graphic filtration afforded an oil identified as a mixture of **27** and **28**, ratio 81:19 (93% total yield). The two products were separated by GC (5 ft × $^1/_4$ in. 20% SE-30 on Gas Chrom Q). **27** (slower): IR (CH_2Cl_2) μ 6.18 (s); ^{1}H NMR ($CDCl_3$) δ 7.35 (s, 5 H), 4.3–4.2 (m, 1 H), 3.7–3.3 (m, 4 H), 2.0–1.8 (m, 4 H); high-resolution mass spectrum, *m/e* (relative intensity) 225.0716 (M[^{37}Cl]$^+$, 5%, $C_{12}H_{14}{}^{37}ClNO$ requires 225.0734), 224.0671 (M[^{37}Cl – H]$^+$, 18%, $C_{12}H_{13}{}^{37}ClNO$ requires 224.0656), 223.0753 (M[^{35}Cl]$^+$, 18%, $C_{12}H_{14}{}^{35}ClNO$ requires 223.0764), 222.0687 (M[^{35}Cl – H]$^+$, 57%, $C_{12}H_{13}{}^{35}ClNO$ requires 222.0685), 105 (100%), 77 (57%). **28** (faster): IR (CH_2Cl_2) μ 6.18 (s); ^{1}H NMR ($CDCl_3$) δ 7.35 (s, 5 H), 5.9–5.7 (m, 2 H), 4.2–3.4 (m, 4 H), 2.2–1.7 (m, 2 H); high-resolution mass spectrum, *m/e* (relative intensity) 187.0991 (M$^+$, 29%, $C_{12}H_{13}NO$ requires 187.0997), 186 (16%), 105 (100%), 77 (36%). For a summary of product ratio vs. reaction condition variations see discussion; for experimental details see ref 15.

***N*-Cyclododecylmorpholine (29).** Cyclododecanone was converted to its morpholine enamine as described by Wakselman.[23] This was hydrogenated over PtO_2 in methanol at 2 atm and **29** was obtained as an oil (NMR and TLC pure) after a standard acid extraction workup: ^{1}H NMR ($CDCl_3$) δ 3.6–3.4 (m, 4 H), 2.6–2.3 (m, 5 H), 1.45–1.35 (m, 22 H); high-resolution mass spectrum, *m/e* (relative intensity) 253.2409 (M$^+$, 16%, $C_{16}H_{33}NO$ requires 253.2405), 224 (9%), 210 (11%), 182 (6%), 126 (100%).

Reaction of 29 with ACE–Cl. N-Dealkylation of **29** as above using 2 equiv of ACE–Cl and 2 equiv of **12** gave cyclododecene in 80% yield. By GC, IR, and NMR the product was identical with a sample of commercial *trans*-cyclododecene. No chlorocyclododecane was found (GC, NMR). For details of other reaction variations, see ref 15.

Acknowledgment. We are grateful to the National Institutes of Health for the Grant (GM 13980) which supported this research. We also thank Dr. John Carson, Dr. Serge Lecolier, and Dr. Jean-Pierre Senet for valuable discussions and David Morrison for experimental support.

Registry No. **10**, 6821-01-8; **11**, 42152-99-8; **12**, 20734-58-1; **13**, 23616-79-7; **14**, 332-14-9; **15**, 622-24-2; **16**, 74246-27-8; **17**, 2651-46-9; **18**, 3733-38-8; **19**, 84-04-8; **20**, 34927-63-4; **21**, 34924-25-9; **22**, 94-62-2; **23**, 90670-01-2; **24**, 90670-02-3; **26**, 90670-03-4; **27**, 90670-04-5; **28**, 71785-91-6; **29**, 58748-24-6; AEC-Cl, 50893-53-3; 10-(3-chloropropyl)phenothiazine, 5909-59-1; 10-(3-chloropropyl)-2-chlorophenothiazine, 2765-59-5; 2,7-bis(4-chlorobutyryl)fluorene, 34927-52-1; 2,7-bis(4-chlorobutyryl)fluoren-9-one, 90670-00-1; tetrahydropiperine, 23434-88-0; 4-piperidinopiperidine, 4897-50-1; cyclodecanone, 830-13-7; *N*-(cyclododec-1-enyl)morpholine, 3725-39-1; *trans*-cyclododecene, 1486-75-5.

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[23] Wakselman, C. *Bull. Soc. Chim. Fr.* **1967**, *10*, 3763.

Photostimulated Reactions of *o*-Bis(phenylsulfonyl)benzene Derivatives with Sodium Arenethiolates in Me_2SO. Evidence for Competing Pathways Involving a Common Intermediate σ Radical

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The effects of incremental additions of benzenethiol on the product distribution of the photostimulated reactions of 2,3-bis(phenylsulfonyl)-1,4-dimethyl- (**1a**) and 1,2-bis(phenylsulfonyl)-3,4,5,6-tetramethylbenzene (**1b**) with sodium benzenethiolate in Me_2SO have been studied. In agreement with the electron-transfer mechanism previously proposed, the benzenethiol, by acting as a hydrogen atom donor trapping agent on the σ radical intermediates **2a**,**b**, favors the formation of the reduction products **5a**,**b** to the detriment of the other possible reaction products (viz., **3a**, **4a**, and **4b**). Substantial evidence that the formation of **3a**, **4a**, and **5a** as well as of **4b** and **5b** occurs via competing pathways involving respectively **2a** and **2b** as common intermediates has been obtained by the observation that the **5a**/**3a**, **5a**/**4a**, and **5b**/**4b** molar ratios can be well linearly correlated with the concentration of the benzenethiol. Inhibition of the reaction rate by the thiol is observed even in the experiments where there is negligible or no formation at all of the substitution product via an $S_{RN}1$ chain process. This observation together with the fact that the raw quantum yield of the reaction of **1b** with benzenethiolate (where only cyclization and reduction products are formed) exceeds unity (ϕ = 4) indicates that the intramolecular arylation leading to **4a**,**b** proceeds, at least in part, via a chain process. An hypothesis on such a chain mechanism is advanced in Scheme III.

In a previous paper[1] we showed that the reaction of 2,3-bis(phenylsulfonyl)-1,4-dimethylbenzene (**1a**) with sodium benzenethiolate in Me_2SO, when subjected to photostimulation by a sunlamp, yields a mixture of the substitution product **3a**, of the cyclization product **4a**, and of the reduction product **5a**.

To account for the experimental results, we proposed the mechanism depicted in Scheme I according to which the reaction initially proceeds through a single electron transfer from the arenethiolate anion to the substrate with formation of the radical anion **1a**$^{-}\cdot$ which fragments into benzenesulfinate anion and the σ radical **2a**. The various reaction products then arise from **2a** through the three competing paths C, D, and E. In particular, path C is supposed to involve a $S_{RN}1$ process, path D a homolytic intramolecular arylation, and path E the abstraction of a hydrogen atom from the medium.

The results we obtained recently[2] from an electrochemical investigation on the cathodic reduction of **1a** were consistent with this mechanism and, in particular, they

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

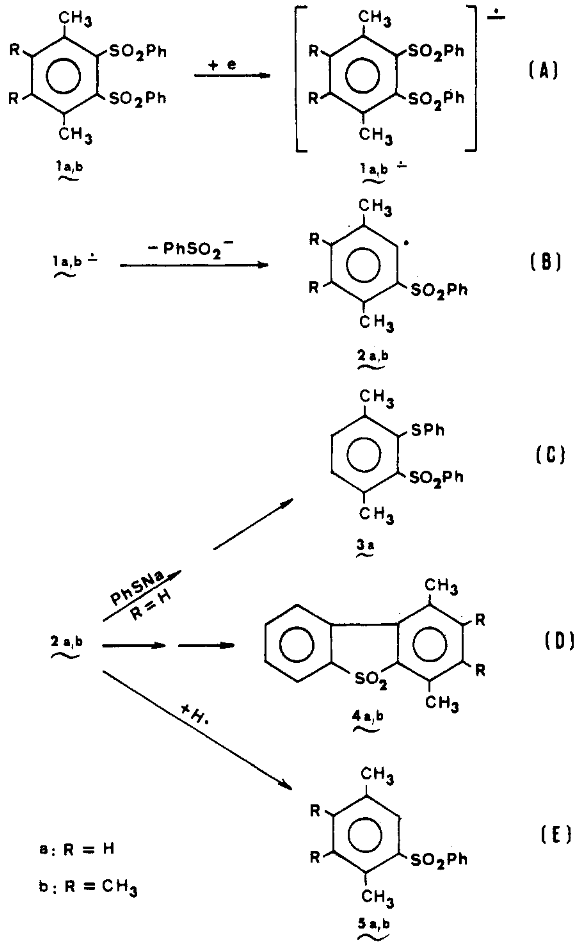
[2] Novi, M.; Dell'Erba, C.; Garbarino, G.; Scarponi, G.; Capodaglio, G. *J. Chem. Soc., Perkin Trans. 2* **1984**, 951.

Table I. Photostimulated Reactions of 2,3-Bis(phenylsulfonyl)-1,4-dimethylbenzene (1a) with PhSNa/PhSH in Me$_2$SO (10 min, 50 °C)[a]

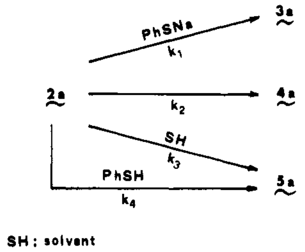
run	1a/PhSNa/PhSH mol ratio	1a recovd,[b] %	% relative yield[b]			molar ratio	
			3a	4a	5a	5a/3a	5a/4a
1	1:1:0		2	77	21		0.27
2	1:1:1	15		57	43		0.75
3	1:1:2.5	45		35	65		1.86
4	1:1:4	56		26	74		2.85
5	1:5:0		33	57	10	0.30	0.17
6	1:5:1	14	21	45	34	1.62	0.76
7	1:5:2.5	32	15	31	54	3.60	1.74
8	1:5:4	61	14	20	66	4.71	3.30

[a] All reactions were carried out under Ar in a Pyrex test tube stoppered with a rubber septum and under irradiation by a 300-W sunlamp. The overall yields, estimated by NMR spectroscopy with 1,4-bis(chloromethyl)benzene as an internal standard, were almost quantitative in every case. [b] All yields, average values of at least 5 independent determinations, were estimated by integration of the NMR peak areas of the methyl groups. The average errors from the mean values listed are ±2%.

Scheme I



Scheme II



showed that (in contrast with what was reported about the behavior of diaryl dulfones in electron-transfer reactions[3,4] but in agreement with Grimshaw's results[5]) a monoelectronic cleavage of a C–SO$_2$Ph bond according to equations A and B of Scheme I is reasonable.

To gain deeper insight into the mechanism, it appeared to us that further experimental evidence was required in order to confirm both the formation of **2a** in the reaction course and the fact that products **3a**–**5a** are formed from this common intermediate via three competing paths.

In this regard we thought that if the three paths C, D, and E are actually competing for **2a**, the addition to the reaction mixture of a good hydrogen atom donor, like the free arenethiol,[6] should favor path E over the other two processes.

The results obtained from the photostimulated reactions of **1a** with sodium benzenethiolate in Me$_2$SO and in the presence of increasing amounts of benzenethiol are collected in Table I. The data clearly show that there is always an increment of the yield of the sulfone **5a** when the molar concentration of the benzenethiol is increased. In the case of the reactions carried out with equimolar amounts of substrate and benzenethiolate, where the yield of the substitution product **3a** is negligible, the yield of **5a** becomes greater as that of **4a** lowers. When the substitution process can effectively compete and the yield of **3a** is appreciable (as in the experiments carried out with 5 molar equiv of benzenethiolate), it is possible to note that the increase in the relative yield of **5a** parallels the decrease in those of both **3a** and **4a**.

In our opinion this merely qualitative examination of the results argues in favor of the hypothesis that competing pathways involving a common intermediate are operative. In principle, the trapped intermediate could be either the radical anion of **1a** or the σ radical **2a**, on which the added benzenethiol might act either as a proton or as a H atom donor, respectively. However the latter possibility is strengthened by the fact that control experiments showed that the rate and the product distribution of the reaction was not significatively influenced by addition of 2.5 molar equiv of PhOH (a donor widely used for proton-transfer reactions on radical anion species[3b,7]). Apparently proton donors do not react with **1a**$^{-}\cdot$ rapidly enough to compete

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(3) (a) De Jong, F.; Janssen, M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 572. Gerdil, R. *Helv. Chim. Acta* **1973**, *56*, 196. (b) Horner, L.; Meyer, E. *Ber. Bunsenges. Phys. Chem.* **1975**, *79*, 136, 143 and references therein cited.

(4) Rossi, R. A.; Bunnett, J. F. *J. Am. Chem. Soc.* **1974**, *96*, 112.

(5) Grimshaw, J.; Trocha-Grimshaw, J. *J. Chem. Soc., Perkin Trans. 1* **1979**, 799.

(6) Ohno, A.; Oae, S. In "Organic Chemistry of Sulfur"; Oae, S., Ed.; Plenum Press: New York, 1977; p 125. Knight, A. R. In "The Chemistry of the Thiol Group"; Patai, S., Ed.; Interscience: New York, 1974; p 473. Pryor, W. A.; Kneipp, K. G. *J. Am. Chem. Soc.* **1971**, *93*, 5584.

(7) Parker, V. D. In "Advances in Physical Organic Chemistry"; Gold, V., Bethell, D., Eds.; Academic Press: New York, 1983; Vol. 19, p 174 and references therein.

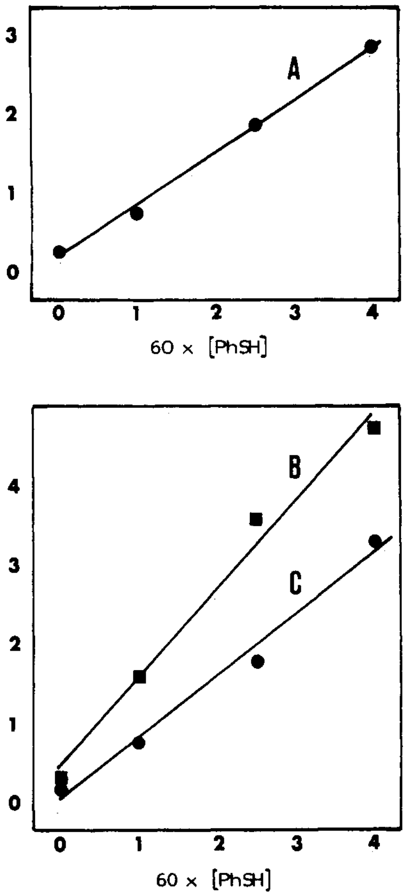

Figure 1. Plots of **5a**/**4a** (●) and **5a**/**3a** (■) molar ratios vs. [PhSH]. A (runs 1–4): [**5a**]/[**4a**] = (0.66 ± 0.03) [PhSH] + (0.20 ± 0.07), (r = 0.998, s = 0.01). B (runs 5–8): [**5a**]/[**3a**] = (1.12 ± 0.10) [PhSH] + (0.46 ± 0.25), (r = 0.992, s = 0.09). C (runs 5–8): [**5a**]/[**4a**] = (0.77 ± 0.07) [PhSH] + (0.04 ± 0.18), (r = 0.991, s = 0.05).

with the fast[2] alternative process of fragmentation of this radical anion into **2a**. This observation in the case of reductive cleavage of ortho-substituted diaryl sulfones is not unprecedented.[5] It is therefore much more likely that, as we anticipated, the added benzenethiol favors the formation of **5a** to the detriment of those of **3a** and **4a** by acting as a H atom donor trapping agent on the intermediate σ radical.[8] Therefore, if Scheme II holds, where both solvent[9] and PhSH are indicated as potential H atom donors in the competing process, taking into account that **3a**, **4a**, and **5a** are not interconverted under the conditions employed and that the concentrations of solvent, benzenethiol, and benzenethiolate (when 5 equiv are used) do not change significantly during the reaction (so that they can be assumed to be constant), a mathematical treatment[10] of the competing paths shown in Scheme II indicates that the yields of **3a**, **4a**, and **5a** should be related as follows:

Table II. Photostimulated Reactions of 1,2-Bis(phenylsulfonyl)-3,4,5,6-tetramethylbenzene (1b) with PhSNa/PhSH in Me_2SO (10 min, 50 °C)[a]

run	**1b**/PhSNa/PhSH mol ratio	**1b** recovd,[b] %	% rel yld[b] **4b**	**5b**	**5b**/**4b** mol ratio
9	1:1:0		87	13	0.15
10	1:1:1	11	70	30	0.43
11	1:1:4	24	52	48	0.92
12	1:1:7	62	41	59	1.44

[a,b] Refer to corresponding footnote in Table I.

$$\frac{d[\mathbf{5a}]}{d[\mathbf{4a}]} = \frac{k_4[\mathrm{PhSH}] + k_3[\mathrm{SH}]}{k_2} = \frac{\text{moles of } \mathbf{5a}}{\text{moles of } \mathbf{4a}}$$

$$\frac{d[\mathbf{5a}]}{d[\mathbf{3a}]} = \frac{k_4[\mathrm{PhSH}] + k_3[\mathrm{SH}]}{k_1[\mathrm{PhSNa}]} = \frac{\text{moles of } \mathbf{5a}}{\text{moles of } \mathbf{3a}}$$

By substituting ($k_{\mathrm{I}} = k_4/k_2$, $k_{\mathrm{II}} = k_3[\mathrm{SH}]/k_2$, $k_{\mathrm{III}} = k_4/k_1[\mathrm{PhSNa}]$, and $k_{\mathrm{IV}} = k_3[\mathrm{SH}]/k_1[\mathrm{PhSNa}]$) it can be shown that there should be a linear correlation between the **5a** to **4a** and the **5a** to **3a** molar ratios and the concentration of the added benzenethiol:

$$\frac{\text{moles of } \mathbf{5a}}{\text{moles of } \mathbf{4a}} \simeq k_{\mathrm{I}}[\mathrm{PhSH}] + k_{\mathrm{II}} \qquad (1)$$

$$\frac{\text{moles of } \mathbf{5a}}{\text{moles of } \mathbf{3a}} \simeq k_{\mathrm{III}}[\mathrm{PhSH}] + k_{\mathrm{IV}} \qquad (2)$$

The least-squares treatment of the data reported in Table I shows that the experimental points fit eq 1 and 2 (Figure 1) well enough to confirm the above mechanistic hypotheses. Moreover, in agreement with eq 1 (by which the **5a** to **4a** molar ratio is independent of the benzenethiolate concentration) a statistical estimation[11] of the k_{I} values obtained for the two series of experiments (runs 1–4 and 5–8) shows that such regression coefficients are not significantly different.

Another interesting point which emerges from the data reported in Table I is that the incremental addition of benzenethiol appreciably lowers the reaction rate, as deducible from the percentages of **1a** recovered at constant reaction times. While this can be justified in the case of runs 5–8 by the trapping of the chain carrying radical of the $S_{RN}1$ process leading to **3a**, the same reason can be hardly adduced in the case of runs 1–4 in which the formation of **3a** is negligible. On the other hand, the possibility that the rate retarding effect of the thiol be also ascribed to the formation of hydrogen-bonded species such as $PhS^-\cdots H\text{-}SPh$ (which would reduce somehow the efficiency of the electron donor) and/or to an inner filter effect can be easily rejected as (a) no homo-hydrogen bonding of the above type occurs[12] for PhS^- in Me_2SO owing to the strong H bond accepting properties of the solvent,[12,13] (b) benzenethiol does not show appreciable absorption at

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(8) To give strongest support to our conclusions a referee suggests we test whether other good hydrogen donors which are not proton donors have an effect similar to that of PhSH. However such a choice in the system in hand appears to be problematic as the H atom donor (QH) has to fulfil the following requirements: (a) It must be an acid much weaker than PhSH to avoid protonation of PhS^-. (b) It has to be a highly reactive donor so that it may intercept an appreciable fraction of the H scavenging radical **2a** when in competition with the intramolecular process of cyclization. (c) It should not absorb an important fraction of the useful light. (d) The radical Q· formed by abstraction of the H atom should not appreciably interfere with the already complex reaction, e.g., by trapping PhS^- (which has a large affinity for radicals) or **2a**. We think that this problem can be better studied and solved in the electrochemically induced reactions of **1a**,**b** where many of the above restrictions are overcome. Such an investigation is in progress.

(9) For a discussion on the importance of the role played by Me_2SO and other organic solvents as H atom donors see: M'Halla, F.; Pinson, J.; Saveant, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 4120. Semmelhack, M. F.; Bargar, T. *Ibid.* **1980**, *102*, 7765. Bunnett, J. F.; Scamehorn, R. G.; Taber, R. P. *J. Org. Chem.* **1976**, *41*, 3677.

(10) Russell, G. A. In "Technique of Organic Chemistry"; Weissberger, A., Ed.; Interscience: New York, 1961; Chapter VIII. Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 751 and references therein.

(11) Crow, E. L.; Davis, F. A.; Maxfield, M. W. "Statistics Manual"; Dovel Publishers: New York, 1960; p 161.

(12) Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1982**, *47*, 3224.

(13) See for instance: Kolthoff, I. M.; Chantooni, M. K.; Bhowmik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23.

wavelengths above 310 nm and therefore it is unlikely to absorb an important fraction of the useful light (2-mm Pyrex filtered light of a sunlamp).

To shed more light on the observed decrease in reaction rate, we investigated the behavior of 1,2-bis(phenylsulfonyl)-3,4,5,6-tetramethylbenzene (**1b**) under experimental conditions similar to those used for **1a** (Table II). On the basis of the results previously obtained in the photostimulated reactions of **1b** with sodium 2,4,6-trimethylbenzenethiolate,[1] in fact, it was possible to anticipate that most likely, even with the unsubstituted benzenethiolate, the $S_{RN}1$ process should not have significantly interfered, especially using 1 molar equiv of nucleophile.

Table II presents evidence that, within the limit of HPLC detectability, in the reactions of **1b** with sodium benzenethiolate there is no formation of substitution product, while, unlike the results found with 2,4,6-trimethylbenzenethiolate,[1] the yield of the reduction product **5b** is appreciable.

In agreement with the results obtained for **1a** and with the mechanistic hypothesis done (Scheme I), the analysis of the data reported in Table II also shows that an increment of the concentration of the added benzenethiol causes the yield of **5b** to increase. Furthermore, also in this case, the **5b** to **4b** molar ratio can be well correlated linearly with the concentration of the benzenethiol:

$$\frac{\text{moles of } \mathbf{5b}}{\text{moles of } \mathbf{4b}} = k_{\mathrm{I}}'[\mathrm{PhSH}] + k_{\mathrm{II}}'$$

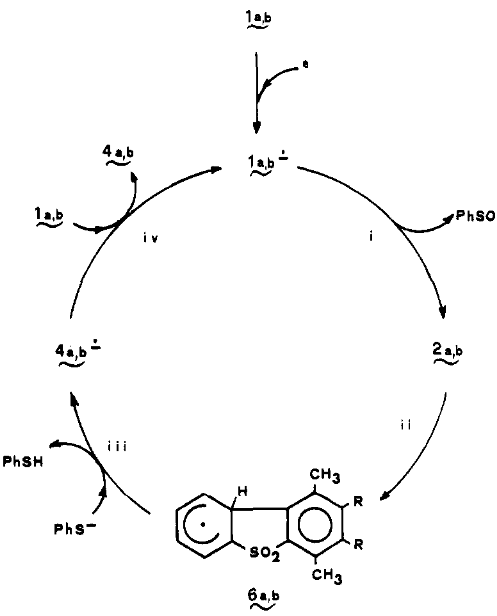
$k_{\mathrm{I}}' = k_4'/k_2' = 0.18 \pm 0.01$, $k_{\mathrm{II}}' = k_3'[\mathrm{SH}]/k_2' = 0.20 \pm 0.04$ ($r = 0.997$, $s = 0.003$) and the meaning of the primed constants is similar to that previously reported in the case of **1a**.

The lower value of the slope found in the experiments carried out on **1b** ($k_{\mathrm{I}}'/k_{\mathrm{I}} \simeq 0.25$) is indicative of a lower sensitivity of the process to the addition of benzenethiol. On the other hand, a similar estimation can also be made on a merely qualitative basis by comparison of the results reported in Tables I (runs 1–4) and II. At the present, the exact meaning of this experimental finding is however unclear.

It is interesting to note that, also in the experiments carried out on **1b**, the addition of benzenethiol decreases the reaction rate as the more the concentration of the trapping thiol is increased the larger is the amount of recovered substrate. The observation of this effect (in spite of the lack of formation of the substitution product) was, in our opinion, indicative of the fact that another substrate consuming chain process was operative. The observed parallelism between decrease in the reaction rate and decrease in the relative yield of **4b** suggested that the intramolecular arylation leading to this cyclization product proceeds, at least in part, via a chain mechanism. This conclusion was successively supported by a quantum yield determination of the reaction of **1b** with 1 molar equiv of benzenethiolate (15-s irradiation by 8 "350 nm" fluorescent lamps in a Rayonet photochemical reactor). As the raw quantum yield measured exceeds unity ($\phi = 4$) there would seem to be little doubt that we are dealing with a chain process. The inhibition of the photostimulated reactions of **1a** by PhSH (observed also in runs 2–4) would be therefore rationalized in view of the logical assumption that a similar process is involved also in the formation of **4a** from **2a**.

A hypothesis as to the character of the chain mechanism leading to **4a,b** is sketched in Scheme III. The crucial point of this scheme is step iii which however is not particularly difficult to accept when it is realized that the cyclohexadienyl radicals **6a,b** are conjugate acids of the radical anions of the cyclization products **4a,b**. We believe it possible that, because of the presence in **6a,b** of a benzylic proton whose intrinsic acidity is enhanced by the ortho sulfonyl group, the benzenethiolate abstracts a proton from these cyclohexadienyl radicals to form the radical anions $\mathbf{4a,b}^{-}\cdot$. Further, as the $\mathbf{4a}/\mathbf{4a}^{-}\cdot$ and $\mathbf{4b}/\mathbf{4b}^{-}\cdot$ couples have a standard potential negative to the reduction potential of the corresponding starting bis(sulfone),[2,14] it is conceivable that the anion radicals $\mathbf{4a,b}^{-}\cdot$ will be immediately oxidized by **1a,b** into the parent dibenzothiophene derivatives (step iv). This electron transfer to **1a,b** will eventually regenerate the radicals **2a,b** as in step B of Scheme I.[15] Reasonable termination steps (not shown in Scheme III) can be (a) trapping of **2a,b**, e.g., by H atom transfer from PhSH, Me_2SO, or **6a,b** or by coupling with PhS^- (which starts the competing $S_{RN}1$ process), or (b) any other well-known aromatization path of cyclohexadienyl radical intermediates of homolytic aromatic substitutions.

Scheme III



In conclusion, the collected results, while strongly supporting the mechanism advanced[1,2] for the electron-transfer reactions occurring on the bis(sulfones) **1a,b**, give indications that homolytic intramolecular arylations can proceed via an unusual chain mechanism. Further investigation is in progress to definitely confirm the mechanistic hypothesis proposed in Scheme III as well as to verify whether similar processes are involved in other intra- and intermolecular homolytic substitutions.

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[14] Novi, M.; Garbarino, G.; Dell'Erba, C., unpublished results.

[15] A species that accepts an electron from PhS^- or from radical anions $\mathbf{4a,b}^{-}\cdot$ more rapidly than the substrates do would be expected to interfere with the initiation step or with the propagation sequence of Scheme III. As the halfwave reduction potential[16] of *m*-dinitrobenzene is approximately 1 V more positive than the reduction potentials[2,14] of **1a,b** the observed[1] inhibition of the reaction by this nitro derivative can be well understood. There are precedents[18] for this expectation that electron transfer to substrates of more positive reduction potential should be faster than to those of more negative reduction potential.

[16] Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Nonaqueous Systems"; Bard, J. A., Ed.; Marcel Dekker: New York, 1970; p 370.

[17] For a discussion of the intervening aptitude of dinitrobenzene derivatives in chain reactions see: Kerber, R. C.; Urry, W.; Kornblum, N. *J. Am. Chem. Soc.* **1964**, *86*, 3904; *Ibid.* **1965**, *87*, 4520. Kornblum, N.; Michel, R. E.; Kerber, R. C. *Ibid.* **1966**, *88*, 5660, 5662. Kornblum, N. *Proc. Int. Congr. Pure Appl. Chem.* **1971**, *4*, 81. Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734.

[18] Swartz, J. E.; Bunnett, J. F. *J. Org. Chem.* **1979**, *44*, 340. Dorfman, L. M. *Acc. Chem. Res.* **1970**, *3*, 224.

Experimental Section

Melting points were taken on an Electrothermal melting point apparatus and are uncorrected. ^1H NMR spectra of deuteriochloroform solutions with Me_4Si as internal standard (δ 0) were recorded on a Varian FT 80 spectrometer. High-pressure liquid chromatography (HPLC) was performed on a Waters Model ALC-202 chromatograph equipped with a Model 440 UV detector monitoring at 254 nm and using a 3.9 × 300 mm μ-Porasil column.

Materials. Sodium benzenethiolate was prepared and Me_2SO was purified as previously reported.[1,19] The preparations and characterization of the substrates and of the authentic samples necessary to the present investigation are described elsewhere.[1] All other commercial solvents and reagents were purified according to literature methods to match reported physical constants.

Photostimulated Reactions of 1a,b with Sodium Benzenethiolate (Experiments 1–12 of Tables I and II). In a Pyrex test tube was dissolved the sulfone **1a** or **1b** (0.15 mmol) in Me_2SO (5 mL) and this was deaerated with argon gas by using 5 freeze–pump–thaw cycles. To this solution either was added 1 mL of a Me_2SO solution of benzenethiol at the appropriate concentration or an additional 1 mL of Me_2SO (experiments 1, 5, and 9), followed by 3 mL of an 0.25 or 0.05 M solution of sodium benzenethiolate in the same solvent. The reaction mixture was deaerated again with argon and stoppered with a rubber septum. The reactions were then irradiated for 10 min in a homemade "merry-go-round" apparatus by a 300-W Osram sunlamp placed 10 cm from the reaction vessel. The successive workup involved dilution with water (5–6 volumes) and 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 was removed on a rotoevaporator under reduced pressure. The residue, dissolved in CH_2Cl_2, was flash chromatographed on a silica gel column by first eluting with hexane, to remove some diphenyl disulfide and the benzenethiol, and then with CH_2Cl_2. All successive fractions (eluted with CH_2Cl_2) were collected together and concentrated on a rotoevaporator, and the residue was analyzed by TLC, ^1H NMR, and HPLC [eluants, CH_2Cl_2/*n*-hexane (4:1, v/v) at 1.7 mL/min for a good separation between **3a** and **5a**, CH_2Cl_2 at 2.0 mL/min or CH_2Cl_2/diisopropyl ether (10:1, v/v) at 0.8 mL/min for a quicker detection of other components of the reaction mixture].

The overall yields of the various experiments, estimated by NMR spectroscopy with 1,4-bis(chloromethyl)benzene as an internal standard, were almost quantitative in every case.

The relative yields reported in Tables I and II (average values of at least 5 independent experiments) were likewise obtained by NMR from the ratios of the integrated areas relative to the methyl absorptions. In the case of experiments 10–12, where some absorptions overlapped, a better reproducibility of the results was achieved by carrying out the NMR analysis first on the mixture of **1b**, **4b**, and **5b** and then, after removing the starting substrate by further chromatography, on the mixture of products alone.

1-(Phenylsulfonyl)-2,3,4,5-tetramethylbenzene (5b). Five independent reactions were carried out as above described on 0.1 g of **1b**, 1 molar equiv of PhSNa and 10 molar equiv of PhSH. After 1 h of irradiation, the reactions were poured together into brine and worked up as above. Column chromatography on silica gel (CH_2Cl_2as eluant) gave compound **5b** in 35% yield: mp 129.5–130.5 °C (EtOH); NMR ($CDCl_3$) δ 7.95 (s, 1 H, H-6), 7.82 (m, 2 H, H-2′ and H-6′ of $PhSO_2$), 7.50 (m, 3 H, H-3′, H-4′, and H-5′ of $PhSO_2$), 2.36, 2.31, 2.24, and 2.16 (4 overlapping s, 12 H in all, 4 CH_3). Anal. Calcd for $C_{16}H_{18}O_2S$: C, 70.0; H, 6.6. Found C, 70.1; H, 6.7.

The successive fractions eluted from the column gave dibenzothiophene **4b** as well as small amounts of unreacted **1b**.

Quantum Yield Determination. A Me_2SO solution (8.4 mL) of equimolar amounts (3.2 10^{-5} mol) of **1b** and PhSNa was prepared, as reported above, in a Pyrex test tube wrapped in aluminium foil.[20] The solution was deaerated with argon gas and immediately sealed with a rubber stopper. After removal of the aluminium foil in a dark room, the test tube was placed (beside an identical test tube containing the actinometer) in a "merry-go-round" rotating within a Rayonet RPR-100 photochemical reactor equipped with 8 fluorescent lamps emitting maximally about 350 nm. A duplicate was run simultaneously; the deviations between duplicate runs did not exceed 2%. In order to test whether correction for a dark reaction had to be done, 2 unirradiated samples were prepared and quenched at the end of the irradiation time.

The amount of light absorbed by the reaction mixtures was measured by the ferrioxalate method.[21] The measurements were performed in duplicate during the irradiation of the reaction mixtures and compared with an unirradiated sample. The values obtained for the flux that entered the test tubes were about 1.5 10^{-5} einstein/min. After 15 s of irradiation the reaction mixtures were poured into brine and carefully worked up as previously described. The residue obtained by evaporation of the ether extracts was dissolved in CH_2Cl_2 and quantitatively transferred into a 10-mL volumetric flask. The amount of reacted substrate was determined by HPLC (CH_2Cl_2/diisopropyl ether (10:1, v/v) as eluant at 0.8 mL/min) with phenol as internal standard. While the irradiated reactions gave an average conversion value of 47%, in the unirradiated samples a 98% recovery of **1b** was determined.

The number of moles of reacted substrate divided by the total amount of light (in einsteins) absorbed by the solution during irradiation gave an average value of the quantum yield of 4.

Registry No. **1a**, 81064-10-0; **1b**, 81064-11-1; **3a**, 81095-45-6; **4a**, 23018-39-5; **4b**, 81064-13-3; **5a**, 2548-26-7; **5b**, 90481-86-0; PhSNa, 930-69-8; PhSH, 108-98-5.

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Fluorination of Polycyclic Aromatic Hydrocarbons: Charge vs. Frontier Orbital Control in Substitution Reactions of Radical Cations

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The anodic fluorination of perylene and pyrene in acetonitrile occurred at potentials consistent with the intermediacy of dications, but that of triphenylene with its radical cation. Fluorination of anthracene compounds at a meso position occurred by the action of iodine/silver(I) fluoride in acetonitrile via radical cation intermediates. Phenanthrene, 9-nitroanthracene, perylene, and pyrene failed to react. These results support the view that the reaction of fluoride-providing anions with cationic species occurs primarily by a charge controlled mechanism.

The anodic fluorination of aromatic hydrocarbons in acetonitrile has been reviewed by Rozhkov,[1] whose group has studied primarily the fluorination of naphthalene, benzene, and their derivatives. We have applied the me-

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