Tetrahedron Vol. 35, pp. 1783 to 1788

0040-4020/79/0715-1783/$02.00/0

TELE- VERSUS NORMAL SUBSTITUTION IN THE REACTION OF 1,4-DIALKYL-2,3-DINITRONAPHTHALENES WITH SODIUM ARENETHIOLATES IN DMSO

M. NOVI, G. GUANTI,* S. THEA, F. SANCASSAN and D. CALABRÒ
Istituto di Chimica Organica dell'Università, C.N.R. Centro di Studio sui Diariloidi e loro Applicazioni, Palazzo delle Scienze, Corso Europa, 16132 Genova, Italy

(*Received in UK 29 December* 1978)

Abstract—1,4-Dimethyl-2,3-dinitronaphthalene (1) reacts with sodium arenethiolates in DMSO to give 2-arylthio-1,4-dimethyl-3-nitronaphthalene (3) [normal substitution product (NSP)] and 1-arylthiomethyl-4-methyl-3-nitronaphthalene (5) [*tele*-substitution product (TSP)]. The percentage of TSP is found to increase with the enhancement of the reaction temperature, the presence of electron-withdrawing substituents in the arenethiolate, the increase of steric hindrance in the nucleophile, and the substitution of two Et for two Me groups in 1. A mechanism, involving a partial tautomerization of 1 into 2,3-dinitro-4-methyl-1-methylene-1,2-dihydronaphthalene (7) followed by attack of the nucleophile on this tautomeric form, is suggested to account for the formation of TSP. The analogous reactions on 1,4-dimethyl-2,3-dinitrobenzene and 5,8-dimethyl- and 5,8-diethyl-6,7-dinitro-1,2,3,4-tetrahydronaphthalene yield only NSPs. Some double bonds localization together with steric compression in the congested naphthalene derivative are suggested to play an important role in driving the reaction along the *tele*-substitution pathway.

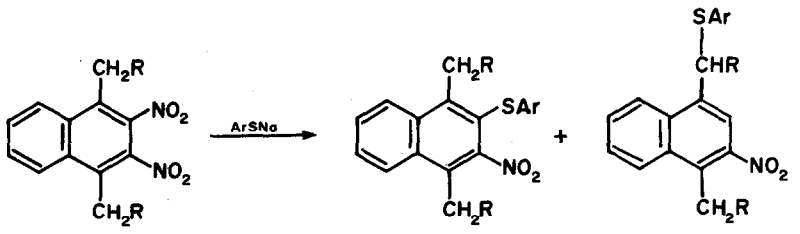
It has long been known that aromatic *o*- and *p*-dinitro compounds react with different nucleophiles to afford generally *o*- or *p*-substituted nitro derivatives.[1] In addition to such behaviour (typical nucleophilic aromatic substitution) examples are known in which no direct replacement of a nitro group occurs.[2] Thus, e.g. 2,3-dinitronaphthalene[2a] reacts with piperidine to give 1 - piperidino - 3 - nitronaphthalene and 3,4-dinitrothiophen[2b] furnishes with sodium arenethiolates aryl 2-(4-nitro)thienyl sulphides (*cine*-substitution reactions). Recently[3] we have found that 1,4 - dimethyl - 2,3 - dinitronaphthalene reacts with piperidine to give 4 - methyl - 3 - nitro - 1 - piperidinomethyl - naphthalene rather than the expected 1,4 - dimethyl - 2 - nitro - 3 - piperidinonaphthalene. Similar behaviour was also shown by 2,5 - dimethyl - 3,4 - dinitrothiophen which affords with sodium arenethiolates 2 - arylthiomethyl - 5 - methyl - 4 - nitrothiophens.[4] These are examples of a novel type of substitution occurring on dinitro-aromatic compounds (*tele*-substitution[3-5]) which involves nucleophilic attack on a side-chain carbon atom with departure of the nearest nitro group.

We have now examined the behaviour of 1,4-dimethyl- (1) and of 1,4 - diethyl - 2,3 - dinitronaphthalene (2) towards sodium arenethiolates in DMSO. Here we report the results of this investigation which was undertaken to provide some insight into the role played by different factors in driving the reaction along the *tele*- instead of the normal substitution pathway.

RESULTS AND DISCUSSION

Naphthalene derivatives 1 and 2 were synthesized by nitration of the corresponding 5,8 - dialkyl - 1,2,3,4 - tetrahydronaphthalenes, followed by aromatization with bromine of the resulting 6,7-dinitrated products.

When substrates 1 or 2 were allowed to react with sodium arenethiolates in DMSO, two products were isolated in good overall yield: the normal substitution product (NSP) [(3) or (4)] and the *tele*-substitution product (TSP) [(5) or (6)] (Scheme 1).



NSP **TSP**

1: R = H
2: R = CH_3

3: R = H
4: R = CH_3

5: R = H
6: R = CH_3

a: Ar = C_6H_5
b: Ar = 2,4,6-$Me_3C_6H_2$
c: Ar = 4-MeC_6H_4
d: Ar = 3-ClC_6H_4

Scheme 1.

The structures of the reaction products were established by analytical and ^{1}H NMR data and their relative percentages (Table 1) determined by ^{1}H NMR analysis of the crude mixture of isomeric sulphides. The structures of **3a** and **5a** were also confirmed by ^{1}H NMR analysis of the corresponding sulphones.

First it was proved that compounds **3–6** were not interconverted under the reaction conditions and that neither light nor di-t-butyl nitroxide[6] influenced their overall and relative yield. Hence a radical or radical anion-chain mechanism seems to be excluded.

Experiments were then performed to determine the effect of reaction temperature, concentration of the reagents, and substituents in the nucleophile on product distribution. The results are reported in the Table, from which the following observations emerge: (a) No significant effect on the relative percentage of the two products was found by changing the sodium arenethiolate concentration (see entries 6 and 7). Thus it is likely that the normal and the *tele*-substitution process follow a kinetic law with the same order in arenethiolate. (b) An enhancement of the reaction temperature gives rise to an increase of the extent of side-chain thioarylation. (c) Electron-withdrawing substituents in the arenethiolate anion favour the *tele*- over the normal substitution process. In the reaction on compound **1**, in fact, some increase of the yield in TSP is observed in going from 4-Me-, to unsubstituted, and to 3-chlorobenzenethiolate (*cf* entries 8, 3 and 9). (d) Steric requirement of the two competing reactions seems to be different: a greater steric hindrance in the nucleophile favours the *tele*-substitution process. On going from benzenethiolate to the more space demanding 2,4,6-trimethylbenzenethiolate, in fact, the NSP-TSP ratio decreases in spite of the electronic effect of substituents which, as above mentioned, acts in the opposite direction.

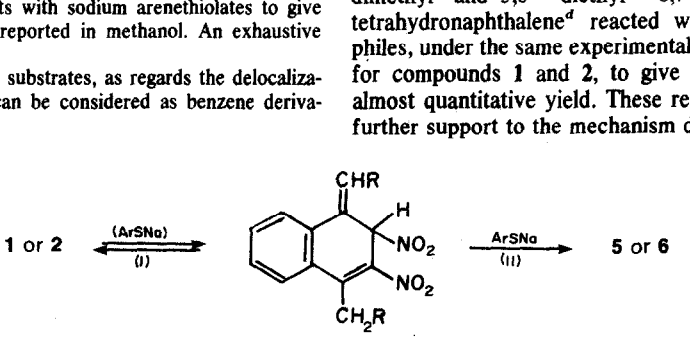
On the basis of these results, it is likely that the NSP forms via the usual addition-elimination pathway, typical of aromatic nucleophilic substitutions. On the other hand, as concerns the TSP, we believe that its formation could be reasonably explained by assuming that under the reaction conditions compounds **1** and **2** partially tautomerize into **7** and **8** respectively. These tautomeric forms furnish the TSPs via displacement involving a three carbon anionotropic rearrangement[7] (Scheme 2).

Although we have no direct evidence of the presence of intermediates **7** or **8**, we believe they are not unreasonable ones as tautomeric equilibria of type (i) are well known for α,β-unsaturated nitro-olefins,[8] to which our substrates can be formally related. As regards step (ii) the hypothesis that allylic-type nitro derivatives like **7** and **8** can undergo nucleophilic displacement with rearrangement cannot be accepted at first glance without some reluctance as, at the best of our knowledge, no example of nucleophilic substitution of this kind is reported to occur on allylic or benzylic derivatives.[a] However, besides the substitution of the nitro-group, step (ii) involves rearomatization of the dihydronaphthalene system and formation of a less congested molecule (the TSP). Probably this is the force which drives the reaction along the path (ii).

The fact that the *tele*-substitution process is favoured by a more space demanding reagent as 2,4,6-trimethylbenzenethiolate is in line with the proposed mechanism. The normal substitution reaction involves attack of the nucleophile on a centre (C-2) which is expected to be more sterically hindered than the one (a side-chain carbon atom) involved in the *tele*-substitution.

Another point worth considering is the fact that in the reactions on compound **2** the extent of side-chain thioarylation is always greater than that observed in the corresponding reactions on dimethyl derivative **1**. This result may be related to the different influence which the extension of the side-chain by a Me group can exert on the two competing reactions. As regards the S_NAr process the increase of unfavourable steric effects on going from **1** to **2** ought to be negligible owing to the high polarizability of the reagent.[b] On the other hand, it is likely that the substitution of two Et for two Me groups in the naphthalene substrate favours the *tele*-substitution process because of a larger stabilization of the intermediate **8** with respect to **7** by hyperconjugation between the Me and the exocyclic double bond.[8]

Comparison of the results now obtained with those found[4] for 2,5 - dimethyl - 3,4 - dinitrothiophen,[c] shows that the reaction course strongly depends also on the aromaticity of the ring. To test better this point we investigated the behaviour of benzene derivatives having a structure similar to that of compound **1**. We found that both 1,4 - dimethyl - 2,3 - dinitrobenzene and 5,8-dimethyl- and 5,8 - diethyl - 6,7 - dinitro - 1,2,3,4 - tetrahydronaphthalene[d] reacted with different nucleophiles, under the same experimental conditions employed for compounds **1** and **2**, to give exclusively NSPs in almost quantitative yield. These results seem to furnish further support to the mechanism depicted in Scheme 2.



7: R = H
8: R = CH_3

Scheme 2.

[a] In general the nitro group is a sluggish leaving group in aliphatic nucleophilic substitutions proceeding through S_N1 and S_N2 mechanism,[9] but it has been found to be easily displaced in radical-anion substitution processes.[6]

[b] E.g. with the iodide anion, in the reactions with 1-bromo-2-X-4,6-dinitrobenzenes in acetone at 80°, $k_{2\text{-Me}}/k_{2\text{-Et}}$ is only *ca.* 1.5.[10]

[c] Preliminary results show that, also in DMSO, 2,5 - dimethyl - 3,4 - dinitrothiophen reacts with sodium arenethiolates to give only TSP as previously[4] reported in methanol. An exhaustive research is in progress.

[d] Tetrahydronaphthalene substrates, as regards the delocalization of the π-electrons, can be considered as benzene derivatives.[11]

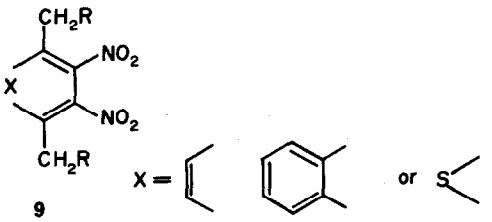
Table 1.

Entry no.	Compd.	Ar in ArSNa	Mol. equiv. of ArSNa	Temp. (°C)	Reaction time (h)	Yield[a,b] (%)	NSP[b,c] (%)	TSP[b,c] (%)
1	1	C_6H_5	5	25	44	91	ca. 100	[d]
2	1	C_6H_5	1.2	60	19	90	94	6
3	1	C_6H_5	1.2	120	1	87	87	13
4	1	Mes[e]	5	25	48	90	80	20
5	1	Mes[e]	1.2	60	24	86	66	34
6	1	Mes[e]	1.2	120	2	80	55	45
7	1	Mes[e]	5	120	1	82	57	43
8	1	4-MeC_6H_4	1.2	120	1	91	91	9
9	1	3-ClC_6H_4	1.2	120	1.5	90	81	19
10	2	C_6H_5	1.2	120	0.5	87	82	18
11	2	Mes[e]	1.2	120	0.5	75	45	55

[a] Overall yield based on the isolated mixture of sulphides. [b] Average values of two or more independent determinations. [c] Percentage of product in the isolated mixture of sulphides determined by ^1H NMR analysis. [d] Indeterminable traces. [e] Mes = 2,4,6-$Me_3C_6H_2$

In fact if tautomers **7** and **8** are the species responsible for the formation of TSPs, a decrease of the extent of *tele*-substitution would be expected to occur by increasing the aromaticity of the system.[12,13]

In conclusion, from the collected data it follows that there are potentially two ways for nucleophilic attack on aromatic dialkyl dinitro derivatives of type (**9**): i.e. the normal and the *tele*-substitution process.



9

Fig. 1.

The prevalence of the one over the other reaction primarily depends on the delocalization of the π-electrons in the ring. When both processes are possible, as in the naphthalene derivatives, the NSP-TSP ratio becomes dependent on various factors as the reaction temperature, type of alkyl groups present in the substrate, and nature of the nucleophile. It is interesting to note in this regard that, unlike the reactions with sodium arenethiolates, the compound **1** reacted with secondary amines, both in neat amine[3] and in DMSO,[e] to give only TSP. The high sensitivity of the rate of S_NAr processes to change in softness of the nucleophile[14] particularly evident[15] in substrates having a leaving nitro-group and a methyl group in *ortho* to the reaction centre, could be a factor responsible for this different behaviour.

[e] Experiments carried out after the publication of Ref. 3 showed that compound **1** heated at 110° in DMSO with two mol. equiv. of secondary amine gave TSP in 84% yield as the only reaction product.

EXPERIMENTAL

^1H NMR spectra of $CDCl_3$ solns were recorded on a Varian XL 100 or on a Perkin–Elmer 60 instrument ($SiMe_4$ as internal reference). Light petroleum had b.p. 30–50°. Organic extracts were dried over Na_2SO_4 and solvents were removed under reduced pressure below 50°.

Materials. Sodium arenethiolates were prepared following the procedure reported for the sodium 4-chlorobenzenethiolate,[6a] kept *in vacuo* and iodometrically titrated before use. Dimethyl sulphoxide, distilled under reduced pressure over calcium hydride and in a N_2 stream, was stored over molecular sieves (type 4A).

Preparation of 1,4-*dimethyl*-2,3-*dinitronaphthalene* **1**

(a) 5,8 - *Dimethyl* - 6,7 - *dinitro* - 1,2,3,4 - *tetrahydronaphthalene* (**10**). 5,8 - Dimethyl - 1,2,3,4 - tetrahydronaphthalene[16] (2 g) was added in small portions to a vigorously stirred mixture of conc H_2SO_4 (50 ml), fuming HNO_3 (15 ml, *d* 1.52), and $CHCl_3$ (50 ml), allowing time for the deep red colour to fade after each addition and taking care that the temp. did not exceed 5°. After adding all the hydrocarbon, the mixture was immediately poured onto ice. The $CHCl_3$ layer was separated and the aqueous one extracted with $CHCl_3$. The combined organic phases, washed with water, with 5% Na_2CO_3aq, and finally with water again, were dried over Na_2SO_4. Evaporation of the solvent gave crude **10** (2.3 g, 74%), which after crystallization from EtOH-dioxan melted at 191–192°. (Found: C, 57.5; H, 5.6; N, 11.25. $C_{12}H_{14}N_2O_4$ requires: C, 57.6; H, 5.6; N, 11.2%); τ 7.32 (4H, m, $2\times CH_2$), 7.80 (6H, s, $2\times CH_3$), and 8.16 (4H, m, $2\times CH_2$).

(b) 1,4 - *Dibromo* - 5,8 - *dimethyl* - 6,7 - *dinitro* - 1,2,3,4 - *tetrahydronaphthalene* (**11**). Br_2 (4.19 ml, 82 mmol) was added to a soln of **10** (9.35 g, 37 mmol) in bromobenzene (18.7 ml). After heating at 100° for 5 hr, the excess Br_2 was eliminated from the mixture under reduced pressure. The pale yellow soln obtained was cooled at 0° and the white ppt filtered off and washed with *ca* 45 ml of light petroleum. From the bromobenzene soln, diluted with the washing light petroleum, a second portion of product precipitated and was collected by filtration. Crystallization from EtOH–dioxan of the two combined portions (12.2 g, 80%) gave pure **11**, m.p. 193°, dec. with HBr evolution. (Found: C, 35.4; H, 2.9; Br, 39.05; N, 6.85. $C_{12}H_{12}Br_2N_2O_4$ requires: C, 35.3; H, 2.95;

Br, 39.2; N, 6.85%); τ 4.47 (2H, m, 2×CHBr), 7.12, 7.23, 7.35, and 7.49 (each 1H, m, 2×CH_2), and 7.60 (6H, s, 2×CH_3). Further addition of light petroleum to the above-mentioned bromobenzene soln caused the precipitation of 1 g of a white solid material. Tlc and ^{1}H NMR spectra showed that this ppt was a mixture of **11** and other by-products which were not further investigated.

(c) 1,4 - *Dimethyl* - 2,3 - *dinitronaphthalene* **1**. Dibromotetraline **11** (2 g) was heated at 200–210° (oil bath) in a broad tube equipped with an external ice-cooling jacket. When the HBr evolution from the melted product lowered, the temp was slowly increased to 250° in 1 hr, occasionally stirring with a glass rod. After cooling of the system the solid product was collected and extracted (Soxhlet) with CH_2Cl_2. Evaporation of the solvent and crystallization from MeOH–Dioxan gave pure **1** (0.78 g, 65%), m.p. 275° (lit.,[17] 260°). ^{1}H NMR ($CDCl_3$) and IR (Nujol) data were in full agreement with those reported.[17]

Preparation of 1,4-*diethyl*-2,3-*dinitronaphthalene* **2**

(a) 5,8 - *Diethyl* - 1,2,3,4 - *tetrahydronaphthalene* (**12**). This compound was synthesized following the procedure reported[16] for the analogous dimethyl derivative. Thus condensation of succinic anhydride with 1,4-diethylbenzene[18] gave 3-(2,5-*diethylbenzoyl*)*propionic acid* (80%), m.p. 72–73°, from petroleum b.p. 80–100°. (Found: C, 71.6; H, 7.65. $C_{14}H_{18}O_3$ requires: C, 71.8; H, 7.7%). Clemmensen reduction of the keto-acid gave 4-(2,5-*diethylphenyl*)*butyric acid* (78%), m.p. 30–31°, from light petroleum. (Found: C, 76.4; H, 9.0. $C_{14}H_{20}O_2$ requires: C, 76.4; H, 9.1%). The aryl-substituted butyric acid was cyclized in H_2SO_4 to give 1 - *oxo* - 5,8 - *diethyl* - 1,2,3,4 - *tetrahydronaphthalene* (70%) as an oil (b.p. 133° at 5 mm Hg), which was characterized as *oxime*, m.p. 72–73° from aqueous EtOH. (Found: C, 77.6; H, 8.7. $C_{14}H_{19}NO$ requires: C, 77.4; H, 8.75%). Finally, Clemmensen reduction of the obtained tetralone gave **12** (82%), b.p. 119–120° at 5 mm Hg. (Found: C, 89.4; H, 10.55. $C_{14}H_{20}$ requires: C, 89.4; H, 10.6%).

(b) 5,8 - *Diethyl* - 6,7 - *dinitro* - 1,2,3,4 - *tetrahydronaphthalene* (**13**). Compound **12** (1 g) was nitrated with a mixture of 96% H_2SO_4 (22.5 ml) and fuming HNO_3 (6.7 ml) in the presence of $CHCl_3$ (23 ml) following the procedure described above for the analogous dimethyl derivative. The only difference was that during the evaporation *in vacuo* of the $CHCl_3$ extracts the last 20 ml of solvent were replaced with EtOH keeping the volume constant by adding alcohol from time to time. Cooling to 0° and filtration of the ppt gave **13** (0.55 g, 37%), m.p. 143–144° from EtOH–Dioxan. (Found: C, 60.2; H, 6.4; N, 10.0. $C_{14}H_{18}N_2O_4$ requires: C, 60.4; H, 6.5; N, 10.1%); τ 6.95–7.60 (8H, m),[f] 8.13 (4H, m, 2×CH_2), and 8.79 (6H, t, J 7.3 Hz, 2×CH_2–CH_3).

(c) 1,4 - *Dibromo* - 5,8 - *diethyl* - 6,7 - *dinitro* - 1,2,3,4 - *tetrahydronaphthalene* (**14**). Br_2 (0.36 ml, 7.2 mmol) was added to a soln of **13** (1 g, 3.6 mmol) in bromobenzene (2 ml) and the mixture heated at 100° until the red colour faded (3–4 hr). A second portion of Br_2 (0.04 ml) was added and the heating continued for 1 hr. After elimination of the excess Br_2 *in vacuo* and cooling at 0° a white solid precipitated from the mixture. Filtration of this ppt and crystallization from EtOH–dioxan gave **14** (0.5 g, 33%), m.p. 183–184°, dec. with HBr evolution. (Found: C, 38.5; H, 3.7; N, 6.45. $C_{14}H_{16}Br_2N_2O_4$ requires: C, 38.55; H, 3.7; N, 6.4%); τ 4.43 (2H, m, 2×CHBr), 6.64–7.80 (8H, m, 2×CH_2 and 2×CH_2–CH_3 partially overlapped), and 8.65 (6H, t, J 7.3 Hz, 2×CH_2–CH_3).

By adding light petroleum to the filtered bromobenzene soln precipitation of 0.4 g of a white solid material occurred. ^{1}H NMR and tlc analysis of this ppt showed the presence of **14** together with a by-product. All attempts to effect chromatographic separation of these two products proved futile. However their mixture was employed for the successive preparation and the compound obtained by dehydrobromination of the unknown by-product identified (see below).

(d) 1,4 - *Diethyl* - 2,3 - *dinitronaphthalene* **2**. Compound **14** (2 g) was heated for 30 min at 200–210° and worked-up as described above for **11**, to give **2** (0.45 g, 35%), m.p. 158–159° from EtOH–dioxan. (Found: C, 61.0; H, 5.1; N, 10.1. $C_{14}H_{14}N_2O_4$ requires: C, 61.3; H, 5.1; N, 10.2%); τ 1.69 and 2.15 (each 2H, AA'BB' system, H-5 and H-8, and H-6 and H-7 resp.), 6.86 (4H, q, J 7.3 Hz, 2×CH_2–CH_3) and 8.55 (6H, t, J 7.3 Hz, 2×CH_2–CH_3).

Further amounts of **2** were obtained from the mixture of brominated derivatives previously described. Two grams of this mixture were heated at 200–210° and worked-up as above. The CH_2Cl_2 extracts were concentrated and chromatographed on a silica gel column using light petroleum–benzene (1:1) as eluant. The first fractions contained 0.16 g of a product to which the 6 - *bromo* - 1,4 - *diethyl* - 2,3 - *dinitronaphthalene* structure was attributed, m.p. 121–122° from petroleum b.p. 80–100°. (Found: C, 47.4; H, 3.65; Br, 22.7; N, 7.9. $C_{14}H_{13}BrN_2O_4$ requires: C, 47.6; H, 3.7; Br, 22.7; N, 7.9%); τ 1.68 (1H, d, J 1.9 Hz, H-5), 1.92 (1H, d, J 9.0 Hz, H-8), 2.18 (1H, dd, J 1.9 and 9.0 Hz, H-7), 6.94 and 6.98 (4H in all, two q partly overlapped, J 7.3 Hz, 2×CH_2–CH_3), and 8.60 (6H, t, J 7.3 Hz, 2×CH_2–CH_3). Further elution gave 0.82 g of **2**.

Reactions with sodium arenethiolates in DMSO

General procedure. Weighed amounts of the substrate and sodium arenethiolate were placed in a flask equipped with a condenser. By means of inlet and outlet tubes the reaction flask was swept with N_2 for 15 min. The solvent, previously saturated with N_2, was then added under magnetic stirring and the reaction kept at suitable temp. in a thermostatic oil bath.

Reaction of **1** *with sodium arenethiolates in DMSO*

A soln of **1** (4 mmol) and sodium arenethiolate (4.8 mmol) in DMSO (60 ml)[g] was kept at the temp. and for the time indicated in the Table. The mixture was then poured into cold water and extracted with benzene. The extracts were dried, concentrated and chromatographed on a silica gel column. The initial fractions, eluted with light petroleum, contained traces of diaryl disulphide. Further elution with light petroleum–benzene (1:1) gave a mixture of two products. A second chromatography of this mixture on silica gel column made the separation of the two components possible. Using the eluants reported below, the following pairs of sulphides were isolated from the reaction with the appropriate sodium arenethiolate: (a) [Eluant 1:2 (v/v) chloroform–light petroleum]. 1,4 - *Dimethyl* - 3 - *nitro* - 2 - *phenylthionaphthalene* **3a**, m.p. 156–157° from EtOH–dioxan. (Found: C, 69.9; H, 4.8; N, 4.5. $C_{18}H_{15}NO_2S$ requires: C, 69.9; H, 4.85; N, 4.55%); τ 1.88 (2H, m, H-5 and H-8), 2.30 (2H, m, H-6 and H-7), 2.85 (5H, m, PhS), and 7.18 and 7.42 (each 3H, s, CH_3). 4 - *Methyl* - 3 - *nitro* - 1 - *phenylthiomethyl* - *naphthalene* **5a**, m.p. 108° from petroleum b.p. 80–100°. (Found: C, 69.8; H, 4.8; N, 4.5. $C_{18}H_{15}NO_2S$ requires: C, 69.9; H, 4.85; N, 4.5%); τ 1.86 (2H, m, H-5 and H-8), 2.40 (3H, m, H-2, H-6, and H-7), 2.78 (5H, m, PhS), 5.55 br (2H, s, CH_2), and 7.24 br (3H, s, CH_3). Double resonance experiments showed that the CH_2 absorption simplified to a doublet (J 0.56 Hz) on irradiation of the Me protons.[h] The observed constant, resulting from coupling between CH_2 and H-2, is in agreement with the value reported in literature.[19] The corresponding sulphones were also prepared. 1,4 - *Dimethyl* - 3 - *nitro* - 2 - *phenylsulphonylnaphthalene* had m.p. 199° from EtOH–dioxan. (Found: C, 63.4; H, 4.4; N, 4.05. $C_{18}H_{15}NO_4S$ requires: C, 63.3; H, 4.4; N, 4.1%) τ 1.92 (4H, m, H-5 and H-8 together with H-2 and H-6 of $PhSO_2$), 2.30 (2H, m, H-6 and H-7), 2.47 (3H, m, H-3, H-4, and H-5 of $PhSO_2$), and 7.13 and 7.42 (each 3H, s, CH_3). 4 - *Methyl* - 3 - *nitro* - 1 - *phenylsulphonylmethylnaphthalene* had m.p. 211–212° from EtOH–dioxan. (Found: C, 63.4; H, 4.4; N, 4.1. $C_{18}H_{15}NO_4S$ requires: C, 63.3; H, 4.4; N, 4.1%); τ 1.7-2.7 (10H, m, H-2, H-5, H-6, H-7, H-8, and $PhSO_2$), 5.18 br (2H, s, CH_2) and 7.17 br (3H, s, CH_3). (b) [Eluant 1:3 (v/v) benzene–petroleum b.p. 80–100°]. 1,4 - *Dimethyl* - 3 -

[f] A multiplet (attributable to the four protons bonded to C-1 and C-4) centered at τ 7.16 partially overlaps the CH_2–CH_3 quartet centered at τ 7.37 (J 7.3 Hz).

[g] In the reactions performed at room temp. 100 ml of DMSO were necessary to solubilize 4 mmol of **1** and 20 mmol of sodium arenethiolate were employed in order to reduce reaction time.

[h] *p*-Interbenzylic coupling is expected to be small but not negligible.[20]

nitro - 2 - (2,4,6 - *trimethylphenylthio*)*naphthalene* **3b**, m.p. 176–177° from EtOH–dioxan. (Found: C, 71.8; H, 6.05; N, 3.95. $C_{21}H_{21}NO_2S$ requires: C, 71.8; H, 6.0; N, 4.0%); τ (2H, m, H-5 and H-8), 2.39 (2H, m, H-6 and H-7), 3.15 br (2H, s, $Me_3C_6H_2S$), 7.47 br (6H, s, $2\times CH_3$) and 7.80 br (9H, s, $3\times CH_3$). 4 - *Methyl* - 3 - *nitro* - 1 - (2,4,6 - *trimethylphenylthiomethyl*)*naphthalene* **5b**, m.p. 91–92° from light petroleum. (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%); τ 1.82 (2H, m, H-5 and H-8), 2.36 (2H, m, H-6 and H-7), 2.81 br (1H, s, H-2), 3.12 br (2H, s, $Me_3C_6H_2S$), 5.83 br (2H, s, CH_2), 7.23 br (3H, s, CH_3) and 7.75 br (9H, s, $3\times CH_3$). (c) [Eluant 1:2 (v/v) $CHCl_3$–light petroleum]. 1,4 - *Dimethyl* - 2 - (4 - *methylphenylthio*) - 3 - *nitronaphthalene* **3c**, m.p. 137–138° from EtOH–dioxan. (Found: C, 70.65; H, 5.25; N, 4.35. $C_{19}H_{17}NO_2S$ requires: C, 70.6; H, 5.3; N, 4.3%); τ 1.93 (2H, m, H-5 and H-8), 2.35 (2H, m, H-6 and H-7), 3.02 br (4H, s, MeC_6H_4S), and 7.18 br, 7.42 br, and 7.76 br (each 3H, s, CH_3). 4 - *Methyl* - 1 - (4 - *methylphenylthiomethyl*) - 3 - *nitronaphthalene* **5c**, m.p. 92–93° from EtOH. (Found: C, 70.3; H, 5.3; N, 4.3. $C_{19}H_{17}NO_2S$ requires: C, 70.6; H, 5.3; N, 4.3%); τ 1.74 (2H, m, H-5 and H-8), 2.30 (3H, m, H-2, H-6, and H-7), 2.80 br (4H, s, MeC_6H_4S), 5.50 br (2H, s, CH_2), and 7.18 and 7.68 (each 3H, s, CH_3). (d) [Eluant 1:1 (v/v) benzene–light petroleum]. 2 - (3 - *Chlorophenylthio*) - 1,4 - *dimethyl* - 3 - *nitronaphthalene* **3d**, m.p. 133.5–134.5° from EtOH–dioxan. (Found: C, 63.0; H, 4.1; N, 4.1. $C_{18}H_{14}ClNO_2S$ requires: C, 62.9; H, 4.1; N, 4.1%); τ 1.83 (2H, m, H-5 and H-8), 2.28 (2H, m, H-6 and H-7), 2.96 (4H, m, ClC_6H_4S), and 7.15 br and 7.38 br (each 3H, s, CH_3). 1 - (3 - *Chlorophenylthiomethyl*) - 4 - *methyl* - 3 - *nitronaphthalene* **5d**, m.p. 117–118° from EtOH–dioxan. (Found: C, 62.8; H, 4.1; N, 4.05. $C_{18}H_{14}ClNO_2S$ requires: C, 62.9; H, 4.1; N, 4.1%); τ 1.82 (2H, m, H-5 and H-8), 2.35 (3H, m, H-2, H-6, and H-7), 2.82 (4H, m, ClC_6H_4S), 5.52 br (2H, s, CH_2), and 7.22 br (3H, s, CH_3).

Further data are given in Table 1.

Reaction of **2** *with sodium benzenethiolate and* 2,4,6-*trimethylbenzenethiolate in DMSO*

The reaction described before for **1** was repeated at 120° upon **2**. Working-up as above, the preliminary chromatography (eluant 1:1 benzene–light petroleum) gave a mixture of two products which was submitted to ^{1}H NMR analysis in order to determine its per cent composition (Table 1). A second column chromatography, using CH_2Cl_2–light petroleum (1:3, v/v) as eluant, made it possible to separate the mixture components. The following pairs of sulphides were obtained from the reaction with the proper sodium arenethiolate: (a) 1,4 - *Diethyl* - 3 - *nitro* - 2 - *phenylthionaphthalene* **4a**, m.p. 107° from petroleum b.p. 80–100°. (Found: C, 71.0; H, 5.6; N, 4.2. $C_{20}H_{19}NO_2S$ requires: C, 71.2; H, 5.6; N, 4.15%); τ 1.88 (2H, m, H-5 and H-8), 2.34 (2H, m, H-6 and H-7), 2.90 (5H, m, PhS), 6.61 and 7.01 (each 2H, q, J 7.5 Hz, CH_2–CH_3), and 8.66 and 8.88 (each 3H, t, J 7.5 Hz, CH_2–CH_3). 4 - *Ethyl* - 3 - *nitro* - 1 - (1 - *phenylthioethyl*) - *naphthalene* **6a**, m.p. 59° from light petroleum. (Found: C, 71.0; H, 5.6; N, 4.15. $C_{20}H_{19}NO_2S$ requires: C, 71.2; H, 5.6; N, 4.15%); τ 1.75 (2H, m, H-5 and H-8), 2.32 (3H, m, H-2, H-6, and H-7), 2.78 (5H, m, PhS), 4.92 (1H, q, J 7.0 Hz, CH–CH_3), 6.81 (2H, q, J 7.5 Hz, CH_2–CH_3), 8.25 (3H, d, J 7.0 Hz, CH–CH_3), and 8.56 (3H, t, J 7.5 Hz, CH_2–CH_3). (b) 1,4 - Diethyl - 3 - *nitro* - 2 - (2,4,6 - *trimethylphenylthio*) - *naphthalene* **4b**, m.p. 145–146° from EtOH. (Found: C, 73.0; H, 6.65; N, 3.7. $C_{23}H_{25}NO_2S$ requires: C, 72.8; H, 6.6; N, 3.7%); τ 1.94 (2H, m, H-5 and H-8), 2.38 (2H, m, H-6 and H-7), 3.14 br (2H, s, $Me_3C_6H_2S$), 6.68 and 7.10 (each 2H, q, J 7.5 Hz, CH_2–CH_3), 7.73 br (9H, s, $3\times CH_3$), and 8.70 and 8.95 (each 3H, t, J 7.5 Hz, CH_2–CH_3). 4 - *Ethyl* - 3 - *nitro* - 1 - [1 - (2,4,6 - *trimethylphenylthio*)*ethyl*] - *naphthalene* **6b**, m.p. 119–120° from EtOH. (Found: C, 72.4; H, 6.6; N, 3.7. $C_{23}H_{25}NO_2S$ requires: C, 72.8; H, 6.6; N, 3.7%); τ 1.80 (2H, m, H-5 and H-8), 2.14 br (1H, s, H-2), 2.37 (2H, m, H-6 and H-7), 3.10 br (2H, s, $Me_3C_6H_2S$), 5.11 (1H, q, J 7.0 Hz, CH–CH_3), 6.77 (2H, q, J 7.5 Hz, CH_2–CH_3), 7.59 br (6H, s, $2\times CH_3$), 7.74 br (3H, s, CH_3), 8.32 (3H, d, J 7.0 Hz, CH–CH_3), and 8.54 (3H, t, J 7.5 Hz, CH_2–CH_3).

Further data are given in Table 1.

Experiments on the influence of light and of di-t-butyl nitroxide on the reaction between **1** *and sodium arenethiolates in DMSO*

A set of three independent experiments was carried out at 60°, under N_2, using 1 mmol of **1**, 1.2 mmol of sodium 2,4,6-trimethylbenzenethiolate and 15 ml of DMSO.

The first (standard) experiment was conducted in the daylight, the second one in the total darkness, and the third one in the presence of di-t-butyl nitroxide[21] as radical scavenger.[6] All the three reactions were performed under identical conditions and worked-up as above described for the same reaction on compound **1**. In any case the reaction mixtures were chromatographed on a silica gel column (eluant light petroleum–benzene 1:1) in order to obtain the mixture of isomeric sulphides.

The overall yield of the three experiments was the same (*ca.* 90%) and ^{1}H NMR analysis of the respective mixtures of sulphides showed no difference in the NSP-TSP ratio (NSP% *ca.* 64 in all the three cases).

Reaction of 1,4-*dimethyl*-2,3-*dinitrobenzene* (**15**)

(a) *With sodium arenethiolates in DMSO.* A soln of **15** (2 mmol)[22] and sodium arenethiolate (2.4 mmol) in 30 ml of DMSO was heated at 120° under N_2. After 15 min the mixture was poured into water and the product extracted with benzene. Filtration of the benzene extracts on a short silica gel column (in order to eliminate traces of thiol and of a coloured tarry material) and evaporation of the solvent gave the crude sulphide in *ca.* 95% yield.

1,4 - *Dimethyl* - 2 - *nitro* - 3 - *phenylthio* - *benzene* had m.p. 62.5–63° from light petroleum. (Found: C, 64.8; H, 5.0; N, 5.4. $C_{14}H_{13}NO_2S$ requires: C, 64.9; H, 5.0; N, 5.4%); τ 2.70 br (2H, s, H-5 and H-6), 2.81 (5H, m, PhS), and 7.68 br (6H, s, $2\times CH_3$).[i] By peracetic acid oxidation of this sulphide the *corresponding sulphone* was also prepared, m.p. 149–150° from EtOH. (Found: C, 57.7; H, 4.4; N, 4.8. $C_{14}H_{13}NO_4S$ requires: C, 57.7; H, 4.5; N, 4.8%); τ 1.90 (2H, m, H-2 and H-6 of $PhSO_2$), 2.38 (3H, m, H-3, H-4, and H-5 of $PhSO_2$), 2.60 (2H, AB system, J 7.9 Hz, H-5 and H-6 of subst. phenyl), and 7.50 br and 7.68 br (each 3H, s, $2\times CH_3$).

1,4 - *Dimethyl* - 2 - *nitro* - 3 - (2,4,6 - *trimethylphenylthio*) - *benzene* had m.p. 144–145° from MeOH–dioxan. (Found: C, 67.9; H, 6.3; N, 4.6. $C_{17}H_{19}NO_2S$ requires: C, 67.8; H, 6.3; N, 4.65%); τ 2.90 br (2H, s, H-5 and H-6), 3.12 br (2H, s, $Me_3C_6H_2S$), 7.78 br (12H, s, $4\times CH_3$), and 7.92 br (3H, s, CH_3).

(b) *With pyrrolidine in neat amine.* A soln of **15** (2 mmol) in neat pyrrolidine (6 ml, 72 mmol) was heated at 110° in sealed ampoule for 4 hr. The mixture was diluted with benzene, washed repeatedly with water to remove the excess amine, dried and filtered on a short silica gel column. Evaporation of the solvent gave 1,4 - *dimethyl* - 2 - *nitro* - 3 - *pirrolidinobenzene* in almost quantitative yield, m.p. 55° from MeOH. (Found: C, 65.5; H, 7.3; N, 12.75. $C_{12}H_{16}N_2O_2$ requires: C, 65.45; H, 7.3; N, 12.7%); τ 2.82 and 3.02 (2H in all, AB system, J 7.89 Hz, H-5 and H-6), 6.87 (4H, m, $2\times CH_2$), 7.74 br and 7.78 br (partly overlapped) (6H in all, s, $2\times CH_3$), and 8.12 (4H, m, $2\times CH_2$).

Reaction of 5,8-*dimethyl*- **10** *or* 5,8 - *diethyl* - 6,7 - *dinitro* - 1,2,3,4 - *tetrahydronaphthalene* **13** *with sodium benzenethiolate and* 2,4,6-*trimethylbenzenethiolate in DMSO*

By working-up as described above for the analogous reactions on the benzene derivative **15**, compounds **10** and **13** gave the expected sulphides in more than 90% yield.

5,8 - *Dimethyl* - 6 - *nitro* - 7 - *phenylthio* - 1,2,3,4 - *tetrahydronaphthalene* had m.p. 78° from MeOH. (Found: C, 68.95; H, 6.1; N, 4.4. $C_{18}H_{19}NO_2S$ requires: C, 69.0; H, 6.05; N, 4.45%); τ 2.90 (5H, m, PhS), 7.35 (4H, m, $2\times CH_2$), 7.72 and 7.88 (each 3H, s, CH_3), and 8.20 (4H, m, $2\times CH_2$). 5,8 - *Dimethyl* - 6 - *nitro* - 7 - (2,4,6 - *trimethylphenylthio*) - 1,2,3,4 - *tetrahydronaphthalene* had m.p. 190° from EtOH–dioxan. (Found: C, 70.9; H, 6.95; N, 3.9. $C_{21}H_{25}NO_2S$ requires: C, 71.0; H, 7.0; N, 3.9%); τ 3.16 br (2H, s, $Me_3C_6H_2S$), 7.40 (4H, m, $2\times CH_2$), 7.77 br (9H, s, $3\times CH_3$), 7.95

[i] The same sulphide (mixed m.p. undepressed and identical ^{1}H NMR spectrum) was also obtained by the usual working-up from 2 - bromo - 1,4 - dimethyl - 3 - nitrobenzene[23] and sodium benzenethiolate in DMSO.

(6H, s, 2×CH_3), and 8.22 (4H, m, 2×CH_2). 5,8 - *Diethyl* - 6 - *nitro* - 7 - *phenylthio* - 1,2,3,4 - *tetrahydronaphthalene* had m.p. 112° from petroleum b.p. 80–100°. (Found: C, 70.3; H, 6.75; N, 4.2. $C_{20}H_{23}NO_2S$ requires: C, 70.4; H, 6.7; N, 4.1%); τ 2.90 (5H, m, PhS), 6.92–7.75 (8H, m),[f] 8.18 (4H, m, 2×CH_2), and 8.86 and 9.04 (each 3H, two t partly overlapped, J 7.5 Hz, 2×CH_2–CH_3). 5,8 - *Diethyl* - 6 - *nitro* - 7 - (2,4,6 - *trimethylphenylthio*) - 1,2,3,4 - *tetrahydronaphthalene* had m.p. 156–157° from petroleum b.p. 80–100°. (Found: C, 71.9; H, 7.5; N, 3.65. $C_{23}H_{29}NO_2S$ requires: C, 72.05; H, 7.6; N, 3.65%); τ 3.20 br (2H, s, $Me_3C_6H_2S$), 7.10–7.86 (17H m, 2×CH_2, 2×CH_2–CH_3, and 3×CH_3 of $Me_3C_6H_2S$), 8.20 (4H, m, 2×CH_2), and 9.00 (6H, two overlapping triplets, J 7.5 Hz, 2×CH_2–CH_3).

Acknowledgements—The authors wish to thank Prof. Carlo Dell'Erba for many valuable and stimulating discussions during the performance of this work.

REFERENCES

[1]F. Pietra and D. Vitali, *J. Chem. Soc.* Perkin II, 385 (1972); J. R. Beck, *Tetrahedron* **34**, 2057 (1978).

[2a]G. Guanti, S. Thea and C. Dell'Erba, *Tetrahedron Letters* 461 (1976); [b]C. Dell'Erba, D. Spinelli and G. Leandri, *Gazzetta* **99**, 535 (1969); M. Novi, G. Guanti, F. Sancassan and C. Dell'Erba, *J. Chem. Soc.* Perkin I, 1140 (1978); [c]D. C. Morrison, *J. Org. Chem.* **27**, 296 (1962); *U.S. Pat.* 3,177,241 (1965); *Chem. Abstr.* **62**, 1614c (1965); *U.S. Pat.* 3,294,838 (1966); *Chem. Abstr.* **66**, 55277p (1967); K. G. Barnett, J. P. Dickens and D. E. West, *J. Chem. Soc.* Chem. Comm. 894 (1976); R. Nasielski-Hinkens, D. Pauwels and J. Nasielski, *Tetrahedron Letters* 2125 (1978).

[3]G. Guanti, S. Thea, M. Novi and C. Dell'Erba, *Ibid.* 1429 (1977).

[4]M. Novi, F. Sancassan, G. Guanti and C. Dell'Erba, *J. Chem. Soc.* Chem. Comm. 303 (1976).

[5]J. F. Arens, *Bull. Soc. Chim. Fr.* 3037 (1968); T. Kauffmann and R. Wirthwein, *Angew. Chem.* Internat. Edn. **10**, 20 (1971); M. Wozniak and H. C. van der Plas, *J. Heterocyclic Chem.* **15**, 731 (1978); E. Smakula Hand and W. W. Paudler, *J. Org. Chem.* **43**, 2900 (1978).

[f]A multiplet (attributable to four protons bonded to C-1 and C-4) centered at τ 7.22 partly overlaps the two CH_2–CH_3 quartets (J 7.5 Hz) centered approximately at τ 7.17 and 7.48.

[6a]N. Kornblum, S. D. Boyd and Noburo Ono, *J. Am. Chem. Soc.* **96**, 2580 (1974); [b]N. Kornblum, *Angew. Chem.* Internat. Edn. **14**, 734 (1975); and refs. therein.

[7]P. B. D. de la Mare, *Molecular Rearrangements* (Edited by P. de Mayo), Chap. 2. Interscience, New York (1967).

[8]A. J. Hubert and H. Reimlinger, *Synthesis* 97 (1969); *Ibid.* 405 (1970); H. Shechter and J. W. Shepherd, *J. Am. Chem. Soc.* **76**, 3617 (1954); Y. V. Baskov and V. V. Perekalin, *Zh. obschei Khim.* **32**, 3106 (1962); Y. V. Baskov, T. Urbanski, M. Witanowski and L. Stefaniak, *Tetrahedron* **20**, 1519 (1964); M. Bourillot, G. Rostaing and G. Descotes, *C. R. Ser. C*, **262**, 1080 (1966); G. Hesse, R. Hatz and H. Konig, *Leibigs Ann.* **709**, 79 (1967); G. Descotes, Y. Bahurel, M. Bourillot, G. Pingeon and R. Ronstaing, *Bull. Soc. Chim. Fr.* 290 (1970).

[9]I. E. Chelnor, I. M. Petrova and V. A. Tartakovskii, *Izvest. Akad. Nauk. S.S.S.R., Ser. Khim.* 2644 (1973); M. Benn and A. C. M. Meesters, *J. Chem. Soc.* Chem. Comm. 597 (1977).

[10]D. T. Downing, R. L. Heppolette and J. Miller, *Chem. & Ind.* 1260 (1953); R. L. Heppolette, J. Miller and V. A. Williams, *J. Chem. Soc.* 2929 (1955).

[11]I. M. Hunsberger, H. S. Gutowsky, W. Powell, L. Morin and V. Bandurgo, *J. Am. Chem. Soc.* **80**, 3294 (1958).

[12]C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, p. 177. Cornell Univ., Ithaca, New York (1953).

[13]A. R. Katritzky, *Lect. in Heterocyclic Chem.* **1**, 39 (1972); A. R. Katritzky and J. M. Lagowsky, *Adv. Heterocyclic Chem.* **1**, 311 (1963); *Ibid.* **2**, 1 (1963).

[14]R. G. Pearson, *Hard and Soft Acids and Bases*. Dowden, Hutchinson & Ross, Stroudsburg, Pennsylvania (1973).

[15]J. D. Reinheimer and J. F. Bunnett, *J. Am. Chem. Soc.* **81**, 315 (1959); G. Bartoli and P. E. Todesco, *Acc. Chem. Res.* **10**, 125 (1977).

[16]E. De Barry Barnett and F. G. Sanders, *J. Chem. Soc.* 434 (1933).

[17]A. Fischer and A. L. Wilkinson, *Can. J. Chem.* **50**, 3988 (1972).

[18]K. von Auwers, *Liebigs Ann.* **419**, 92 (1919).

[19]P. R. Wells, *Aust. J. Chem.* **17**, 967 (1964).

[20]M. Barfield and B. Chakrabarti, *J. Am. Chem. Soc.* **91**, 4346 (1969).

[21]E. G. Rozantsev and V. D. Sholle, *Synthesis* **4**, 190 (1971).

[22]K. A. Kobe and H. Levin, *Ind. Engng Chem.* **42**, 352 (1950).

[23]I. J. Rinkes, *Rec. Trav. Chim.* **58**, 218 (1939).