# Normal $S_NAr$, Telesubstitution, and Electron-Transfer Pathways in the Reactions of Methyl-Substituted *o*-Bis(phenylsulfonyl)benzene Derivatives with Sodium Arenethiolates in Dimethyl Sulfoxide

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1,4-Dimethyl-2,3-bis(phenylsulfonyl)- (**6a**) and 1,2-bis(phenylsulfonyl)-3,4,5,6-tetramethylbenzene (**6b**) react with sodium benzenethiolate or 2,4,6-trimethylbenzenethiolate in $Me_2SO$ at 120 °C to give mainly products (**7a,b**, **9**, and **10a**) resulting from the normal substitution of a phenylsulfonyl with an arylthio group together with some (1–11%) 1,4-dimethyl- (**8a**) or 1,2,3,4-tetramethyldibenzothiophene 5,5-dioxide (**8b**). Besides these two kinds of products, the reaction of the more congested substrate (**6b**) with the sterically more demanding 2,4,6-trimethylbenzenethiolate affords 1-(phenylsulfonyl)-2,4,5-trimethyl-3-[[(2,4,6-trimethylphenyl)thio]methyl]benzene (**11a**) via a telesubstitution process. When the above-reported experiments on **6a,b** are carried out at 50 °C under photostimulation (sunlamp), a much faster reaction occurs, and the product distribution drastically changes, dibenzothiophenes **8a** and **8b** always being the main products. The observed effect of photostimulation and the fact that the reactions, at 50 °C, do not proceed significantly in the dark and, under irradiation, are inhibited by added *m*-dinitrobenzene are evidence that processes involving radical anion intermediates occur. The experimental results are interpreted by (a) the intervention of an electron-transfer path accounting for the formation of **8a,b**, (b) a competition between the $S_NAr$ and the $S_{RN}1$ mechanisms in the formation of the normal substitution products, and (c) an ionic mechanism, like those previously proposed for the analogous reactions on thiophene and naphthalene derivatives, for the telesubstitution path.

In previous papers[1,2] we showed that aromatic dimethyl dinitro derivatives (**1a–c**) can react with sodium arenethiolates in $Me_2SO$ in two ways (Scheme I). The first one, the normal substitution (NS) reaction, gives sulfides **3** through the usual $S_NAr$ mechanism. The second one, for which we proposed the mechanism depicted in Scheme I, affords sulfides **5** via a side-chain thioarylation [telesubstitution[3] (TS) reaction].

The prevalence of one reaction path over the other primarily depends on the aromaticity of the system. Thus, while the benzene derivative **1a** undergoes only NS reactions, under the same experimental conditions both processes occur on the naphthalene derivative **1b**. The dinitrothiophene **1c**, on the other hand, where localization of the $\pi$ electrons in the ring is greater than in **1a** and **1b**, gives exclusively telesubstitution products.

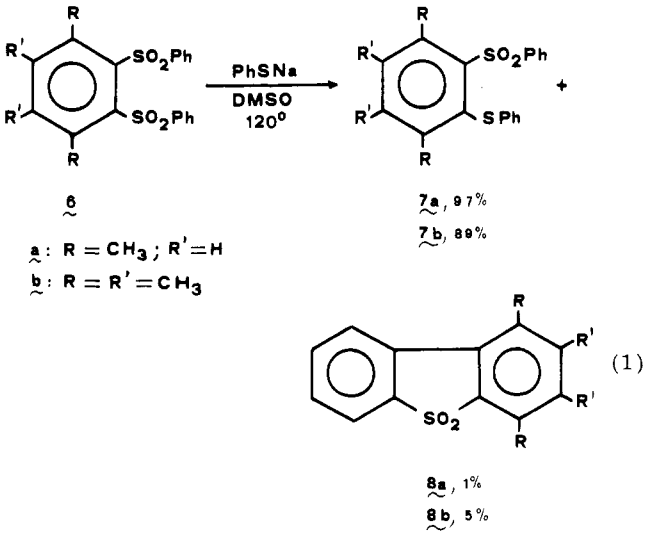
When both processes are possible, as in **1b**, the use of sterically hindered arenethiolates such as 2,4,6-trimethylbenzenethiolate and of dipolar aprotic solvents at high temperature (e.g., $Me_2SO$ at 120 °C) plays a role in driving the reaction along the telesubstitution pathway. As far as the substrate is concerned, we also found[4] that (a) the replacement (in **1b**) of the two nitro groups by phenylsulfonyl groups results in a remarkable increase in the normalized yield of the TS product (from 16% to 100% with PhSNa as nucleophile in $Me_2SO$ at 120 °C) and that (b) the presence of an electron-withdrawing substituent (W) ortho to the leaving group seems to be necessary to promote the TS process. The TS product, in fact, does not further react with nucleophiles, although a tautomerization involving the residual Me—C=C—W system (W = $NO_2$, $SO_2Ph$) is in theory possible. The effect of the W group should be both electronic and steric in nature, and the tautomerization of the aromatic substrate, a key step in the TS process, could be favored inter alia by formation of a sterically less congested molecule.

In the present paper we report on the behavior of 2,3-bis(phenylsulfonyl)-1,4-dimethylbenzene (**6a**) and of the more congested 1,2-bis(phenylsulfonyl)-3,4,5,6-tetramethylbenzene (**6b**) toward two representative[2,4] sodium arenethiolates in $Me_2SO$.

The aim of this investigation was to test whether the factors favoring the TS process in the naphthalene series[2,4] could force the benzene system along this pathway as well.

## Results and Discussion

The reaction of 2,3-bis(phenylsulfonyl)-1,4-dimethylbenzene (**6a**) or of the homologous tetramethyl derivative (**6b**) with an excess of sodium benzenethiolate in $Me_2SO$ at 120 °C afforded good yields of sulfides (**7a,b**) together with traces (1–5%) of 1,4-dimethyl- (**8a**) or 1,2,3,4-tetramethyldibenzothiophene 5,5-dioxide (**8b**, eq 1).




Under identical experimental conditions, with the more sterically hindered sodium 2,4,6-trimethylbenzenethiolate,

(1) Novi, M.; Sancassan, F.; Guanti, G.; Dell'Erba, C. *J. Chem. Soc., Chem. Commun.* **1976**, 303.
(2) Novi, M.; Guanti, G.; Thea, S.; Sancassan, F.; Calabrò, D. *Tetrahedron* **1979**, *35*, 1783.
(3) The term "telesubstitution" is used in accordance with recent IUPAC recommendations (Gold, V. *Pure Appl. Chem.* **1979**, *51*, 1725) to denote reactions in which the entering group takes up a position more than one atom away from the atom to which the leaving group was attached.
(4) Novi, M.; Guanti, G.; Dell'Erba, C.; Calabrò, D.; Petrillo, G. *Tetrahedron* **1980**, *36*, 1879.

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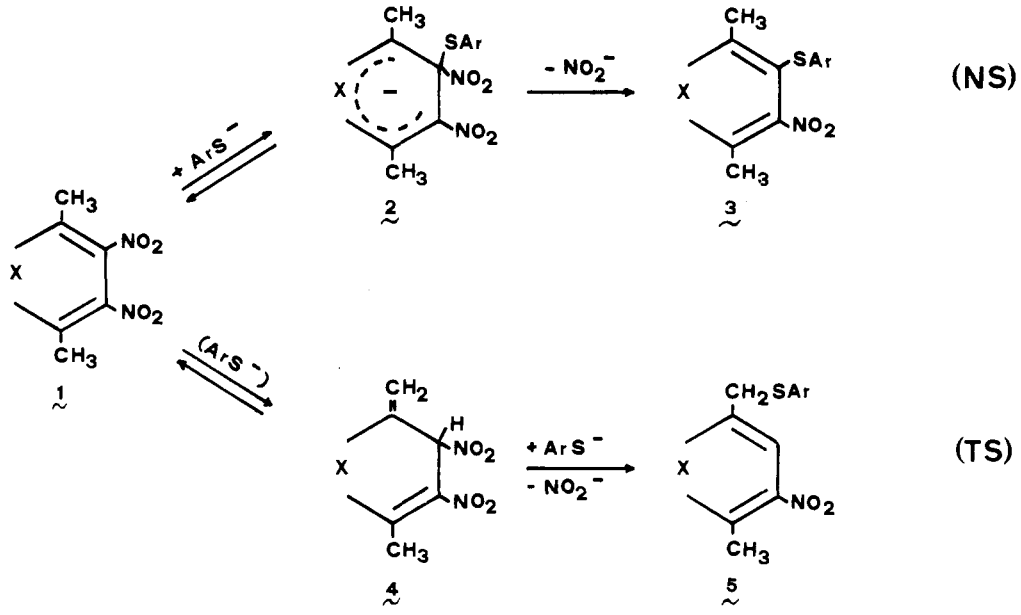
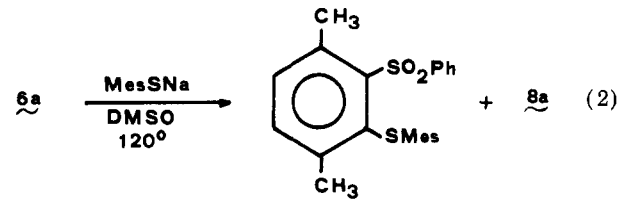
Scheme I




a: X =  ; b: X =  ; c: X = 

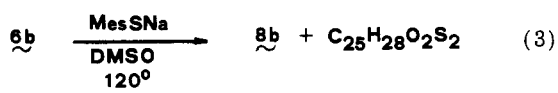
the sulfone **6a** analogously gave 91% of 1,4-dimethyl-2-(phenylsulfonyl)-3-[(2,4,6-trimethylphenyl)thio]benzene (**9**) together with 7% of the cyclization product **8a** (eq 2).




Mes = 2,4,6-$Me_3C_6H_2$

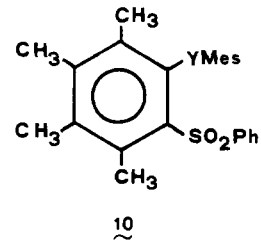
Once again the benzene system proved reluctant to undergo a TS process like that depicted in Scheme I. Interestingly enough, however, another reaction, the one leading to the dibenzothiophene dioxide derivatives, is competing with the NS reaction.

The analogous reaction carried out on the tetramethyl derivative **6b** (eq 3) afforded **8b** in 11% yield along with




Mes = 2,4,6-$Me_3C_6H_2$

86% of a crystalline material, $C_{25}H_{28}O_2S_2$, corresponding to the substitution of a $PhSO_2$ with a mesitylthio group in **6b**. though this material showed a single spot by TLC, its $^1H$ NMR spectrum revealed that it was a mixture (ca. 2.3:1) of two isomeric sulfides. In particular, the singlets at $\delta$ 7.98 and 3.81 exhibited by the minor component (typical absorptions of an isolated aromatic proton and of a methylene group, respectively) suggested that a substitution with thioarylation on a methyl group of **6b** had occurred. The sulfones, obtained by oxidation of the above mixture, could be separated by column chromatography, and the major component was identified as 1-(phenylsulfonyl)-2-[(2,4,6-trimethylphenyl)sulfonyl]-3,4,5,6-tetramethylbenzene (**10b**). As far as the other sulfone is concerned, the $^1H$ NMR data alone, though indicating a telesubstitution product structure for the corresponding sulfide, were not sufficient to establish the exact location of the [(2,4,6-trimethylphenyl)sulfonyl]methyl group. $^1H$ NMR analyses were therefore carried out with the aid of $Yb(fod)_3$ as a shift reagent, and **11b** was assigned as the most probable structure.



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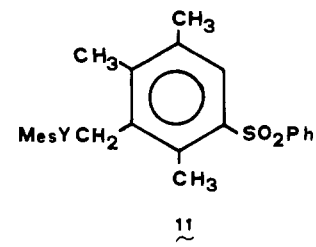

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a: Y = S

b: Y = $SO_2$

Mes = 2,4,6-$Me_3C_6H_2$

In summary, treatment of **6b** with sodium 2,4,6-trimethylbenzenethiolate led to the formation of three products, the NS one (**10a**), the TS one (**11a**), and the cyclized one (**8b**) in 60%, 26%, and 11% yields, respectively. Thus, in agreement with the preliminary statements, on going from **6a** to **6b** (i.e., making both the molecule more congested and the $S_NAr$ process less favorable for electronic reasons), even the benzene system, as a consequence of an appropriate concomitance of factors,[2,4] can undergo a TS reaction like that found for the analogous and "less aromatic" naphthalene derivatives. Such behavior is reminiscent of certain o-dinitrobenzene derivatives[5] which, by the choice of a particular electronic

(5) Self, D. P.; West, D. E.; Stillings, M. R. *J. Chem. Soc., Chem. Commun.* **1980**, 281 and references therein.

Table I. Reaction of 2,3-Bis(phenylsulfonyl)-1,4-dimethylbenzene (6a) with ArSNa in $Me_2SO$

| expt | ArSNa | 6a/ArSNa molar ratio | conditions[a] | time, min | 6a recovd, % | % yield[b] 7a or 9 | 8a | 12 |
|---|---|---|---|---|---|---|---|---|
| 1 | PhSNa | 1:5 | 120 °C[c] | 20 | | 97 | 1[d] | |
| 2 | PhSNa | 1:5 | light, 50 °C | 10 | | 31 | 55 | 11 |
| 3 | PhSNa | 1:1 | light, 50 °C | 10 | | 2 | 74 | 22 |
| 4 | PhSNa | 1:5 | dark, 50 °C | 10 | 93 | 5 | | |
| 5 | PhSNa | 1:5 | light, 50 °C, MDNB[e] | 10 | 91 | 6 | | |
| 6 | MesSNa[f] | 1:5 | 120 °C[c] | 40 | | 91 | 7 | |
| 7 | MesSNa[f] | 1:5 | light, 50 °C | 10 | | 9 | 79 | 9 |
| 8 | MesSNa[f] | 1:1 | light, 50 °C | 10 | | | 84 | 12 |
| 9 | MesSNa[f] | 1:5 | dark, 50 °C | 10 | 98[g] | | | |
| 10 | MesSNa[f] | 1:5 | light, 50 °C, MDNB[e] | 10 | 99[g] | | | |
| 11 | none | | light, 50 °C | 10 | 98[g] | | | |

[a] All reactions were carried out under Ar in a Pyrex test tube stoppered with a rubber septum. Reactions performed in the "dark" were wrapped in aluminum foil, and "light" reactions were irradiated by a sunlamp (see Experimental Section). [b] All yields, average values of at least two independent determinations, are absolute and, unless otherwise stated, were determined by $^1H$ NMR (see Experimental Section). [c] Both at the diffuse laboratory light and in the dark. [d] Approximate value as determined by HPLC. [e] In the presence of *m*-dinitrobenzene (MDNB) at the 30 mol % level (with respect to the substrate). [f] Mes = 2,4,6-$Me_3C_6H_2$. [g] Isolated yields.

Table II. Reaction of 1,2-Bis(phenylsulfonyl)-3,4,5,6-tetramethylbenzene (6b) with ArSNa in $Me_2SO$

| expt | ArSNa | 6b/ArSNa molar ratio | conditions[a] | time, min | 6b recovd, % | % yield[b] 7b or 10a | 8b | 11a |
|---|---|---|---|---|---|---|---|---|
| 12 | PhSNa | 1:5 | 120 °C[c] | 110 | | 89 | 5 | |
| 13 | MesSNa[f] | 1:5 | 120 °C[c] | 360 | | 60 | 11 | 26 |
| 14 | MesSNa[f] | 1:5 | light, 50 °C | 10 | | | 95[g] | |
| 15 | MesSNa[f] | 1:1 | light, 50 °C | 10 | | | 98[g] | |
| 16 | MesSNa[f] | 1:5 | dark, 50 °C | 10 | 98[g] | | | |
| 17 | MesSNa[f] | 1:5 | light, 50 °C, MDNB[e] | 10 | 97[g] | | | |
| 18 | none | | light, 50°C | 10 | 97[g] | | | |

[a-c, e-g] Refer to corresponing footnote in Table I.

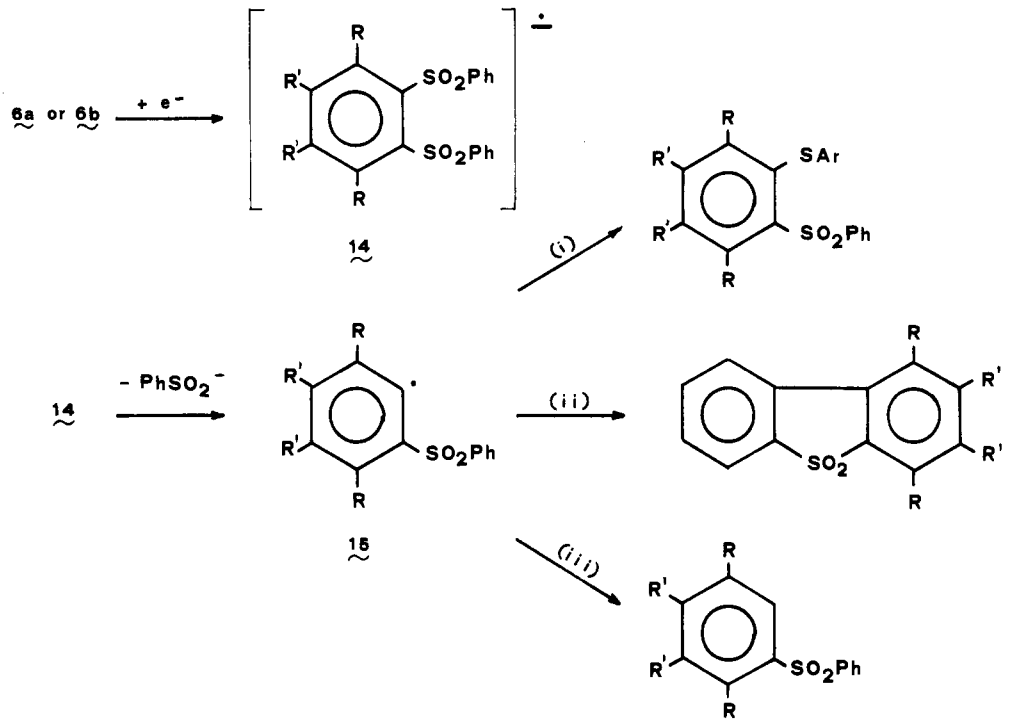
and steric structural situation, can be made to undergo nucleophilic cine- and telesubstitution of the nitro group in addition to normal aromatic substitution. To the best of our knowledge, however, the formation of **11a** from **6b** is the first example of TS reaction in the benzene series involving attack of the nucleophile upon a side-chain methyl group with departure of the leaving group from the ring. Moreover, if the structure assigned to **11a** were confirmed,[6] the position of telesubstitution (on a methyl para rather than ortho to the leaving group) would be quite a novel observation as well.

As regards the mechanism(s) by which the various isolated compounds can form, it should be noted that in previous research on naphthalene and thoiphene derivatives[1,2,4] we obtained evidence that ionic mechanisms, like those sketched in Scheme I, are involved in the formation of normal and telesubstitution products. On the other hand, it is well-known,[7-10] that nucleophilic substitution reactions involving sodium arenethiolates as reagents can easily proceed via electron-transfer pathways. Moreover, the observation that the present system affords cyclization products (like **8a,b**), which were not observed[4] in the similar reactions of 1,4-dimethyl-2,3-bis(phenylsulfonyl)-naphthalene, prompted us to test whether radical-anion intermediates were involved in the formation of compounds **7-9**, **10a**, and **11a**. We therefore studied the reactions of the sulfones **6a,b** with the same arenethiolates in $Me_2SO$ under irradiation with white light, which is known to exert.[9-11] a strong initiating influence on electron-transfer processes.

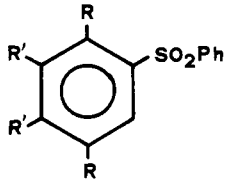
The results obtained in the photostimulated reactions (carried out at 50 °C) together with those of some control experiments are summarized in Tables I and II, where for comparison the data of related reactions performed at 120 °C are also reported. The following interesting points emerge from the collected data. (a) No significative changes in both product distribution and reaction rate were found when the experiments at 120 °C were carried out in room light and in the dark. (b) Under photostimulation (at 50 °C) the disappearance of the starting material is far faster than in the corresponding reactions run at 120 °C. The most striking example is the case of the reaction of **6b** with 2,4,6-trimethylbenzenethiolate which requires 6 h at 120 °C to go to completion with 5 molar equiv of nucleophile (expt 13), whereas under photostimulation this reaction is complete (expts 14 and 15) in only 10 min even on using 1 molar equiv of reagent. (c) Under irradiation the composition of the reaction mixture changes drastically, the dibenzothiophenes always being the main products. Indeed, the experiments on **6b** (expts 14 and 15) gave only **8b** in almost quantitative yields. (d) The yields of the dibenzothiophene derivatives vary as a

(6) A single-crystal X-ray structure determination of **11b** is in progress.
(7) (a) Kornblum, N.; Davies, T. M.; Earl, G. W.; Holy, N. L.; Kerber, R. C.; Musser, M. T.; Snow, D. H. *J. Am. Chem. Soc.* **1967**, *89*, 725. (b) Kornblum, N.; Davies, T. M.; Earl, G. W.; Greene, G. S.; Holy, N. L.; Kerber, R. C.; Manthey, J. W.; Musser, M. T.; Snow, D. H. *Ibid.* **1967**, *89*, 5714. Zoltewicz, J. A.; Oestreich, T. M. *Ibid.* **1973**, *95*, 6863. Kornblum, N.; Boyd, S. D.; Ono, N. *Ibid.* **1974**, *96*, 2580. (c) Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1974**, *39*, 3173. (d) Bunnett, J. F.; Creary, X. *Ibid.* **1974**, *39*, 3611. Bunnett, J. F.; Creary, X.; Sundberg, J. E. *Ibid.* **1976**, *41*, 1707. Kornblum, N.; Fifolt, M. J. *Ibid.* **1980**, *45*, 360. Alonso, R. A.; Rossi, R. A. *Ibid.* **1980**, *45*, 4760. Norris, R. K.; Smith-King, R. J. *J. Chem. Soc., Chem. Commun.* **1981**, 79.
(8) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734.
(9) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.
(10) Todres, Z. V. *Phosphorus Sulfur* **1981**, *9*, 353.
(11) Russell, G. A.; Norris, R. K. In "Organic Reactive Intermediates"; McManus, S. P., Ed.; Academic Press: New York, 1973; Chapter 6. Russell, G. A.; Norris, R. K. *Rev. React. Intermed. Org. React.* **1972**, *1*, 65.

Scheme II



function of the nature of both the substrate (cf. expts 7 and 14, 8 and 15) and the arenethiolate (cf. expts 2 and 7). They also vary with the concentration of the arenethiolate (cf. expts 2 and 3, 7 and 8). (e) In the case of the experiments performed on **6a**, the formation of 1,4-dimethyl-2-(phenylsulfonyl)benzene (**12**) was observed,

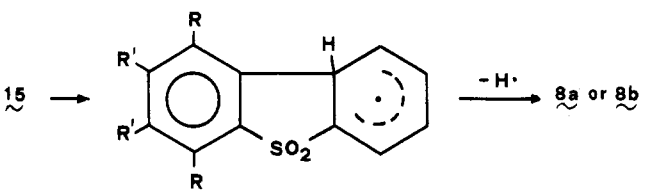


**12**: R = $CH_3$ ; R' = H
**13**: R = R' = $CH_3$

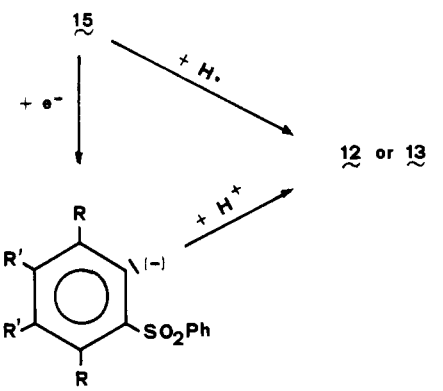
whereas no traces of the analogous tetramethyl derivative (**13**), could be detected in the reactions of **6b**. (f) A decrease in the arenethiolate concentration (cf. expts 2 and 3, 7 and 8) gives rise to less of the substitution product (**7a** or **9**) with a concomitant increase in the yield of **8a** and **12**. The reactions also seem to be sensitive to the steric bulk of the arenethiolate, as a lower yield of sulfide is always obtained on going from benzenethiolate to the more bulky 2,4,6-trimethylbenzenethiolate (cf. expts 2 and 7, 3 and 8). (g) Under the photostimulated reaction conditions, but in the absence of arenethiolate (expts 11 and 18), the sulfones **6a** and **6b** are stable and could be quantitatively recovered. A contribution to the formation of **8a** and **8b** by the photolysis of the starting material can therefore be disregarded.

The observed effect of photostimulation, the isolation of the reduction product **12**, and, of no less importance, the fact that the reactions (at 50 °C) do not proceed significantly in the dark (expts 4, 9, and 16) and are inhibited by 30 mol % (with respect to the benzene substrate) of *m*-dinitrobenzene (expts 5, 10, and 17) suggest[8,9] that an electron-transfer process occurs. It is conceivable, in fact (Scheme II), that photons stimulate electron transfer from the arenethiolate anion to the substrate, forming the radical anion **14**. To account for the experimental results,

Scheme III

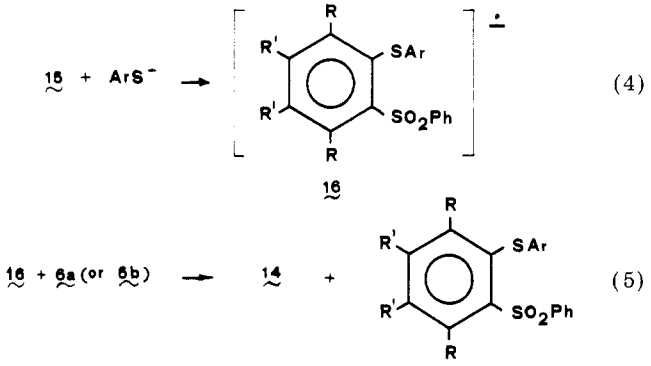


Scheme IV



we suggest the possibility that **14** decomposes by extruding a benzenesulfinate anion to yield the intermediate radical **15**,[12] which then could in principle react by the following pathways:[8,9] (i) undergo the usual radical plus anion trapping reaction of the $S_{RN}1$ process to give eventually the substitution products **7a,b**, **9**, and **10a** (eq 4 and 5); (ii) cyclize, by intramolecular free-radical substitution, to dibenzothiophene derivatives **8a** or **8b** (Scheme III); (iii) abstract a hydrogen atom or, after acceptance of an electron, a proton from the solvent system to afford sulfones

(12) The intermediate radical **15** could also form by scission of the C–SAr bond in the radical anions deriving from sulfides **7a,b**, **9**, and **10a**. However, control experiments showed that, under the photostimulated reaction conditions and in the presence of the corresponding arenethiolate, these sulfides are stable enough and that no dibenzothiophenes **8a,b** are formed.



(4)



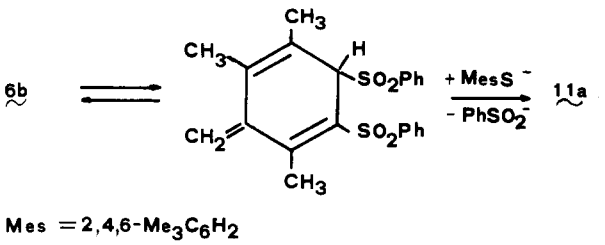
(5)

12 or 13 (Scheme IV). The results show that all three pathways compete in the photostimulated reactions of **6a**. On the contrary, the experiments carried out on **6b** suggest that path ii is much faster than the others as neither **10a** nor **13** are formed. The effect of the change in the concentration and in the steric bulk[13] of the arenethiolate on the product distribution can be well explained in light of the above advanced hypotheses.

In conclusion, on the basis of the obtained results, we believe that in the experiments on **6a** and **6b** carried out at 120 °C small amounts of dibenzothiophenes **8a** and **8b** are formed through a slow electron-transfer dark reaction. It is well-known,[8,15] in fact, that quite often light is not necessary for electron-transfer reactions to proceed, but, as observed in the present case, it can provide significant acceleration. As regards the formation of the normal substitution products (**7a,b**, **9**, and **10a**), it is very likely that the usual $S_NAr$ mechanism is operative, although a small contribution by the $S_{RN}1$ process to the yield of **7a** and **9** cannot be disregarded. Finally, to explain the formation of **11a** from **6b**, the ionic mechanism depicted in Scheme V is, in our opinion, the most reasonable one, as (a) no electron-transfer pathways seem to be involved in the telesubstitution reaction, (b) the latter only occurs in the case of the more congested substrate and with the more sterically hindered arenethiolate, in agreement with our previous results on this topic, and (c) support for the base-catalyzed tautomerization represented in Scheme V was found in H/D exchange experiments carried out in $Me_2SO$-$d_6$. Partially reacted **6b**, recovered from reactions (at 120 °C for 2 h) with sodium 2,4,6-trimethylbenzenethiolate in the presence of 90% deuterated parent thiol, showed 60% average deuteriation of the methyl groups with a slightly larger extent of deuteriation at the ones located in 4- and 5-positions.

It is noteworthy that, to the best of our knowledge, the formation of **7a** and **9** from **6a** under photostimulation appears to be the first example of substitution of the phenylsulfonyl group in aromatic sulfones via an $S_{RN}1$ pathway.[16,17] Moreover, the transformation of **15** into

Scheme V



Mes = 2,4,6-$Me_3C_6H_2$

dibenzothiophene derivatives **8a,b** shows that, when a suitably placed phenyl substituent is present, an intramolecular cyclization of the $\sigma$-radical intermediates[19] of $S_{RN}1$ processes can compete with or even prevail over the other well-known reaction paths. Further investigations are in progress to definitely confirm the mechanism proposed for the photostimulated reactions and to gain more insight into the behavior of aromatic sulfones in electron-transfer reactions.

## Experimental Section

**General Methods.** Melting points were taken on an Electrothermal melting point apparatus and are uncorrected. $^1H$ NMR spectra, reported in parts per million ($\delta$), were recorded on a Varian FT 80 spectrometer using $Me_4Si$ as an internal standard. High-pressure liquid chromatography (HPLC) was performed on a Waters Model ALC-202 chromatograph equipped with a Model 440 UV detector and using a 3.9 × 300 mm $\mu$-Porasil column with a flow rate of 2.0 mL/min (dichloromethane as eluant) and monitoring at 254 nm.

Experiments carried out under Ar were deaerated by using five freeze–pump–thaw cycles and either stoppered by a rubber septum or left under a positive gas pressure (ca. 40 mm, regulated with a mercury bubbler). Reactions performed in $Me_2SO$ were routinely worked up by dilution with water (5–6 volumes) and threefold extraction with benzene, followed by washing of the combined extracts with an equal volume of brine. The benzene extract was dried ($Na_2SO_4$) and the solvent removed on a rotoevaporator under reduced pressure. Sulfides were oxidized to the corresponding sulfones with an excess of 34% hydrogen peroxide in glacial acetic acid at 100 °C.

**Materials.** Sodium arenethiolates were prepared as previously described,[2] kept in vacuo, and iodometrically titrated before use. Dimethyl sulfoxide, distilled under reduced pressure over calcium hydride and in a $N_2$ stream, was stored over molecular sieves (Type 4A). All other commercial solvents and reagents were purified according to literature methods to match reported physical constants. An authentic sample of 1,4-dimethyl-2-(phenylsulfonyl)benzene [mp 111 °C (lit.[20] mp 111–112 °C)] was prepared as reported in the literature.

**Preparation of 6a. (a) 1,4-Dimethyl-2-(phenylsulfonyl)-3-(phenylthio)benzene (7a).** A solution of 1,4-dimethyl-2-nitro-3-(phenylsulfonyl)benzene[2] (0.96 g, 3.3 mmol) and PhSNa (0.53 g, 1.2 molar equiv) in $Me_2SO$ (30 mL) was heated under Ar at 120 °C for 1 h. The usual workup followed by column chromatography on silica gel (65% hexane, 35% benzene) gave 1,4-dimethyl-2-nitro-3-(phenylthio)benzene: 0.13 g (15%); melting point undepressed on admixture with an authentic[2] sample. Further elution with dichloromethane gave **7a** as a white solid: 0.97 g (83%); mp 138–139 °C (EtOH); NMR ($CDCl_3$) $\delta$ 7.85 (m, 2 H, H-2′ and H-6′ of $PhSO_2$), 7.27 (m, 5 H, H-5 and H-6 and H-3′, H-4′, and H-5′ of $PhSO_2$), 6.94 and 6.48 (2 m, 3 H and 2 H, respectively, PhS), 2.95 (s, 3 H, $CH_3$), 2.15 (s, 3 H, $CH_3$). Anal. Calcd for $C_{20}H_{18}O_2S_2$: C, 67.8; H, 5.1. Found: C, 67.7; H, 5.1. NMR spectra of **7a** recorded after incremental additions of the lanthanide shift reagent Yb(fod)$_3$ confirmed the assignments and

(13) The question of whether $S_{RN}1$ reactions are sensitive to steric effects is still controversial.[7a,14] Some experimental results, however, seem to suggest that the combination of arenethiolate anions with aryl radicals "is apparently hindered significantly by *ortho* methyl group".[7c]

(14) Norris, R. K.; Randles, D. *Aust. J. Chem.* **1976**, *29*, 2621.

(15) Scamehorn, R. G.; Bunnett, J. F. *J. Org. Chem.* **1977**, *42*, 1449.

(16) It is reported that the phenylsulfonyl is not a good nucleofugic group in aromatic $S_{RN}1$ reactions. In the reaction with acetone enolate ion stimulated by solvated electrons, in fact, diphenyl sulfone is cleaved to phenyl anion to yield only benzene.[9,18]

(17) Preliminary results show that the presence of the methyl groups in the polysubstituted benzene ring of **6a,b** should play an important role in driving the reaction with arenethiolates along the reported electron-transfer pathways. The reaction of 1,2-bis(phenylsulfonyl)benzene with sodium benzenethiolate in $Me_2SO$, which at 120 °C gives quantitatively 1-(phenylsulfonyl)-2-(phenylthio)benzene, seems to be insensitive to photostimulation.

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

(19) For related examples see: Grimshaw, J.; Haslett, R. J. *J. Chem. Soc., Perkin Trans. 1* **1980**, 657 and previous papers in the series.

(20) Holt, G.; Pagdin, B. *J. Chem. Soc.* **1960**, 2508.

the structure proposed: in particular the absorptions exhibited both by H-5 and H-6 were evidenced as half of an AB system ($J$ = 7.9 Hz).

**(b) Oxidation of 7a to 6a.** Oxidation of **7a** as reported in General Methods gave **6a** in almost quantitative yield: mp 198–199 °C (EtOH); NMR ($CDCl_3$) δ 7.87 [m, 4 H, 2 × (H-2′ and H-6′ of $PhSO_2$)], 7.50 [m, 6 H, 2 × (H-3′, H-4′, and H-5′ of $PhSO_2$)], 7.39 (s, 2 H, H-5 and H-6), 2.53 (s, 6 H, 2 $CH_3$). Anal. Calcd for $C_{20}H_{18}O_4S_2$: C, 62.2; H, 4.7. Found: C, 62.0; H, 4.7.

**Preparation of 6b. (a) 1-Nitro-2-(phenylthio)-3,4,5,6-tetramethylbenzene (17).** 1,2-Dinitro-3,4,5,6-tetramethylbenzene[21] (0.45 g, 2 mmol) and PhSNa (0.29 g, 2.2 mmol) were dissolved in $Me_2SO$ (20 mL) and heated under Ar at 120 °C for 15 min. The usual workup gave nearly quantitative yield of **17**: mp 96.5–97 °C (petroleum ether, bp 80–100 °C); NMR ($CDCl_3$) δ 7.14 (m, 5 H, PhS), 2.38 (s, 3 H, $CH_3$), 2.30 (s, 6 H, 2 $CH_3$), 2.22 (s, 3 H, $CH_3$). Anal. Calcd for $C_{16}H_{17}NO_2S$: C, 66.9; H, 5.9; N, 4.9. Found: C, 67.0; H, 5.8; N, 4.8.

**(b) 1-Nitro-2-(phenylsulfonyl)-3,4,5,6-tetramethylbenzene (18).** This compound was prepared by oxidation of **17** in the usual way: mp 166–167 °C (EtOH); NMR ($CDCl_3$) δ 8.0 (m, 2 H, H-2 and H-6 of $PhSO_2$), 7.58 (m, 3 H, H-3, H-4, and H-5 of $PhSO_2$), 2.40 (s, 3 H, $CH_3$), 2.33 (s, 3 H, $CH_3$), 2.22 (s, 6 H, 2 $CH_3$). Anal. Calcd for $C_{16}H_{17}NO_4S$: C, 60.2; H, 5.3; N, 4.4. Found: C, 61.2; H, 5.0; N, 4.4.

**(c) 1-(Phenylsulfonyl)-2-phenylthio-3,4,5,6-tetramethylbenzene (7b).** A solution of **18** (1 g, 3.13 mmol) and PhSNa (0.5 g, 1.2 molar equiv) in $Me_2SO$ (30 mL) was heated 3 h at 120 °C under Ar. After the usual workup, the concentrated reaction extracts were chromatographed on a silica gel column. With hexane–benzene (2/1) as the eluant, compound **17** (0.23 g, 26%) was collected. Successive elution with dichloromethane afforded **7b**: 0.86 g (72%); mp 188 °C (EtOH–dioxane); NMR ($CDCl_3$) δ 7.83 (m, 2 H, H-2 and H-6 of $PhSO_2$), 7.20 (m, 3 H, H-3, H-4, and H-5 of $PhSO_2$), 6.93 and 6.53 (2 m, 3 H and 2 H, respectively, PhS), 2.83 (s, 3 H, $CH_3$), 2.32 (s, 3 H, $CH_3$), 2.25 and 2.21 (2 overlapping s, 6 H in all, 2 $CH_3$). Anal. Calcd for $C_{22}H_{22}O_2S_2$: C, 69.1; H, 5.75. Found: C, 68.1; H, 5.75.

**(d) Oxidation of 7b to 6b.** Oxidation of **7b** in the usual way gave almost quantitatively **6b** as a white solid: mp 232 °C (EtOH–dioxane); NMR ($CDCl_3$) δ 7.80 [m, 4 H, 2 × (H-2 and H-6 of $PhSO_2$)], 7.48 [m, 6 H, 2 × (H-3, H-4, and H-5 of $PhSO_2$)], 2.30 (s, 6 H, 2 $CH_3$), 2.20 (s, 6 H, 2 $CH_3$). Anal. Calcd for $C_{22}H_{22}O_4S_2$: C, 63.8; H, 5.3. Found: C, 63.7; H, 5.2.

**Reaction of 6a in $Me_2SO$ at 120 °C. (a) With Sodium Benzenethiolate.** A solution of **6a** (0.116 g, 0.3 mmol) and PhSNa (0.198 g, 1.5 mmol) in $Me_2SO$ (18 mL) was heated under Ar at 120 °C for 20 min. The usual workup followed by column chromatography (silica gel, dichloromethane) gave 0.103 g (97%) of **7a**, identical with an authentic sample (NMR, TLC).

When the reaction was checked by HPLC (see below) traces of dibenzothiophene **8a** were also detected.

**(b) With Sodium 2,4,6-Trimethylbenzenethiolate.** The reaction mixture resulting from treatment of **6a** (1.16 g, 3 mmol) with sodium 2,4,6-trimethylbenzenethiolate (2.6 g, 15 mmol) in 180 mL of $Me_2SO$ (40 min at 120 °C under Ar), was worked up as described in the general methods. Column chromatography on silica gel (dichloromethane as eluant) gave compound **9**: 1.07 g (90%); mp 225 °C (EtOH–dioxane); NMR ($CDCl_3$) δ 8.10 (m, 2 H, H-2′ and H-6′ of $PhSO_2$), 7.48 (m, 3 H, H-3′, H-4′, and H-5′ of $PhSO_2$), 7.05 (br s, 2 H, H-5 and H-6), 6.69 (br s, 2 H, $Me_3C_6\mathbf{H}_2$), 2.91 (s, 3 H, $CH_3$), 2.17 (s, 3 H, $CH_3$), 1.69 (s, 9 H, 3 $CH_3$). Anal. Calcd for $C_{23}H_{24}O_2S_2$: C, 69.7; H, 6.1. Found: C, 69.6; H, 6.05. NMR spectra of **9** recorded after incremental additions of $Yb(fod)_3$ confirmed the assignments and the structure proposed: in particular, by addition of an equivalent amount of the shift reagent, the absorption exhibited by H-5 and H-6 was evidenced as an AB system ($J$ = 8 Hz).

The successive fractions eluted from the column gave 36 mg (5%) of dibenzothiophene derivative **8a**: mp 197–198 °C (EtOH) (lit.[22] mp 195–198 °C); NMR ($CDCl_3$) δ 7.85 (m, 2 H, H-6 and H-9), 7.55 (m, 2 H, H-7 and H-8), 7.19 (AB pattern, $J$ = 7.8 Hz, 2 H, H-2 and H-3), 2.68 and 2.64 (2 overlapping s, 6 H in all, 2 $CH_3$).

**Reaction of 6b in $Me_2SO$ at 120 °C. (a) With Sodium Benzenethiolate.** A solution of **6b** (1.24 g, 3 mmol) and PhSNa (1.98 g, 15 mmol) in 180 mL of $Me_2SO$ was heated under Ar at 120 °C for 110 min. The usual workup followed by column chromatography (silica gel, dichloromethane) gave 0.97 g (85%) of **7b** (identified by NMR and mixed mp with an authentic sample) and dibenzothiophene derivative **8b**: 32 mg (4%); mp 255 °C (EtOH–dioxane); NMR ($CDCl_3$) δ 7.88 (m, 2 H, H-6 and H-9), 7.50 (m, 2 H, H-7 and H-8), 2.63, 2.58, 2.30, and 2.25 (4 s, 3 H each, 4 $CH_3$). Anal. Calcd for $C_{16}H_{16}O_2S$: C, 70.6; H, 5.9; S, 11.8. Found: C, 70.5; H, 5.9; S, 11.7.

**(b) With Sodium 2,4,6-Trimethylbenzenethiolate.** Sulfone **6b** (1.24 g, 3 mmol) was reacted with sodium 2,4,6-trimethylbenzenethiolate (2.6 g, 15 mmol) as described above (reaction time 6 h). The usual workup and chromatography (silica gel, $CHCl_3$) gave the following. (i) A solid mixture (1.07 g, 84%) of two isomeric sulfides (**10a** and **11a**; see text) corresponding to the substitution of a $PhSO_2$ with a (2,4,6-trimethylphenyl)thio group in **6b**: NMR ($CDCl_3$) δ 8.15 (m, 2 H of **10a**), 7.98 (s, 1 H of **11a**), 7.80 (m, 2 H of **11a**), 7.49 (m, 3 H of **10a** + 3 H of **11a**), 6.81 (br s, 2 H of **11a**), 6.68 (br s, 2 H of **10a**), 3.81 (s, 2 H of **11a**), 2.77 (s, 3 H of **10a**), 2.31, 2.27, 2.23, 2.16, and 2.11 (5 overlapping s, 9 H of **10a** + 18 H of **11a**), 1.77 and 1.74 (2 overlapping s, 9 H of **10a**). Anal. Calcd for $C_{25}H_{28}O_2S_2$: C, 70.7; H, 6.6; S, 15.1. Found: C, 70.6; H, 6.8; S, 15.0. The **10a** to **11a** molar ratio, as determined from the NMR spectrum, was found to be ca. 2.3:1. Any attempt to separate the mixture components proved futile and they were successively characterized as sulfones (see below). (ii) Dibenzothiophene **8b** (73 mg, 9%), identical with an authentic sample (TLC, NMR) was also obtained.

**Reaction of 6b with Sodium 2,4,6-Trimethylbenzenethiolate in $Me_2SO$-$d_6$ and in the Presence of S-Deuterated 2,4,6-Trimethylbenzenethiol.** A solution of sodium 2,4,6-trimethylbenzenethiolate (0.13 g, 0.75 mmol) and 90% S-deuterated parent thiol (0.113 mL, 0.75 mmol) in $Me_2SO$-$d_6$ (3 mL) was added to a solution of **6b** (62 mg, 0.15 mmol) in 6 mL of $Me_2SO$-$d_6$. The reaction mixture was deaerated with argon gas, stoppered with a rubber septum and heated at 120 °C for 2 h. After the sample cooled at room temperature, an excess (ca. 4 mL) of $CH_3COOD$ was added, and the reaction solution was poured into water. Unreacted **6b** was isolated by a standard workup followed by column chromatography (silica gel, $CHCl_3$). $^1H$ NMR analysis of **6b**, carried out also with the aid of $Yb(fod)_3$ as a shift reagent, showed 65% deuteration at the methyl groups located in 4- and 5-positions and 55% deuteration at the ones in the 3- and 6-positions.

**Experiments 1, 6, 12, and 13 (Tables I and II).** The above-reported reactions of **6a** or **6b** with sodium arenethiolates at 120 °C were repeated on 0.15 mmol of substrate. After a careful standard workup, the reaction mixtures were chromatographed on silica gel (hexane) to remove diaryl disulfide and arenethiol. The successive fractions (eluted with dichloromethane) were collected together and rotoevaporated, and the residue was analyzed by TLC, $^1H$ NMR, and HPLC. The absolute amounts of products were estimated by NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard.

**Oxidation of the Mixture of Isomeric Sulfides 10a and 11a.** The above-reported mixture of **10a** and **11a** (0.9 g) was oxidized with hydrogen peroxide in the usual way. After a standard workup, the mixture components were separated by low-pressure chromatography on silica gel 60 prepacked Lobar (Merck) columns with $CHCl_3$–$Et_2O$ (10/1) as the eluant.

**First Elution Product, 11b**: 0.28 g (0.61 mmol); mp 195–196 °C (EtOH); NMR ($CDCl_3$) δ 8.11 (br s, 1 H, H-6), 7.75 (m, 2 H, H-2′ and H-6′ of $PhSO_2$), 7.50 (m, 3 H, H-3′, H-4′, and H-5′ of $PhSO_2$), 6.77 (br s, 2 H, $Me_3C_6\mathbf{H}_2$), 4.54 (s, 2 H, $CH_2$), 2.35, 2.30, 2.28, and 2.24 (4 overlapping s, 15 H in all, 5 $CH_3$), 2.06 (s, 3 H, $CH_3$). Anal. Calcd for $C_{25}H_{28}O_4S_2$: C, 65.8; H, 6.1. Found: C, 65.7; H, 6.3.

To a solution of **11b** in $CDCl_3$ (ca. 60 mg/mL) were added aliquots of the lanthanide shift reagent $Yb(fod)_3$ in the range 0.03–0.20 mmol/mmol of **11b**. When the LIS vs. the $Yb(fod)_3$ to substrate molar ratio was plotted, straight lines were obtained with relative slopes as follows: 1.00 (H-6), 0.86 (H-2′ and H-6′ of $PhSO_2$), 0.79 ($CH_2$), 0.73 ($CH_3$), 0.49 (2 $CH_3$), 0.21 ($Me_3C_6\mathbf{H}_2$),

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0.21 ($CH_3$), 0.15 (H-3′ and H-5′ of $PhSO_2$), 0.13 (H-4′ of $PhSO_2$), 0.10 ($CH_3$), 0.08 ($CH_3$). The similarity in slope (0.21 and 0.15) between the meta protons of the mesityl and phenyl groups indicates that the two sulfonyl groups coordinate the lanthanide ion to a similar extent. Therefore, the fact that one methyl of the parent ring is shifted (0.73) even more than the two *o*-methyls of the mesityl group (0.49) can be explained by assuming that the former is close to both the sulfonyl groups as in the proposed structure **11b**.

**Second elution product, 10b:** 0.64 g (1.41 mmol); mp 203–204 °C (EtOH); NMR ($CDCl_3$) δ 7.79 (m, 2 H, H-2′ and H-6′ of $PhSO_2$), 7.47 (m, 3 H, H-3′, H-4′, and H-5′ of $PhSO_2$), 6.78 (br s, 2 H, $Me_3C_6H_2$), 2.38 (s, 3 H, $CH_3$), 2.23, 2.20, 2.18, and 2.15 (4 overlapping s, 18 H in all, 6 $CH_3$). Anal. Calcd for $C_{25}H_{28}O_4S_2$: C, 65.8; H, 6.1. Found: C, 65.7; H, 6.1.

**Photostimulated Reactions of 6a,b and Control Experiments of Tables I and II.** In a Pyrex test tube was dissolved the sulfone **6a** or **6b** (0.15 mmol) in $Me_2SO$ (6 mL) or in 6 mL of a $7.5 \times 10^{-5}$ M $Me_2SO$ solution of *m*-dinitrobenzene (expts 5, 10, and 17), and this was deaerated with argon gas by using five freeze–pump–thaw cycles. To this solution either was added 3 mL of a $Me_2SO$ solution of sodium arenethiolate at the appropriate concentration (0.25 or 0.05 M) or an additional 3 mL of $Me_2SO$ (expts 11 and 18). The reaction mixture was deaerated again with argon and stoppered with a rubber septum. Reactions carried out in the "dark" were performed with the test tube wrapped in aluminum foil. Reactions performed in "light" were irradiated in a homemade "merry-go-round" apparatus by a 300-W Osram sunlamp placed 10 cm from the reaction vessel. All reactions were worked up as reported in General Methods and chromatographed by first eluting with hexane (except expts 11 and 18), to remove some diaryl disulfide and the corresponding arenethiol, and then with dichloromethane. All successive fractions (eluted with dichloromethane) were collected together and concentrated on a rotary evaporator, and the residue was analyzed by TLC, $^1H$ NMR, and HPLC. The absolute yields reported in Tables I and II were estimated by NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard.

**Registry No. 6a**, 81064-10-0; **6b**, 81064-11-1; **7a**, 81095-45-6; **7b**, 81064-12-2; **8a**, 23018-39-5; **8b**, 81064-13-3; **9**, 81064-14-4; **10a**, 81064-15-5; **10b**, 81064-16-6; **11a**, 81064-17-7; **11b**, 81064-18-8; **12**, 2548-26-7; **17**, 81064-19-9; **18**, 81064-20-2; PhSNa, 930-69-8; MesSNa, 6127-91-9; $Me_2SO$, 67-68-5; 1,4-dimethyl-2-nitro-3-(phenylsulfonyl)-benzene, 74157-74-7; 1,4-dimethyl-2-nitro-3(phenylthio)benzene, 74157-73-6; 1,2-dinitro-3,4,5,6-tetramethylbenzene, 18801-63-3.

# *o*-Naphthoquinodimethanes and *o*-Phenanthroquinodimethanes. Isoindene-Related Species

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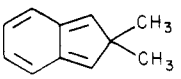
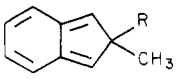
Three isoindene-related naphthoquinodimethane and phenanthroquinodimethane species were synthesized and trapped with 4-phenyl-1,2,4-triazoline-3,5-dione. They are 2,2-dimethyl-2*H*-benz[*e*]indene (**3**), 2,2-dimethyl-2*H*-benz[*f*]indene (**4**), and 2,2-dimethyl-9*H*-cyclopenta[*b*]phenanthrene (**10**). Compound **3** could be isolated and characterized by $^1H$ NMR. The effect of solvent on the bisacylation of naphthalene and phenanthrene by dimethylmalonyl chloride is discussed. Also the use of the Vilsmeier reagent generated from $PBr_3$/DMF if highly recommended as a general reagent for conversion of alcohols to alkyl bromides.

In a recent series of papers we examined the generation and the thermal and photochemical behavior of 2,2-dimethylisoindene (**1**) and other 2-alkyl-2-methylisoindenes (**2**).[1-5] **1** was itself able to be isolated either as a gas or



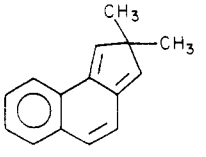
**1**



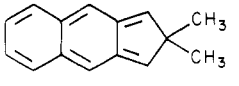
**2**, R = $CH_3CH_2$, $(CH_3)_2CH$, $PhCH_2$, c-$C_3H_5CH_2$

in dilute solution, and it was fully characterized spectroscopically, the first time such an *o*-benzoquinodimethane species had been able to be so fully characterized.[2,3] Its $^1H$ NMR spectrum showed complex vinylic absorptions at δ 6.08 (4 H) and 6.55 (2 H) in addition to a six-proton singlet at δ 1.16, all consistent with **1** having nonaromatic character.

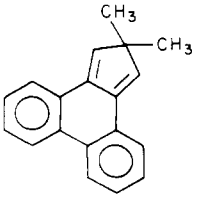
We considered it of interest to attempt to prepare and isolate related 1,2- and 2,3-naphtho- and 9,10-phenanthroquinodimethane species **3–5**. No such iso-



**3**



**4**



**5**

indene-type species have been previously generated, much less isolated, although related 2,3-naphthoquinodimethane derivatives **6** and **7** have recently been reported and

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