ipso- and *tele*-Substitution Pathways in the Reactions of 1,3-Dimethyl-2,4-dinitro- and 1,3-Dimethyl-2-nitro-4-phenylsulphonyl-naphthalene with Sodium Arenethiolates in Dimethyl Sulphoxide

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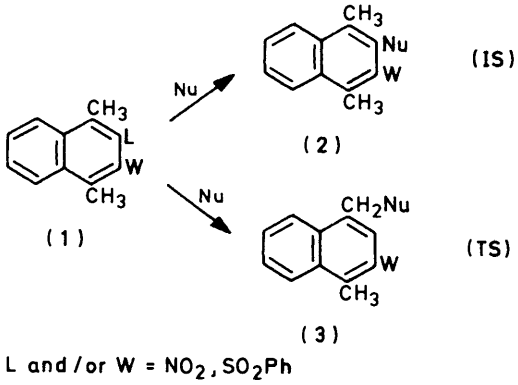
1,3-Dimethyl-2,4-dinitronaphthalene (4) reacts with sodium 2,4,6-trimethylbenzenethiolate in dimethyl sulphoxide at 120 °C giving a mixture of an *ipso*-substitution product, 1,3-dimethyl-2-nitro-4-(2,4,6-trimethylphenylthio)naphthalene (6a), and of two *tele*-substitution products, *viz.* 3-methyl-2-nitro-1-(2,4,6-trimethylphenylthiomethyl)- (7a) and 1-methyl-2-nitro-3-(2,4,6-trimethylphenylthiomethyl)-naphthalene (8a). Lower relative yields of *tele*-substitution products were obtained when the reaction temperature was decreased and when the less bulky sodium benzenethiolate was used as nucleophile. The reaction of 1,3-dimethyl-2-nitro-4-phenylsulphonylnaphthalene (5) with sodium 2,4,6-trimethylbenzenethiolate (Me_2SO, 120 °C) gave only the *tele*-substitution products (7a) and (8a). The obtained results show that among the possible *ipso*- and *tele*-substitution products only those deriving from the departure of the nucleofugic group present in the α-position are formed. Probable mechanisms accounting for the experimental results are discussed.

In previous papers [1a-c] we showed that treatment with nucleophiles of naphthalene derivatives having structures like (1) can result in two competing kinds of displacement: the *ipso*- (IS) and the *tele*-substitution (TS) process (Scheme 1). Depending on the nature of both the nucleophile and the W and L groups and, in general, on the experimental conditions, the TS can prevail over the IS or in some cases be the only possible process. Examples of this kind of TS reaction occurring in the thiophen [2] and benzene [3] series were likewise reported by us and some mechanistic implications discussed.

In the previously studied compounds, however, the L and W groups were always in vicinal positions. Therefore, in order to better define the scope and limitations of these TS processes, we have extended our studies to the reactivity of 1,3-dimethyl-2,4-dinitro- (4) and 1,3-dimethyl-2-nitro-4-phenylsulphonyl-naphthalene (5). The results obtained from the reactions of compounds (4) and (5) with two representative [1b,c] sodium arenethiolates, under the same experimental conditions used for substrates (1), are herein reported.



Scheme 1.

Results and Discussion

The reaction of compound (4) with sodium 2,4,6-trimethylbenzenethiolate in dimethyl sulphoxide (DMSO) at 120 °C (Scheme 2) gave an 80% yield of a mixture of an *ipso*-substitution product, 1,3-dimethyl-2-nitro-4-(2,4,6-trimethylphenylthio)naphthalene (6a), and of two *tele*-substitution products, *viz.* 3-methyl-2-nitro-1-(2,4,6-trimethylphenylthiomethyl)- (7a) and 1-methyl-2-nitro-3-(2,4,6-trimethylphenylthiomethyl)-naphthalene (8a). The ratio (6a) : (7a) : (8a), as determined by ^1H n.m.r., was 48 : 28 : 24. Structure assignment for sulphides (6a), (7a), and (8a) follow both from their elemental analyses and ^1H n.m.r. data and, mainly, from ^1H n.m.r. analysis carried out on the corresponding nitro-sulphones and/or amino-sulphides with the aid of $Yb(fod)_3$ as a shift reagent (see Experimental section).

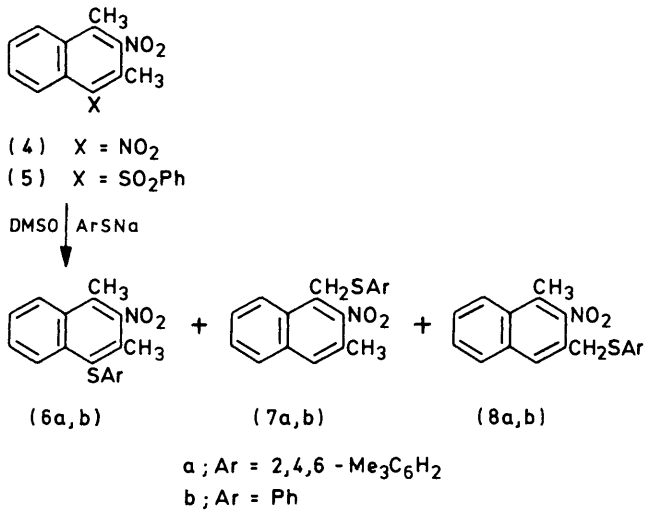
An increase in the yield of the *ipso*-substitution product was found when (*a*) the reaction temperature was decreased to 60 °C [the (6a) : (7a) : (8a) molar ratio being 64 : 18 : 18], and (*b*) the less bulky benzenethiolate was used as nucleophile at 120 °C. In this case, in fact, substrate (4) afforded 1,3-dimethyl-2-nitro-4-phenylthionaphthalene (6b) in 81% yield along with 10% of a mixture (*ca.* 3 : 2) of two *tele*-substitution sulphides, which could not be isolated.† Thus, in the reaction on substrate (4), as previously found for (1),[1b] the TS paths are also favoured with respect to the IS ones on increasing the reaction temperature and the nucleophile bulk.

Confirming previous results [1c] which showed that the substitution of a nitro-group with a phenylsulphonyl group strongly favours the TS pathway, the reaction of 1,3-dimethyl-2-nitro-4-phenylsulphonylnaphthalene (5) with sodium 2,4,6-trimethylbenzenethiolate gave only the *tele*-substitution products (7a) and (8a), in 52 and 29% yield respectively. No trace of the expected *ipso*-substitution product (6a) could be detected.

It is interesting to note that in the observed *ipso*- and *tele*-substitutions only the α-electron-withdrawing substituent can act as the leaving group. Conversely, the values of the (7) : (8) ratios obtained with both the substrates are indicative of a low selectivity as regards the methyl groups involved in the TS processes.

Control experiments showed that (*a*) compounds (6)—(8) were not interconverted under the reaction conditions; (*b*) the overall and relative yields of the various sulphides did not change when the reactions on substrate (4) were carried out either under photostimulation (sunlamp) or in the presence of

† The assignment of the particular structures (7a) and (8a) to these *tele*-substitution products can be made only on the basis of the results obtained using 2,4,6-trimethylbenzenethiolate as nucleophile (see Experimental section for more details).



Scheme 2.

di-t-butyl nitroxide (a free-radical scavenger)[4] or of azobenzene (a good electron acceptor).[5] Hence a radical or a radical-anion chain mechanism seems to be excluded.

As far as the formation of the *ipso*-substitution products (6a) and (6b) is concerned, the classical addition–elimination mechanism appears to be operative as (*a*) the relative ease of nucleophilic displacement of aromatic nitro-groups by thiolate anions *via* S_NAr has been verified by numerous studies;[6] (*b*) these reactions, when carried out in dipolar aprotic solvents, can be activated also from non-conjugated positions;[7] (*c*) in an independent experiment we ascertained that 1,3-dinitronaphthalene (9) reacts with sodium benzenethiolate, under the same conditions used for substrate (4), to give likewise the sulphide deriving from *ipso*-substitution of the α-nitro-group, *i.e.* 3-nitro-1-phenylthionaphthalene (10). The preferential substitution of the nitro-group in the α-position of compounds (4) and (9) can therefore be explained on the basis of the well-known greater reactivity of these naphthalene positions in aromatic nucleophilic substitutions.

As regards the formation of the *tele*-substitution products (7) and (8), on the basis of the experimental results, it is reasonable to think that ionic mechanisms, similar to that previously suggested for such processes,[1,3] are operative. It is conceivable, in fact, that under the basic reaction conditions compounds (4) and (5) partially tautomerize into the methylene-dihydronaphthalene derivatives (13) and (15), which then undergo nucleophilic attack on the exocyclic methylene group with consequent departure of either a nitro or the phenylsulphonyl group from a γ- or ε-ring position (Scheme 3, paths A,A′ and C,C′). It is interesting to observe that the intermediate anions (11) and (12) could, in principle, give rise to other two methylene-dihydronaphthalene derivatives [(14) and (16)] from which the *tele*-substitution products (17) and (18) should form. The fact that only compounds (7) and (8) are obtained indicates that paths A,A′ and C,C′ are much more favoured over, respectively, the B,B′ and D,D′ ones. A different rate in the nucleophilic substitution steps A′—D′ could be taken into account to explain the experimental results. However, as we have already proposed for the *tele*-substitution reactions occurring on 1,4-dimethyl-2-nitro-3-phenylsulphonylnaphthalene,[1c] it is possible that the different thermodynamic stabilities of the intermediate tautomers (13)—(16) play a role in driving the reaction exclusively along paths A and C. The inherent instability[9] of polycyclic molecules which are constrained to exist in a completely non-aromatic structure [as in (16)] can account for the preferential formation of (15) from (12). In a similar way, the lack of formation of compound (17) could reflect, in our opinion, the lower stability of (14) with respect to (13).

The results obtained with substrate (5) are consistent with the proposed mechanism. In fact, the substitution of the nitro-group in the 4-position with the phenylsulphonyl group, which is considered to be a worse leaving group in aromatic nucleophilic substitutions,[10] can cause the S_NAr to be less favourable and allow the *tele*-substitution to predominate. In concomitance with this, the presence of the phenylsulphonyl group in place of the nitro-group can lead to a faster formation of tautomers (13) and (15) owing to an increase in their relative stability. In fact, on the basis of the results found for tautomeric equilibria of substituted olefins,[11] intermediates (13) and (15) (L = SO_2Ph) should be regarded as more stable than the corresponding intermediates with L = NO_2, for the simultaneous presence of the more favoured vinyl-nitro and allyl-sulphonyl systems. Moreover, for the same reasons, they should also be more stable than intermediates (14) and (16), respectively, in agreement with the lack of formation of compounds (17) and (18) in the TS path.

Support for the ionic mechanism represented in Scheme 3 was found also in H–D exchange experiments carried out in [$^2H_6$]dimethyl sulphoxide. Partially reacted (4) and (5), recovered from reactions with sodium 2,4,6-trimethylbenzenethiolate and in the presence of *S*-deuteriated parent thiol, showed relevant deuteriation at both the methyl groups. Surprisingly enough, the 1-Me to 3-Me deuteriation ratios [1.1 for (4) and 2.2 for (5)] were not very different from the ratios in which compounds (7) and (8) were formed in the corresponding reactions on substrates (4) and (5). The exact meaning of this result is not yet well defined; however, in our opinion, it can be regarded as consistent with the involvement of anions (11) and (12) in the paths leading to the formation of the *tele*-substitution products (7) and (8).

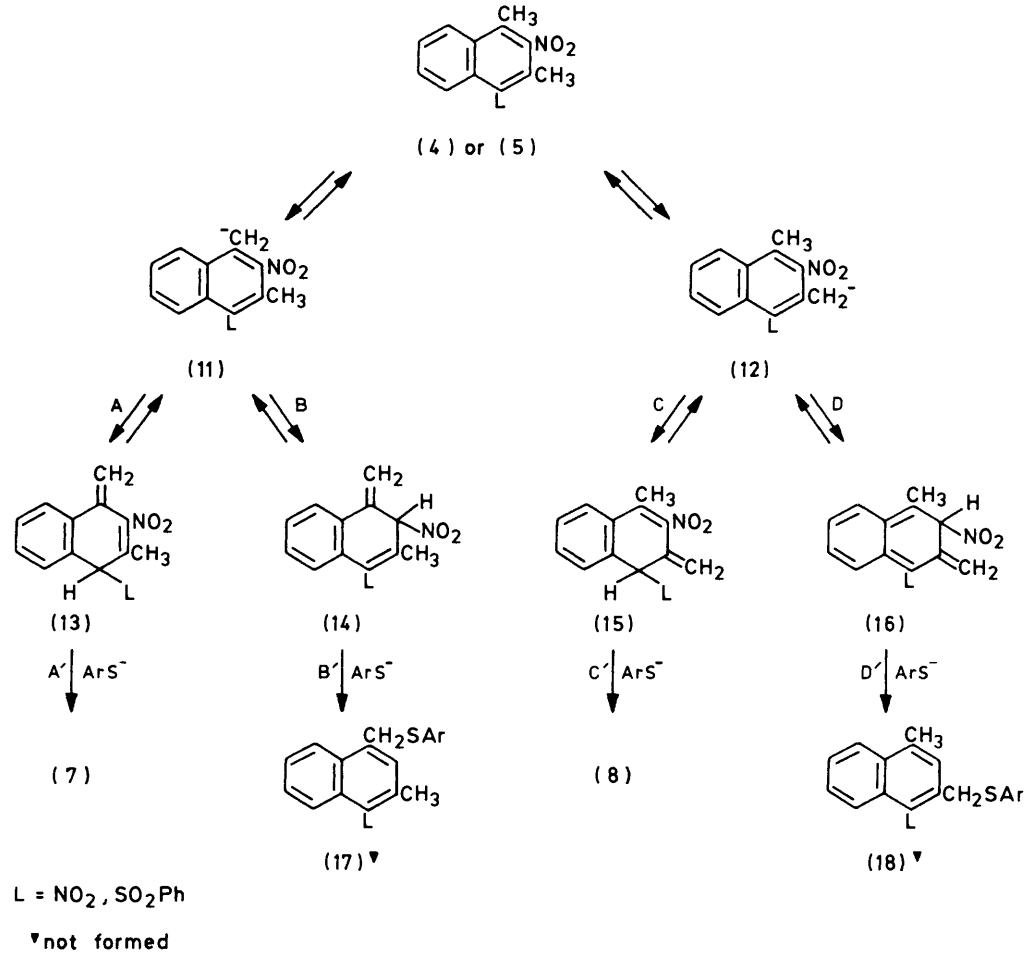
In conclusion, the obtained results show that the known *tele*-substitution reactions can also occur on alkyl aromatic derivatives having two non-*ortho* electron-withdrawing groups. Also in this case, as already found for substrates (1), the TS competes against the IS and becomes the only possible process when the phenylsulphonyl group acts as the leaving group. An intriguing feature of the nucleophilic displacements occurring on substrates (4) and (5) is that among the possible reaction products (two IS and four TS products) only those deriving from the departure of the nucleofugic group in the α-position are formed.

Experimental

General.—M.p.s were taken on an Electrothermal melting point apparatus and are uncorrected. ^1H N.m.r. spectra were recorded on a Varian FT-80 spectrometer ($SiMe_4$ as internal standard).

Experiments carried out under argon were deaerated using five freeze-pump-thaw cycles and either stoppered by a rubber septum or left under a positive gas pressure (*ca.* 30 mmHg, regulated with a mercury bubbler). Reactions performed in DMSO were routinely worked up by dilution with water (5—6 vol), three-fold 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. Nitro-sulphides were oxidized to the corresponding nitro-sulphones with an excess of 34% hydrogen peroxide in glacial acetic acid at 100 °C. Amino-sulphides were prepared by reduction with tin of the corresponding nitrosulphides in ethanol–hydrogen chloride.

In some cases structural assignments were made by ^1H n.m.r. analysis carried out with the aid of $Yb(fod)_3$ as a shift



Scheme 3.

reagent: unless otherwise stated, to a solution of the compound to be examined in $CDCl_3$ (*ca.* 60 mg/ml) aliquots of the lanthanide shift reagent were added in the range 0.03—0.20 mmol per mmol of compound. Structure assignments were done by examining the relative slopes of the straight lines obtained by plotting lanthanide-induced shifts (L.I.S.) *vs.* $Yb(fod)_3$ to substrate molar ratio.

Materials.—Sodium arenethiolates were prepared and DMSO purified as previously reported.[1b]

Preparation of 1,3-*Dimethyl*-2,4-*dinitronaphthalene* (4).—(*a*) 5,7-*Dimethyl*-6,8-*dinitro*-1,2,3,4-*tetrahydronaphthalene* (19). 5,7-Dimethyltetralin [12] (6 g) was nitrated with a mixture of 96% sulphuric acid (150 ml) and fuming nitric acid (45 ml; *d* 1.52) in the presence of chloroform (150 ml) following the procedure [1b] described for the 5,8-dimethyl isomer. The residue obtained by evaporation of the chloroform extracts was taken up with ethanol and filtered. The *dinitro-derivative* (19) (6.5 g, 69%) had m.p. 155—157 °C (from ethanol) (Found: C, 57.8; H, 5.7; N, 11.1. $C_{12}H_{14}N_2O_4$ requires C, 57.6; H, 5.6; N, 11.2%); δ ($CDCl_3$) 2.67 (4 H, m, 2 × CH_2), 2.16 (6 H, s, 2 × CH_3), and 1.82 (4 H, m, 2 × CH_2).

(*b*) 1,4-*Dibromo*-5,7-*dimethyl*-6,8-*dinitro*-1,2,3,4-*tetrahydronaphthalene* (20). Bromine (2.25 ml, 44 mmol) was added to a solution of compound (19) (5 g, 20 mmol) in bromobenzene (10 ml) and the mixture heated at 100 °C for 3 h. A second portion of bromine (0.2 ml) was added and the heating continued for 2 h. Hydrobromic acid and the excess of bromine were eliminated from the reaction solution under reduced pressure (20 mmHg) heating at 70—80 °C. After cooling with an ice-bath and addition of light petroleum (b.p. 30—50 °C) (50 ml), a white solid precipitated. The product was filtered off and washed with further light petroleum (50 ml). Crystallization with ethanol–dioxan (150 ml; 4 : 1) gave *compound* (20) (2.7 g; 33%), m.p. 198—200 °C (decomp. with HBr evolution) (Found: C, 35.2; H, 2.9; Br, 39.05; N, 6.9. $C_{12}H_{12}Br_2N_2O_4$ requires C, 35.3; H, 2.95; Br, 39.2; N, 6.85%); δ ($CDCl_3$) 5.71 (1 H, m, CHBr), 5.51 (1 H, m, CHBr), 2.81, 2.68, 2.57, and 2.47 (4 H in all, partly overlapping m's, 2 × CH_2), and 2.37 and 2.19 (each 3 H, s, 2 × CH_3).

(*c*) 1,3-*Dimethyl*-2,4-*dinitronaphthalene* (4). Compound (20) (2 g) was heated for 30 min at 200—210 °C (oil-bath) in a broad tube equipped with an external ice-cooling jacket. When the HBr evolution from the melted product decreased, the temperature was slowly increased to 250 °C and kept at this value for *ca.* 15 min. After cooling of the system, the residue was collected and extracted (Soxhlet) with dichloromethane. The dichloromethane extracts were concentrated and chromatographed on a silica-gel column using hexane–dichloromethane (3 : 1) as eluant. After the first fractions, containing traces of by-products which were not investigated, the dinitronaphthalene (4) (0.7 g, 58%) was eluted from the column. *Compound* (4) had m.p. 201—202 °C (from ethanol–dioxan) (Found: C, 58.5; H, 4.1; N, 11.4. $C_{12}H_{10}N_2O_4$

requires C, 58.5; H, 4.1; N, 11.4%); δ ($CDCl_3$) 8.10 (1 H, m, 8-H), 7.70 (3 H, m, 5-, 6-, and 7-H), 2.65 (3 H, s, CH_3), and 2.37 (3 H, s, CH_3).

Reaction of Compound (4) *with Sodium* 2,4,6-*Trimethylbenzenethiolate in DMSO.*—(*a*) *At* 120 °C. A solution of compound (4) (1 g, 4.07 mmol) and sodium 2,4,6-trimethylbenzenethiolate (0.85 g, 1.2 mol equiv.) in DMSO (60 ml) was kept, under argon, at 120 °C for 2 h. The reaction was worked up as reported in the general methods and chromatographed on a silica-gel column. The initial fractions, eluted with hexane, contained a mixture of 2,4,6-trimethylbenzenethiol and the corresponding disulphide. Further elution with hexane–benzene (1 : 1) gave 1.14 g of a mixture of three products. Samples of this mixture were saved to determine the relative composition by ^1H n.m.r.

The components of the mixture could be separated by low pressure chromatography on silica-gel 60 prepacked Lobar (Merck) columns using hexane–dichloromethane (3 : 1) as eluant.

The first elution product was identified as 1,3-*dimethyl*-2-*nitro*-4-(2,4,6-*trimethylphenylthio*)*naphthalene* (6a), m.p. 190—191 °C (from ethanol–dioxan) (Found: C, 71.7; H, 6.0; N, 4.0. $C_{21}H_{21}NO_2S$ requires C, 71.8; H, 6.0; N, 4.0%); δ ($CDCl_3$) 8.59 (1 H, m, 5-H), 7.99 (1 H, m, 8-H), 7.52 (2 H, m, 6- and 7-H), 6.80 br (2 H, s, $Me_3C_6H_2S$), 2.55 (3 H, s, CH_3), and 2.22 and 2.15 (each 6 H, s, 4 × CH_3). The absorptions at δ 8.59, 7.99, and 7.52 showed an ABCD pattern typical [13] of four vicinal protons in an aromatic condensed ring. Further support to the structure proposed for compound (6a) was achieved from ^1H n.m.r. analysis, carried out with Yb(fod)$_3$ as a shift reagent, on the corresponding nitro-sulphone: 1,3-*dimethyl*-2-*nitro*-4-(2,4,6-*trimethylphenylsulphonyl*)-*naphthalene* (21) had m.p. 215—216 °C (from ethanol–dioxan) (Found: C, 65.9; H, 5.5; N, 3.65. $C_{21}H_{21}NO_4S$ requires C, 65.8; H, 5.5; N, 3.65%); δ ($CDCl_3$) 8.97 (1 H, m, 5-H), 8.05 (1 H, m, 8-H), 7.58 (2 H, m, 6-H and 7-H), 6.86 br (2 H, s, $Me_3C_6H_2$), 2.62 (3 H, s, CH_3), 2.53 (3 H, s, CH_3), 2.38 (6 H, s, 2 × CH_3), and 2.26 (3 H, s, CH_3). L.I.S. analysis gave straight lines with relative slopes: 1.00 (5-H), 0.70 (3-Me), 0.66 (2- and 6-Me of $Me_3C_6H_2$), 0.20 ($Me_3C_6H_2$), 0.16 (1-Me), 0.10 (8-H), 0.05 (4-Me of $Me_3C_6H_2$), and 0.04 (6- and 7-H).

To the second elution product the structure of 3-*methyl*-2-*nitro*-1-(2,4,6-*trimethylphenylthiomethyl*)*naphthalene* (7a) was assigned, m.p. 116—117 °C (from ethanol) (Found: C, 71.9; H, 6.0; N, 4.0. $C_{21}H_{21}NO_2S$ requires C, 71.8; H, 6.0; N, 4.0%); δ ($CDCl_3$) 8.03 (1 H, m, 8-H), 7.62 (4 H, m, 4-, 5-, 6-, and 7-H), 6.91br (2 H, s, $Me_3C_6H_2$), 4.14 (2 H, s, CH_2), 2.41 (9 H, s, 3 × CH_3), and 2.26 (3 H, s, CH_3). Decisive structural evidence for (7a) came from the analysis of the ^1H n.m.r. spectrum and of the shifts induced by incremental additions of Yb(fod)$_3$ to the corresponding nitro-sulphone (22). 3-*Methyl*-2-*nitro*-1-(2,4,6-*trimethylphenylsulphonylmethyl*)-*naphthalene* (22) had m.p. 228—230 °C (from ethanol–dioxan) (Found: C, 65.9; H, 5.5; N, 3.6. $C_{21}H_{21}NO_4S$ requires C, 65.8; H, 5.5; N, 3.65%); δ ($CDCl_3$) 8.12 (1 H, m, 8-H), 7.76 (2 H, m, 4- and 5-H), 7.55 (2 H, m, 6- and 7-H), 6.92br (2 H, s, $Me_3C_6H_2$), 5.00 (2 H, s, CH_2), 2.49 (6 H, s, 2 × CH_3), 2.41 (3 H, s, CH_3), and 2.30 (3 H, s, CH_3). L.I.S. analysis gave straight lines with relative slopes: 1.00 (CH_2), 0.60 (2- and 6-Me of $Me_3C_6H_2$), 0.55 (8-H), 0.21 ($Me_3C_6H_2$), 0.16 (3-Me), 0.14 (6- and 7-H), 0.14 (4-H), 0.08 (4-Me of $Me_3C_6H_2$), and 0.07 (5-H).

The third elution product was identified as 1-*methyl*-2-*nitro*-3-(2,4,6-*trimethylphenylthiomethyl*)*naphthalene* (8a), m.p. 88—89 °C from light petroleum (b.p. 80—100 °C) (Found: C, 71.8; H, 6.0; N, 4.0. $C_{21}H_{21}NO_2S$ requires C, 71.8; H, 6.0; N, 4.0%); δ ($CDCl_3$) 8.01 (1 H, m, 8-H), 7.57 (3 H, m, 5-, 6-, and 7-H), 7.20 (1 H, s, 4-H), 6.85br (2 H, s, $Me_3C_6H_2$), 3.87 (2 H, s, CH_2), 2.60 (3 H, s, CH_3), 2.32 (6 H, s, 2 × CH_3), and 2.24 (3 H, s, CH_3). In this case, to obtain structural information about compound (8a), it was necessary to transform it into the corresponding aminosulphide (23). 2-*Amino*-1-*methyl*-3-(2,4,6-*trimethylphenylthiomethyl*)*naphthalene* (23) had m.p. 114—116 °C (from light petroleum, b.p. 80—100 °C) (Found: C, 78.2; H, 7.2; N, 4.4. $C_{21}H_{23}NS$ requires C, 78.5; H, 7.2; N, 4.4%); δ ($CDCl_3$) 7.82 (1 H, m, 8-H), 7.55 (1 H, m, 5-H), 7.20 (3 H, m, 4-, 6-, and 7-H), 6.86br (2 H, s, $Me_3C_6H_2$), 4.26br (2 H, NH_2), 3.93 (2 H, s, CH_2), 2.44 (3 H, s, CH_3), 2.40 (6 H, s, 2 × CH_3), and 2.22 (3 H, s, CH_3). L.I.S. analysis gave straight lines with relative slopes: 1.00 (CH_2), 0.96 (1-Me), 0.46 (4-H), 0.44 (2- and 6-Me of $Me_3C_6H_2$), 0.28 (8-H), 0.19 ($Me_3C_6H_2$), 0.12 (5-H), 0.11 (6- and 7-H), and 0.10 (4-Me of $Me_3C_6H_2$).

The overall yield in the isolated mixture of isomeric sulphides was 80% and the average composition, determined by ^1H n.m.r. analysis from two independent experiments, was (6a) : (7a) : (8a) = 48 : 28 : 24.

(*b*) *At* 60 °C. The above reaction was repeated at 60 °C on compound (4) (0.1 g, 0.4 mmol). After being heated for 48 h, the reaction mixture was worked up and chromatographed as described above to give a mixture (96 mg, 68%) of sulphides (6a), (7a), and (8a) (which was analyzed by ^1H n.m.r.) and unchanged starting substrate (13 mg, 13%). The (6a) : (7a) : (8a) molar ratio was found to be 64 : 18 : 18.

Reaction of Compound (4) *with Sodium Benzenethiolate in DMSO at* 120 °C.—Proceeding as described above for the reaction with sodium 2,4,6-trimethylbenzenethiolate, compound (4) (1 g, 4.07 mmol) was treated with sodium benzenethiolate at 120 °C for 2 h. The preliminary column chromatography (hexane–benzene 1 : 1) gave a mixture (1.14 g) of sulphides.

Low-pressure chromatography on silica-gel 60 prepacked Lobar (Merck) columns gave the following fractions: (i) a product (1.02 g) identified as 1,3-*dimethyl*-2-*nitro*-4-*phenylthionaphthalene* (6b) (81%), m.p. 114—115 °C (from ethanol) (Found: C, 70.0; H, 4.85; N, 4.5. $C_{18}H_{15}NO_2S$ requires C, 69.9; H, 4.85; N, 4.5%); δ (CD_3COCD_3) 8.62 (1 H, m, 5-H), 8.22 (1 H, m, 8-H), 7.68 (2 H, m, 6- and 7-H), 7.10 (5 H, m, PhS), 2.67 (3 H, s, CH_3), and 2.58 (3 H, s, CH_3). Structural proof for compound (6b) also rested on the spectral data of the corresponding nitro-sulphone (5) and on ^1H n.m.r. analysis carried out with the aid of Yb(fod)$_3$ on the corresponding amino-sulphide (24). 1,3-*Dimethyl*-2-*nitro*-4-*phenylsulphonylnaphthalene* (5) had m.p. 212—213 °C (from ethanol–dioxan) (Found: C, 63.3; H, 4.4; N, 4.1. $C_{18}H_{15}NO_4S$ requires C, 63.3; H, 4.4; N, 4.1%); δ (CD_3COCD_3) 9.07 (1 H, m, 5-H), 8.25 (1 H, m, 8-H), 7.97 (2 H, m, 2′- and 6′-H of $PhSO_2$), 7.67 (5 H, m, 6-, 7-H, and 3′-, 4′-, and 5′-H of $PhSO_2$), 2.81 (3 H, s, CH_3), and 2.67 (3 H, s, CH_3). 2-*Amino*-1,3-*dimethyl*-4-*phenylthionaphthalene* (24) had m.p. 123—124 °C (from ethanol) (Found: C, 77.5; H, 6.05; N, 5.0. $C_{18}H_{17}NS$ requires C, 77.4; H, 6.1; N, 5.0%); δ ($CDCl_3$) 8.48 (1 H, m, 5-H), 7.89 (1 H, m, 8-H), 7.30 (2 H, m, 6- and 7-H), 6.97 (5 H, m, PhS), 3.88br (2 H, NH_2), 2.60 (3 H, s, CH_3), and 2.49 (3 H, s, CH_3). L.I.S. analysis gave straight lines with relative slopes: 1.00 (Me), 0.96 (Me), 0.29 (8-H), 0.25 (5-H), 0.16 (PhS), 0.14 (6- and 7-H). (ii) A solid mixture (0.125 g) of two isomeric sulphides corresponding to the substitution of a nitro-group with a phenylthio-group in compound (4) (Found: C, 70.0; H, 4.9; N, 4.5; S, 10.4. $C_{18}H_{15}NO_2S$ requires C, 69.9; H, 4.85; N, 4.5; S, 10.3%); δ ($CDCl_3$) 8.16 [m, 1-H of (7b) + 1-H of (8b)], 7.72 [m, 4-H of (7b) + 4-H of (8b)], 7.30 [m, 5-H of (7b) + 5-H of (8b)], 4.58 [s, 2-H of (8b)], 4.33 [2-H of (7b)], 2.62 [3-H of (7b)], and 2.41 [3-H of

(8b)]. The ^{1}H n.m.r. data (in particular the singlets at δ 4.58 and 4.33, typical absorptions of methylene groups linked to an aromatic moiety) suggest that this material was a mixture of two *tele*-substitution sulphides (ratio 3 : 2). Any attempt to effect chromatographic separation of the mixture components proved futile and the assignment of the 3-methyl-2-nitro-1-phenylthiomethyl- (7b) and 1-methyl-2-nitro-3-phenylthiomethyl-naphthalene (8b) structures was done in a tentative way.

Experiments on the Influence of Light, Di-t-butyl Nitroxide, and Azobenzene on the Reaction between Compound (4) *and Sodium Arenethiolates in DMSO.*—A set of five independent experiments was carried out at 60 °C, under argon, using compound (4) (0.5 mmol), sodium 2,4,6-trimethylbenzenethiolate (0.6 mmol) and DMSO (7 ml).

The first (standard) experiment was conducted at the diffuse laboratory light, the second one under irradiation by a 300-W sunlamp, the third one in the total darkness, the fourth one in the presence of di-t-butyl nitroxide (1 mol equiv.), and the fifth one in the presence of azobenzene (1 mol equiv.). All five reactions were performed under identical experimental conditions and worked up as described above for the same reaction on (4).

Within the limit of experimental error, the overall yield of the five experiments was the same and ^{1}H n.m.r. analysis of the respective mixtures of sulphides showed no difference in the ratio of the various products.

Reaction of Compound (5) *with Sodium* 2,4,6-*Trimethylbenzenethiolate in DMSO at* 120 °C.—The reaction described above for compound (4) was repeated with compound (5) (0.68 g, 2 mmol). After being heated at 120 °C for 1 h, the reaction mixture was worked up and chromatographed as previously reported to give compound (7a) (0.365 g, 52%) and compound (8a) (0.205 g, 29%). Sulphides (7a) and (8a) were identified by comparison of their ^{1}H n.m.r. spectra with those of authentic samples prepared from compound (4).

Reaction of Compound (4) *or* (5) *with Sodium* 2,4,6-*Trimethylbenzenethiolate in* [$^2H_6$]*Dimethyl Sulphoxide and in the Presence of* S-*Deuteriated* 2,4,6-*Trimethylbenzenethiol.*—A solution of sodium 2,4,6-trimethylbenzenethiolate (0.127 g, 0.73 mmol) and 82% *S*-deuteriated parent thiol (0.22 ml, 1.46 mmol) in [$^2H_6$]dimethyl sulphoxide (3 ml) was added to a solution of (4) or (5) (0.61 mmol) in [$^2H_6$]dimethyl sulphoxide (6 ml). The reaction mixture was deaerated with argon gas, stoppered with a rubber septum and heated at 120 °C for 10 min. After cooling to room temperature, an excess (*ca.* 4 ml) of CH_3COOD was added and the reaction solution poured into water. Unchanged (4) or (5) was isolated by standard work-up followed by column chromatography. ^{1}H N.m.r. analysis of the recovered (4) or (5) showed the following deuteriation percentages: 24% (1-Me) and 16% (3-Me) for compound (4); 31% (1-Me) and 14% (3-Me) for compound (5). The assignment of the two methyl absorptions was made with the aid of Yb(fod)$_3$ as a shift reagent. With compound (4), low but significant induced shifts were observed only for the signals of the two methyls and 5-H, indicating some extent of complexation at the two nitro-groups [Δδ: 0.24 (3-Me), 0.18 (5-H), and 0.11 (1-Me) after addition of 1 mol equiv. of shift reagent]. With compound (5), where the complexation affects mainly the sulphonyl group, the addition of Yb(fod)$_3$ (0.2 mol equiv.) caused the following induced shifts: Δδ 0.35 (5-H), 0.20 (3-Me), and 0.04 (1-Me).

Reaction of Compound (9) *with Sodium Benzenethiolate in DMSO at* 120 °C.—A solution of compound (9) (0.22 g, *ca.* 1 mmol) and sodium benzenethiolate (0.16 g, 1.2 mol equiv.) in DMSO (15 ml) was heated at 120° C for 1 h. Work-up gave 3-*nitro*-1-*phenylthionaphthalene* (10) (0.27 g, 96%), m.p. 134—135 °C (from ethanol) (Found: C, 68.5; H, 4.0; N, 5.0. $C_{16}H_{11}NO_2S$ requires C, 68.3; H, 3.9; N, 5.0%); δ ($CDCl_3$) 8.64 (1 H, d, *J* 2.05 Hz, 4-H), 8.40 (1 H, m, 8-H), 8.09 (1 H, d, *J* 2.05 Hz, 2-H), 8.03 (1 H, m, 5-H), 7.71 (2 H, m, 6-H and 7-H), and 7.36 (5 H, m, PhS).

The assigned structure was confirmed by ^{1}H n.m.r. analysis, carried out on the corresponding sulphone (25), using Yb(fod)$_3$ as a shift reagent. 3-*Nitro*-1-*phenylsulphonylnaphthalene* (25) had m.p. 194—195 °C (from ethanol) (Found: C, 61.3; H, 3.5; N, 4.5. $C_{16}H_{11}NO_4S$ requires C, 61.3; H, 3.5; N, 4.5%); δ ($CDCl_3$) 9.20 (1 H, d, *J* 2.3 Hz, 2-H), 8.98 (1 H, d, *J* 2.3 Hz, 4-H), 8.75 (1 H, m, 8-H), 8.02 (3 H, m, 5-H and 2′- and 6′-H of $PhSO_2$), 7.75 (2 H, m, 6- and 7-H), and 7.53 (3 H, m, 3′-, 4′-, and 5′-H of $PhSO_2$). L.I.S. analysis gave straight lines with relative slopes: 1.00 (8-H), 0.73 (2′- and 6′-H of $PhSO_2$), 0.65 (2-H), 0.13 (4-H), 0.13 (3′-, 4′-, and 5′-H of $PhSO_2$), 0.11 (6- and 7-H), and 0.08 (5-H).

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