tablished before the start of reaction 1.

For the pH-jump experiments, the addition complex had to be generated at high enough pH to assure nearly complete conversion of BMN into T^- but at low enough pH to avoid rapid decomposition of malononitrile and/or hydrolysis of BMN. A pH ~8 borate buffer gave the best results.

Acknowledgment. This research was supported by Grant CHE80-24261 from the National Science Foundation.

Registry No. T^-, 88157-08-8; $CH(CN)_2^-$, 41470-37-5; benzylidenemalononitrile, 2700-22-3; malononitrile, 109-77-3; piperidine, 110-86-1; morpholine, 110-91-8.

Supplementary Material Available: Tables S1–S5, containing data on the following reactions: reaction of BMN with $CH(CN)_2^-$ at pH 9.11 and 7.97 in water at 25 °C (Table S1), reaction of BMN with $CH(CN)_2^-$ at single $CH(CN)_2^-$ concentrations (pH jumps) in water at 25 and 20 °C (Table S2), reaction of BMN with $CH(CN)_2^-$ at pH 12.72 in water at 20 °C (Table S3), reaction of BMN with $CH(CN)_2^-$ in 50% Me_2SO–50% water at 20 °C (Table S4), reaction of BMN with $CH(CN)_2^-$ at single $CH(CN)_2^-$ concentrations (pH jumps) in 50% Me_2SO–50% water at 20 °C (Table S5) (5 pages). Ordering information is given on any current masthead page.

Relative Reactivities of Nucleophiles Derived from Group 6A toward Aryl Radicals[1]

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Received March 24, 1983

Competition experiments have been carried out in liquid ammonia at reflux temperature to determine the relative rate constants for the coupling reactions of nucleophiles derived from group 6A of the periodic table toward aryl radicals. The nucleophiles studied were of the type PhZ^- (Z = S, Se, Te). It has been proposed that these nucleophiles react under photochemical stimulation with haloaromatic substrates through the $S_{RN}1$ mechanism of aromatic substitution. The experimental results suggest that the coupling reaction aryl radical–PhZ^- anion can be reversible or irreversible depending on the nature of the aryl moiety and the PhZ^- nucleophile. Relative rate constants have been determined under conditions of irreversible coupling of the nucleophiles PhZ^- (Z = S, Se, Te) with 2-quinolyl radicals. Results here reported indicate an increasing reactivity as we go down the group: PhO^- (0.0), PhS^- (1.00), $PhSe^-$ (5.8), $PhTe^-$ (28). The relative rate constant when one of the coupling reactions is reversible supports our mechanistic suggestions.

We have reported the photostimulated reaction of phenyl selenide ion and phenyl telluride ion nucleophiles with haloaromatic substrates in liquid ammonia. It has been proposed that these reactions occur by the $S_{RN}1$ mechanism of aromatic nucleophilic substitution.[2,3]

Inspection of the species PhZ^- nucleophilicities, Z being an element of group 6A of the periodic table, shows that phenoxide ion does not react with haloarenes,[4] while benzenethiolate ion,[5] phenyl selenide ion,[3] and phenyl telluride ion[3] react with good yields of substitution products in general. We determined the relative reactivity of the last three nucleophiles just mentioned toward aryl radicals.

All the reactions were carried out in liquid ammonia as the solvent at −33 °C and under photostimulation. Similar competition experiments have been previously reported.[6] In these experiments two nucleophiles were allowed to react with aromatic radicals generated from the haloaromatic substrate.

The propagation steps for $S_{RN}1$ reactions of one aromatic substrate with two nucleophiles Nu_1 and Nu_2 are shown in Scheme I.

Scheme I

$$(\mathrm{ArX})^{-\cdot} \rightarrow \mathrm{Ar}\cdot + \mathrm{X}^- \qquad (1)$$

$$\mathrm{Ar}\cdot + \mathrm{Nu_1}^- \xrightarrow{k_{\mathrm{Nu1}}} (\mathrm{ArNu_1})^{-\cdot} \qquad (2)$$

$$\mathrm{Ar}\cdot + \mathrm{Nu_2}^- \xrightarrow{k_{\mathrm{Nu2}}} (\mathrm{ArNu_2})^{-\cdot} \qquad (3)$$

$$(\mathrm{ArNu_1})^{-\cdot} + \mathrm{ArX} \rightarrow \mathrm{ArNu_1} + (\mathrm{ArX})^{-\cdot} \qquad (4)$$

$$(\mathrm{ArNu_2})^{-\cdot} + \mathrm{ArX} \rightarrow \mathrm{ArNu_2} + (\mathrm{ArX})^{-\cdot} \qquad (5)$$

As it has been pointed out, the ratio of concentration of substitution products, $ArNu_1$ and $ArNu_2$, derived from the nucleophiles Nu_1^- and Nu_2^-, respectively, would be indicative of the relative rate constants (k_{Nu_1}/k_{Nu_2} of both reactions (eq 2 and 3). This will be so if the propagation steps are more frequent than the termination steps and if the nucleophiles and the intermediate radical anions are not involved in side reactions.[6]

It is known that the benzenethiolate ion reacts with aryl radicals to give an intermediate radical anion, whose main reaction is the electron transfer to the aromatic substrate. The reaction products of this nucleophile with different

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[1] Research supported in part by the Consejo Nacional de Investigaciones Cientificas y Técnicas and the Subsecretaria de Ciencia y Tecnologia, Argentina.

[2] Pierini, A. B.; Rossi, R. A. *J. Organomet. Chem.* **1978**, *144*, c12; **1979**, *168*, 163.

[3] Pierini, A. B.; Rossi, R. A. *J. Org. Chem.* **1979**, *44*, 4667.

[4] Rossi, R. A.; Pierini, A. B. *J. Org. Chem.* **1980**, *45*, 2914.

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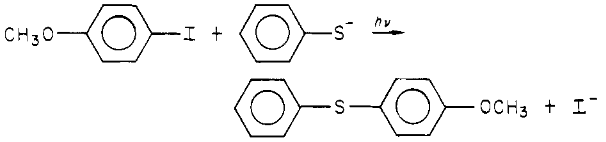
Table I. Photostimulated Reactions of Phenyl Telluride and Phenyl Selenide Ions in Liquid Ammonia

expt	ArX	concn, M	PhZ^-	concn, M	irradn time, min	% yield of X^- [a]	products obtained[b] (% yield)
1	4-iodoanisole	0.036	$PhSe^-$	0.036	260	75	Ph_2Se (20), *p*-anisyl phenyl selenide (25), bis(*p*-anisyl) selenide (19)
2	2-bromopyridine	0.025	$PhSe^-$	0.025	220	92	Ph_2Se (4, 5),[c] phenyl 2-pyridil selenide (72),[c] bis(2-pyridyl) selenide (2)[c]
3	2-chloroquinoline	0.025	$PhSe^-$	0.025	220	54	phenyl 2-quinolyl selenide (46)
4	2-chloroquinoline	0.028	$PhTe^-$	0.031	220	60	Ph_2Te (11), phenyl 2-quinolyl telluride (43)
5	2-chloroquinoline	0.004	$PhTe^-$	0.016	220[d]	*e*	phenyl 2-quinolyl telluride (8)[f]
6	2-chloroquinoline	0.004	$PhTe^-$	0.007	220[g]	<5	phenyl 2-quinolyl telluride (4)[f]
7			$PhTe^-$	0.031	220		Ph_2Te (20)[h]

[a] Determined potentiometrically. [b] Product isolated, unless otherwise quoted. [c] Determined by GLC with 1-chloronaphthalene as an internal standard to quantify Ph_2Se and phenyl 2-pyridyl selenide and triphenylphosphine to quantify bis(2-pyridyl) selenide. [d] Dark reaction wrapped with aluminum foil. [e] Not determined. [f] Determined by GLC. [g] Dark reaction carried out in the presence of *p*-dinitrobenzene (11%) with respect to the substrate. [h] Quantified by GLC with 1-chloronaphthalene as an internal standard.

compounds, including *p*-iodoanisole, were the expected substitution products (eq 6).[7]



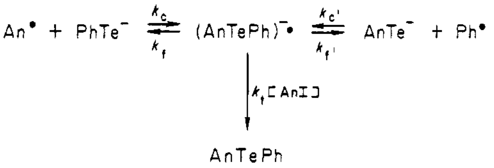
(6)

However, the photostimulated reaction of phenyl telluride ion with *p*-iodoanisole and 1-chloronaphthalene as substrates gave three substitution products.[3] These results were ascribed to the fragmentation of the intermediate radical anion, which leads to the scrambling of aryl rings (Scheme II).

Scheme II

$$\mathrm{AnI} + \mathrm{PhTe}^- \xrightarrow{h\nu} (\mathrm{AnI})^{-}\cdot + \mathrm{PhTe}\cdot \tag{7}$$

$$(\mathrm{AnI})^{-}\cdot \rightarrow \mathrm{An}\cdot + \mathrm{I}^- \tag{8}$$



$$\begin{tikzcd}
\mathrm{An}^\bullet + \mathrm{PhTe}^- \arrow[r, shift left, "k_c"] & (\mathrm{AnTePh})^{-\bullet} \arrow[l, shift left, "k_f"] \arrow[r, shift right, "k_{f'}"'] \arrow[d, "k_t[\mathrm{AnI}]"] & \mathrm{AnTe}^- + \mathrm{Ph}^\bullet \arrow[l, shift right, "k_{c'}"'] \\
& \mathrm{AnTePh} &
\end{tikzcd} \tag{9}$$

$$\mathrm{AnTe}^- + \mathrm{An}\cdot \rightleftarrows (\mathrm{An_2Te})^{-}\cdot \xrightarrow{k_t[\mathrm{AnI}]} \mathrm{An_2Te} \tag{10}$$

$$\mathrm{PhTe}^- + \mathrm{Ph}\cdot \rightleftarrows (\mathrm{Ph_2Te})^{-}\cdot \xrightarrow{k_t[\mathrm{AnI}]} \mathrm{Ph_2Te} \tag{11}$$

An = *p*-anisyl

In this system $k_f \approx k_t[\mathrm{ArX}]$, but with benzenethiolate ion as the nucleophile $k_f \ll k_t[\mathrm{ArX}]$. As the frangibility of the radical anions (large k_f) depends on the bond-dissociation energy of the C–Z bond that fragments into aryl radicals and PhZ^- and on the molecular orbital of the aromatic moiety,[8] we decided to study the photostimulated reaction of phenyl selenide ion and phenyl telluride ion with several haloaromatic compounds to determine which one gives scrambled products as well as which gives the straightforward substitution product and also to determine the relative reactivities of PhZ^- (Z = S, Se, and Te) nucleophiles with aryl radicals.

Results

Photostimulated Reactions with Phenyl Selenide and Phenyl Telluride Ions. We have reported that the photostimulated reaction of phenyl selenide ion with 1-chloronaphthalene, 9-bromophenanthrene, and 4-chlorobiphenyl gave the straightforward substitution product (eq 12).[3]

$$\mathrm{ArX} + \mathrm{PhSe}^- \xrightarrow{h\nu} \mathrm{ArSePh} + \mathrm{X}^- \tag{12}$$

ArX = 1-chloronaphthalene, 9-bromophenanthrene, 4-chlorobiphenyl

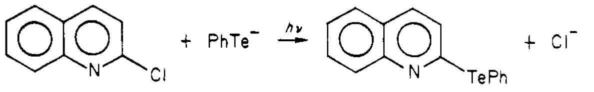
In the photostimulated reaction with iodo- or bromobenzene, diphenyl selenide was the main product, but in such a symmetrical system it was not possible to determine the reversibility of the coupling step. In the photostimulated reaction of *p*-iodoanisole with phenyl selenide ion (an asymmetrical system) we obtained scrambling of aryl rings (eq 13; expt 1, Table I). This was the case, though

$$\mathrm{ArX} + \mathrm{PhSe}^- \xrightarrow{h\nu} (\mathrm{Ph})_2\mathrm{Se} + \mathrm{PhSeAr} + \mathrm{ArSeAr} \tag{13}$$

ArX = *p*-iodoanisole, 2-bromopyridine

to a lesser extent, when 2-bromopyridine was the substrate (expt 2, Table I). However, in the photostimulated reaction with 2-chloroquinoline the only product obtained was the straightforward substitution one (eq 12, ArX = 2-chloroquinoline; expt 3, Table I).

Phenyl telluride ion gave a scrambling reaction with *p*-iodoanisole and 2-chloronaphthalene.[3] We studied the photostimulated reaction of phenyl telluride ion with the substrate 2-chloroquinoline due to the fact that quinoline has a lower antibonding π^* molecular orbital than naphthalene and benzene. In this reaction we found the straightforward substitution product 2-quinolyl phenyl telluride (43%) together with diphenyl telluride (11%) (eq 14; expt 4, Table I).



(14)

Although there is a small dark reaction in the same period of time which is partially inhibited by *p*-dinitrobenzene, a very well-known inhibitor of the $S_{RN}1$ reactions (expts 5 and 6, Table I).

The scrambling reaction could account for the diphenyl telluride thus formed, but after an exhaustive search we failed to find bis(2-quinolyl) telluride, one of the expected scrambled products. This might prove that the diphenyl telluride must come from another route and not through the $S_{RN}1$ mechanism as sketched in Scheme II. In fact, the photostimulated reaction of phenyl telluride ion in liquid ammonia and in the absence of 2-chloroquinoline

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[7] Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1975**, *40*, 3740.
[8] Rossi, R. A. *Acc. Chem. Res.* **1982**, *15*, 164.

Table II. Competition Experiments of ArX with Two Nucleophiles

		concn $\times 10^3$,	nucleophile Nu_1^-		nucleophile Nu_2^-		$h\nu$,[a]	rel yield,[b] %		
expt	ArX[d]	M	identity	concn, M	identity	concn, M	min	$ArNu_1$	$ArNu_2$	k_{Nu_1}/k_{Nu_2}[c]
1	2-ClQ[d]	8.2	$PhSe^-$	0.024	PhS^-	0.024	220	83	18	5.16
2	2-ClQ	8.0	$PhSe^-$	0.016	PhS^-	0.032	220	72	23	6.23
3	2-ClQ	6.4	$PhSe^-$	0.012	PhS^-	0.030	220	67	33	5.88
										av 5.8 ± 0.4
4	2-ClQ	8.0	$PhTe^-$	0.024	$PhSe^-$	0.024	220	81	19	4.83
5	2-ClQ	7.2	$PhTe^-$	0.014	$PhSe^-$	0.029	220	66	34	4.42
6	2-ClQ	8.0	$PhTe^-$	0.024	$PhSe^-$	0.024	220	83	17	5.55
7	2-ClQ	6.6	$PhTe^-$	0.013	$PhSe^-$	0.026	140	35[e]	18[e]	4.50[f]
										av 4.8 ± 0.4
8	PhI	6.4	$PhSe^-$	0.098	PhS^-	0.010	150	28[g]	40[g]	0.059
9	PhI	6.4	$PhSe^-$	0.064	PhS^-	0.010	150	15[g]	42[g]	0.045
10	PhI	6.4	$PhSe^-$	0.064	PhS^-	0.010	150	15[g]	54[g]	0.057
										av 0.054 ± 0.006
11	PhI	5.6	$PhTe^-$	0.011	$PhSe^-$	0.011	220	97	3	[h]
12	PhI	2.4	$PhTe^-$	0.0048	$PhSe^-$	0.019	140	14	5	[i, j]

[a] Irradiation time. [b] Relative yields determined by assuming the formation of $ArNu_1$ and $ArNu_2$ in 100% yield. [c] Ratio determined by using eq 17. [d] 2-ClQ = 2-chloroquinoline. [e] Quantified by GLC with 9-bromophenanthrene as an internal standard together with 40% of unreacted 2-chloroquinoline and 15% of diphenyl telluride. [f] Ratio determined with eq 18. [g] Quantified by GLC with 1-chloronaphthalene as an internal standard. In all these ratios benzene was detected but not quantified. [h] $k_{-Te}/k_{-Se} \approx 2$ (see text). [i] Benzene detected but not quantified. [j] $k_{-Te}/k_{-Se} = 1.8$.

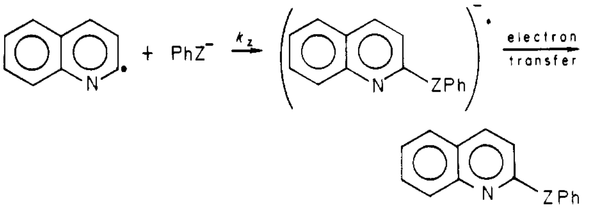
gave a 20% yield of diphenyl telluride (eq 15; expt 7, Table I).

$$PhTe^- \xrightarrow{h\nu} (Ph)_2Te \tag{15}$$

Although we have not investigated the mechanism of the photostimulated reaction of eq 15, it is independent of the $S_{RN}1$ reaction of phenyl telluride ion with 2-chloroquinoline.

Competition Experiments

Irreversible Coupling of PhZ^- Nucleophiles. 2-Quinolyl radical reacts with PhZ^- (S, Se, Te) nucleophiles in an irreversible reaction (no scrambled products, eq 16).



(16)

Z = S, Se, Te

In this system it is possible to study the relative reactivities of pairs of nucleophiles toward the 2-quinolyl radicals.

Benzenethiolate Ion vs. Phenyl Selenide Ion. Once the yields of the substitution products 2-quinolyl phenyl sulfide (PhSQ) and 2-quinolyl phenyl selenide (PhSeQ) were determined in the photostimulated reaction of 2-chloroquinoline with benzenethiolate and phenyl selenide ions in excess, it was possible to calculate k_{Se}/k_S by using eq 17 (Table II). $[PhS^-]_0$ and $[PhSe^-]_0$ are initial concentrations, and $[PhSQ]_t$ and $[PhSeQ]_t$ are concentrations of the products at time t.[9] This equation is based on the assumption that the reactions of both nucleophiles with the 2-quinolyl radicals are first order in the anions.

$$\frac{k_{Se}}{k_S} = \frac{\ln \dfrac{[PhSe^-]_0}{[PhSe^-]_0 - [PhSeQ]_t}}{\ln \dfrac{[PhS^-]_0}{[PhS^-]_0 - [PhSQ]_t}} \tag{17}$$

Phenyl Selenide Ion vs. Phenyl Telluride Ion. The relative reactivities of both nucleophiles were determined by using eq 17 (Table II).

Considering that the phenyl telluride ion concentration decreases by an independent and parallel reaction (eq 15), we investigated the variation of the ratio k_{Te}/k_{Se} using a modified equation. If the ratio of concentrations of product diphenyl telluride and 2-quinolyl phenyl telluride ($Ph_2Te/PhTeQ$) is constant during the reaction, it will be possible to determine the ratio k_{Te}/k_{Se} by taking into account the decrease of phenyl telluride ion concentration by the parallel reaction by using eq 18.

$$\frac{k_{Te}}{k_{Se}} = \frac{1}{C} \times \frac{\dfrac{[PhTe^-]_2}{[PhTe^-]_0 - C\,[PhTeQ]_t}}{\dfrac{[PhSe^-]_0}{[PhSe^-]_t - [PhSeQ]_t}} \tag{18}$$

$$\text{where} \quad C = \frac{[Ph_2Te]}{[PhTeQ]} + 1$$

In order to determine if $(Ph)_2Te/PhTeQ$ is a constant, we performed the photostimulated reaction of phenyl telluride ion with 2-chloroquinoline under the same experimental conditions as those in the competitive reactions, determining the ratio $(Ph)_2Te/PhTeQ$ as a function of time. It can be seen from Table III that from 60 to 140 min of reaction the ratio is almost a constant, the ratio increasing slightly at 240 min of reaction time.

In a competitive reaction of phenyl selenide and phenyl telluride ions during 140 min, with calculation of the ratio k_{Te}/k_{Se} by using the modified eq 18, the ratio was similar, within the experimental error (Table II), to those determined by means of eq 17, considering only an $S_{RN}1$ mechanism as being in play.

In reactions carried out with a large excess of phenyl selenide and phenyl telluride ions and long irradiation times we found an increase in the yield of diphenyl telluride and a decrease in the substitution product phenyl 2-quinolyl telluride, but as the results obtained in the competition experiments do not vary at different irradiation times, we concluded that this reaction does not in-

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[9] Bunnett, J. F. "Investigation of Rates and Mechanisms of Reactions", 3rd. ed.; Lewis, E. S., Ed.; Wiley-Interscience: New York, 1974; Part I, p 159.

Table III. Photostimulated Reaction of 2-Chloroquinoline with $PhTe^-$ Ion: $[Ph_2Te]/[PhTeQ]$[a] Ratio as a Function of Time

irradn time, min	$[Ph_2Te]/[PhTeQ]$	irradn time, min	$[Ph_2Te]/[PhTeQ]$
60	0.68	140	0.88 (expt 7, Table II)
90	0.66	240	1.46
115	0.60	240	1.23 (expt 4, Table II)
140	0.67	240	1.10 (expt 5, Table II)
		240	1.21 (expt 6, Table II)

[a] PhTeQ stands for phenyl 2-quinolyl telluride.

Table IV. Relative Reactivities of PhZ^- (Z = O, S, Se, Te) Nucleophiles toward 2-Quinolyl Radicals

nucleophile	rel reactivity	nucleophile	rel reactivity
PhO^-	0.0	$PhSe^-$	5.8
PhS^-	(1.00)[a]	$PhTe^-$	28.0

[a] Reference.

Table V. Relative Nucleophilicities toward Aryl Radicals

nucleophile	radical	A[a]	B[b]
Ph_2P^-	phenyl[c]	5.9	74
Ph_2PO^-	phenyl[c]	2.7	34
$PhTe^-$	2-quinolyl	2.2	28
$(EtO)_2PO^-$	phenyl[c]	1.4	18
$(CH_3)_3CCOCH_2^-$	phenyl[c]	(1.0)	13
$PhSe^-$	2-quinolyl	0.46	5.8
PhS^-	phenyl[c]–2-quinolyl	0.08	(1.00)

[a] $(CH_3)CCOCH_2^-$ as reference. [b] PhS^- as reference. [c] Taken from ref 6.

terfere with the results reported in Table II.

From Table II it is possible to calculate the relative reactivities of PhZ^- nucleophiles (Z = O, S, Se, and Te) toward 2-quinolyl radicals (Table IV).

Comparative Reactivities of Irreversible–Reversible Coupling of Nucleophiles with Phenyl Radicals. As has already been discussed, benzenethiolate ion reacts with *p*-iodoanisole, giving the straightforward substitution product, and this means that the intermediate radical anion in the coupling of *p*-anisyl radical with benzenethiolate ion only transfers its electron to give the observed substitution product.[7]

However, phenyl selenide ion gave scrambled products in the photostimulated reaction with *p*-iodoanisole, and this means that the intermediate radical anion formed in the coupling of *p*-anisyl radicals with phenyl selenide ion fragments to give starting materials and also to give *p*-anisyl selenide ion and phenyl radicals.

To avoid the complication of scrambled substitution products, we did the competition experiments using iodobenzene as the substrate. Phenyl radicals react irreversibly with benzenethiolate ion (eq 19) and reversibly with phenylselenide ion (eq 20).

$$Ph\cdot + PhS^- \xrightarrow{k_S} (PhSPh)^{-}\cdot \xrightarrow{k_{tS}[PhI]} PhSPh \qquad (19)$$

$$Ph\cdot + PhSe^- \underset{k_{-Se}}{\overset{k_{Se}}{\rightleftarrows}} (PhSePh)^{-}\cdot \xrightarrow{k_{tSe}[PhI]} PhSePh \qquad (20)$$

We did the competition reaction of benzenethiolate and phenyl selenide ions with iodobenzene and used eq 17 to find the *apparent* reactivities of both nucleophiles toward phenyl radicals (Table II).

Comparative Reactivities of Reversible Coupling of Nucleophiles with Phenyl Radicals. Phenyl selenide and phenyl telluride ions react reversibly with phenyl radicals (eq 20 and 21). The ratio of rates is given by eq 22.

$$Ph\cdot + {}^{-}TePh \underset{k_{-Te}}{\overset{k_{Te}}{\rightleftarrows}} (PhTePh)^{-}\cdot \xrightarrow{k_{tTe}[PhI]} PhTePh \qquad (21)$$

$$\frac{d[Ph_2Te]}{d[Ph_2Se]} = \frac{k_{tTe}k_{Te}[PhTe^-]/k_{-Te} + k_{tTe}[PhI]}{k_{tSe}k_{Se}[PhSe^-]/k_{-Se} + k_{tSe}[PhI]} \qquad (22)$$

The $k_{tSe}[PhI]$ should be similar or smaller than k_{-Se} because scrambled products are obtained and, furthermore, because as the reaction proceeds the iodobenzene concentration decreases to zero. If it is assumed that $k_{-Se} > k_{tSe}[PhI]$, eq 22 can be transformed into eq 23.

$$\frac{k_{Te}/k_{-Te}}{k_{Se}/k_{-Se}} = \frac{[PhSe^-]_0}{[Ph_2Se]_t} \ln \frac{[PhTe^-]}{[PhTe]_0 - [Ph_2Te]_t} \qquad (23)$$

In this system the reaction carried out with a ratio of nucleophile/iodobenzene of 2 gave diphenyl telluride as the main product (97%) together with diphenyl selenide (3%) (expt 11, Table II). If it is taken into account that diphenyl telluride is formed not only through the $S_{RN}1$ mechanism but also by an independent reaction (eq 15) and that the ratio k_{Te}/k_{Se} will be the same with 2-quinolyl radicals as well as with phenyl radicals, k_{-Te}/k_{-Se} is approximately equal to 2. This result suggests a similar fragmentation rate for the diphenyl selenide and diphenyl telluride radical anions, with a difference in ΔH^{*} activation of 0.3 kcal/mol (−33 °C). In the reactions carried out with large excess of phenyl selenide ion we noticed an increase in the yield of benzene. Under these experimental conditions we were unable to determine the relative reactivities.

Discussion

The reaction of benzenethiolate ion with aryl radicals always leads to the substitution product. Phenyl selenide ion gave scrambled products with *p*-anisyl and 2-pyridyl radicals but straightforward substitution product with 4-biphenyl, 9-phenanthryl, 1-naphthyl, and 2-quinolyl radicals, while phenyl telluride ion gave scrambling with *p*-anisyl and 1-naphthyl radicals but the straightforward substitution product with 2-quinolyl radicals. These facts resemble the results of the photostimulated reaction of Ph_2M^- (M = P, As, and Sb) nucleophiles with aryl radicals.[8,10-13]

When an aryl radical couples with a PhZ^- (Z = S, Se, Te) nucleophile, a radical anion is formed. If the π^* is the lowest antibonding molecular orbital of the parent compound, a π^* radical anion is formed, and the electron transfer of the odd electron to the substrate is the main reaction pathway which leads to the straightforward substitution product. However, if the π^* MO has similar or higher energy than the σ^* MO of the C–Z bond, the radical anion could have a σ^*–π^* isomerism, and it could fragment from the σ^* state to give scrambling of aryl rings. Whether the system will have σ^*–π^* isomerism or only the π^* radical anion will depend on the gap of energy of both states.[13-15]

The π^* molecular orbital depends on the aryl moiety and is related to its reduction potential while the σ^* antibonding molecular orbital is related to the bond dissociation energy of the C–Z bond which decreases as we go down in a group of the periodic table.

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(10) Swartz, J. E.; Bunnett, J. F. *J. Org. Chem.* **1979**, *44*, 340.

(11) Rossi, R. A.; Alonso, R. A.; Palacios, S. M. *J. Org. Chem.* **1981**, *46*, 2498.

(12) Alonso, R. A.; Rossi, R. A. *J. Org. Chem.* **1982**, *47*, 77.

(13) Rossi, R. A.; de Rossi, R. H. *ACS Monogr.* **1983**, *No. 178*, 212.

(14) Rossi, R. A. *J. Chem. Educ.* **1982**, *59*, 310.

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The results obtained agree with this interpretation. Thus benzenethiolate ion will always give unscrambled products (π^* radical anion intermediates). With phenyl selenide ion the scrambling reaction will be observed with aryl radicals derived from arenes with reduction potentials of −2.7 V or more negative, while straightforward substitution product will be observed with aryl radicals whose parent arene has a reduction potential of −2.6 V or more positive. Phenyl telluride ion will give a scrambling reaction with aryl radicals derived from arenes with a reduction potential of −2.5 V or more negative but the straightforward substitution product with aryl radicals derived from arenes with reduction potentials of −2.1 V or more positive.[8]

The photostimulated reaction of 2-chloroquinoline with PhZ^- (Z = S, Se, Te) nucleophiles only gave the straightforward substitution product, which means that the intermediate radical anion only transfers its odd electron without the competing fragmentation reaction. This substrate allowed us to determine the actual reactivities of the nucleophiles (Table IV). The order of reactivities of this series ($PhTe^- > PhSe^- > PhS^- \gg PhO^-$) increases as the nucleophiles become softer. Since aryl radicals are soft electrophiles, they react faster as the nucleophiles becomes softer.

Having a common nucleophile, benzenethiolate ion, this series can be compared with the reactivity order determined by Bunnett[6] (Table V).

A quite different reactivity order was found when the competition experiments were carried out between benzenethiolate and phenyl selenide ions with iodobenzene. In this system the irreversible coupling of benzenethiolate ion with phenyl radical gave a radical anion that only transfers its odd electron, but phenyl selenide ion gave a reversible coupling with phenyl radicals, which decreases the apparent reactivity by a factor of 100 (from 5.8 to 0.05).

Phenyl telluride ion also reacts reversibly with phenyl radical, and in a competition experiment with phenyl selenide ion this allowed us to estimate the fragmentation ratio (k_{-Te}/k_{-Se}) of the radical anions. They were found to be very close. The apparent reactivity is similar with these two nucleophiles in the competition with 2-quinolyl radicals (irreversible couplings) and with phenyl radical (reversible couplings).

Experimental Section

Melting points have not been corrected. NMR spectra were performed with a Varian T-60 nuclear magnetic resonance spectrometer with CCl_4 as the solvent, unless otherwise indicated; the spectra are reported in parts per million relative to Me_4Si (δ).

Mass spectral measurements were obtained with a Finnigan Model 3300 mass spectrometer.

Gas chromatographic analyses were performed on a Varian Aerograph Series 2400 with a flame-ionization detector equipped with a Data Procesor Chromatopac C-R1A, Shimadzu. Analyses were performed by using a 1.5% OV-101 on 80–100-mesh Chromosorb P, 1.52 mm × 3.2 mm column.

Column chromatography was performed on neutral aluminum oxide (Merck) and eluted with petroleum ether.

Materials. All the halo aromatic compounds were analytical grade, commercially available products used as received. Diphenyl diselenide and diphenyl ditelluride were synthetized as described.[3] The nucleophiles phenyl selenide, phenyl telluride and benzenethiolate ions were prepared in situ, following the same procedure as reported.[2,3]

Photostimulated Reactions. These reactions were carried out in a photochemical reactor equipped with four 250-W lamps with maximum emission at 350 nm (Philips, Model HPT, water refrigerated).

Photostimulated Reaction of Phenyl Selenide and Phenyl Telluride Ions. The reaction of these nucleophiles with 2-chloroquinoline is representative: 250 mL of ammonia, previously dried over sodium, was distilled to a 500-mL, three-necked, round-bottomed flask equipped with a cold finger, nitrogen inlet, and magnetic stirrer. To the ammonia was added diphenyl diselenide (3 mmol) followed by the addition of small pieces of Na metal until persistence of the blue color, at that time diphenyl ditelluride (3 mmol) was added, and phenyl telluride ion was generated by the addition of the exact amount of sodium needed (6 mmol).

2-Chloroquinoline (2.01 mmol) was added, and then the solution was irradiated for different time periods. The reaction was quenched by adding methyl iodide. Ammonia was allowed to evaporate. Water was added to the residue, and the mixture was then extracted three times with diethyl ether. Halide ions were determined potenciometrically in the aqueous phase. The ether extracts were analyzed by GLC. All the products were identified by comparison of their retention times with those of authentic samples. The compounds were quantified by the standard internal or external method.

Identification of Products. 2-Quinolyl Phenyl Telluride. This compound was isolated by column chromatography and recrystallized from petroleum ether: mp 46–48 °C; MS, *m/e* (relative intensity) 335 (10), 334 (49.5), 333 (23), 332 (45.3), 331 (22), 330 (35), 329 (17), 328 (11), 206 (16), 205 (60), 204 (60), 203 (7), 128 (100), 101 (70), 77 (5), 76 (85), 51 (8), 50 (46).

2-Quinolyl phenyl sulfide was isolated by column chromatography: mp 47.5–48.5 °C (lit.[16] mp 48–49 °C); MS, *m/e* (relative intensity) 239 (2.1), 238 (10.8), 237 (46.9), 236 (100), 204 (2.6), 163 (84.1), 128 (19.5), 101 (17), 109 (2.3), 77 (8.1), 51 (6.5).

2-Quinolyl Phenyl Selenide. This compound gave the same melting point and mass spectrum as previously reported.[3]

Bis(*p*-anisyl) selenide was isolated by column chromatography: mp 54–55 °C (lit.[17] mp 55–56 °C) MS, *m/e* (relative intensity) 296 (3.1), 294 (22.3), 292 (10.6), 291 (4.3), 290 (3.7), 214 (100), 199 (85.6), 184 (2.16), 128 (15), 187 (9.4), 185 (4.7), 172 (8.9), 171 (27.9), 170 (4.1), 156 (8.5), 154 (0.6), 107 (10.5), 92 (7), 77 (5.6); ^1H NMR δ 3.70 (6 H_1, s), 6.5–6.9 (4 H_1, m), 7.1–7.5 (4 H_1, m).

***p*-Anisyl phenyl selenide** was isolated by column chromatography (liquid): MS, *m/e* (relative intensity) 266 (4.6), 264 (30.3), 262 (13.9), 261 (5.5), 260 (5.4), 184 (100), 169 (49.3), 141 (32), 115 (14.6), 77 (15), 51 (109); ^1H NMR δ 3.6 (3 H_1, s), 6.5–6.8 (2 H_1, m), 6.9–7.6 (7 H_1, m).

2-Pyridyl phenyl selenide: liquid; ^1H NMR δ 6.68–7.0 (2 H_1, m), 7.08–7.40 (4 H_1, m), 7.45–7.80 (2 H_1, m), 8.15–8.38 (1 H_1, m).

Bis(2-pyridyl) selenide: liquid; ^1H NMR δ 6.8–7.6 (6 H_1, m), 8.25–8.46 (2 H_1, m).

Acknowledgment. Alicia B. Peñéñory gratefully acknowledges receipt of a fellowship from the Consejo Nacional de Investigaciones Cientificas y Técnicas, Argentina. INFIQC is jointly sponsored by the Consejo Nacional de Investigaciones Cientificas y Técnicas and the Universidad Nacional de Córdoba. This work is partially supported by the SUBCYT.

Registry No. 2-Quinolyl phenyl telluride, 87803-46-1; 2-quinolyl phenyl sulfide, 22190-12-1; 2-quinolyl phenyl selenide, 71672-71-4; bis(*p*-anisyl) selenide, 22216-66-6; *p*-anisyl phenyl selenide, 80448-01-7; 2-pyridyl phenyl selenide, 87803-47-2; bis(2-pyridyl) selenide, 66491-49-4; 4-iodoanisole, 696-62-8; 2-bromopyridine, 109-04-6; 2-chloroquinoline, 612-62-4; diphenyl diselenide, 1666-13-3; diphenyl ditelluride, 32294-60-3; $PhSe^-$, 14971-39-2; $PhTe^-$, 65081-67-6; PhS^-, 13133-62-5; PhO^-, 3229-70-7; PhI, 591-50-4; Na, 7440-23-5.

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