°C for 3 h. The reaction mixture was worked up as before to yield 10.2 g (70%) of material, bp 180-230 °C (10.0 torr). It solidified in the receiver and was recrystallized from methanol, giving white rhombic crystals of 1,1-diisodurylethene, mp 87-88 °C.

Reaction of Isodurene with Propionyl Chloride at 100 °C. The procedure was the same as that for reaction of acetyl chloride with isodurene at 100 °C except that 8.5 g (0.092 mol) of propionyl chloride was used. Vacuum distillation gave two fractions. The first fraction, 2.3 g (12%), bp 95 °C (1.2 torr), was identified by GC/MS as propioisodurene: ¹H NMR (CDCl₃) δ 1.3 (t, 3 H), 2.05-2.28 (t, 12 H), 2.7 (q, 2 H), 6.85 (s, 1 H); mass spectrum, calcd for $C_{13}H_{18}O[M^+] m/e$ 190.13511, found 190.13494. The second fraction, 2.23 g (78%), bp 195 °C (1.0 torr), became a hard glass upon cooling: GC/MS showed it to be a pure compound; ¹H NMR (CDCl₃) δ 1.6 (d, 3 H), 1.9–2.3 (t, 24 H), 5.72 (q, 1 H), 6.78 (s, 2 H, Ar H); mass spectrum, calcd for $C_{23}H_{30}$ [M⁺] m/e 306.23474, found 306.23462.

Reaction of Propioisodurene with Isodurene at 150-160 °C. A mixture of 20 g (0.15 mol) of isodurene, 9.5 g (0.05 mol) of propioisodurene, and 1.33 g (0.01 mol) of AlCl₃ was heated at 160 °C for 3 h. The reaction mixture was worked up in the usual way to give 1.0 g (10%) of propioisodurene, bp 95 °C (1.2 torr), and 12.2 g (80%) of 1,1-diisodurylpropene, bp 195 °C (1.0 torr), as a viscous yellow oil, which solidified into a hard glass upon cooling.

Reaction of Prehnitene with Acetyl Chloride and Pro**pionyl Chloride.** When prehnitene was treated with acetyl chloride or propionyl chloride and AlCl₃ under the conditions used with durene and isodurene, the products were recovered prehnitene, acetoprehnitene or propioprehnitene, and smaller amounts of other products. Although these other products were not identified, it was established by GC/MS analysis that no more than traces (1%) of 1,1-diprehnitylethene and 1,1-diprehnitylpropene were present in the product mixtures.

Reaction of Acetoprehnitene and Propioprehnitene with Prehnitene. When acetoprehnitene or propioprehnitene was treated with prehnitene and AlCl₃ under the conditions used with acetodurene or propiodurene and the corresponding arenes, mainly the starting materials were recovered, along with small amounts of other compounds. Although these other compounds were not identified, it was established by GC/MS analysis that no more than traces (1%) of 1,1-diprehnitylethene and 1,1-diprehnitylpropene were present in the product mixtures.

Acknowledgment. Support for this work by the Robert A. Welch Foundation is gratefully acknowledged.

Registry No. 1, 95-93-2; 2, 527-53-7; 3a, 2142-79-2; 3b, 2040-16-6; 4a, 2142-78-1; 4b, 91390-77-1; 7a, 91390-74-8; 7b, 91390-75-9; 8a, 91390-76-0; 8b, 91390-78-2; acetyl chloride, 75-36-5; propionyl chloride, 79-03-8; prehnitene, 488-23-3; acetoprehnitene, 34764-71-1; propioprehnitene, 91390-79-3.

Reduction Process in the Photostimulated Reaction of Benzeneselenate Ion with Haloarenes

Alicia B. Peñéñory, Adriana B. Pierini, and Roberto A. Rossi*

Instituto de Investigaciones en Físico Química de Córdoba (INFIQC), Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, sucursal 16-C.C. 61, 5016 Córdoba, Argentina

Received January 9, 1984

Benzeneselenate (PhSe⁻) and benzenetellurate (PhTe⁻) ions react under photostimulation with haloarenes by the S_{RN} 1 mechanism of nucleophilic substitution.¹⁻³

The frangibility of the radical anion 1 formed in the coupling reaction between the anions and the aromatic

Table I. Photostimulated Reactions of Benzeneselenate Ions with Different Substrates in Liquid Ammonia^a

			PhSe⁻.	yield, %	
expt	substrate	$M \times 10^3$	$M \times 10^3$	$\overline{Ph_2Se}$	PhH
16	PhI	22.4	22.6	55	3.5
2°	PhI	4.2	16.2	44	31
3°	PhI	2.1	16.0	13	91
4^d	PhI	2.1	16.1	28	17
5			30.4	0	2
6	Ph_2Se	1.7	16.3	18	51
7	2-ClQ ^e	1.8	16.0	95^{f}	1
8	2-ClQ ^e	3.4	16.5	98 ^f	1
9	Ph_2S	1.6	14.5	0	1

^a140 min of irradiation with four 250-W lamps. ^bPhI recovered 38.5%. "No PhI recovered unreacted. d Irradiation with two 250-W lamps; PhI recovered was no quantified. e2-ClQ = 2chloroquinoline. [†]2-Quinolyl phenyl selenide.

radical depends on both the nature of the radical and the nucleophile involved. This fact will determine the product distribution and the relative reactivities of the nucleophiles toward radicals.⁴

When the reaction takes place under irreversible conditions, $k_{\rm t}({\rm ArX}) \gg k_{\rm f} \approx k_{\rm f'}$, the product observed is the expected substitution one, ArZPh (Z = Se, Te), while three compounds, ArZPh, Ar₂Z, and Ph₂Z, are obtained when the reversible conditions prevail. In this case, $k_f \approx k_{f'} \approx$ $k_{\rm t}({\rm ArX}) \ ({\rm eq} \ 1).$

$$Ar^{*} + PhZ^{-} \xrightarrow{k_{c}} (ArZPh)^{-} \cdot \xrightarrow{k_{c}} ArZ^{-} + Ph \cdot (1)$$

$$\downarrow k_{t}(ArX)$$

$$ArZPh$$

$$Z = Se, Te$$

In the reaction of benzeneselenate ion with phenyl radicals we have found a decrease in the percentage of the substitution product together with an increase in the percentage of the reduction one (hydrogen substitution) as a function of the concentration of the nucleophile.⁴ In this paper we report the study of this reduction process.

Results and Discussion

The photostimulated reaction of iodobenzene with PhSe⁻ and PhTe⁻ ion with a ratio of concentration (1:2:2) gave Ph_2Te (97%) and Ph_2Se (3%). In order to increase the yield of Ph₂Se in the competition experiments we increased the concentration of PhSe⁻ ion. In the reaction carried out with a ratio of PhI:PhTe⁻:PhSe⁻ of 1:2:8, we found Ph_2Te (14%) and Ph_2Se (5% yield) while the percentage of halide liberated was 92%.

This decrease in the overall yield of substitution product must result from the excess of PhSe⁻ ion. In the photostimulated reaction of PhSe⁻ with PhI (1:1) the ratio of Ph₂Se:PhH was approximately 16. The ratio Ph₂Se:PhH was ~ 1.5 with a ratio PhSe⁻:PhI of 4, and it was 0.15 with a ratio PhSe⁻:PhI of 8 (Table I). In the reaction carried out with the latter ratio of nucleophile to substrate but with half the number of irradiation lamps, the ratio $Ph_2Se:PhH$ was ~1.6.

These results clearly show that the concentration of benzene, the reduction product, depends on the concentration of nucleophile and on the light intensity.

A mechanism that accounts for the formation of benzene could be the electron transfer from the nucleophile to phenyl radical (eq 2). This reaction is in competition with

Pierini, A. B.; Rossi, R. A. J. Organomet. Chem. 1978, 144, C12.
 Pierini, A. B.; Rossi, R. A. J. Org. Chem. 1979, 44, 4667.
 Pierini, A. B.; Rossi, R. A. J. Organomet. Chem. 1979, 168, 163.

⁽⁴⁾ Peñéñory, A. B.; Pierini, A. B.; Rossi, R. A. J. Org. Chem. 1984, 49, 486.

the coupling reaction (eq 3). This reduction mechanism could be rejected because under this condition the ratio $Ph_2Se:PhH$ should be independent of the concentration of the nucleophile and of the light intensity.

Another possibility could be the photodecomposition of the nucleophile (eq 4). $PhTe^{-}$ ion is known to decompose under irradiation to give 20% of $Ph_2Te.^4$

$$PhSe^{-} \xrightarrow{n\nu} PhH$$
 (4)

This mechanism could be ruled out because PhSe⁻ ion failed to give benzene in appreciable amounts (Table I, expt 5) when irradiated.

A third mechanism would be the photodetachment of an electron from the nucleophile to give a solvated electron which would reduce the phenyl radicals to phenyl ions, which would ultimately be protonated to form benzene (eq 5 and 6).⁵

$$PhSe^{-} \xrightarrow{h\nu} PhSe_{-} + e_{NH_{3}}^{-}$$
(5)

$$Ph \cdot + e_{NH_3}^{-} \rightarrow Ph^{-} \xrightarrow{NH_3} PhH$$
 (6)

In this mechanism the ratio $Ph_2Se:PhH$ will depend on the light intensity and on the concentration of the nucleophile.

On the other hand if the electron transfer were a photostimulated reaction from the nucleophile to the substitution product, the concentration of phenyl radicals would increase during the reaction, leading ultimately to benzene (eq 7-9).⁶

$$PhSe^{-} + Ph_2Se \xrightarrow{h\nu} (Ph_2Se)^{-} + PhSe$$
(7)

$$(Ph_2Se)^{-} \rightarrow PhSe^{-} + Ph.$$
(8)

$$Ph \rightarrow PhH$$
 (9)

In this mechanism the ratio of reduction to substitution product also depends on the light intensity and on the concentration of the nucleophile.

The photostimulated reaction of PhSe⁻ with Ph₂Se gave benzene (51%) (Table I, expt 6), which means that the nucleophile does react with the substitution product to give benzene when irradiated; therefore, the last two mechanisms can account for it. To differentiate between the two possibilities of reduction, we performed the photostimulated reaction of 2-chloroquinoline with a large excess of nucleophile.

If the photodetachment of an electron is the mechanism in play, the yield of quinoline must be as large as benzene because there should not be an important difference between the rates of electronation of phenyl vs. 2-quinolyl radicals. If on the other hand the mechanism operating were the photostimulated electron transfer from the nucleophile to the substitution product, although 2-quinolyl phenyl selenide is a better electron acceptor than Ph_2Se , there should not be an increase in the concentration of the reduction product since the 2-quinolyl phenyl selenide radical anion did not fragment in our experimental conditions.

In the photostimulated reaction of 2-chloroquinoline with PhSe⁻ in a ratios of 1:4 and 1:8, the yield of 2-quinolyl phenyl selenide was 95–98% and neither benzene nor quinoline was found (<1% yield). On the other hand, in the photostimulated reaction of PhSe⁻ with Ph₂S in a ratio of 9:1 no benzene was found. The formation of Ph₂S radical anion has been ascribed to an irreversible coupling reaction under our experimental conditions.

The fact that Ph_2S reacts with acetone enolate ion under photostimulation to give high yields (66%) of phenylacetone after 30 min of irradiation time indicates that in the absence of good electron acceptors, diphenyl sulfide radical anion mainly fragments to give phenyl radicals.⁷ The absence of benzene in the reaction of $PhSe^-$ with Ph_2S could also be ascribed to a poor electron-transfer reaction from the nucleophile to the substrate.

As a conclusion the mechanism of reduction is the photostimulated electron transfer from the nucleophile to the substitution product. This reaction is important when the aryl radical reacts under reversible conditions with the nucleophiles. When it reacts irreversibly (slow fragmentation rate of the radical anion) this mechanism of reduction does not operate significantly.

Experimental Section

Gas chromatographic analyses were performed on a 2400 Varian Aerograph Series with a flame ionization detector equipped with a Data Procesor Chromatopac C-RIA Schimadzu. Analyses were performed on a 3% SE-30 on 80–100 mesh Chromosorb P, 1.52 mm \times 3.2 mm column.

Materials. Diphenyl ditelluride and diphenyl diselenide were synthesized as described.³ Diphenyl selenide and 2-quinolyl phenyl selenide were synthesized by the $S_{RN}1$ mechanism.² All the other materials were analytical grade, commercially available products used as received. PhSe⁻, PhTe⁻, and PhS⁻ ions were prepared in situ by following the procedure reported.^{2,3}

Photostimulated Reaction. All the reactions were carried out in 250 mL of freshly distilled ammonia at reflux temperature and under N_2 atmosphere. In the competition experiments PhSe⁻ ion was first formed by reaction of diphenyl diselenide (3 mmol) with small pieces of sodium metal slowly added until decoloration of the solution. Then, diphenyl ditelluride (3 mmol) was added and PhTe⁻ (6 mmol) generated by the addition of the exact amount of metal (6 mmol).

The haloaromatic substrate was added and the reaction was irradiated during the period of time indicated in a photochemical reactor equipped with four 250-W lamps with maximum emission at 350 nm (Philips, Model HPT, water refrigerated).

The reaction was then quenched by addition of ammonium nitrate and 100 mL of diethyl ether. Once the ammonia was evaporated water was added. The halide ions were determined potentiometrically in the aqueous layer while its ether extracts were analyzed by GLC. All the products were identified by comparison of their retention times with authentic samples and quantified by using internal standards.

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

Registry No. PhSe⁻, 14971-39-2; PhTe⁻, 65081-67-6; PhI, 591-50-4; Ph₂S, 139-66-2; 2-ClQ, 612-62-4; 2-PhSeQ, 71672-71-4.

⁽⁵⁾ Saeva, F. D.; Olin, G. R. J. Am. Chem. Soc. 1975, 97, 9631. Fisher, M.; Romme, G.; Claesson, S.; Szwara, M. Proc. R. Soc. London, Ser. A 1972, 327, 481. Fox, M. A.; Kobir-Ud-Din, J. Phys. Chem. 1979, 83, 1800.
(6) In poor hydrogen-donating solvents (NH₃), the main reduction process of aryl radicals is the electron-transfer reaction from the radical anions intermediates. See: Amatore, C.; Pinson, J.; Savéant, J. M.; Thiebault, A. J. Am. Chem. Soc. 1981, 103, 6930.

⁽⁷⁾ Rossi, R. A.; Bunnett, J. F. J. Org. Chem. 1973, 38, 1407.