The $S_{RN}1$ reactions of 1,8-diiodonaphthalene

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Dedicated to Professor Roberto A. Rossi on his 60th birthday

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Abstract

The reactions of 1,8-diiodonaphthalene with the enolate ions from pinacolone and acetone, and with *p*-toluenethiolate, mesitylenethiolate, and diethylphosphite ions in DMSO or liquid ammonia have been studied. In these $S_{RN}1$ (or related radical) processes, disubstitution, without isolation of the monosubstituted monoiodo compound takes place with the enolate ions to give ultimately (after a subsequent aldol condensation) substituted dihydrophenalenes. With *p*-toluenethiolate ion a novel thiaxanthene system results. With mesitylenthiolate ion and diethylphosphite ions, monosubstitution with monoreduction occurs. Deuterium labeling experiments show that the major source of hydrogen (deuterium) necessary for the reduction process arises from DMSO by a radical abstraction reaction.

Keywords: $S_{RN}1$ Reaction, 1,8-disubstituted naphthalenes, radical substitution

Introduction

The $S_{RN}1$ radical chain substitution mechanism, first recognised in aromatic nucleophilic substitutions in 1970,[1] is a well-established mechanism for substitution reactions in aryl halides and dihaloarenes.[2] The $S_{RN}1$ mechanism (nucleophile-initiated) for substitution in dihaloarenes is represented in Scheme 1 (equations *1-7*). A variety of nucleophiles have been used in these reactions, including ketone enolates,[3] aromatic thiolates[4,5] and dialkylphosphites.[6]

In the reactions of dihaloarenes, the decision as to which of the two nucleofuges or both are replaced depends on the nature of the two groups and their relative positions, the nature of the nucleophile and the reaction conditions.[2] For diiodoarenes the dissociation of the radical anion of the intermediate monosubstituted compound, IArNu (equation *4*) normally appears to be faster than the electron transfer step (Equation *5*), and disubstitution, without the isolation of monosubstituted monoiodo compounds, takes place.[6,7]

$$Nu^- + XArY \longrightarrow Nu^\bullet + XArY^{-\bullet} \quad (1)$$

$$XArY^{-\bullet} \longrightarrow XAr^{\bullet} + Y^{-} \quad (2)$$

$$XAr^{\bullet} + Nu^{-} \longrightarrow XArNu^{-\bullet} \quad (3)$$

$$XArNu^{-\bullet} \longrightarrow ArNu^{\bullet} + X^{-} \quad (4)$$

or

$$XArNu^{-\bullet} + XArY \longrightarrow XArNu + XArY^{-\bullet} \quad (5)$$

$$ArNu^{\bullet} + Nu^{-} \longrightarrow ArNu_2^{-\bullet} \quad (6)$$

$$ArNu_2^{-\bullet} + XArY \longrightarrow ArNu_2 + XArY^{-\bullet} \quad (7)$$

Scheme 1. $S_{RN}1$ reaction of arylidene dihalides, ArXY.

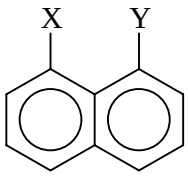
The $S_{RN}1$ reactions of a dihalogenated system in which the halogens are on different rings in a fused polycyclic aromatic system appear to be unreported. The choice of substrate in this study, the readily prepared[8] 1,8-diiodonaphthalene **1**, was based on the special *peri* relationship between the halogens and the expected avoidance of monosubstitution versus disubstitution as discussed above. The proximity of the two iodines in **1** might lead to interesting steric or chemical interactions between the incoming nucleophiles or other interesting interactions during the various $S_{RN}1$ reaction steps. This paper reports the reaction of **1** with the potassium enolates **2** and **3**, sodium *p*-toluenethiolate **4**, sodium and potassium mesitylenethiolate **5a** and **5b** and the potassium salt of its deuterated derivative **5c**, and potassium diethylphosphite **6**.

Results and Discussion

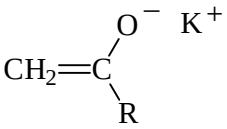
Enumeration and identification of products

The reaction of **1** with the salts **2**-**6** gave the products **7**-**14** as detailed in Table 1. A number of these products were known compounds and were identified by comparison with independently synthesized samples (see Experimental). The proportion of deuterium in **7**-$\boldsymbol{d_1}$ and **12**-$\boldsymbol{d_1}$ that contain containing deuterium in the 1- or 8-position, or in **7**-$\boldsymbol{d_2}$ that contains deuterium in both the 1- and 8-positions was estimated by ^{1}H NMR and mass spectrometry.

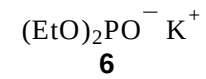
Initially, reactions of **1** with the pinacolone enolate **2** were carried out in DMSO. At higher concentration of substrates (Table 1, entry 1) naphthalene **7** (double-reduced product) and the monosubstituted monoreduced product **8** were formed, whereas at lower concentrations naphthalene **7** was the only product (entries 2-4).



	X	Y
1	I	I
7	H	H
7-*d*$_1$	D	H
7-*d*$_2$	D	D
8	t-BuCOCH$_2$	H
12	2,4,6-Me$_3$C$_6$H$_2$S	H
12-*d*$_1$	2,4,6-Me$_3$C$_6$H$_2$S	D
14	(EtO)$_2$P(O)	H



2 R = t-Bu
3 R = Me



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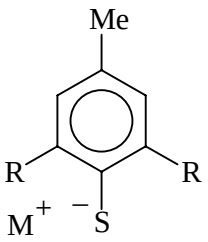


	M	R
4	Na	H
5a	Na	Me
5b	K	Me
5c	K	CD_3

When the reaction between **1** and **2** was performed in liquid ammonia, (entries 5 and 6) the product was identified from its mass spectral (parent ion at *m/z* 324 for $C_{22}H_{28}O_2$) and ^{1}H NMR data (see Figure 1 for the final assignments of resonances) to be the tricyclic dihydrophenalene **9**. The expansion of the ^{1}H NMR signals for the three benzylic protons in the region δ 5.40-3.40 in **9** are displayed in Figure 2. Irradiation of the signal at δ 3.72 (H-3) resulted in the simplification of the signals at δ 3.41 (^1J 16.1 Hz), δ 7.26 (^4J 1.8 Hz) and δ 7.67 (^6J 1.2 Hz), where the parenthetical *J* values represent the coupling constant to H-3. Thus the proton on C-3 at δ 3.72 is coupled to geminal (H-3e), *ortho* (H-4) and *para* (H-6) protons respectively and from the size of the *ortho* and *para* couplings, was assigned to be out of the plane of the naphthalene ring; that is it is H-3a, axial with respect to the saturated six-membered ring. Therefore the signal at δ 3.41 can be assigned as the equatorial proton H-3e (Figure 1). Irradiation of H-3e resulted in the simplification of the signals at δ 3.72 (^1J 16.1 Hz), δ 5.33 (^4J 1.6 Hz) and a reduction of the width-at-half-height ($W_{h/2}$) of the aromatic proton at δ 7.26 (^4J 0.6 Hz). The loss of a ^4J coupling of 1.6 Hz from H-1 indicates that the four bonds joining H-1 and H-3$_e$ are coplanar, confirming that H-1 and H-3$_e$ are both equatorial. Clear nuclear Overhauser effects (NOE) were observed. Irradiation of the *t*-butyl group (δ 0.80), α to the hydroxy group, enhanced the signals for both H-1 and H-3$_e$ (see Experimental). There was no enhancement of the signal for the pivaloyl *t*-butyl group (δ-1.34) confirming that the other *t*-butyl group (δ 0.80) is axial. The aromatic signals in **9** were assigned on the basis of long-range and normal aromatic ring coupling constants and these assignments are shown in Figure 1.

The corresponding reaction of **1** with acetone enolate **3** in liquid ammonia gave a good yield of the 2-phenalenol **10**, (see Table 1, entry 7). By analogy with **9**, the structure of this product was assigned by ^{1}H NMR spectroscopy (see Figure 1 for assignments) and mass spectrometry. The assignment of the proton resonances at δ 2.94 and δ 3.50 to the two protons on C-3 as H-3e (an equatorial proton) and H-3a (an axial proton) respectively, was performed by irradiation experiments and magnitude of long-range coupling constants (see Experimental).

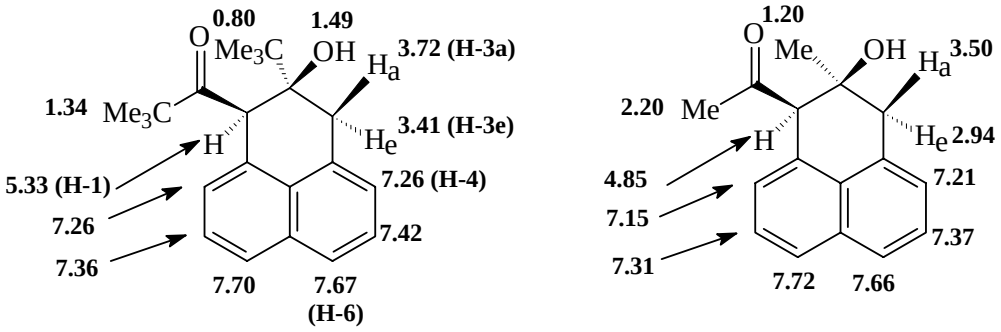


Figure 1. ^{1}H NMR spectroscopic data for 2-phenalenols **9** and **10**.

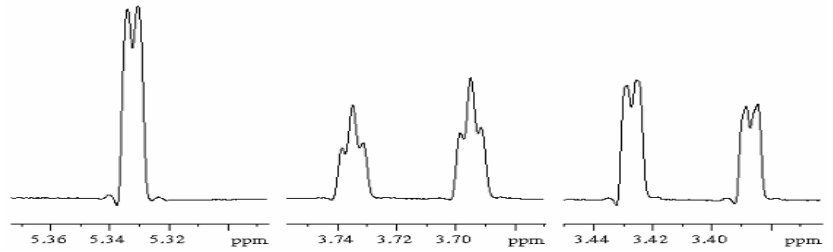


Figure 2. The 400 MHz ^{1}H NMR spectrum of the benzylic protons in **9**.

The reaction of **1** with thiolate **4** gave the thiaxanthene **11** (see Table 1, entries 9 and 10), whose structure was confirmed by mass spectrometry (parent ion at *m/z* 248 for $C_{17}H_{12}S$) and ^{1}H NMR spectroscopic data (including NOE experiments). The assignments of resonances are given in Figure 3. Irradiation of the methyl signal (δ 2.36) gave a 1.0 % enhancement of H-8 (δ 7.00) and a 1.0 % enhancement of H-10 (δ 7.74). Irradiation of H-10 (δ 7.74) gave a 3.7% enhancement of H-1 (δ 7.87). Irradiation of H-3 (δ 7.59) enhanced H-4 (δ 7.42), although the magnitude of enhancement could not be measured due to some overlap of H-4 and H-2. The remaining protons were assigned by using 2-dimensional nuclear Overhauser effect spectroscopy (NOESY).

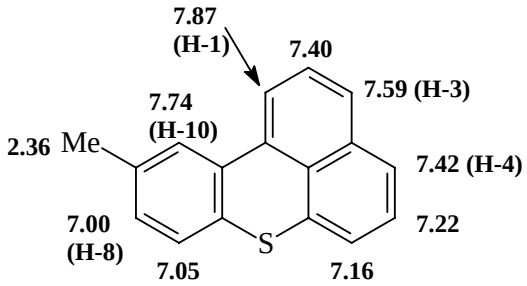


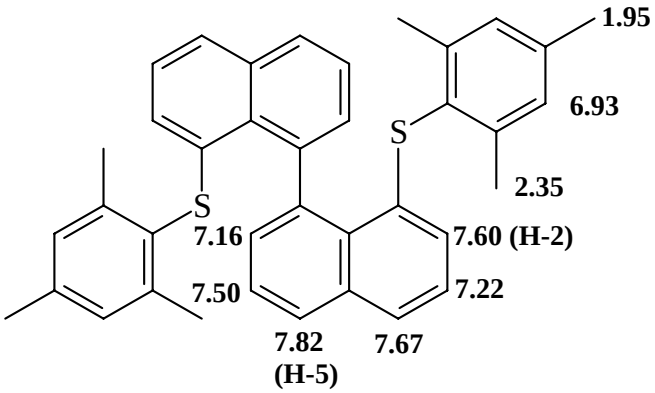
Figure 3. ^{1}H NMR chemical shift data for the thiaxanthene **11**.

Table 1. $S_{RN}1$ Reactions of **1** with **2-6**[a]

Entry	Concentration of substrate **1** [M]	Salt, [M]	Solvent	Time (h)	Product (% yield)
1	0.50	**2** [2.0]	DMSO	1	**7** (5); **8** (62)
2	0.10	**2** [0.40]	DMSO	1	**7** (66)[b]
3	0.010	**2** [0.040]	DMSO	1.5	**7** (60)[b]
4	0.010	**2** [0.040]	DMSO-d_6	1.5	**7** + **7-*d*$_1$** + **7-*d*$_2$** (60)[b,c]
5	0.10	**2** [0.40]	NH_3	2	**9** (16)[d]
6	0.030	**2** [0.12]	NH_3	2	**9** (60)
7	0.010	**3** [0.040]	NH_3	2	**10** (80)
8	0.040	**4** [0.16]	NH_3	2	-[e]
9	0.015	**4** [0.060]	NH_3	2	**11** (5)[d,f]
10	0.016	**4** [0.064]	DMSO	3.5	**11** (49; 55[g])[d]
11	0.047	**5a** [0.19]	DMSO	2	**12** (15); **13 (**75)
12	0.010	**5a** [0.040]	DMSO	2	**12** (12); **13** (73)
13	0.020	**5b** [0.080]	DMSO	2	**12** (20)[d]
14	0.0090	**5b** [0.040]	DMSO	2	**12** (45)[d]
15	0.0090	**5b** [0.033]	DMSO-d_6	2	**12** + **12-*d*$_1$** (71; 82[b,h])
16	0.0090	**5c** [0.035]	DMSO	2	**12** (78)[b]
17	0.0080	**6** [0.032]	NH_3	3.5	**14** (56)

[a] Reactions were carried out under 500 W mercury vapor lamp irradiation under an atmosphere of nitrogen. General conditions are specified in the Experimental Section. Percentage yields are isolated yields unless otherwise stated. [b] Yield estimated by ^{1}H NMR with 2,4,6-trinitrotoluene (TNT) as internal standard (see Experimental for safety note). [c] The ratio of naphthalene **7** and its 1-monodeuterio **7-*d*$_1$** and 1,8-dideuterio-isomers **7-*d*$_2$** was not determined. Integration of the signal for the α-protons in the aromatic region in the ^{1}H NMR spectrum showed that 92±3% incorporation of deuterium had taken place. [d] Recovery of **1** was not quantified. [e] **1** (91%) was recovered. [f] **1** (90%) was recovered. [g] Yield of **11** estimated by GLC with phenanthrene as internal standard. [h] Ratio of **12**:**12-*d*$_1$** was determined by mass spectroscopy (see Experimental) to be 1:9.

The reaction of **1** and the sodium mesitylenethiolate **5a** yielded the monosubstituted-monoreduced compound **12** and the dimer **13** (see Table 1, entries 11 and 12). A sample of **12** was separately prepared from the reaction of 1-iodonaphthalene and **5a**. The structure of **13** (unstable to exposure to light and air) was determined by mass spectrometry [parent ion peak at m/z 554 (M+• $C_{38}H_{34}S_2$) and a strong peak (84%) at m/z 277 ($C_{19}H_{17}S$ and/or double charged parent ion)] and ^{1}H NMR spectroscopic data. The ^{1}H NMR assignments for **13** are given in Figure 4. Interesting support for both the gross structure of **13** and confirmation of the assignments for the protons in **13** come from NOE experiments. Irradiation of the methyl groups *ortho* to sulfur (at δ 2.35) gave, not unexpectedly, substantial enhancement (5.0%) of the signals for the protons (at δ 6.93) *ortho* to the methyl groups being irradiated, but also gave a 1.4% enhancement of H-7 and H-7′ (δ 7.16) and a 1.1% enhancement of H-2 and H-2′ (δ 7.60). Inspection of molecular models reveals that these later two sets of aromatic protons lie reasonably close in space to the protons in the aromatic methyl groups in **13**.



13

Figure 4. ^{1}H NMR spectroscopic data for the dimer **13**.

The reaction of **1** with the potassium salts **5b** and **5c** gave no detectable amounts of the dimer **13** and yielded *only* **12** in DMSO and its deutero derivative **12-*d*$_1$** in DMSO-d_6 (entries 13-16).

The reaction of **1** with the phosphonate **6** (entry 17) gave only the monosubstituted monoreduced product **14**, whose NMR data was identical with reported data,[9] and which was also identical with an independently prepared sample formed in the reaction of 1-iodonaphthalene with **6**.

One observation pertinent to the reactions in liquid ammonia was that those carried out under more concentrated conditions led to lower conversion into products (*e.g.*, compare entry 5 with 6 and 8 with 9). An explanation for this behavior is not obvious.

Mechanistic implications

From the results of the reaction of **1** with the enolates **2** and **3** it is clear that liquid ammonia (Table 1, entries 6 and 7) is a superior solvent over DMSO for double substitution reactions. In

the latter solvent at higher concentrations only monosubstitution accompanied by monoreduction, giving **8**, occurs whilst at lower concentrations double reduction forming naphthalene **7** predominates. Swartz found evidence for hydrogen (deuterium) abstraction from DMSO by phenyl radicals in the reaction of potassium benzenethiolate with bromobenzene under conditions of electrochemical initiation,[10] so we deemed it worthwhile to confirm this conclusion under conditions of nucleophile-initiated (equation 1) reaction. When the reaction of **1** was carried out with the enolate **2** in DMSO-d_6, the resulting mixture of naphthalene **7** and deuterated naphthalenes **7-*d*$_1$** and **7-*d*$_2$** contained 92% deuterium in the 1- and 8-positions (Table 1, entry 4). This result confirms that reduction products (represented in Equations *8-10* as ArH) are principally being formed by hydrogen (deuterium) atom abstraction from the DMSO (H-Solv) by the intermediate aryl radical ($Ar^{\bullet}$), as represented in equation *8*, rather than by a second electron-transfer step followed by protonation of the resulting aryl anion as represented in equations *9* and *10*, where the electron in equation 9 arises from the pinacolone enolate ion and H-B represents the proton sources, t-butyl alcohol and/or pinacolone. The overwhelming incorporation of deuterium, when DMSO-d_6 is the solvent, clearly demonstrates deuterium abstraction from the solvent by an aryl radical, since an aryl anion would be *protonated* by the relatively stronger acids (t-butyl alcohol and/or pinacolone) in the system in preference to deuteriation by the far less acidic solvent, DMSO-d_6.

$$Ar^{\bullet} + H{-}Solv \longrightarrow ArH + Solv^{\bullet} \quad (8)$$

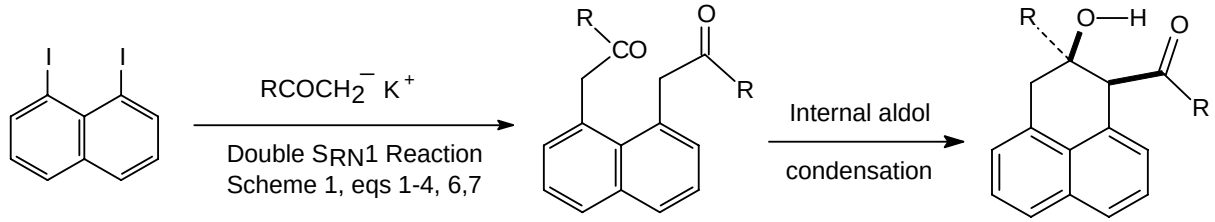
$$Ar^{\bullet} + e^{-} \longrightarrow Ar^{-} \quad (9)$$

$$Ar^{-} + H{-}B \longrightarrow ArH + B^{-} \quad (10)$$

Another piece of evidence for the formation of reduced products by a radical abstraction process is revealed in comparison of the product distributions in Table 1, entries 1 and 2. Decreasing the concentrations of the substrate **1** and the electron donating salt **2** should decrease the rate of the reduction process if it proceeded through equation 9 (electron from the pinacolone enolate). The contrary is observed and monosubstitution takes place at higher concentrations. This concentration dependence would indicate that the radical + anion coupling reaction (symbolized in equation 3) between naphthyl radicals and the pinacolone enolate and the hydrogen abstraction reaction from DMSO (equation 8) do not differ by more than 2-3 orders of magnitude. This latter conclusion is entirely consistent with the independently determined values for the rate constants (k_H = 6.4 x 10^6 M^{-1} s^{-1})[11] involving naphthyl radicals (without peri-substituents) in hydrogen abstraction reactions with DMSO and the rate constant for coupling of the α-naphthyl radical with the enolate anion of pinacolone (2.9 x 10^9 M^{-1} s^{-1}).[12]

In the reactions of **1** with **2** or **3** in liquid ammonia it is clear that double $S_{RN}1$ substitution takes place, with the distinctive absence of any traces of monosubstituted monoiodo compounds, and the resulting disubstituted products undergo ready internal aldol condensations to give **9** and **10** respectively, as summarized in Scheme 2. Under the strongly basic (equilibrating) conditions it would appear that the more thermodynamically stable diastereomers, in which the acyl and

alky groups are trans-diaxial, are formed exclusively. Since no detectable amounts of the intermediate disubstituted products were found, it would appear, unlike the analogous reactions of *o*-dibromobenzene with **2** and **3** reported by Bunnett and Singh,[13] that very efficient aldol condensation takes place in the 1,8-disubstituted naphthalene system. It is interesting to note that neither of the aldol products **9** or **10** underwent elimination of water, unlike the processes occurring with the products from the reaction of *o*-dibromobenzene and **3**. It is also worthy of note, by way of contrast, that the reaction of o-dihalobenzenes with the enolates of aryl alkyl ketones to give neither double substitution nor monosubstitution with reduction have been reported very recently.[14]

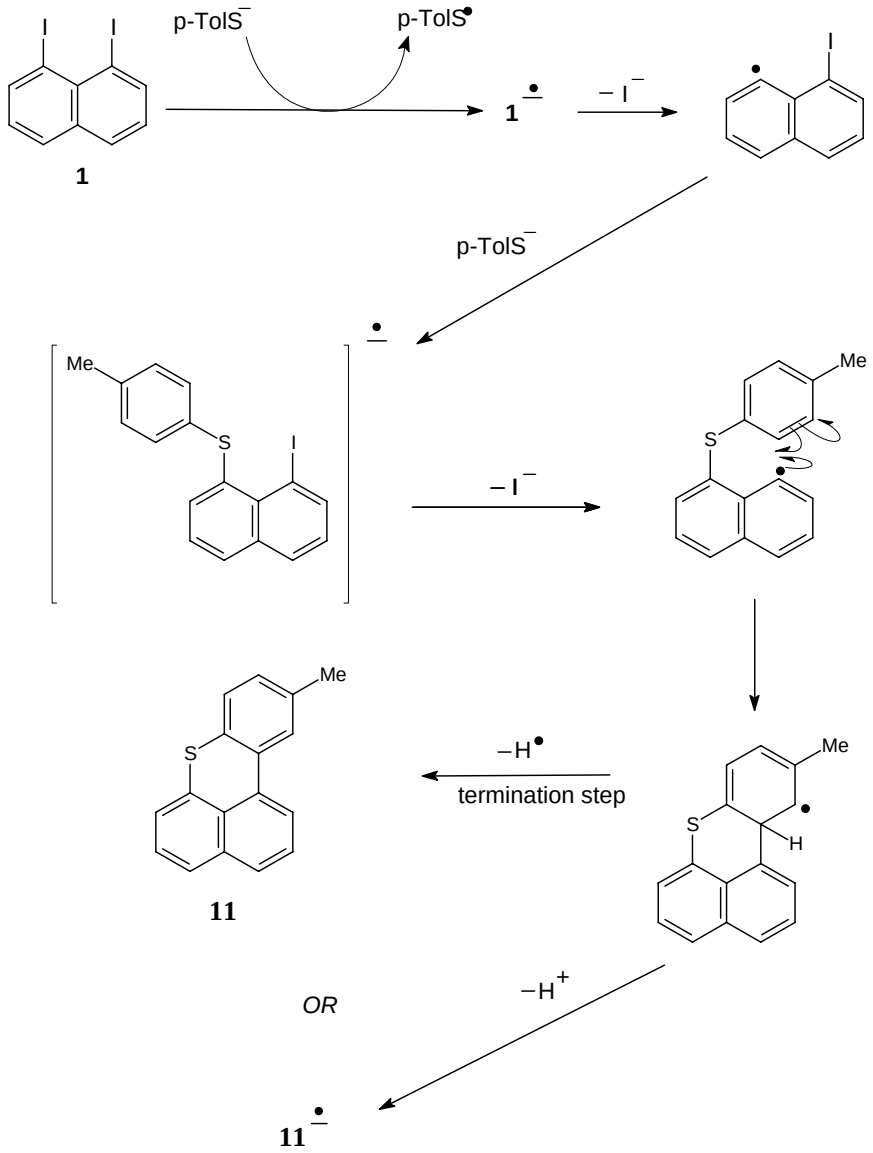


9 R = t-Bu
10 R = Me

Scheme 2

The reaction between **1** and **4** proceeded poorly in liquid ammonia (see Table 1, entries 8 and 9), but in DMSO gave moderate yields of the thiaxanthene **11** (see entry 10). There was no detectable formation of the simple disubstituted product nor of monosubstituted reduced products in any of these reactions, in contrast with the reported reactions of benzenethiolate with various dihalobenzenes, including *o*-chloroiodobenzene.[5] Whilst these cyclizations are novel in the naphthalene system, substitution reactions in DMSO involving benzenethiolate ions with *o*-bis(phenylsulfonyl)benzene derivates have been found to lead to cyclization in which the intermediate radical cyclizes onto the existing phenylsulfonyl moiety.[15] In another o—substituted benzene system (in the absence of benzenethiolate ions), substituted phenyl radicals cyclize onto the *o*-position of adjacent *S*-benzyl groups.[16]

A probable mechanism for the formation of **11**, is shown in Scheme 3. The intermediate α-naphthyl radical is presumably more hindered by the *peri*-substituent than the corresponding phenyl radicals in *o*-substituted phenyl systems and this, together with the additional effect of changed geometry involved in the 1,8-arrangement in naphthalene systems, leads to exclusive formation of the cyclized product **11**, rather than the disubstituted product normally expected from a double $S_{RN}1$ process. Given the strongly basic conditions, the loss of a proton to give a chain-propagating radical anion is more attractive than the alternative terminating step involving an unidentified hydrogen atom-abstracting agent (indicated as "-H•"in Scheme 3). This deprotonation step has also been proposed in related proceses.[15,16]



Scheme 3

In order to prevent this internal cyclization by having methyl groups *ortho* to the sulfur atom, the reactions of the **1** with sodium or potassium mesitylenethiolate, **5a** or **5b**, respectively were performed. When sodium hydride was used as the base, *i.e.* the salt was **5a,** the monosubstituted monoreduced compound **12** and the dimerized monosubstituted compound **13** were formed (see Table 1, entries 11 and 12). When potassium t-butoxide was used as the base, *i.e.* the salt was **5b**, only the monosubstituted-monoreduced product **12** was produced (Table 1, entries 13 and 14). Although it is clear that the additional methyl groups prevent the internal cyclization reaction, the intermediate radical, however, does not couple with a further mesitylenethiolate ion and instead it either couples with itself to form the dimer **13**, or undergoes a hydrogen abstraction reaction to form **12**.

The formation of the dimer **13** is quite remarkable and its counter-ion dependence requires comment. The formation of **13** does not seem to be concentration dependent. This can be seen by comparing the data in entries 11 and 12 (Table 1), where there is over a twenty-fold difference in *the product of molarities* of the substrate **1** and **5a** (8.9×10^{-3} M^2 and 0.4×10^{-3} M^2 respectively). Also in one of the reactions with the potassium salt **5b** (see entry 13) the corresponding *product of molarities* is 1.6×10^{-3} M^2, and this value lies between the concentrations in entries 11 and 12 involving the sodium salt **5a**. It is very difficult to explain this difference in reaction products, but perhaps the dimer formation is related to the lower solvation of the sodium cation by DMSO. This may result in tight association between the sodium ions and the intermediate radical anions. If this tight association leads to aggregation of radical anions then the resulting proximity of radicals could lead to dimerization. Another indication that the radicals in the reaction of **1** with **5b** are more available to solvent than in reactions with **5a** is given by the increase in the formation of the monosubstituted monoreduced product 12 (compare entries 12 and 14).

In order to determine the source of the hydrogen atoms needed to produce the product **12**, the reaction of **1** and the potassium salt **5b** was performed in DMSO-d_6 (99.9% deuterium). The resulting product was a mixture of 90% of **12-d_1** and 10% of **12** as determined by mass spectroscopy (see Table 1, entry 15 and Experimental). This result shows that the major pathway for the formation of the reduced product **12** (**12-d_1**) is hydrogen (deuterium) abstraction from DMSO as shown in the general equation *8*. In this case, however, some hydrogen is coming from a source other than the DMSO and so the carbanion process in equations *9* and *10* cannot be totally excluded. Hydrogens could also be *abstracted* from *ortho*-methyl groups in the mesitylthiyl moiety. To exclude this not unreasonable possibility, given the proximity of these groups to the α-naphthyl radical, the reaction was performed with mesitylenethiolate specifically deuterated in its methyl groups to >96%, *i.e.*, by use of salt **5c** (see Table 1, entry 16). Inspection of the product **12** by ^{2}H NMR spectroscopy revealed that no deuterium had been incorporated into the 8-position, clearly showing that the deuterium was not arising from the *o*-methyl groups.

The reaction of the **1** with phosphite salt **6** in liquid ammonia gave only the monosubstituted monoreduced product **14** in moderate yield (see Table, entry 17). No disubstituted product could be detected in the crude reaction product. This behavior contrasts with that of *o*-diiodobenzene, where the reaction with **6** gave a good yield of the disubstituted product (70%) and a yield of only 15% of the monosubstituted monoreduced product.[7]

Although no specific trapping or inhibition effects were undertaken in this study there is no doubt that all the reactions proceeded by processes involving radical anions and radicals. This is amply demonstrated by failure to isolate any monohalo-monosubstituted compounds, formation of cyclized products from reactions with **4** (the clear results of radical processes), demonstration of hydrogen (or deuterium) abstraction from DMSO (or DMSO-d_6) in the formation of reduced products and formation of the dimer **13**.

Conclusions

The *peri* relationship of the iodo groups of **1** cause some interesting effects in its $S_{RN}1$ reactions with the enolates **2** and **3**, the thiolates **4**, **5a**, **5b** and **5c**, and the phosphite **6** when compared with the corresponding reactions of *o*-dihalobenzenes with these nucleophiles. In the reaction with **2** and **3** the change in geometry did not affect the ready double substitution of the iodines in **1** that took place without detectable formation of monosubstituted monoiodo compounds, but did allowed facile aldol condensation of the intermediate disubstituted compound to proceed to completion leading to the phenalen-2-ols **9** and **10** exclusively. The change in geometry together with the added stability of the monosubstituted α-naphthyl radicals formed during the reaction, stopped the second substitution occurring during the reactions of the thiolates **5a**, **5b** and **5c** and the phosphite salt **6** by either formation of cyclized products, *e.g.*, thiaxanthene **11** or dimerisation to form **13**, or by the formation of monosubstituted-monoreduced compounds. In the reactions of **1** with the hindered thiolate salts **5a** or **5b** and the phosphite salt **6** either a steric or subtle electronic effect prevents attack of the intermediate monosubstituted radical, formed in equation *4* (Scheme 2) by the appropriate nucleophilic anion (radical + anion trapping), instead an alternative reduction process, principally abstraction of hydrogen from the solvent, takes place. The internal cyclization in the reaction of **1** with thiolate **4**, and the failure to couple with a second thiolate ion in the reactions with **5a-c** contrast with the facile double substitution in the *o*-disubstituted benzene system.

Experimental Section

General Procedures. Melting points were determined thermoelectrically on a Reichert hot-stage microscope and are uncorrected. "Chromatography", refers to flash chromatography as described by the method of Still,[17] carried out on silica gel (Merck 60, 230-240 mesh) as the stationary phase and with the eluent mixture as specified. Thin layer chromatography (TLC) was performed on Merck Kieselgel HF254 (type 60) paper. ^{1}H NMR and spectra were determined on a Bruker AMX400 (400 MHz) spectrometer. Chemical shifts (δ in ppm) are given as downfield from internal TMS. Where noted, yields of products were determined in some instances by ^{1}H NMR spectroscopy on known aliquots of reaction mixtures containing added TNT (2,4,6-trinitrotoluene) and these spectra were recorded on a Bruker AC200 (200 MHz) spectrometer. Coupling constants (*J* in Hz) are accurate to ± 0.1 Hz. Infrared spectra (unless otherwise stated as nujol mulls) were recorded on either a Biorad 20-80 FTIR or Perkin Elmer 1600 series FTIR spectrophotometers and ultraviolet spectra (in EtOH, unless otherwise stated) were recorded with a Hitachi 150-20 spectrophotometer in the specified solvents at room temperature. Mass spectra at 70 eV using electron impact mode were determined with an AEI model MS902. Mass charge ratios (*m/z*) are quoted in the form X(Y), where X is the *m/z* and Y is the percentage abundance relative to the base peak. Peaks with percentage abundance values less than 5% are not quoted unless significant. Microanalyses were carried out by either the Chemical and Micro Analytical

Service Pty. Ltd., Melbourne, or the Microanalysis Unit at the University of New South Wales, Sydney. Distillations performed under reduced pressure on a Buchi GKR-50 Kugelrohr are reported as "(oven temp. x-y °C/z mmHg)". Commercial samples of 2,4,6-trinitrotoluene (in up to 10 g quantities) can be safely recrystallized to constant MP from ethanol and then dried under vacuum to produce an excellent internal standard (two sharp signal from the aromatic methyl and the aromatic protons), readily soluble in $CDCl_3$. We have used this process without incident since 1978.[18]

1,8-Diiodonaphthalene (1). Naphthalene-1,8-diamine was tetrazotised and treated with potassium iodide by the method of Hodgson and Whitehurst[8] to give **1** (35%) mp 107-108 °C (lit.[19] mp 109 °C).

Mesitylenethiol. Lithium aluminum hydride (6.0 g) was placed in a Soxhlet apparatus whose delivery system was protected by dry glass wool rather than the usual Soxhlet thimble. A solution of mesitylenesulfonyl chloride (10.0 g, 46 mmol) prepared by the method of Carten and Huntress[20] in anhydrous tetrahydrofuran (300 mL) was heated under reflux whilst attached to the Soxhlet system for 3 h. On completion of the reaction the excess of lithium aluminum hydride was quenched by addition of an EtOH/benzene solution (50%, 160 mL). The lithium and aluminum salts were dissolved in an excess of H_2SO_4 (10%), and a further amount of benzene (40 mL) was added. The reaction mixture was worked up in the usual manner followed by purification by distillation (Kugelrohr) to give mesitylenethiol (5.5 g, 79%) as a colorless oil (oven temp. 73-79 ºC/2 mm Hg; lit.[21] bp 109.5-11 °C/18 mm Hg).

Mesitylene-d_9. The procedure of Chen and coworkers[22] was modified as follows:- Sodium hydride (50% suspension in paraffin, 1.1 g) was added to a solution of mesitylene (5.0 g, 42 mmol) in DMSO-d_6 (99.5% deuterium, 10.0 g) at 100 °C and stirred under nitrogen for 24 h. Water (20 mL) was added and the mixture was worked up in the usual fashion and the crude (dried) product was subjected to the above treatment two further times, to give mesitylene-d_9, bp 162-164 °C (4.75 g, 95%). The deuterium incorporation in the methyl groups was determined by ^{1}H NMR spectroscopy to be > 96%.

Mesitylenesulfonyl-d_9 chloride. Mesitylene-d_9 (2.0 g, 15 mmol) was dissolved in dichloromethane (10 mL), cooled to 0 °C and chlorosulfonic acid (4.0 mL) was added dropwise whilst the temperature was maintained between 0-5 °C. After the usual work-up mesitylenesulfonyl-d_9 chloride, mp 54-55 °C (3.3 g, 94%) was obtained and was used in the next step without any further purification.

Mesitylenethiol-d_9. By use of the method for the preparation of mesitylenethiol, mesitylenesulfonyl- d_9 chloride (3.3 g) was converted into to d_9-mesitylenethiol (2.0 g, 80%) as a colorless oil (oven temp. 80-81 °C/2 mmHg).

General procedures for S_{RN}1 reactions. In DMSO. The substrate of was placed in a dry addition funnel and fitting it to a two-neck pyrex flask. The potassium enolate **2** or thiolates **5b** or **5c** were generated *in situ* immediately prior to use by addition of 1.1-1.2 equivalents of potassium t-butoxide to a solution of the appropriate ketone or thiol in DMSO. The solution was

then deoxygenated by passage of a stream of dry nitrogen for 10 min followed by the addition of the substrate. The sodium thiolates **4** or **5a** were generated *in situ* immediately prior to use by the addition of an excess of sodium hydride (50% dispersion in oil) to a solution of the corresponding thiol in DMSO. After 5 min the solution was filtered under vacuum into the pyrex flask and was deoxygenated by the passing of a stream of dry nitrogen for 10 min followed by the addition of the substrate dissolved in deoxygenated DMSO. Irradiations were performed by a 500 W mercury vapor lamp (350 nm) at a distance of 20 cm from the flask. The volumes of DMSO in the component solutions led to the concentrations reported in Table 1. **In liquid ammonia.** The general procedure involved placing the substrate in a dry addition funnel and fitting it to a three-neck pyrex flask fitted with a dry ice condenser with 2-propanol/dry ice as a cooling mixture. For reactions with **2** or **3**, potassium t-butoxide was added to the flask and placed under nitrogen. Sodium-dried liquid ammonia was distilled into the flask at room temperature. The appropriate ketone (pinacolone or acetone respectively) was injected into the flask and stirred for 10 min., then the substrate was added and irradiated as described above. For reaction with **4**, potassium t-butoxide and *p*-toluenethiol were added to the flask under nitrogen. Sodium-dried liquid ammonia was distilled into the flask at room temperature, after which the substrate was added and the mixture irradiated as described above. For reactions with **6**, potassium metal was placed in the flask and flushed with nitrogen. Sodium-dried liquid ammonia was distilled into the flask at room temperature and enough diethyl phosphite was injected into the flask to discharge the blue color then the substrate was added and the mixture irradiated as described above. Reaction mixtures were then 'worked up in the usual manner' and this signifies the following procedures: Reactions in DMSO were quenched with water, followed by three-fold extraction into Et_2O. The combined Et_2O extracts were washed with water, 3M sodium hydroxide (where necessary), and brine and dried ($MgSO_4$) and the solvent was removed under reduced pressure to give a crude product. Reactions in liquid ammonia were quenched with 2M ammonium nitrate followed by extraction into Et_2O. The combined Et_2O extracts were treated as above.

Mesityl 1-naphthyl sulfide (12). The reaction mixture from the treatment of 1-iodonaphthalene (254 mg, 1.0 mmol) with **5a** prepared from mesitylenethiol (305 mg, 2.0 mmol) in DMSO (100 mL) was worked up in the usual manner. Chromatography with light petroleum as eluent followed by crystallization from EtOH gave **12** (240 mg, 86%) mp 119-120 °C. Anal. Calcd. for $C_{19}H_{18}S$ (278.41): C, 82.0; H, 6.5. Found: C, 81.8; H 6.7. λ_{max} 312 nm (ε 9.9 x 10^3). ν_{max} 1601, 1564, 1503, 1463, 1380, 970, 854 cm^{-1}. δ_H ($CDCl_3$) 2.34 (Me *para* to S), 2.38 (Me *ortho* to S), 6.56 (H-2, $J_{2,3}$ = 7.5 Hz, $J_{2,4}$ = 1.6 Hz), 7.05 (H-3′ and 5′), 7.17 (H-3, $J_{2,3}$ = 7.5 Hz, $J_{3,4}$ = 8.1 Hz) 7.51 (H-6, $J_{5,6}$, = 8.0 Hz, $J_{6,7}$ = 7.1 Hz, $J_{6,8}$ = 1.4 Hz), 7.55 (H-4, $J_{2,4}$ = 1.6 Hz, $J_{3,4}$ = 8.1 Hz), 7.56 (H-7, $J_{5,7}$ = 1.6 Hz, $J_{6,7}$ = 7.1 Hz, $J_{7,8}$ = 8.3 Hz), 7.83 (H-5, $J_{5,6}$ = 8.0 Hz, $J_{5,7}$ = 1.6 Hz, $J_{5,8}$ 0.7 Hz), 8.38 (H-8, $J_{5,8}$ = 0.7 Hz, $J_{6,8}$ = 1.6 Hz, $J_{7,8}$ = 8.3 Hz). *m/z* 280 (M+2, 8%), 279 (M+1, 24), 278 (M, 100), 248 (13), 150 (86), 128 (11), 115 (19), 91 (8), 77 (12).

Diethyl 1–naphthylphosphonate (14). The reaction mixture from the treatment of 1-iodonaphthalene (360 mg, 1.4 mmol) with **6** prepared from diethyl phosphite and potassium (110 mg, 2.8 mmol) in liquid ammonia (100 mL) was worked up in the usual manner. Distillation gave **14** (296 mg,

80%) (oven temp. 165 °C/2 mmHg), whose ^{1}H NMR spectroscopic data were identical with the literature data.[9]

S_{RN}1 Reactions of 1 (also see Table 1)

Reaction of 1 with 2 (Table 1, entry 1). The reaction mixture from the treatment of **1** (0.95 g, 2.5 mmol) with **2**, prepared from pinacolone (1.0 g, 10.0 mmol) and potassium t-butoxide (1.12 g, 10.0 mmol) in DMSO (5 mL) was worked up in the usual manner. Chromatography with 15% ethyl acetate/light petroleum as eluent gave two products. The least polar component eluted was identified as naphthalene **7** (16 mg, 5%) by ^{1}H NMR spectroscopy and TLC. The more polar component, after crystallization from EtOH was identified as 3,3-dimethyl-1-(1-naphthyl)-2-butanone **8** (351 mg, 62%) mp 67-69 °C (lit.[23] mp 67-69 °C).

Table 1, entry 2. The reaction mixture from the treatment of **1** (0.19 g, 0.5 mmol) with **2** prepared from pinacolone (0.20 g, 2.0 mmol) and potassium t-butoxide (0.25 g, 2.2 mmol) in DMSO (5.0 mL) was worked up in the usual manner. Chromatography with 15% ethyl acetate/light petroleum as eluent gave **7** (66% as estimated by ^{1}H NMR spectroscopy with TNT as internal standard).

Table 3, entry 3. The reaction mixture from the treatment of **1** (193 mg, 0.50 mmol) with **2** prepared from pinacolone (0.20 g, 2.0 mmol) and potassium t-butoxide (0.25 g, 2.2 mmol) in DMSO (50 mL) gave **7** (60% as determined by ^{1}H NMR spectroscopy with TNT as internal standard).

Table 1, entry 4. The reaction mixture from the treatment of **1** (0.19 mg, 0.50 mmol) with the **2** prepared from pinacolone (0.20 g, 2.0 mmol) and potassium t-butoxide (0.25 g, 2.2 mmol) in DMSO-d_6 (5.0 mL) gave a mixture of **7**, 1-deuteronaphthalene (**7-*d*$_1$**) and 1,8-dideutero-naphthalene (**7-*d*$_2$**) (39 mg, 60% as determined by ^{1}H NMR spectroscopy with TNT as internal standard). Integration of the α- and β-aromatic regions in the ^{1}H NMR spectrum of the reaction product indicated >92% α-deuteration.

Reaction of 1 with 2 (Table 1, entry 6). The reaction mixture from the treatment of **1** (0.57 g, 1.5 mmol) with **2** prepared from pinacolone (0.60 g, 6.0 mmol) and potassium t-butoxide (0.74 g, 6.6 mmol) in liquid ammonia (50 mL) was worked up in the usual manner. Chromatography with 15% ethyl acetate/light petroleum as eluent, after crystallized from EtOH, gave **1-(2,2-dimethyl-1-oxopropyl-2-t-butyl-1,2-dihydrophenalen-2-ol (9)** (0.29 g, 60%) mp 156-160 °C. Anal. Calcd. for $C_{22}H_{28}O_2$: (324.46): C, 81.4; H, 8.7. Found: C, 81.5; H, 8.9. λ_{max} 298 nm (ε 7.5 x 10^3). ν_{max} 1695, 1597, 1479, 1396, 1297, 1066, 980, 816 cm^{-1}. δ_H ($CDCl_3$) 0.80 (CMe_3), 1.34 (CMe_3), 1.49 (OH), 3.41 (H-3e, $J_{1,3e}$ = 1.6 Hz, $J_{3a,3e}$ = 16.1 Hz), 3.72 (H-3a, $J_{3a,3e}$ = 16.1 Hz, $J_{3a,4}$ = 1.4 Hz, $J_{3a,6}$ = 1.2 Hz), 5.33 (H-1, $J_{1,3e}$ = 1.6 Hz, $J_{1,9}$ 0.5 = Hz), 7.26 (H-4, $J_{3a,4}$ = 1.8 Hz, $J_{4,6}$ = 1.2 Hz, $J_{4,5}$ = 7.0 Hz, $J_{3e,4}$ = 0.6 Hz), 7.26 (H-9, $J_{1,9}$ = 0.5 Hz, $J_{7,9}$ = 1.3 Hz, $J_{8,9}$ = 7.1 Hz), 7.36 (H-8, $J_{7,8}$ = 8.2 Hz, $J_{8,9}$ = 7.1 Hz), 7.42 (H-5, $J_{4,5}$ = 7.0 Hz, $J_{5,6}$ = 8.3 Hz), 7.67 (H-6, $J_{3a,6}$ = 1.2 Hz, $J_{4,6}$ = 1.2 Hz, $J_{5,6}$ = 8.3 Hz), 7.70 (H-7, $J_{7,8}$ = 8.2, $J_{7,9}$ = 1.3 Hz). Irradiation of *t*-butyl (δ 0.80) gave a 0.76% enhancement of H-3e (δ 3.41) and a 1.7% enhancement of H-3a (δ 3.72). Irradiation of *t*-butyl (δ 1.34) gave a 0.4% enhancement of H-1 (δ 5.33) and 0.4% enhancement of H-9. Irradiation of H-3e (δ 3.41) gave a 23.5% enhancement of H-3a (δ 3.72) and an 8.2% enhancement of *t*-butyl (δ 0.80). Irradiation of H-3a (δ 3.72) gave a 25.8% enhancement of H3e

(δ 3.41). *m/z* 324 (M, 1%), 222 (69), 221 (64), 183 (46), 182 (18), 181 (39), 166 (34), 165 (80), 153 (19), 152 (17), 57 (100).

Reaction of 1 with 3 (Table 1, entry 7). The reaction mixture from the treatment of **1** (0.95 g, 2.5 mmol) with **3** prepared from acetone (0.58 g, 10.0 mmol) and potassium t-butoxide (1.20 g, 11.0 mmol) in liquid ammonia (250 mL) was worked up in the usual manner. Chromatography with 20% ethyl acetate/light petroleum as eluent followed by crystallization from EtOH gave white crystals of **1-(acetyl)-2-methyl-1,2-dihydrophenalen-2-ol (10)** (480 mg, 80%) mp 134-135 °C. Anal. Calcd. for $C_{16}H_{16}O_2$ (240.30): C, 80.0; H, 6.7. Found: C, 80.3; H, 6.8. λ_{max} ($CHCl_3$) 240 (ε 1.1 x 10^3), 290 nm (7.5 x 10^3). ν_{max} 1356, 1698, 3014, 3474 cm^{-1}. ^{1}H. NMR δ_H ($CDCl_3$) 1.20 (CH_3), 2.20 ($COCH_3$), 2.94 (H-3e, $J_{1,3e}$ = 1.3 Hz, $J_{3a.,3e}$ = 15.9 Hz), 3.50 (H-3a, $J_{3a.,3e}$ = 15.9 Hz), 4.85 (H-1, $J_{1,3e}$ = 1.3 Hz), 7.15 (H-9, $J_{7,9}$ = 1.2 Hz, $J_{8,9}$ = 7.1 Hz), 7.21 (H-4, $J_{4,5}$ = 7.0 Hz, $J_{4,6}$ = 1.1 Hz), 7.31 (H-8, $J_{8,9}$ = 8.3 Hz, $J_{8,9}$ = 7.1 Hz), 7.37 (H-5, $J_{4,5}$ = 7.0 Hz, $J_{5,6}$ = 8.2 Hz), 7.66, H-6, $J_{4,6}$ = 1.1 Hz, $J_{5,6}$ 8.2 = Hz), 7.72 (H-7, $J_{7,8}$ = 8.3 Hz, $J_{7,9}$ = 1.2 Hz). Double irradiation experiments: irradiation of H-3_a (δ 3.50) resulted in the simplification of H-3_e (δ 2.94, loss of J = 15.9 Hz), H-4 (δ 7.21, loss of J = 0.7 Hz) and H-6 (δ 7.66, loss of J = 0.8 Hz); irradiation of H-3_e (δ 2.94) resulted in the simplification of H-1_e (δ 4.85, loss of J = 1.3 Hz) and H-3_a (δ 3.50, loss of J = 15.9 Hz) and there was no detectable effect on the width-at-half-height ($W_{h/2}$) of the aromatic protons H-4 and H-6. *m/z* 240 (M 0.3%), 180 (23), 179 (100), 178 (17), 165 (30), 153 (17), 152 (17), 43 (12).

Reaction of 1 with 4 (Table 1, entry 9). The reaction mixture from the treatment of **1** (0.57 g, 1.5 mmol) with **4** prepared from *p*-toluenethiol (0.75 g, 6.0 mmol) and potassium t-butoxide (0.74 g, 6.6 mmol) in liquid ammonia (100 mL) was worked up in the usual manner. Chromatography with light petroleum as eluent gave starting **1** (0.52 g, 91%) and a more polar component that on crystallization from EtOH gave **9-methylbenz[m,n]thioxanthene** (**11**) (20 mg, 5%) mp 111-112 °C. Anal. Calcd. for $C_{17}H_{12}S$ (248.34): C, 82.2; H, 4.9; S, 12.9. Found: C, 82.1; H, 4.9; S, 12.9. λ_{max} ($CHCl_3$) 242 nm (ε 3.2 x 10^4). ν_{max} 1611, 1567, 1480, 1405 cm^{-1}. δ_H ($CDCl_3$) 2.36 ($ArCH_3$, $^4J_{Me,8}$ = $^4J_{Me,10}$ = 0.7 Hz), 7.00 (H-8, $J_{7,8}$ = 8.0 Hz, $J_{8,10}$ = 1.8 Hz, $J_{8,Me}$ = 0.7 Hz), 7.05 (H-7, $J_{7,8}$ = 8.0 Hz), 7.16 (H-6, $J_{5,6}$ = 7.3 Hz, $J_{4,6}$ = 1.3 Hz), 7.22 (H-5, $J_{5,6}$ = 7.3 Hz, $J_{4,5}$ = 8.1 Hz), 7.40 (H-2, $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 8.2 Hz), 7.42 (H-4, $J_{4,5}$ = 8.1 Hz, $J_{4,6}$ = 1.3 Hz), 7.59 (H-3, $J_{1,3}$ = 1.0 Hz, $J_{2,3}$ = 8.2 Hz), 7.74 (H-10, $J_{8,10}$ = 1.8 Hz, $J_{10,Me}$ = 0.7 Hz), 7.87 (H-1, $J_{1,2}$ = 7.5 Hz, $J_{1,3}$ = 1.0 Hz). Irradiation of Me (δ 2.36) gave a 1.0% enhancement of H-8 (δ 7.00) and a 1.0% enhancement of H-10 (δ 7.74). Irradiation of H-1 (δ 7.87) gave a 0.6% enhancement of H-2 (δ 7.40) and a 6% enhancement of H-10 (δ 7.74). Irradiation of H-3 (δ 7.59) gave an enhancement of H-4 (δ7.42), which could not be measured due to overlap with H-2 (δ7.40). *m/z* 250 (M+2 ,7%), 249 (M+1, 21), 248 (M, 100), 215 (27), 124 (12), 122 (12).

Reaction of 1 with 4 (Table 1, entry 10). The reaction mixture from the treatment of **1** (0.31 g, 0.81 mmol) with **4** prepared from *p*-toluenethiol (0.40 g, 3.2 mmol) in DMSO (50 mL) was worked up in the usual manner. Chromatography with light petroleum as eluent followed by crystallization from EtOH gave **11** (98 mg, 49%) mp 111-112 °C (55% estimated yield by GLC with phenanthrene as internal standard.).

Reaction of 1 with the with the sodium salt 5a (Table 1, entry 11). The reaction mixture from the treatment of **1** (0.18 g, 0.47 mmol) with **5a** prepared from mesitylenethiol (0.29 g, 1.9 mmol) in DMSO (10 mL) was worked up in the usual manner. Chromatography with 2% dichloromethane/light petroleum as eluent gave a less polar component that on crystallization from EtOH gave mesityl 1–naphthyl sulfide (**12**) (20 mg, 15%), identical with the sample prepared above. The more polar component on crystallization from ethyl acetate under nitrogen, gave 8,8′-(dimesitylthio)-1,1′-binaphthalene (**13**) (98 mg, 75%) mp 128 °C (decomp.) that darkened on exposure to light and air. Exact mass Calcd. for $C_{38}H_{34}S_2$: 554.2102. Found: 554.2096. λ_{max} (CH_3CN) 219 (ε 6.4 x 10^4), 308 nm (1.5 x 10^4). ν_{max} (CH_3CN) 2258, 2243, 1632, 1443, 1427, 1420, 1368, 1043, 918 cm^{-1}. δ_H ($CDCl_3$) 1.95 (CH_3 *para* to S*)*, 2.35 (CH_3 *ortho* to S), 6.93 (mesityl H), 7.16 (H-7 and H-7′, $J_{5,7}$ = $J_{5',7'}$ = 1.4 Hz, $J_{6,7}$ = $J_{6',7'}$ = 7.0 Hz), 7.22 (H-3 and H-3′, $J_{2,3}$ = $J_{2',3'}$ = 7.5 Hz, $J_{3,4}$ = $J_{3',4'}$ = 8.2 Hz), 7.50 (H-6 and H-6′, $J_{5,6}$ = $J_{5',6'}$ = 8.2 Hz, $J_{6,7}$ = $J_{6',7'}$ = 7.0 Hz), 7.60 (H-2 and H-2′, $J_{2,3}$ = $J_{2',3'}$ = 7.5, $J_{2,4}$ = $J_{2',4'}$ = 1.2 Hz), 7.67 (H-4 and H-4′, $J_{2,4}$ = $J_{2',4'}$ = 1.2 Hz, $J_{3,4}$ = $J_{3',4'}$ = 8.2 Hz), 7.82 (H-5 and H-5′, $J_{5,6}$ = $J_{5',6'}$ =8.2 Hz, $J_{5,7}$ = $J_{5',7'}$ = 1.4 Hz). Irradiation of Me *ortho* to S gave a 5% enhancement of the mesityl H (δ 6.93), a 1.4% enhancement of H-7 and H-7′ (δ 7.16) and a 1.1% enhancement of H-2 and H-2′ (δ 7.60). *m/*z 555 (M+1, 17%), 554 (M, 39), 372 (77), 277 (84), 262 (100), 254 (29), 229 (39), 151 (18), 103 (23), 91 (25), 69 (18), 57 (31), 56 (25), 39 (23).

The reaction of 1 with the potassium salt 5b (Table 1, entry 13). The reaction mixture from the treatment of **1** (0.76 g, 2.0 mmol) with **5b** prepared from mesitylenethiol (1.23 g, 8.0 mmol) and potassium t-butoxide (0.98 mg, 8.7 mmol) in DMSO (100 mL) was worked up in the usual manner. Chromatography with light petroleum as eluent followed by crystallization from EtOH gave **12** (0.11 g, 20%) identical with sample prepared above. Similarly the reaction in **entry 14** gave **12** (0.125 g, 45%).

Table 1, entry 15. The reaction mixture from the treatment of **1** (34 mg, 0.09 mmol) with **5b** prepared from mesitylenethiol (50 mg, 0.33 mmol) and potassium t-butoxide (40 mg, 0.036 mmol) in DMSO-d_9 (10 mL) was worked up in the usual manner. Chromatography with light petroleum as eluent to give a mixture of **12** and *mesityl 1–(8-deuteronaphthyl) sulfide* (**12-d_1**) (82% as determined by ^{1}H NMR spectroscopy with TNT as internal standard). 90% overall deuteration of the 8-position was determined by MS: *m/z* 281 (M+2, 6%), 280 (M+1, 12), 279 (100), 150 (66), 119 (15), 115 (15) and NMR spectroscopy.

Table 1, entry 16. The reaction mixture from the treatment of **1** (34 mg. 0.09 mmol) with the potassium salt **5c** prepared from mesitylenethiol-d_9 (57 mg, 0.35 mmol) and potassium t-butoxide (44 mg, 0.39 mmol) in DMSO (10 mL) was worked up in the usual manner. Chromatography with light petroleum as eluent gave *mesityl-d_9 1-naphthyl sulfide* (**12-d_9**) (78% as determined by ^{1}H NMR spectroscopy with TNT as internal standard).

Reaction of 1 with 6 (Table 1, entry 17). The reaction mixture from the treatment of **1** (0.15 g, 0.39 mmol) with the potassium salt **6** prepared from diethyl phosphite (0.22 mg, 1.6 mmol) and potassium t-butoxide (0.20 g, 1.8 mmol) in liquid ammonia (50 mL) was worked up in the usual

manner. Distillation gave **14** (68 mg, 56%) (Kugelrohr bp 65 °C/0.6 mbar) (identical by TLC and ^{1}H NMR spectroscopy with authentic sample prepared above).

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