[31] 2b,[32] 2c,[32] 2d',[33] 2e',[31] 2f',[31] 2g',[34] 2h',[35] 2i',[31] 2j',[36] 2k',[37] 2l',[35] 2o',[36] 2p,[38] 2r',[31] 2s,[39] 2t,[40] 4u,[41] 4v',[41] 4w',[41] and 11.[26b]

3-Chloro-1-(phenylsulfonyl)benzene 2m': m.p. 110—111 °C (petroleum, b.p. 80—100 °C) (Found: C, 57.1; H, 3.7. $C_{12}H_9ClO_2S$ requires C, 57.0; H, 3.6%); ^{1}H NMR: δ 8.01—7.76 (4H, m) and 7.62—7.42 (5H, m).

2-Fluoro-1-(phenylsulfonyl)benzene 2n': m.p. 105—106 °C (petroleum, b.p. 80—100 °C) (Found: C, 61.1; H, 4.0. $C_{12}H_9FO_2S$ requires C, 61.0; H, 3.8%); ^{1}H NMR: δ 8.22—7.95 (3H, m) and 7.66—6.97 (6H, two partly overlapping multiplets).

The sulfide 2q and the bis(sulfide) 10 were new compounds but no attempt of isolating them as pure analytical samples was made and the oily residues of the respective chromatographic fractions

were directly oxidized to the corresponding sulfones. 2-Chloro-4-methyl-1-(phenylsulfonyl)benzene 2g', m.p. 90—91 °C (petroleum, b.p. 80—100 °C) (Found: C, 58.4; H, 4.1. $C_{13}H_{11}ClO_2S$ requires C, 58.5; H, 4.2%); ^1H NMR: δ 8.22 (1H, app. d, J 8.5 Hz), 8.00—7.87 (2H, m), 7.63—7.40 (3H, m), 7.30—7.20 (2H, m), and 2.38 (3H, s). 1,2-Bis(phenylsulfonyl)-4-methylbenzene 10', m.p. 185-187 °C (EtOH) (Found: C, 61.1; H, 4.3. $C_{19}H_{16}O_4S_2$ requires C, 61.3; H, 4.3%); ^1H NMR: δ 8.36 and 8.28 [2H in all, a doublet (J 8.1 Hz) partly overlapped with a broad singlet], 8.04—7.87 (4H, m), 7.67—7.40 (7H, m), and 2.54 (3H, s).

1-[(4-Chlorophenyl)thio]-4-{[(4-phenylthio)phenyl]thio}benzene 12 was a white crystalline solid, m.p. 119—121 °C (petroleum, b.p. 80—100 °C) (Found: C, 66.0; H, 3.8. $C_{24}H_{17}ClS_3$ requires C, 66.0; H, 3.9%); ^1H NMR: δ 7.33 (4H, app. br. s), 7.25 and 7.22 (13H in all, app. br. s).

Authentic samples of dibenzothiophene 5[42] and of 2-methyldibenzothiophene 6[43] were prepared as reported in literature.

Controlled-potential electrolysis.— Experiment 2d in the Table was conducted with 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. Correction for the background current was achieved by the method of plotting the charge as a function of time and extrapolating the linear portion back to zero time. Cells were flushed with and kept under a positive pressure of high purity argon which was previously passed through columns of granular silica gel. A platinum bead and a platinum flag were used as working electrodes respectively in cyclic voltammetric experiments and controlled-potential electrolyses. A platinum wire served as a counter electrode and $Ag/AgNO_3$ 0.01 M in Me_2SO was used as a reference electrode.

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