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PHOTOSTIMULATED REACTIONS OF HALOARENES WITH BENZENESELENATE IONS BY THE $S_{RN}1$ MECHANISM. COMPETITION BETWEEN ELECTRON TRANSFER AND FRAGMENTATION OF RADICAL ANION INTERMEDIATES

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The photostimulated reaction of *p*-iodoanisole (*p*-IAn) and 2-bromopyridine with $PhSe^-$ ions in liquid ammonia gave Ph_2Se, ArSePh and Ar_2Se (Ar = *p*-anisyl, 2-pyridyl) by the $S_{RN}1$ mechanism. These products are formed due to the competition between two steps of the proposed mechanism, the fragmentation of the radical anion intermediate formed in the coupling of aryl radicals with the $PhSe^-$ ion, and the electron transfer from the radical anion to an electron acceptor. These photostimulated reactions were carried out in different solvents in order to study their influence on the rates of the two competing reactions. They were also studied at high concentrations of *p*-haloanisoles in acetonitrile (ACN), and it was found that the straightforward substitution product AnSePh was formed only at a 2.5 M concentration of *p*-IAn, 7·8 M *p*-BrAn and 15·6 M *p*-ClAn. The last compound did not react with the $PhSe^-$ ion at concentrations as high as 15·6 M, but the substitution reaction took place in the presence of 0·025 M *p*-IAn (entrainment reaction). The relative reactivity of $PhSe^-$ vs PhS^- toward 2-quinolyl radicals was studied and it was found that $PhSe^-$ reacts 2·7 times faster than PhS^- in ACN.

INTRODUCTION

The mechanism known as radical nucleophilic substitution or $S_{RN}1$ is well known.[1] The three main steps of the propagation cycle are outlined in Scheme 1.

$$(RX)^{-\cdot} \longrightarrow R^{\cdot} + X^- \quad (1)$$

$$R^{\cdot} + Nu^- \longrightarrow (RNu)^{-\cdot} \quad (2)$$

$$(RNu)^{-\cdot} + RX \longrightarrow RNu + (RX)^{-\cdot} \quad (3)$$

$$RX + Nu^- \longrightarrow RNu + X^- \quad (4)$$

Scheme 1

Summation of these three steps leads to equation (4), which is a nucleophilic substitution but with radical and radical anions as intermediates. When there is no spontaneous formation of the radical anion of the substrate to initiate the reaction, it can be catalysed with solvated electrons in liquid ammonia[2] or with electrons from an electrode,[3] but the most common initiation step is photostimulation.[1,4]

Although it is known that many systems react to give a substitution product, such as in equation (4), it is also known that in some systems other products are formed. For instance, in the photostimulated reaction of *p*-iodoanisole (*p*-IAn, **1a**) or 2-bromopyridine (2-BrPy, **1b**) with benzeneselenate ($PhSe^-$) ions **2** not only the straightforward substitution product ArSePh (**3**) was obtained, but also the symmetrical diphenyl selenide (**4**) and the diaryl selenide (**5**) were formed [equation (5)].[5]

$$\underset{\mathbf{1}}{ArX} + \underset{\mathbf{2}}{PhSe^-} \xrightarrow{h\nu} \underset{\mathbf{3}}{ArSePh} + \underset{\mathbf{4}}{Ph_2Se} + \underset{\mathbf{5}}{Ar_2Se} \quad (5)$$

1a = *p*-IAn **3a**, Ar = *p*-anisyl **5a**, Ar = *p*-anisyl
1b = 2 – BrPy **3b**, Ar = 2-pyridyl **5b**, Ar = 2-pyridyl

This scrambling of aromatic rings has been ascribed to a reversible coupling and fragmentation of the radical anion intermediates during the $S_{RN}1$ chain process, and more steps should be added to Scheme 1 to account for the products obtained, as shown in Scheme 2.[5,6]

The aryl phenyl selenide radical anion $\mathbf{6}^{-\cdot}$ formed by coupling of the aryl radical with $PhSe^-$ ion undergoes three competitive reactions, namely, reversion to start-

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$$ArX + PhSe^- \xrightarrow{h\nu} (ArX)^{-\cdot} + PhSe^{\cdot} \quad (6)$$

$$(ArX)^{-\cdot} \longrightarrow Ar^{\cdot} + X^- \quad (7)$$

$$Ar^{\cdot} + PhSe^- \underset{k_f}{\overset{k_c}{\rightleftharpoons}} (ArSePh)^{-\cdot} \underset{k_r'}{\overset{k_f'}{\rightleftharpoons}} ArSe^- + Ph^{\cdot} \quad (8)$$

$$\mathbf{6}^{-\cdot}$$

$$\downarrow k_f[ArX]$$

$$ArSePh + (ArX)^{-\cdot}$$

$$\mathbf{3}$$

$$Ar^{\cdot} + ArSe^- \rightleftharpoons (Ar_2Se)^{-\cdot} \xrightarrow{k_f[ArX]} Ar_2Se + (ArX)^{-\cdot} \quad (9)$$

$$\mathbf{5}$$

$$Ph^{\cdot} + PhSe^- \rightleftharpoons (Ph_2Se)^{-\cdot} \xrightarrow{k_f[ArX]} Ph_2Se + (ArX)^{-\cdot} \quad (10)$$

$$\mathbf{4}$$

Scheme 2

ing materials, electron transfer to the substrate to give the substitution product **3** and fragmentation of the Ph—Se bond to give the areneselenate ion $ArSe^-$ and phenyl radical [equation (8)]. In equation (8) two new intermediates are formed, $ArSe^-$ and phenyl radical. They can further react with each other to give the same radical anion $\mathbf{6}^{-\cdot}$, or they can diffuse apart and $ArSe^-$ competes as a nucleophile with aryl radical to give ultimately **5** [equation (9)], whereas phenyl radical can be trapped by $PhSe^-$ ion to give **4** [equation (10)].

The fragmentation of the radical anion $\mathbf{6}^{-\cdot}$ occurs because the energy levels of the antibonding π^* MO of the aromatic system and the antibonding σ^* MO of the C—Se bonds are close enough, and from the antibonding σ^* MO fragmentation occurs [equation (11)].[6,7]

$$Ar^{\cdot} + {}^-SePh \rightleftharpoons [Ar\overset{-}{-}SePh \leftrightarrow ArSe\overset{-}{-}Ph] \rightleftharpoons ArSe^- + Ph^{\cdot} \quad (11)$$

σ^* radical anion

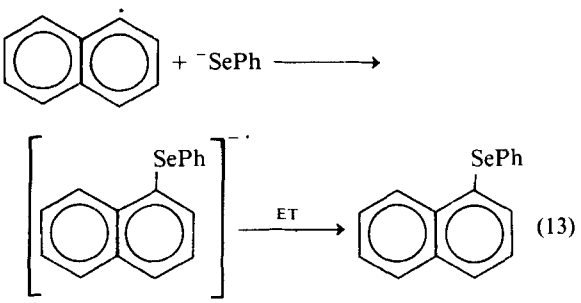
These scrambling reactions have been found not only with $PhSe^-$ ions but also with $PhTe^-$,[8] Ph_2As^- and Ph_2Sb^- ions,[9] so we consider it important to establish how to avoid these scrambling reactions.

One possibility to avoid the fragmentation of radical anion intermediates, such as $\mathbf{6}^{-\cdot}$, is by increasing its stability, which can be done by lowering its antibonding π^* MO.[6] For instance, the photostimulated reactions of 1-chloronaphthalene (**1c**) or 2-chloroquinoline (**1d**) with $PhSe^-$ ions in liquid ammonia given good yields of the substitution product 1-naphthyl phenyl selenide (**3c**) and 2-quinolyl phenyl selenide (**3d**), respectively, by the $S_{RN}1$ mechanism of nucleophilic substitution [equation (12)].[8]

$$\underset{\mathbf{1}}{ArX} + \underset{\mathbf{2}}{PhSe^-} \xrightarrow{h\nu} \underset{\mathbf{3}}{ArSePh} + X^- \quad (12)$$

1c = 1-chloronaphthalene — **3c**, Ar = 1-naphthyl
1d = 2-chloroquinoline — **3d**, Ar = 2-quinolyl

In these cases, the radical anions formed by coupling of 1-naphthyl or 2-quinolyl radicals with $PhSe^-$ ion fragment too slowly in comparison with the electron-transfer reaction to the substrate, and only the substitution product is obtained without scrambled products. In this case a π^* radical anion is formed [equation (13)].[6]



(13)

π^* radical anion

When it is not possible to lower the antibonding π^* MO of the aromatic system, and considering that there is a competition between the rate of fragmentation (k_f) and the rate of ET [k_f(ArX)] [equation (8)], the scrambling reaction could be avoided by increasing the stability of the radical anion intermediate when changing the solvent, or increasing the rate of ET by means of increasing the concentration of the acceptor ArX.

It is known that the fragmentation rate of radical anions depends on the temperature and the solvent.[10] Saveant and Thiebault[10a] studied the rate of fragmentation of halobenzophenones radical anions in liquid ammonia, acetonitrile (ACN) and dimethylformamide (DMF) at different temperatures. For instance, they found that the rate of fragmentation of 4-bromobenzophenone radical anion is $2 \times 10^5 s^{-1}$ in liquid ammonia, $8{\cdot}2 \times 10^4 s^{-1}$ in DMF and $2{\cdot}4 \times 10^3 s^{-1}$ in ACN at 20 °C (extrapolated), but in liquid ammonia it was $5{\cdot}9 \times 10^2 s^{-1}$ at −40 °C.

It is well known that $S_{RN}1$ reactions also occur in solvents other than liquid ammonia,[1b,3,11] so we decided to study the effect of the different solvents and different concentrations of *p*-haloanisoles (*p*-XAn) on the scrambling of aromatic rings in the photostimulated reaction with $PhSe^-$ ions.

The relative reactivity of PhS^- and $PhSe^-$ ions toward 2-quinolyl radicals has been studied. The determined ratio k_{PhSe^-}/k_{PhS^-} was 5·8 in liquid ammonia.[5]

We studied this relative reactivity in ACN in order to determine the solvent effect on the relative reactivity of pair of nucleophiles toward aromatic radicals.

RESULTS

Reactions in different solvents

The nucleophile $PhSe^-$ was insoluble in dioxane, and there was no reaction with *p*-IAn under irradiation (expt 5, Table 1). However, $PhSe^-$ ions were soluble in dioxane with 6% v/v of DMSO (the minimum amount of DMSO to dissolve the KPhSe), and in this reaction medium the photostimulated reaction gave the same three selenides as in the reaction in liquid ammonia together with a ca 10% yield of the reduction product anisole. The photostimulated reaction of 2-BrPy in dioxane–6% DMSO gave the three selenides as in liquid ammonia (expt 7, Table 1), although in an overall lower yield. Irradiation of only the nucleophile $PhSe^-$ under the same experimental conditions did not give Ph_2Se (expt 8, Table 1).

In *t*-BuOH–water there was no reaction with 2-BrPy. In pure *t*-BuOH the only product detected was 2-pyridyl phenyl selenide, although in low yield (Expts 10 and 11, Table 1).

In ACN the photostimulated reaction with *p*-IAn gave the three selenides as in liquid ammonia, but in relative lower yields (expt 12, Table 1). 2-BrPy gave the three selenides although in even lower yields (expt 13, Table 1).

The photostimulated reaction of 1-bromonaphthalene or **1d** with $PhSe^-$ ions in ACN gave good yields of the straightforward substitution product without scrambling of aromatic rings (expts 14 and 15, Table 1). The same behaviour was observed in liquid ammonia as reported previously.[5,8]

The photostimulated reaction of **1d** with PhS^- ion as nucleophile gave good yields of 2-quinolyl phenyl sulphide (expt 16, Table 1). There was some reaction in the dark (16% yield of Cl^- ions) which was inhibited by *p*-dinitrobenzene (expts 17 and 18, Table 1).

Table 1. Photostimulated reactions of aryl and hetaryl halides with $PhSe^-$ ions in different solvents[a]

Expt	ArX[b]	Concentration ($M \times 10^3$)	$PhSe^-$ ($M \times 10^3$)	Solvent	Product yields (%)[c]			
					ArSePh	Ar_2Se	Ph_2Se	ArH
1[d]	*p*-IAn	36	36	NH_3	25	19	20	[e]
2[d]	2-BrPy	25	25	NH_3	72	2	4·5	[e]
3[f]	1-ClNp	16	34	NH_3	73	0	0	[e]
4[d]	2-ClQ	25	25	NH_3	54	0	0	[e]
5	*p*-IAn	39	90	Dioxane	<1	–	–	–
6	*p*-IAn	18	45	Dioxane–6% DMSO	18	10	22	10
7	2-BrPy	19	36	Dioxane–6% DMSO	12	3	5	
8	–	–	45	Dioxane–6% DMSO			<1	
9	2-BrPy	83	83	*t*-BuOH–H_2O (1 : 1)	<1			
10	2-BrPy	33	82	*t*-BuOH	16	[g]	[g]	
11	2-BrPy	13	32	*t*-BuOH	18	[g]	[g]	
12	*p*-IAn	19	63	ACN	17	7	8	9
13	2-BrPy	26	63	ACN	13	2	2	1
14	1-BrNp	25	63	ACN	88	0	0	[e]
15	2-ClQ	25	63	ACN	70	0	0	1
16	2-ClQ	25	73[h]	ACN	94	0	0	[e]
17[i]	2-ClQ	26	61[h]	ACN	[j]	0	0	[e]
18[i,k]	2-ClQ	26	61[h]	ACN	0[l]	0	0	[e]

[a] Irradiation time 4 h at room temperature.
[b] An = anisyl; Py = pyridyl; Np = naphthyl; Q = quinolyl.
[c] Determined by GLC, using the internal standard method.
[d] Ref. 5.
[e] Not quantified.
[f] Ref. 8.
[g] Not detected by GLC.
[h] PhS^- ions as nucleophile.
[i] Dark reaction.
[j] Cl^- ions 16% yield; the substitution product was detected but not quantified.
[k] 20 mol% of *p*-dinitrobenzene was added.
[l] Cl^- ion in ca 5% yield.

Table 2. Photostimulated reactions of *p*-haloanisoles with $PhSe^-$ in acetonitrile[a]

Expt	IAn (M)	BrAn (M)	ClAn (M)	I^- (%)	X^- (%)	Product yields (%)[b] AnH	Ph_2Se	PhSeAn	An_2Se
1	0·019	–	–	[c]	–	9	8	17	7
2	1·0	–	–	93	–	5	2	68	⩽1
3	2·0	–	–	89[d]	–	5	2	56	⩽1
4	2·5	–	–	100	–	10	0	67	0
5	0·024	2·0	–	23	18[e]	8	5	23	5
6	0·025	3·9	–	26	13[e]	10	⩽1	22	⩽1
7	0·024	7·8	–	21	35[e]	10	0	31	0
8	–	7·8	–	–	34[e]	3	0	26	0
9	0·025	–	3·9	19	22[f]	4	8	28	8
10	0·025	–	7·8	24	24[f]	10	5	25	3
11	0·025	–	11·7	18	32[f]	16	3	20	1
12	0·025	–	15·6	18	22[f]	12	⩾1	13	0
13	–	–	15·6	–	⩽5[f]	0	0	0	0

[a] Irradiation time 4 h at room temperature; An = *p*-anisyl; $PhSe^-$ = 0·063 M.
[b] Determined by GLC using the internal standard method.
[c] Not quantified.
[d] Irradiation time 2 h.
[e] Bromide ions.
[f] Chloride ions.

Reactions with different concentrations of *p*-Haloanisoles in ACN

The photostimulated reaction of *p*-IAn (0.019 M) with $PhSe^-$ ions (0·063 M) gave PhSeAn (17%), Ph_2Se (8%) and An_2Se (7%) (expt 1, Table 2). When the photostimulated reaction was performed with *p*-IAn at 1·0 M concentration, PhSeAn was formed in 68% yield with an important decrease in the symmetrical selenides (expt 2, Table 2). When the concentration of **1a** was increased to 2·5 M, the only product formed was PhSeAn (expt 4, Table 2).

The photostimulated reaction of *p*-IAn (0·024 M) with $PhSe^-$ ions (0·063 M), but in the presence of *p*-BrAn (2 M), gave more AnSePh and less symmetrical selenides (expt 5, Table 2). In the presence of *p*-BrAn (3·9 M), the symmetrical selenides were formed in ⩽1% yield; AnSePh was the only product formed when *p*-BrAn was present at 7·8 M (expt 7, Table 2). The photostimulated reaction of *p*-BrAn (7·8 M) and $PhSe^-$ (0.063 M) also gave only AnSePh.

The photostimulated reaction of *p*-IAn (0·025 M) with $PhSe^-$ ions (0·063 M) and *p*-ClAn (3·9 M) gave almost the same results as in the absence of *p*-ClAn. However, an increase in the concentration of *p*-ClAn resulted in a decrease in the symmetrical selenides, which almost disappeared at a *p*-ClAn concentration of 15·6 M. There was no photostimulated reaction of *p*-ClAn (15·6 M) with $PhSe^-$ ions in the absence of *p*-IAn (expt 13, Table 2).

Competition experiments. Relative Reactivity of $PhSe^-$ and PhS^- ions toward 2-quinolyl radicals in ACN

Once the yields of the substitution products 2-quinolyl phenyl sulphide (PhSQ) and 2-quinolyl phenyl selenide (PhSeQ) had been determined in the photostimulated reaction of 2-chloroquinoline with PhS^- and $PhSe^-$ ions in excess, it was possible to calculate k_{PhSe^-}/k_{PhS^-} by using equation (14) (see Table 3), where $[PhS^-]_0$ and

Table 3. Competition experiments of 2-chloroquinoline with PhS^- and $PhSe^-$ ions in acetonitrile[a]

2-ClQ (M × 10^3)	PhS^- (M × 10^3)	$PhSe^-$ (M × 10^3)	2-QSPh (%)[b]	2-QSePh (%)[b]	k_{PhSe^-}/k_{PhS^-} ratio
10	31	36	21	70	3·10
10	46·5	20	51	49	2·52
10	36·6	31	35	65	2·47
					Av. 2·7 ± 0·3

[a] Irradiation time 4 h at room temperature 2-ClQ = 2-chloroquinoline; 2-QSPh = 2-quinolyl phenyl sulphide; 2-QSePh = 2-quinolyl phenyl selenide.
[b] Determined by GLC using the internal standard method.

$[PhSe^-]_0$ are the initial concentrations and $[PhSQ]_t$ and $[PhSeQ]_t$ are the concentrations of the products at time t.[5,12] This equation is based on the assumption that the reactions of both nucleophiles with the 2-quinolyl radicals are first order in the anions.

$$\frac{k_{PhSe^-}}{k_{PhS^-}} = \frac{\ln\left(\frac{[PhSe^-]_0}{[PhSe^-]_0 - [PhSeQ]_t}\right)}{\ln\left(\frac{[PhS^-]_0}{[PhS^-]_0 - [PhSQ]_t}\right)} \qquad (14)$$

We found that $PhSe^-$ ions are 2·7 times more reactive than PhS^- ions toward 2-quinolyl radicals in ACN.

DISCUSSION

It is known that the fragmentation rate of radical anions is solvent dependent because, in the transition state for the fragmentation step of a radical anion which has the negative charge delocalized over the whole molecule, the charge has to be localized on the bond which fragments;[7a] more polar solvents stabilize this transition state, increasing the rate of the fragmentation step.[13]

In the photostimulated reactions in dioxane there was no reaction owing to the insolubility of the nucleophile in this solvent. The nucleophile was soluble in dioxane–6% DMSO. In this solvent mixture, in which there is an apparent decrease in the polarity of the bulk solvent, we obtained almost the same results as in liquid ammonia. The expected decrease in the fragmentation rate by decreasing the polarity of the solvent was probably cancelled by the almost 60 °C difference in temperature of the reaction from liquid ammonia (−33 °C) to room temperature of this solvent mixture.

In *tert*-butyl alcohol–water (1 : 1) there was no reaction of 2-BrPy with $PhSe^-$ ions. In pure *tert*-butyl alcohol there was some reaction of 2-BrPy with the nucleophile, and no scrambling could be detected. In this case the low polarity of *tert*-butyl alcohol decreases the fragmentation rate of the radical anion intermediate.

The photostimulated reaction in ACN of **1a** or **1b** gave scrambling of products, and 1-bromonaphthalene or **1d** gave only the substitution product. This solvent behaved as liquid ammonia, both being of similar polarity. However, when the reactions of **1a** were performed with increasing concentrations, there was a decrease in the scrambled products, and at 2·5 M only the substitution product AnSePh was formed.

In the photostimulated reaction of **1a** with $PhSe^-$ and in the presence of *p*-BrAn at high concentration there was also a decrease in the scrambled products, but now the concentration of *p*-BrAn necessary to prevent the fragmentation was 7.8 M.

p-BrAn (0·045 M) reacts sluggishly with $PhSe^-$ (0·045 M) in liquid ammonia ($\leqslant 5\%$).[8] In ACN and at 7·8 M *p*-BrAn there was a 26% yield of the substitution product PhSeAn without scrambling of the products.

In the photostimulated reaction of **1a** with $PhSe^-$ in the presence of *p*-ClAn there was a decrease in the scrambled product only at high concentrations of *p*-ClAn. In order to obtain only the substitution product, a concentration as high as 15·6 M of *p*-ClAn was necessary.

p-ClAn reacted neither under photostimulation in liquid ammonia[8] nor in ACN at 15·6 M. The fact that in the presence of *p*-IAn (0·025 M) and 15·6 M *p*-ClAn only PhSeAn was formed indicates that *p*-IAn initiates the reaction, and the radical anion intermediate formed in the coupling of *p*-anisyl radical with $PhSe^-$ transfers its odd electron to *p*-ClAn (*entrainment* reaction[1] of *p*-ClAn by *p*-IAn).

Taking into account that the rate of fragmentation of the radical anion intermediate competes with the rate of the electron transfer (ET) to the substrate, and that the rate of ET depends on, in addition to solvent and temperature, the reduction potential of both species,[14] the ET reaction should be almost diffusional (see below).

Although the reduction potential of PhSeAn is not known, the reduction potential of the related compound Ph_2Se is −2·54 V (ACN),[15] which is more negative than *p*-ClAn ($E_{1/2} = -2{\cdot}15$ V, ACN),[16] *p*-BrAn ($E_{1/2} = -1{\cdot}95$ V, ACN)[16] and *p*-IAn ($E_{1/2} = -1{\cdot}26$ V, ACN).[16] Although the half-wave potential of Ph_2Se is vs SCE, and the *p*-haloanisoles are vs Ag/AgBr, the difference in these reference electrodes is ca 0·2 V.[17]

In the coupling of *p*-anisyl radical with $PhSe^-$ ion, the radical anion $(AnSePh)^{-\cdot}$ is formed, and although the ET to *p*-IAn should be diffusional (difference in $E_{1/2}$ ca 1·2 V), a concentration of 2·5 M of *p*-IAn was used to prevent its fragmentation. With *p*-BrAn (difference in $E_{1/2}$ of ca 0·5 V) and with *p*-ClAn (difference in $E_{1/2}$ of ca 0·3 V), a concentration of 7·8 and 15·6 M had to be used, respectively. These results indicate a very fast fragmentation rate of the radical anion $(AnSePh)^{-\cdot}$, and that the more negative the reduction potential of the *p*-haloanisoles, the higher is the concentration needed to prevent its fragmentation.

Assuming that the rate constant of the electron transfer from $(PhSeAn)^{-\cdot}$ to *p*-IAn (k_t) is ca 10^{10} l mol^{-1} s^{-1} in ACN,[18] and considering that when the products of the fragmentation of the radical anion are not observed, the ratio between the rate of electron transfer to the rate of fragmentation is 100 : 1, we can therefore estimate that the rate constant of fragmentation (k_f) of the radical anion is $\leqslant 10^8$ s^{-1}. The rate of the electron transfer from $(PhSeAn)^{-\cdot}$ to *p*-IAn is

$$\text{rate}_{ET} = k_t[(AnSePh)^{-\cdot}]\,[p\text{-IAn}] \qquad (15)$$

The fragmentation rate of the same radical anion is

$$\text{rate}_f = 2k_f[(AnSePh)^{-\cdot}] \qquad (16)$$

The factor of 2 arises from the fact that we observed only half of the fragmentation products (the fragmentation to $An^{\cdot} + PhSe^{-}$ does not give scrambled products). If the ratio of equation (15) to equation (16) is 100:1 when no scrambled products are observed ([*p*-IAn] = 2·5 M), we can write

$$2k_f[(AnSePh)^{-\cdot}] \approx k_t[(AnSePh)^{-\cdot}][p\text{-IAn}] \times 10^{-2} \quad (17)$$

from which we can estimate k_f as $\leqslant 10^8$ s^{-1} using $k_t = 10^{10}$ l mol^{-1} s^{-1}.

With the value of ca 10^8 for k_f, and with the same procedure, we can estimate the k_t from $(PhSeAn)^{-\cdot}$ to *p*-BrAn to be ca 2.6×10^9 l mol^{-1} s^{-1} and *p*-ClAn 1.3×10^9 l mol^{-1} s^{-1} under these experimental conditions.

In the competition experiments between $PhSe^-$ and PhS^- toward 2-quinolyl radicals, we found that there is a decrease in the selectivity compared with the results in liquid ammonia (2.7 in ACN compared with 5·8 in liquid ammonia). This fact can also be ascribed to the 60 °C difference in temperature, but we must also take into account the difference in the solvent, and different solvation from polar protic (liquid ammonia) to polar aprotic (ACN) can modify the reactivity of the nucleophiles. There is a precedent that changing the solvent produces a modification in the reactivity, and it was reported that in DMSO there is a decrease also in the selectivity of radicals toward nucleophiles.[19]

EXPERIMENTAL

General Methods. ^{1}H NMR spectra were recorded on a Varian T-60 instrument. Infrared spectra were recorded on a 5 SXC Nicolet FTIR spectrophotometer. Mass spectral measurements were obtained with a Finnigan Model 3300 mass spectrometer and gas chromatographic analyses were performed on a Varian Aerograph Series 2400 instrument with a flame ionization detector by using a column packed with 3% SE-30 on Chromosorb P (0·5 m × 3 mm i.d.) or 5% OV-17 on Chromosorb P (1·5 m × 3 mm i.d.). Irradiation was conducted in a reactor equipped with four 250-W UV lamps emitting maximally at 350 nm (Philips Model HPT, water refrigerated).

Materials. *p*-Chloroanisole (Aldrich), *p*-bromoanisole (Aldrich), *p*-iodoanisole (Fluka), 2-chloroquinoline (Aldrich), 2-bromopyridine (Aldrich), 1-bromonaphthalene (Aldrich) and 1-chloronaphthalene (Fluka) were used as received. Benzenethiol (Aldrich) was distilled under reduced pressure and stored in ampoules under nitrogen. Diphenyl selenide and diphenyl diselenide were prepared as reported.[20] Benzene selenol was prepared as reported[21] and distilled under reduced pressure and stored in ampoules under nitrogen. All the other selenides and sulphides were prepared as reported.[5,8] 1,4-Dioxane (Merck) was dried with KOH pellets, refluxed over sodium metal, distilled and stored with $LiAlH_4$. It was redistilled before each reaction. DMSO (Merck) was dried over molecular sieves (Merck, 4 Å). and then vacuum distilled under nitrogen and stored over molecular sieves (4 Å). ACN (spectroscopy grade, Merck) was dried over molecular sieves (4 Å) and distilled under nitrogen.

Photostimulated reactions of benzeneselenate ions **2** *with 2-bromopyridine in* tert-*butyl alcohol.* The following procedure is representative of these reactions: to a three-necked 250-ml round-bottomed flask, equipped with a nitrogen inlet and a magnetic stirrer, were added 80 ml of *tert*-butyl alcohol, which was then degassed. Diphenyl diselenide (389 mg, 1·25 mmol) was added, followed by sodium borohydride (108 mg, 2·86 mmol) to form **2**.[22] Then 2-bromopyridine (0·10 ml, 1·04 mmol) was added and irradiated for 4 h at room temperature. The reaction was quenched with 30 ml of water and air was bubbled into the reaction mixture (to oxidize **2** to diphenyl diselenide). The organic phase was separated and the aqueous solution was extracted three times with diethyl ether. In the aqueous solution Br^- ions were determined potentiometrically (18% yield). The organic solution was dried (anhydrous Na_2SO_4) and by GLC 2-pyridyl phenyl selenide was quantified in comparison with an authentic sample (internal standard 1-chloronaphthalene) (0.184 mmol, 18% yield). No other selenides were detected by GLC ($\leqslant 0{\cdot}5\%$).

Photostimulated reaction of benzeneselenate ions **2** *with p-iodoanisole in dioxane.* Following the same procedure, diphenyl diselenide (403 mg, 1·29 mmol) was added to 130 ml of dioxane and potassium metal (111 mg, 2·84 mmol) was added to the yellow solution. The solution was boiled and a fine precipitate of **2** was formed. *p*-Iodoanisole (241 mg, 1·03 mmol) was added and irradiated for 4 h at room temperature. The reaction was quenched by adding ammonium nitrate and water (10 ml). By potentiometric analysis there were no I^- ions, and by GLC there were no substitution products compared with authentic samples of the selenides. The nucleophile **2** was prepared using the same procedure, but DMSO was added to the white precipitate until it was dissolved (6%, v/v). The selenides and the I^- ions were analysed by the same procedure and are reported in Table 1.

Photostimulated reactions of **2** *with p-haloanisoles in ACN.* The experiments were similar to those reported above; nucleophile **2** was prepared from benzeneselenol and potassium *tert*-butoxide and the results are given in Table 2.

Competition experiments in ACN. To a three-necked 250-ml round-bottomed flask, equipped with a nitrogen inlet and a magnetic stirrer, were added 63 ml of ACN and the solution was degassed. Then benzenethiol (0·20 ml. 1·95 mmol) and benzeneselenol (0·18 ml, 2·25 mmol) were added from ampoules. Potassium *tert*-butoxide (444.2 mg, 3·96 mmol) was added. After 30 min, 2-chloroquinoline (106 mg, 0·65 mmol) was added and the solution irradiated for 4 h at room temperature. The reaction was quenched by adding methyl iodide (4·8 mmol) and 20 ml of water, and ca 50 ml of ACN were removed by distillation. The residue was extracted three times with diethyl ether, dried over anhydrous Na_2SO_4 and quantified by GLC, using pure samples of the substitution products with phenanthrene as internal standard. The results are given in Table 3. In blank experiments, benzenethiolate and benzeneselenate ions were recovered in 94% and 93% yields, respectively (quantified by GLC as the methyl derivatives, using naphthalene as an internal standard).

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