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Photostimulated Reactions of *o*-Dihalobenzenes with Nucleophiles Derived from the 2-Naphthyl System. Competition between Electron Transfer, Fragmentation, and Ring Closure Reactions

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The photostimulated reaction of *o*-dihalobenzenes **2** with 2-naphthoxide ions **1-O** gave the substitution product on carbon 1 of the naphthyl moiety with retention of halogen (I, Br, and Cl) **3** as well as the ring closure product benzo[*b*]naphtho[1,2-*d*]furan (**4**), with product **3** being an intermediate in the formation of **4**. The products obtained in the photostimulated reaction of 2-naphthalenethiolate ions **1-S** with **2** depend on the halogens. When both nucleofugal groups are iodine, only the ring closure product benzo[*b*]naphtho[1,2-*d*]thiophene (**10**) is obtained. With *o*-bromoiodobenzene, the photostimulated reaction gave **10** and the substitution product on sulfur with retention of bromine, while with *o*-chloroiodobenzene the only observed product was the substitution product on sulfur with retention of chlorine. The photostimulated reaction of **2** with 2-naphthaleneselenolate ions **1–Se** gave the same amount of cyclized product benzo[*b*]naphtho[1,2-*d*]selenophene (**14**) and the substitution product on selenium without retention of halogen **15**, although in an overall low yield. It is suggested that all these reactions occur by the $S_{RN}1$ mechanism. Theoretical studies support the different behavior found with the nucleophiles derived from the 2-naphthyl system.

The aromatic radical nucleophilic substitution, or $S_{RN}1$, reaction has been shown to be an excellent route for performing nucleophilic substitution of unactivated aromatic compounds possessing suitable leaving groups. The mechanism of the reaction is a chain process. The propagation steps are shown in Scheme I.[1]

Scheme I depicts a nucleophilic substitution in which radicals and radical anions are intermediates. It has been shown that aromatic radicals are able to react by the $S_{RN}1$ mechanism with many different types of nucleophiles.[1] However, alkoxide ions do not couple with aryl radicals, and primary or secondary alkoxides reduce them to arenes.[2] On the other hand, anions from phenols react at the ortho and para carbon of their aromatic moieties.[3,4]

In regard to nucleophiles derived from the 2-naphthyl system, 2-naphthoxide ions **1-O** react with haloarenes only on carbon 1 of the naphthyl moiety. 2-Naphthalenethiolate ions **1-S** react mainly on the S atom and only to a small extent on carbon 1 of the naphthalene ring whereas 2-naphthaleneselenolate ions **1-Se** react exclusively on the Se atom.[5]

The bidentate behavior of these nucleophiles derived from the 2-naphthyl system led us to consider the possibility of performing a ring closure reaction in their reaction with an aromatic substrate bearing two leaving groups in ortho position. There are precedents of ring closure reactions with bidentate nucleophiles and *o*-dihalobenzenes.[6]

Scheme I

$$(RX)^{\bullet-} \rightarrow R^{\bullet} + X^{-} \quad (1)$$

$$R^{\bullet} + Nu^{-} \rightarrow (RNu)^{\bullet-} \quad (2)$$

$$(RNu)^{\bullet-} + RX \rightarrow RNu + (RX)^{\bullet-} \quad (3)$$

$$RX + Nu^{-} \rightarrow RNu + X^{-} \quad (4)$$

In the coupling reaction of 2-naphthoxide ions **1-O** with an *o*-halophenyl radical, a radical anion would be formed, which upon fragmentation in the chain propagation cycle of the $S_{RN}1$ mechanism has the possibility to generate an aromatic σ radical very close to the oxygen functionality. The fact that the intramolecular coupling between them would give a relative stable radical anion would increase the possibility of reaction.

In the case of 2-naphthalenethiolate **1-S** and 2-naphthaleneselenolate ions **1-Se**, the nucleophilic heteroatom reacts faster than the carbon 1 of the naphthyl moiety. Thus in the reaction of these nucleophiles with an *o*-halophenyl radical, the intermediate radical anion formed would fragment to give an aromatic σ radical close to the carbon 1 of the naphthyl moiety. The spacial proximity[7] between both reacting centers and the fact that the intramolecular coupling between them would give a relative stable radical would increase the possibility of the ring closure reaction.

We here report the photostimulated reaction of these bidentate nucleophiles derived from the 2-naphthyl system with *o*-dihalobenzenes in liquid ammonia.

Results and Discussion

2-Naphthoxide Ions (1-O). In the liquid ammonia photostimulated reaction of **1-O** with *o*-diiodobenzene **(2a)**

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[1] For reviews, see: (a) Norris, R. K. *The Chemistry of Functional Groups*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, UK, 1983; Supplement D, Chapter 16. (b) Rossi, R. A.; de Rossi, R. H. *Aromatic Substitution by the $S_{RN}1$ Mechanism*; ACS Monograph 178; American Chemical Society: Washington, DC, 1983.

[2] Bunnett, J. F.; Wamser, C. C. *J. Am. Chem. Soc.* **1967**, *89*, 6712. Bunnett, J. F.; Takayama, H. *J. Am. Chem. Soc.* **1968**, *90*, 5173. Rossi, R. A.; Bunnett, J. F. *J. Org. Chem.* **1973**, *38*, 1407.

[3] (a) Beugelmans, R.; Bois-Choussy, M. *Tetrahedron Lett.* **1988**, *29*, 1289. (b) Beugelmans, R.; Bois-Choussy, M.; Tang, Q. *Tetrahedron Lett.* **1988**, *29*, 1705. (c) Pierini, A. B.; Baumgartner, M. T.; Rossi, R. A. *Tetrahedron Lett.* **1988**, *29*, 3451.

[4] Petrillo, G.; Novi, M.; Dell'Erba, C.; Tavani, C.; Berta, G. *Tetrahedron* **1990**, *46*, 7977 and references cited therein.

[5] Pierini, A. B.; Baumgartner, M. T.; Rossi, R. A. *J. Org. Chem.* **1991**, *56*, 580.

[6] Pierini, A. B.; Baumgartner, M. T.; Rossi, R. A. *J. Org. Chem.* **1987**, *52*, 1089.

[7] Houk, K. N.; Tucker, J. A.; Dorigo, A. F. *Acc. Chem. Res.* **1990**, *23*, 107. Sherrod, M. J.; Menger, F. M. *Tetrahedron Lett.* **1990**, *31*, 459 and references cited therein.

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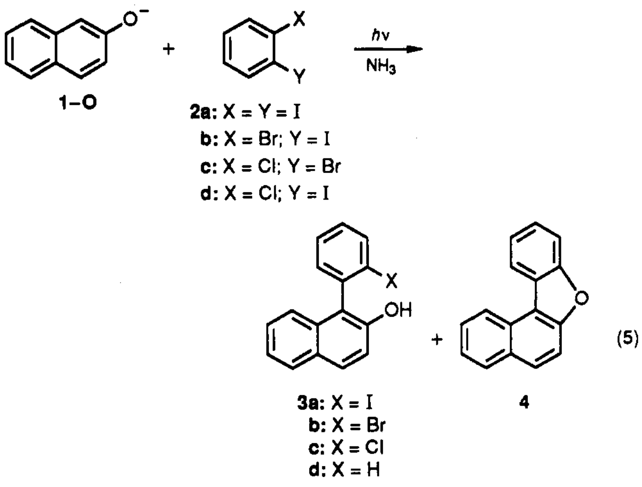
Table I. Photostimulated Reactions of *o*-Dihalobenzenes with Nucleophiles 1-O, 1-S, and 1-Se in Liquid Ammonia[a]

expt	nucleophile (M × 10^3)	substrate (M × 10^3)	X^- [b]	products (%)[c]	
1	**1-O** (11.2)	**2a** (10.2)	42	**3a** (20)	**4** (16)
2	**1-O** (34.0)	**2a** (10.2)	63	**3a** (45)	**4** (24)
3[d]	**1-O** (8.3)	**2a** (2.6)	66	**3a** (3)	**4** (44)
4	**1-O** (5.1)	**2a** (10.4)	31	**3a** (22)	**4** (15)
5[e]	**1-O** (34.0)	**2a** (10.2)	<3		
6	**1-O** (34.0)	**2b** (10.4)	I^- 61 Br^- 30	**3b** (35)	**4** (17)
7	**1-O** (34.0)	**2b** (10.4)	I^- 69 Br^- 42	**3b** (32)	**4** (24)
8[f]	**1-O** (34.0)	**2b** (10.4)	I^- 39 Br^- 31	**3b** (7)	**4** (13)
9	**1-O** (11.4)	**2c** (11.9)	Br^- 45 Cl^- 27	**3c** (17)	**4** (20)
10	**1-S** (9.8)	**2a** (9.7)	81		**10** (62)
11[f]	**1-S** (6.3)	**2a** (5.1)	63		**10** (51)
12[e]	**1-S** (9.8)	**2a** (5.1)	<3		
13	**1-S** (12.9)	**2b** (10.4)	I^- 100 Br^- 42	**11b** (56)	**10** (46)
14[f]	**1-S** (5.1)	**2b** (6.2)	I^- 35 Br^- 11	**11b** (26)	**10** (18)
15	**1-S** (13.9)	**2d** (10.9)	I^- 93	**11c** (81)	
16[f]	**1-S** (7.4)	**2d** (5.4)	I^- 21	**11c** (15)	
17	**1-S** (12.5)	**2c** (11.4)	Br^- 14	**11c** (3)	**10** (4)
18	**1-Se** (4.9)	**2a** (5.1)	80	**15** (15)	**14** (15)[g]

[a] Irradiation time: 180 min. [b] Quantified potentiometrically based on substrate concentration, considering two halogen per mole. [c] Quantified by GLC using the internal standard method. [d] Irradiation time: 300 min. [e] Dark reaction. [f] *p*-Dinitrobenzene (20 mol %) was added. [g] PhI was formed in 20% yield.

in the presence of an excess of potassium *tert*-butoxide, we obtained the substitution product **3a** (20%), the cyclized product **4** (16%), and a small amount of PhI (≈2%) (Table I, expt 1) (eq 5). The reduced substitution product **3d** was not detected by GLC compared with an authentic sample.[8]



1-O

2a: X = Y = I
b: X = Br; Y = I
c: X = Cl; Y = Br
d: X = Cl; Y = I

3a: X = I
b: X = Br
c: X = Cl
d: X = H

4

(5)

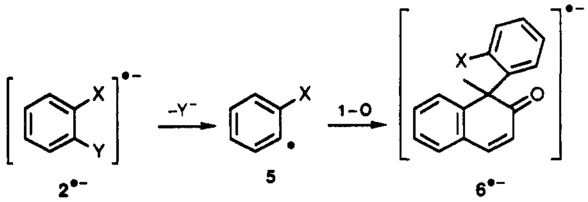
The overall percentage of products increased when a 3-fold excess of **1-O** was employed (Table I, expt 2). Under more dilute conditions and at a longer irradiation time (Table I, expt 3), **4** was the main reaction product (only 3% of **3a**). There is less overall reaction when the concentration of **1-O** is lowered, while no reaction was observed in the dark.

In the photostimulated reaction of **1-O** with *o*-bromoiodobenzene (**2b**), compounds **3b** and **4** were formed, the percentage of iodide ions eliminated being almost twice that of the bromide ions (Table I, expts 6 and 7). The photostimulated reaction was inhibited by 20 mol % of *p*-dinitrobenzene (*p*-DNB) (Table I, expt 8), a well known inhibitor of $S_{RN}1$ reactions.[1]

In the photostimulated reaction with *o*-bromochlorobenzene (**2c**), compounds **3c** (17%) and **4** (20%) were obtained, the elimination of bromide ions being 45% whereas that of chloride ions was only 27% (Table I, expt 9).

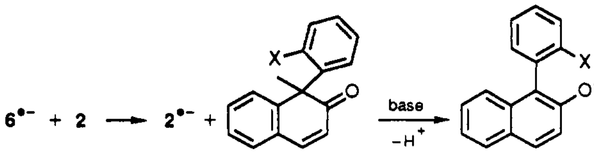
These results strongly support the $S_{RN}1$ mechanism as the reactions did not occur in the dark; they were inhibited by *p*-DNB, and the order of nucleofugicity of the leaving groups was I > Br > Cl. The formation of product **3** in all these reactions can be explained according to eqs 6 and 7.

Once **2** receives one electron from **1-O** under irradiation, it forms the radical anion $\mathbf{2}^{\bullet-}$, which fragments to give the *o*-halophenyl radical **5**. This radical reacts with **1-O** at carbon 1 of the naphthyl moiety to give the radical anion intermediate $\mathbf{6}^{\bullet-}$ (eq 6) which transfers its odd electron to **2** to give $\mathbf{2}^{\bullet-}$ and **6**. The latter is deprotonated to give the anion $\mathbf{3}^-$ in the basic reaction conditions (eq 7).



$\mathbf{2}^{\bullet-}$ **5** $\mathbf{6}^{\bullet-}$

(6)



6 $\mathbf{3}^-$

(7)

The formation of the ring closure product **4** could be rationalized through two different reaction paths. One possibility is the fragmentation of the radical anion $\mathbf{6}^{\bullet-}$ at the C–halogen bond to give the radical **7**, which is

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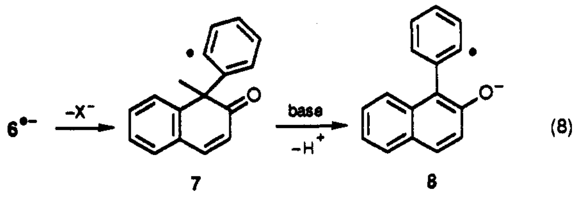
(8) For a preliminary communication, see: Pierini, A. B.; Baumgartner, M. T.; Rossi, R. A. *Tetrahedron Lett.* **1992**, *33*, 2323.

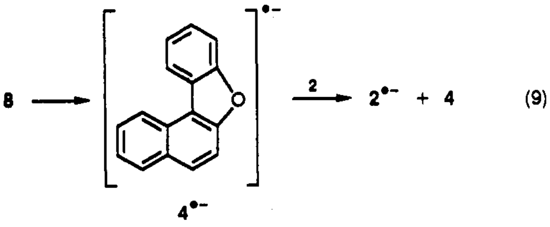
Table II. Ratio of Products 3a/4 vs Irradiation Time[a]

irradiation time (min)	3a/4	irradiation time (min)	3a/4
15	21.5	120	2.8
30	11.2	180	1.5
45	5.5	240	0.6
60	4.9	300	0.1

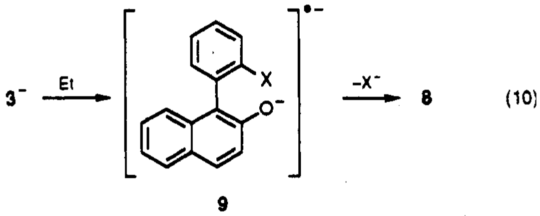
[a] Reaction conditions: [1-O] = 8.3×10^{-3} M; [2a] = 2.6×10^{-3} M.

deprotonated to give the radical and anion 8 (eq 8). The aromatic σ radical is located in this intermediate very close to the oxygen nucleophile and thus is able to couple with it to give the radical anion $4^{\bullet -}$, which by an ET reaction with 2 finally gives the cyclized product 4 (eq 9).





Another possibility is a stepwise process in which the anion of the substitution product 3 is an intermediate. This compound can receive another electron to give the radical dianion 9, which could fragment to the radical and anion 8 (eq 10). Intermediate 8 will finally give 4 as shown in eq 9. The reaction of 3a in presence of an excess of 1-O gives 4 under photostimulation in liquid ammonia (no reaction was observed in the dark).

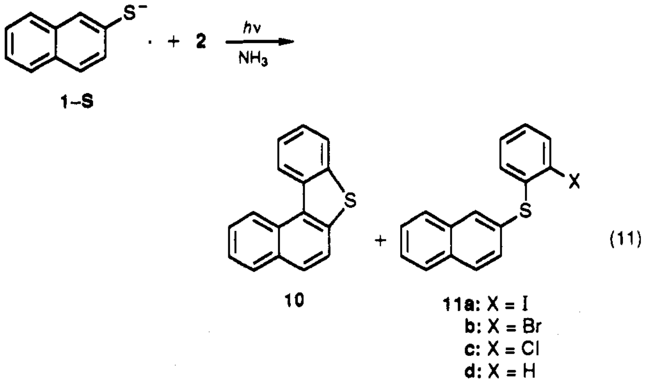


To estimate the degree of competition between the bond fragmentation and the ET reactions proposed for the radical anion $6^{\bullet -}$, we carried out the reaction of 2a with 1-O, taking samples at different times in order to quantify the ratio of products 3a/4. After 15 min the relationship was 21.7 (almost all the product was 3a). This ratio decreased with time, and after 300 min of irradiation the relationship was 0.1 (Table II). These results suggest that indeed the radical anion $6^{\bullet -}$ transfers the odd electron and a proton to give 3^- and that this anion is able to receive another electron to give the intermediate anion and radical 8, which cyclizes to 4.

Based on these results, we can propose a relative slow fragmentation rate for $6^{\bullet -}$ in the sense of eq 8. There are precedents indicating that radical anions with low LUMO have a slow rate of fragmentation and that even iodoarene radical anions are stable. For instance, it has been shown that the polarographic reduction of 9-(2-iodophenyl)-acridine gave reduction of the acridine ring without C–I bond fragmentation[9] and that the 1-iodoanthraquinone radical anion does not fragment unless it is irradiated.[10]

All these results show that 1-O reacts with *o*-dihaloarenes by the $S_{RN}1$ mechanism through a stepwise process in which the monosubstitution product 3 is an intermediate and that the oxygen functionality is able to react intramolecularly and quite efficiently with aromatic σ radicals to give the cyclized product. Even the reaction of 3^- with sodium metal in liquid ammonia afforded the cyclized product 4.[8]

2-Naphthalenethiolate Ions (1-S). The photostimulated reaction of 1-S with 2a gave 62% of the cyclized product benzo[*b*]naphtho[1,2-*d*]thiophene (10) (Table I, expt 10)[11] (eq 11). Neither the reduced product 11d nor the substitution product with retention of iodine 11a were formed.

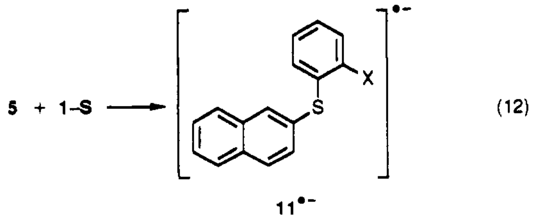


This reaction was slightly inhibited by *p*-DNB, and it does not occur in the dark (Table I, expts 11 and 12).

The photostimulated reaction of 1-S with 2b gave 100% of iodide ions, and only 42% of bromide ions, together with 46% of product 10 and 56% of product 11b (Table I, expt 13). In the reaction with 2d, only iodide ions were eliminated, the only product formed being 11c (Table I, expt 15). These reactions were inhibited by *p*-DNB (Table I, expts 14 and 16). With 2c, there was only 14% of bromide ion elimination and a very small amount of chloride ion elimination. Compound 10 was obtained in ca. 4%, together with 3% of 11c (Table I, expt 17).

All these results can be explained according to the propagation cycle of the $S_{RN}1$ mechanism, but with some additional steps, according to eqs 12–15.

Once 2 receives one electron from 1-S under irradiation, it fragments to give the *o*-halophenyl radical 5. This radical couples with 1-S mainly at the sulfur atom to give the radical anion $11^{\bullet -}$ (eq 12). This radical anion has two



$$11^{\bullet -} + 2 \longrightarrow 2^{\bullet -} + 11 \qquad (13)$$

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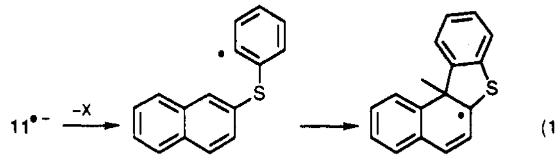
[9] Lingane, J. J.; Swain, C. G.; Fields, M. *J. Am. Chem. Soc.* **1943**, *65*, 1348.

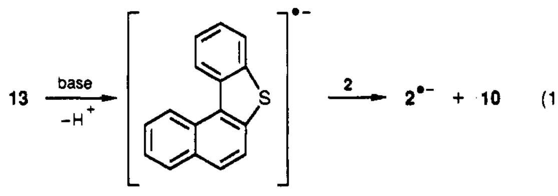
[10] Bethell, D.; Compton, R. G.; Wellington, R. G. *J. Chem. Soc., Perkin Trans. 2*, 1992, 147 and references cited therein.

[11] A small amount (ca. 8%) of a product ascribed to the disubstitution compound by mass spectrum was also isolated.

competitive reactions: ET to the substrate **2** to give product **11** (eq 13) or fragmentation to give halide ions and the radical **12**, which quite effectively attacks the carbon 1 of the naphthyl moiety to give the cyclized radical **13** (eq 14). This radical loses a proton in the basic reaction conditions to give the radical anion **10**$^{\bullet-}$ of the cyclized product, which by ET to the substrate **2** gives finally the product **10** observed. It has been previously shown that certain radicals are able to react with a base to give a radical anion which enters in the $S_{RN}1$ propagation cycle.[12]



12 13 (14)



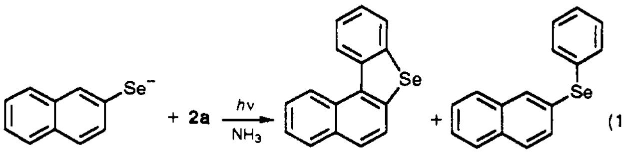
10•− (15)

When the substrate has two iodines as the nucleofugal groups (**2a**), the rate of fragmentation of the radical anion **11a**$^{\bullet-}$ is faster than the ET, thus only the cyclized product **10** is formed in high yield. When one of the leaving groups is iodine and the other is bromine, iodide ions are eliminated in ca. 100% yield and bromide ions in only a 42% yield, which is in agreement with the greater nucleofugicity of iodine compared with bromine. This result implies that in the radical anion **11b**$^{\bullet-}$, the rate of bond fragmentation is similar to the rate of ET reaction.

When the substrate has iodine and chlorine as leaving groups, only iodide ions are eliminated, and only the product **11c** is formed. This indicates that the rate of ET of the radical anion **11c**$^{\bullet-}$ is much faster than the C–Cl bond fragmentation.

On the other hand, when the substrate has bromine and chlorine as leaving groups, there is a decrease in the overall yield of the reaction, but in this case both products **11c** and **10** were observed, which suggests that the radical anion **11c** has similar ET and C–Cl bond fragmentation rates, probably because in this case the substrate **2c** is a poorer electron acceptor than **2d**, decreasing the intermolecular ET reaction and increasing the C–Cl bond fragmentation.

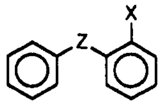
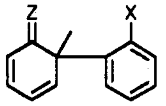
2-Naphthaleneselenolate Ions (1-Se). The photostimulated reaction of **1-Se** with **2a** gave 80% of iodide ions, but only 15% yield of the cyclized product benzo[*b*]naphtho[1,2-*d*]selenophene (**14**), 15% yield of reduced product **15**, and some tar (Table I, expt 18) (eq 16).



1-Se 14 15 (16)

Even though this reaction was performed under different experimental conditions (not shown in the table), there were always decomposition products and the overall low yield of reaction could not be modified.

Table III. AM1 Calculated Heat of Formation (kcal/mol) for Radical Anions (X = I)

radical anion	Z = O	Z = S
	22.5	39.4
	8.4	55.3

However, in this reaction there is an important yield of the reduction product **15**. The comparison of these results with those obtained in the reaction of **2a** with **1-S**, where the *only* product observed was the ring closure product **10**, suggests that in the radical **12** the ring closure reaction is faster than the reduction when the heteroatom is S while it becomes slower and similar to the reduction rate when it is replaced by Se. In this latter case both products are formed in similar yields.

Another possibility is that the cyclized product **14** is formed, and with our experimental condition (irradiation and basic medium) **14** decomposes.

Theoretical Studies. We next determined theoretically the properties of the radical anions formed in the coupling reaction between *o*-halophenyl radicals and **1-O** and **1-S** nucleophiles, including the electronic nature and energy differences as well as the possible effects of these factors in the fragmentation reaction. The calculations were performed with the semiempirical AM1 method[13,14] and the PhO$^-$ and PhS$^-$ ions were taken as representative.

In Table III are presented the heats of formation calculated for the carbon and heteroatom arylated radical anions formed in the reaction. The same as in the reaction of methyl radicals with PhO$^-$ ions,[15] the C-arylated radical anions are more stable than the corresponding O-arylated ones. For PhS$^-$ ions, the most stable radical anions are those corresponding to sulfur substitution.

According to these calculations, the unpaired spin distribution in the most stable radical anions **6**$^{\bullet-}$ (X = Cl, Br, I) is located mainly on the π system of the ketyl substituted ring which is separated from the *o*-halophenyl moiety by an sp^3 carbon atom.

In Table IV are presented the differences in energy between the π and σ (unpaired electron in the C–X bond) radical anion isomers while the charge and the unpaired spin distribution are shown in Figure 1.

As can be seen, changes in unpaired spin and negative charge distribution take place upon isomerization, the main geometric difference between the π and σ radical anions being the length of the C–X bond which is slightly longer in the σ isomer.

The difference in heat of formation $\Delta H_{\pi-\sigma}$ calculated for both **6**$^{\bullet-}$ isomers follows the order Cl > Br > I. If the energy difference between both isomers is taken as an

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(12) Russell, G. A.; Kim, G. H. *Tetrahedron Lett.* **1990**, *31*, 6273.

(13) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. G.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902, available from the Quantum Chemistry Program Exchange (QCPE), program 506.

(14) Geometries of stable species were calculated by minimizing the energy with respect to all geometrical variables. All stationary points were characterized by calculating force constants.

(15) Pierini, A. B.; Borosky, G. M.; Baumgartner, M. T. *Int. J. Quantum Chem.* **1992**, *44*, 759.

Table IV. AM1 Calculated Heat of Formation (kcal/mol) for Radical Anions $6^{\bullet-}$ and $11^{\bullet-}$

radical anion	halogen	radical anion type	ΔH_f	$\Delta H_{\pi-\sigma}$
$6^{\bullet-}$	Cl	π	−15.3	24.4[a]
		σ	9.1	
$6^{\bullet-}$	Br	π	−3.0	14.8
		σ	11.8	
$6^{\bullet-}$	I	π	8.4	10.9
		σ	19.3	
$11^{\bullet-}$	Cl	π	18.0	18.7[a]
		σ	36.7	
$11^{\bullet-}$	Br	π	28.6	8.2
		σ	36.8	
$11^{\bullet-}$	I	π	39.4	0.1
		σ	39.5	

[a] This value represents the $\pi - \sigma$ potential energy surface crossing point.

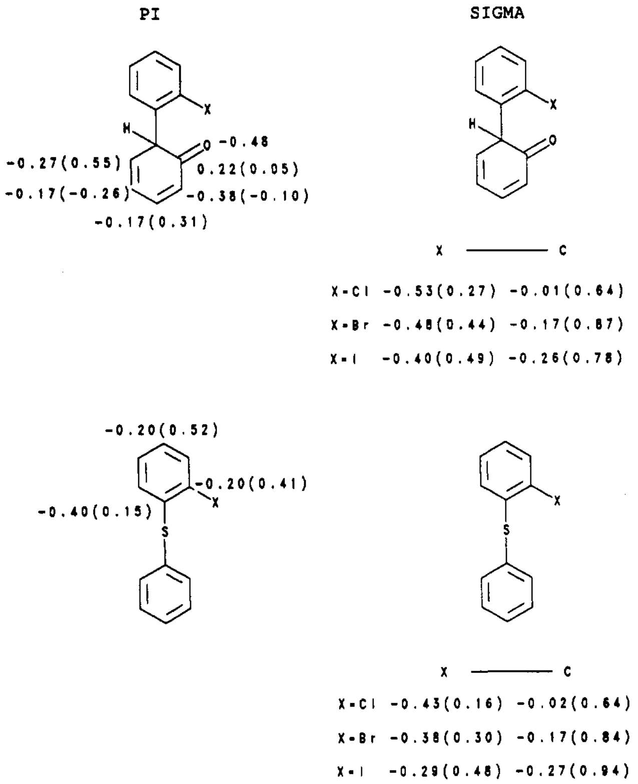

Figure 1. Charge and spin density (in parentheses) for $6^{\bullet-}$ and $11^{\bullet-}$.

indication of the possibility of the intramolecular ET (from the π system to the σ C–X bond) we can conclude, based on the experimental evidences, that for differences of 10 kcal/mol or higher and for the preferred spatial position calculated for both rings, the intramolecular ET (fragmentation in the sense of eq 8) is not favored in these systems. On the contrary, the intermolecular ET prevails leading to the compound with retention of halogen.

On the other hand, our calculations indicate that the radical dianion **9** has the extra electron localized in the C–I σ bond, which suggests a fast rate of fragmentation.

The most stable S-substituted radical anions are also of π nature, but in this case the charge and spin distribution are mainly located on the halogen-substituted aryl ring (Figure 1). The difference in heat of formation for both radical anions follows the same order as that calculated for the O radical anions. Comparison of the values indicates that the intramolecular ET is not favored for X = Cl, while ET takes place easily for X = I with X = Br falling in between.

This theoretical behavior proposed is confirmed by our experimental results: the cyclized product **10** was the only observed product in the reaction of **1-S** with **2a**, **11c** was formed together with **10** in the reaction of **1-S** with **2b**, and **11d** was the only product observed in the reaction with **2d**.

Experimental Section

General Method. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 200 nuclear magnetic resonance spectrometer, and all spectra are reported in parts per million relative to Me_4Si (δ), with $CDCl_3$ as the solvent. Mass spectra were obtained with a Finnigan 3300 f-100 mass spectrometer. Infrared spectra were recorded on a Nicolet FTIR 5-SXC spectrophotometer. Gas chromatographic analyses were performed on a Shimadzu GC-8A or Konik instrument with a flame ionization detector and a Shimatzu Cr-3A or Spectra Physics SP-2400 data system, using a column packed with 5% 0V17 on Chromosorb G (1.5 m × 3 mm). Column chromatography was performed on silica gel (70–270-mesh ASTM). Irradiation was conducted in a reactor equipped with four 250-W lamps emitting maximally at 350 nm (Philips Model HPT, water refrigerated). Potentiometric titration of halide ions was performed with a pH meter (Seybold Wien) using a Ag/Ag$^+$ electrode and a $AgNO_3$ standard. Melting points were obtained with a Büchi 510 apparatus and are not corrected. The high resolution mass spectra were run at the University of Chicago.

Materials. 2-Naphthol (Merck), 2-naphthalenethiol (Aldrich), potassium *tert*-butoxide (Fluka), *o*-diiodobenzene (Aldrich), *o*-bromoiodobenzene (Aldrich), *o*-bromochlorobenzene (Aldrich), and *o*-chloroiodobenzene (Aldrich) were commercially available and used as received. 2-Naphthaleneselenolate ions were prepared from di(2-naphthyl) diselenide and potassium metal in liquid ammonia. Di(2-naphthyl) diselenide was prepared from selenium metal and 2-iodonaphthalene by photostimulated reaction in liquid ammonia.[16]

Photostimulated Reaction of 2-Naphthoxide Ions with *o*-Diiodobenzene. The following procedure is representative of these reactions. The equipment used has been previously described.[1b] To 130 mL of distilled ammonia were added potassium *tert*-butoxide (7 mmol) and then 2-naphthol (3 mmol). After 15 min *o*-diiodobenzene (1.5 mmol) was added and the reaction mixture was irradiated for 180 min. The reaction was quenched with an excess of ammonium nitrate. The ammonia was allowed to evaporate and water (50 mL) was added to the residue, and it was extracted twice with diethyl ether (50 mL each). The iodide ions in the aqueous solution were determined potentiometrically. The organic extract was quantified by GLC (internal standard method). The solvent was removed under reduced pressure. The residue, after column chromatography on silica gel [eluted with petroleum ether:diethyl ether (90:10)], gave benzo[*b*]naphtho[1,2-*d*]furan [mp 31 °C (lit.[8,17] mp 31 °C): ^{1}H NMR δ 7.43–8.67 (m); ^{13}C NMR (C quaternary) 154.22, 155.82; IR (KBr) 3064, 2074, 1214, 803, 740 cm^{-1}; MS (25 eV, relative intensity) *m/e* 220 (4), 219 (36), 218 (M$^+$, 100), 190 (13), 189 (58), 164 (4), 163 (13)] and 1-(2-iodophenyl)-2-naphthol[8] [^{1}H NMR (60 MHz), CCl_4 (TMS) δ 4.83 (s, OH), 7.04–8.15 (m); ^{13}C NMR (C quaternary) 102, 149.65, 153.21; MS (25 eV, relative intensity) *m/e* 348 (2), 347 (18), 346 (M$^+$, 100), 220 (27), 219 (97), 218 (51), 201 (38), 191 (69), 190 (28), 189 (98), 165 (16)].

Reaction of 2-Naphthoxide Ions with *o*-Diiodobenzene in the Dark. Following the same procedure as described before, except that the reaction flask was wrapped with aluminum foil, the iodide ion liberated was found in less than 3% yield after 180 min.

1-(2-Bromophenyl)-2-naphthol was isolated by column chromatography and eluted with petroleum ether:diethyl ether (90:10):[8] MS (25 eV, relative intensity) *m/e* 300 (11), 298 (11), 219 (41), 218 (100), 191 (30), 190 (12), 189 (52), 163 (7).

1-(2-Chlorophenyl)-2-naphthol was isolated by column chromatography and eluted with petroleum ether:diethyl ether

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(17) Russell, P. B.; Osdene, T. S. *J. Org. Chem.* **1966**, *31*, 2646.

(90:10):[8] MS (25 eV, relative intensity) *m/e* 256 (6), 255 (3), 254 (17), 219 (27), 218 (29), 201 (16), 191 (13), 189 (34).

Benzo[*b*]naphtho[1,2-*d*]thiophene was isolated by column chromatography and eluted with petroleum ether, mp 100–1 °C (lit.[18] mp 101–2 °C): MS (25 eV, relative intensity) *m/e* 236 (6), 235 (16), 234 (100), 232 (19), 203 (1), 202 (7), 200 (3), 190 (1), 189 (8), 188 (3); IR (KBr) 3054, 2964, 2928, 2856, 1712, 1429, 1362, 1210, 1134, 793, 719, 655, 562, 500 cm^{-1}.

2-Bromophenyl 2-naphthyl sulfide was isolated by column chromatography and eluted with petroleum ether: MS (70 eV, relative intensity) *m/e* 318 (10), 317 (32), 316 (100), 315 (33), 314 (99), 236 (65), 235 (90), 234 (90), 233 (24), 204 (2), 203 (9), 202 (38), 201 (5), 191 (2), 190 (21), 189 (14), 188 (10), 127 (35), 126 (22); MS (high resolution) 315.9766 (calcd 315.9744), 313.9801 (calcd 313.9765); ^{13}C NMR (C quaternary) 138.73, 133.89, 123.31; (CH) 133.03, 132.88, 130.20, 129.86, 129.31, 127.77, 127.68, 126.83, 126.68.

2-Chlorophenyl 2-naphthyl sulfide was isolated by column chromatography and eluted with petroleum ether: MS (70 eV, relative intensity) 274 (1), 273 (4), 272 (23), 271 (10), 270 (60), 237 (4), 236 (22), 235 (100), 234 (94), 233 (7), 232 (7), 203 (4), 202 (17), 201 (2), 200 (2), 191 (1), 190 (2), 187 (7), 127 (16); MS (high resolution) 272.0237 (calcd 272.0241), 270.0263 (calcd 270.0270); ^{13}C NMR (C quaternary) 136.50, 133.87, 133.18, 132.84; (CH) 162.59, 130.20, 130.06, 129.76, 129.26, 127.62, 127.28, 126.17, 126.71.

Photostimulated Reaction of 2-Naphthaleneselenolate Ions with *o*-Diiodobenzene. To 150 mL of distilled ammonia were added 2,2-dinaphthyl diselenide (1 mmol) and then potassium metal in excess in small pieces. When all the substrate had reacted, *o*-diiodobenzene (1.6 mmol) was added and the reaction mixture was irradiated for 180 min. The residue, after column chromatography on silica gel (eluted with petroleum ether), gave benzo[*b*]naphtho[1,2-*d*]selenophene [^{1}H NMR δ 9.11–7.21 (m); ^{13}C NMR δ (C quaternary) 139.393, 135.511, 132.319, 130.348, 129.502; MS (eV, relative intensity) *m/e* 288 (1), 286 (6), 284 (38), 282 (100), 281 (20), 280 (55), 279 (22), 278 (26), 207 (2), 205 (4), 203 (17), 202 (59), 201 (21), 200 (24); MS (high resolution) 281.9975 (calcd 281.9948)] and 2-naphthyl phenyl selenide [mp = 52–3 °C; ^{1}H NMR δ 7.2–8 (m); ^{13}C NMR δ (C quaternary) 132.387, 130.457, 127.754, 126.213; MS (eV, relative intensity) *m/e* 288 (2), 287 (3), 286 (15), 285 (6), 284 (42), 282 (26), 281 (8), 280 (10), 207 (4), 206 (9), 205 (31), 204 (100), 203 (32), 202 (24), 201 (3)]. This product was compared with an authentic product prepared by the photostimulated reaction of benzeneselenolate ion and 2-iodonaphthalene in liquid ammonia.

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