

PHOTOSTIMULATED REACTIONS OF 1-IODOADAMANTANE AND IODOBENZENE
 WITH THIOLATE, SELENATE, AND TELLURATE IONS

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ABSTRACT - The photostimulated reaction of 1-iodoadamantane (1-IAd) with benzenethiolate ion gave the substitution product 1-adamantylphenylsulfide. With benzeneselenate ion (PhSe^-) it gave three products: diphenylselenide, 1-adamantylphenylselenide and di(1-adamantyl) selenide. With benzenetellurate ions it gave the substitution product 1-adamantylphenyltelluride and diphenyltelluride, the latter is ascribed to the photodecomposition of the nucleophile. The photostimulated reaction of 1-IAd with 1-naphtaleneselenate ion only gave the substitution product without scrambling of products.

The photostimulated reaction of PhI with 1-adamantane-selenate ion gave the same three products as the reaction of 1-IAd and PhSe^- ion, but with different ratios of products. The reaction with 1-adamantanetellurate ion gave mainly diphenyltelluride, together with the substitution product 1-adamantylphenyltelluride.

The relationship of the fragmentation rates of Ad-Z and Ph-Z bonds in radical anions of structure $(1-\text{AdZPh})^{\cdot-}$ were studied, and $k_f^{\text{AdZ}} / k_f^{\text{PhZ}}$, being Z=S is 3.7, Z=Se is 9.5 and Z=Te is 13.

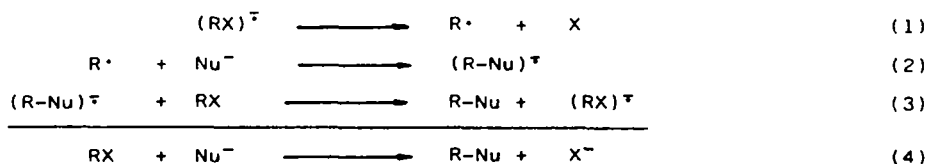
These results suggest that in the photostimulated reactions the products obtained depend on the energy levels of the antibonding σ^* MO and the σ^* MO of the $\text{C-Z}(\text{Z=S, Se and Te})$ bonds of the radical anion intermediate.

The fragmentation rates of the radical anion intermediates depend on the energy levels of the MO'S involved.

INTRODUCTION

The mechanism of radical nucleophilic substitution, or $\text{S}_{\text{RN}}1$, is a chain process that has radicals and radical anions as intermediates.¹ The main steps of the propagation cycle of this mechanism are fragmentation of the radical anion of the substrate (eq. 1), coupling of the radical with the nucleophile (eq. 2), and electron transfer from the radical anion of the substitution product to the substrate (eq.3), a step which completes the chain propagation cycle (Scheme I). Termination steps which depend on the reaction conditions, also occur.

SCHEME I



Summation of these three steps leads to eq. 4, which is a nucleophilic substitution, but with radical and radical anions as intermediates.

The main substrates in these reactions have been alkyl derivatives activated by an electron-withdrawing group,^{1a} unactivated aryl derivatives,^{1b,1c} vinyl halides,² perfluoroalkyl iodides,³ bridgehead halides,⁴ bromocyclopropane⁵ and neopentyl bromide.⁶

We have previously reported that 1-haloadamantanes react under light stimulation with diphenylphosphide and diphenylarsenide ions, as well as with disodium selenide and disodium telluride in liquid ammonia by the $S_{RN}1$ mechanism.⁴ We have now studied the photostimulated reaction of 1-iodoadamantane with benzenethiolate, benzeneselenate and benzenetellurate ions as nucleophiles as well as iodobenzene as substrates and 1-adamantaneselenate and 1-adamantanetellurate ions as nucleophiles.

RESULTS

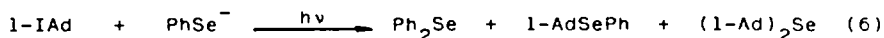
Photostimulated Reactions of 1-Iodoadamantane with Benzenethiolate Ions.

The photostimulated reaction of 1-iodoadamantane (1-IAd) with benzenethiolate ions (PhS^-) in liquid ammonia gave 58% yield of iodide ion and 45% yield of isolated 1-adamantylphenylsulfide (1-AdSPh) after 3hs of irradiation (Table I, expt. 1) (eq. 5).



Photostimulated Reaction of 1-Iodoadamantane with Benzeneselenate Ions.

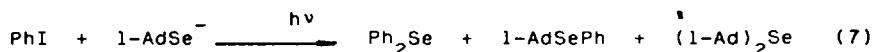
The photostimulated reaction of 1-IAd with benzeneselenate ions (PhSe^-) gave three products: diphenylselenide (Ph_2Se), 1-adamantylphenylselenide (1-AdSePh) and di(1-adamantyl) selenide ($(1\text{-Ad})_2\text{Se}$) (eq. 6)



The relative yield of these three products are: Ph_2Se , 10%, 1-AdSePh, 74% and $(1\text{-Ad})_2\text{Se}$ 16% (Table I, exp. 2-5).

Photostimulated Reaction of Iodobenzene with 1-Adamantaneselenate Ions.

The photostimulated reaction of iodobenzene (PhI) with 1-adamantaneselenate ions (1-AdSe^-) gave the same three products as in the photostimulated reaction of 1-IAd with PhSe^- (see eq. 6). However, the relative amount of the three products is different (Table I, exp. 6-7); Ph_2Se (34%), 1-AdSePh (34%) and $(1\text{-Ad})_2\text{Se}$ (31.5%) (eq. 7).



Photostimulated Reaction of 1-Iodoadamantane with Benzenetellurate Ions.

The photostimulated reaction of 1-IAd with benzenetellurate ions (PhTe^-) gave 46% of iodide ion after 3hs of irradiation and only two products were found, diphenyltelluride (Ph_2Te , 31% of relative yield) and 1-adamantylphenyltelluride (1-AdTePh, 69% of relative yield) (eq. 8).



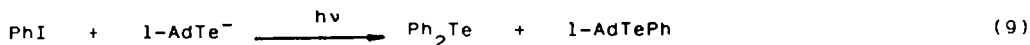
Despite careful search di(1-adamantyl)telluride $(1\text{-Ad})_2\text{Te}$ was not found as product in these reactions.

Photostimulated Reaction of 1-Iodoadamantane with 1-Adamantanetellurate Ions.

One of the expected products of the scrambling reaction of eq. 8 was $(1\text{-Ad})_2\text{Te}$. We thought to synthesize it by photostimulated reaction of 1-IAd and 1-AdTe^- ion, but only adamantane and 1,1'-diadamantyl were formed.

Photostimulated Reaction of Iodobenzene and 1-Adamantanetellurate Ions.

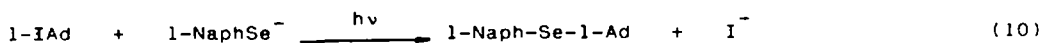
In the photostimulated reaction of PhI with 1-AdTe^- ions as nucleophile, two products were formed Ph_2Te (84% of relative yield) and 1-AdTePh (16% of relative yield) after 3 hs of irradiation (Table I, exp. 9) (eq. 9).



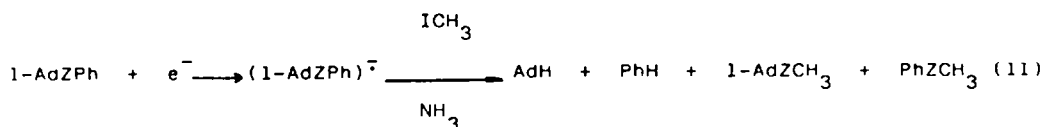
After careful search, no $(1\text{-Ad})_2\text{Te}$ as product was found in this reaction.

Photostimulated Reaction of 1-Iodoadamantane with 1-Naphthaleneselenate Ions.

The photostimulated reaction of 1-IAd with 1-naphthaleneselenate ions (1-NaphSe^-) gave 80% of iodide ion after 2.5 hs of irradiation, and 1-naphthyl-1-adamantylselenide (1-Naph-Se-1-Ad) was formed in 50% of isolated yield (eq. 10). Di(1-adamantyl)selenide was not found by gc ($< 0.1\%$ yield).

Reaction of 1-AdZPh (Z = S, Se and Te) with Sodium Metal in Liquid Ammonia.

The reaction of 1-AdZPh with sodium metal, in liquid ammonia and after quenching the reaction with methyl iodide, gave benzene, adamantane, 1-AdZCH_3 and PhZCH_3 (eq. 11).



The relationship of products was, Z = S, AdH/PhH 3.7; Z = Se, AdH/PhH = 9.5 and Z = Te, AdH/PhH = 13.

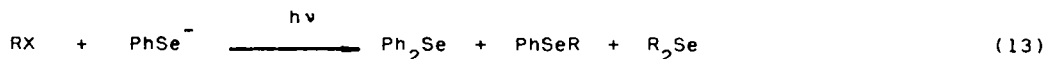
DISCUSSION

In several cases, the $S_{\text{RN}}1$ mechanism occurs without stimulation of any type other than temperature, but when a substrate and a nucleophile do not have the appropriate combination of electron affinity-ionization potential for spontaneous transfer of one electron from the nucleophile to the substrate, the reaction does not take place unless it is promoted by other means, being the photostimulation one of the most used methods.¹ The nature of the initiation step and the actual mechanism of this photostimulated process is not clear, but it gives the first reactive intermediate to start the chain propagation steps of the $S_{\text{RN}}1$ mechanism (eq. 12).



The photostimulated reaction of haloarenes with PhS^- ions in liquid ammonia gave the substitution product arylphenylsulfide in good yields.⁷ On the other hand

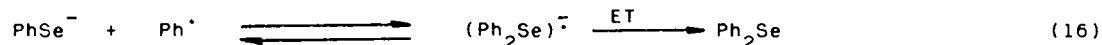
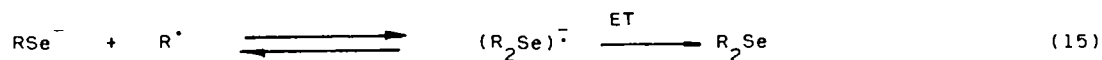
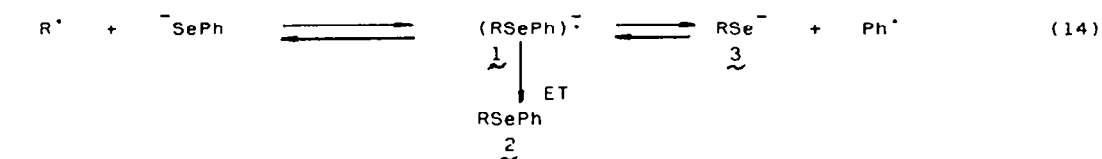
the photostimulated reaction of PhSe^- ions as nucleophile with some haloarenes, such as 1-chloro naphthalene or 2-chloroquinoline also gave the substitution product in good yields,⁸ but with other haloarenes, such as p-iodoanisole or 2-chloropyridine, three products were formed: diphenylselenide, arylphenylselenide and diarylselenide, being aryl: p-anisyl or 2-pyridyl (eq. 13).⁹



R = p-anisyl; 2-pyridyl

These results were explained by adding more steps to the Scheme I of the $\text{S}_{\text{RN}}1$ mechanism, as is shown in Scheme II.

SCHEME II

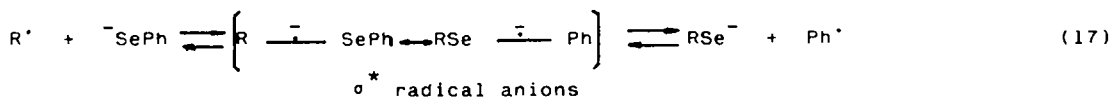


R = p-anisyl; 2-pyridyl

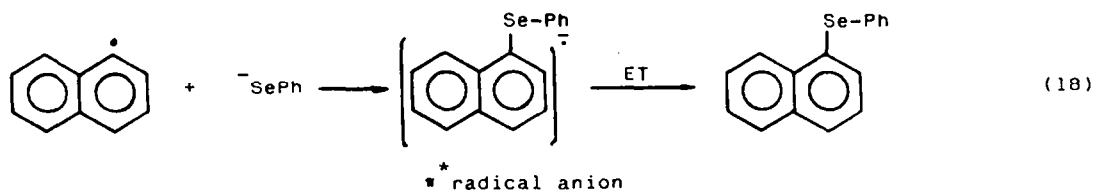
ET = Electron transfer

The arylphenylselenide radical anion 1 formed by coupling of aryl radical with PhSe^- ion undergoes three competitive reactions, namely: reversion to starting materials, electron transfer to the substrate to give the substitution product aryl phenylselenide 2, and fragmentation of the Ph-Se bond to give the areneselenate ion RSe^- 3 and phenyl radical (eq. 14).

In eq. 14 of Scheme II two new intermediates are formed, areneselenate ion 3 and phenyl radical. They can further react with each other to give the radical anion 1, or they can diffuse apart and 3 competes as nucleophile with aryl radicals to give ultimately diarylselenide (eq. 15), whereas phenyl radicals can be trapped by PhSe^- ion to give diphenylselenide (eq. 16). The fragmentation of the radical anion 1 occurs because the energy levels of the antibonding π^* MO and the antibonding σ^* MO of the C-Se bonds are close enough, and from the antibonding σ^* MO fragmentation occurs (eq. 17)¹⁰⁻¹¹



However, if the aromatic moiety has a low lying antibonding π^* MO, such as naphthalene or quinoline, the radical anion formed by coupling of 1-naphtyl or 2-quinolyl radicals with PhSe^- ion, will not fragment and only the substitution product is obtained without scrambled products, in this case a π^* radical anion is formed (eq. 18)



The photostimulated reaction of *p*-iodoanisole and 1-chloronaphthalene with PhTe^- ion gave scrambled products in the sense of eq. 13, but only gave the substitution product with 2-chloroquinoline as substrate.⁹

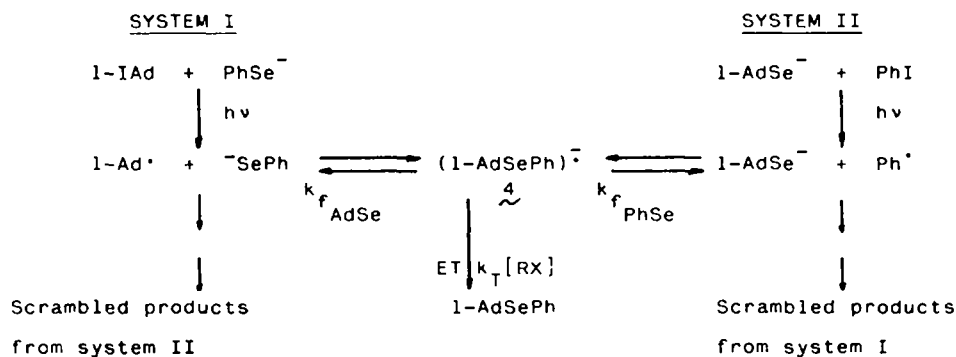
The results of the photostimulated reaction of haloarenes with PhS^- , PhSe^- and PhTe^- ions indicate that the products obtained depend on the reduction potential of the aryl moiety (antibonding π^* MO) and on the bond strength of the Ph-Z ($\text{Z} = \text{S}, \text{Se}$ and Te) bonds.⁹⁻¹⁰

In the photostimulated reaction of 1-IAAd with PhS^- ions only the substitution product 1-AdSPh was obtained, a similar result as with the photostimulated reaction of PhI with PhS^- ions.

In the photostimulated reaction of 1-IAAd with PhSe^- ions, named system I by us, three products were obtained: Ph_2Se , 1-AdSePh and $(1\text{-Ad})_2\text{Se}$. The presence of these scrambled products can be easily explained following Scheme II, being $\text{R} = 1\text{-adamantyl}$.

The photostimulated reaction of PhI with 1-AdSe $^-$ ion, (exchange of leaving group and nucleophilic center in both moieties), which we named system II, lead to the same radical anion intermediate 4 as in system I by coupling of phenyl radical with 1-AdSe $^-$ ion, and it also gave the same three products observed in system I, however the relative amount of the scrambled products were different (Scheme III).

SCHEME III



As the rate of electron transfer from the radical anion 4 to the substrates 1-IAAd or PhI should be similar and probably diffusion controlled,¹⁰ the differences in the relative amount of scrambled products from system I and system II, suggest a different fragmentation rate of the bonds Ad-Se and Ph-Se in the radical anion intermediate 4.

There are different amounts of scrambled products because the reversible reactions (coupling of radical with the nucleophiles to form radical anions, and then fragmentation) are competing with irreversible reactions (electron transfer to the substrate).

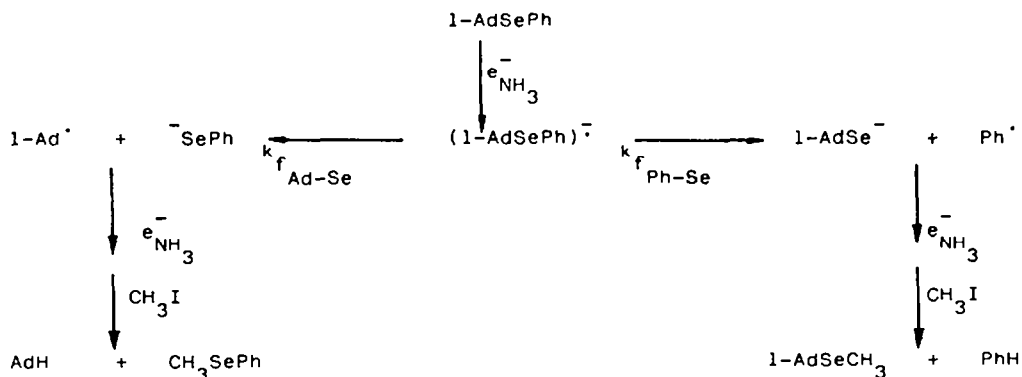
If both fragmentation rates $k_{f_{\text{AdSe}}}$ and $k_{f_{\text{PhSe}}}$ were similar, the same amount of scrambled products should be expected from systems I and II.

On the other hand, if $k_{f_{\text{AdSe}}} \gg k_{f_{\text{PhSe}}}$ scrambled products would be formed only from system II but not from system I.

In the reaction of system I we obtained the substitution product 1-AdSePh in 74% yield, and the scrambled products Ph_2Se and $(1\text{-Ad})_2\text{Se}$ in about 10% yield. In the reaction of System II, the substitution product and the scrambled products gave similar yields (about 30% each). These results suggest that $k_{f_{\text{AdSe}}} > k_{f_{\text{PhSe}}}$.

In order to confirm that there is a different rate of fragmentation of Ad-Se and Ph-Se bonds, we formed the same radical anion intermediate in these reactions by another route such as the reaction of 1-AdSePh with solvated electrons in liquid ammonia and trapped of the ions formed by its fragmentation by reaction with iodomethane (Scheme IV).

SCHEME IV



The ratios between $\text{PhSeMe}/1\text{-AdSeMe}$ and AdH/PhH corresponds to $k_{f_{\text{AdSe}}}/k_{f_{\text{PhSe}}}$ and the average gave 9.5 ± 0.8 .

These results are in agreement with those obtained from system I and II and confirm the different rates of fragmentation of Ad-Se and Ph-Se bonds.

As we discussed before, the naphthyl moiety stabilized the radical anion 1-naphthylphenylselenide, and only the substitution product is formed.

In the photostimulated reaction of 1-naphthaleneselenate ion with 1-IAd, we found only the substitution product 1-naphthyl-1-adamantylselenide. This result shows that the naphthyl moiety avoids the fragmentation of the radical anion, and does not matter if it is in the substrate or in the nucleophile.

In the photostimulated reaction of 1-IAd with PhTe^- ion, which was named System I, we found Ph_2Te and the substitution product 1-AdTePh, but we were unable to find $(1\text{-Ad})_2\text{Te}$.

As we discussed before, if $k_{f_{\text{AdTe}}} \gg k_{f_{\text{PhTe}}}$, mainly the substitution product 1-AdTePh should be formed in the reaction of System I with no scrambled products, and the presence of Ph_2Te could be ascribed to the photostimulated decomposition of the nucleophile PhTe^- . (eq. 19)



It is known that Ph_2Te is formed when PhTe^- is irradiated in liquid ammonia.⁹

On the other hand, in the photostimulated reaction of 1-AdTe^- ion with PhI which we named System II, we found mainly Ph_2Te (84% relative yield) and a small yield of the substitution product 1-AdTePh . In system II the formation of Ph_2Te can be ascribed only to the fragmentation of the Ad-Te bond of the radical anion intermediate $(1\text{-AdTePh})^\cdot$. The photodecomposition of 1-AdTe^- ion in the sense of eq. (19), should give $(1\text{-Ad})_2\text{Te}$ but it was not found as product in these reactions. All these results suggest that $k_{f\text{AdTe}} \gg k_{f\text{PhTe}}$.

In the reaction of 1-AdTePh with solvated electrons in liquid ammonia, in the sense of scheme IV, we found 93% of adamantane and only 7% of benzene. This means that $k_{f\text{AdTe}}/k_{f\text{PhTe}}$ is about 13.

From this relationship of rates of fragmentation, only the substitution product 1-AdTePh is observed in the reaction of system I. The presence of Ph_2Te is ascribed to the photodecomposition of the nucleophile PhTe^- ion.

In the reaction of system II, Ph_2Te is mainly observed, coming from the fragmentation of the radical anion intermediate.

CONCLUSIONS

The photostimulated reaction of 1-IAd with PhS^- , PhSe^- and PhTe^- as nucleophiles gave different results. Only the substitution product 1-AdSPh is obtained with PhS^- because in the competing reactions $k_t[1\text{-IAd}] \gg k_{f\text{AdS}}/k_{f\text{PhS}}$. With PhSe^- , there is a scrambling of products, but the substitution product is mainly obtained due to the fact that $k_{f\text{AdSe}}/k_{f\text{PhSe}}$ is 9.5. However, if the nucleophile has a low antibonding π^* MO, as the naphthaleneselenate ion, no scrambling of products is formed because in this radical anion intermediate the odd electron is localized in the naphthyl moiety, and no fragmentation occurs.

With PhTe^- , only the substitution product is obtained because the difference in the rates of fragmentation is too large to form scrambled products,

$$k_{f\text{AdTe}}/k_{f\text{PhTe}} = 13.$$

In the photostimulated reaction of PhI with 1-AdSe^- , similar yields of products are observed, and with 1-AdTe^- , the principal product comes from the fragmentation of the radical anion intermediate.

In the competition of the fragmentation rates of radical anions of the structure $(1\text{-Ad-Z-Ph})^\cdot$, being $Z = \text{S, Se and Te}$, the weaker the bond is, the more differences in rates are found. Thus, the relationship of $k_{f\text{AdZ}}/k_{f\text{PhZ}}$, with $Z = \text{S}$ is only 3.7, and with Se , 9.5 and with Te is 13.

These differences in fragmentation rates suggest that there are, differences in the antibonding σ^* MO of the Ad-Z and Ph-Z bonds, being the former lower in energy, and the differences increase as we go down in the periodical table.

EXPERIMENTAL SECTION

General methods: NMR spectra were recorded on a Varian T-60 nuclear magnetic resonance spectrometer. Mass spectral measurements were obtained with a Finnigan Model 3300 mass spectrometer. Gas chromatographic analyses were performed on a Varian Aerograph Series 2400 instrument with a flame-ionization detector using a column packed with

1.5% OV-101 on Chromosorb P(1.5m x 3mm). Irradiation was conducted in a reactor equipped with three 250-W UV lamps emitting maximally at 350 nm (Phillips Model HPT, water refrigerated).

Materials: Reagents were all commercially available materials unless otherwise indicated and were purified by standard procedures. Liquid ammonia was dried over sodium and distilled under nitrogen into the reaction flask. The sodium metal was cut into small pieces and washed free of oil with dried diethyl ether immediately before addition to the reaction flask.

1-Iodoadamantane, (1-AdSe)₂ and (1-AdTe)₂ were obtained from previous work^{4b}; the nucleophiles 1-AdSe⁻, PhS⁻, PhSe⁻ and PhTe⁻ were obtained from (1-AdSe)₂, (1-AdTe)₂, Ph₂S₂, Ph₂Se₂, Ph₂Te₂ and two equiv. of sodium metal in liquid ammonia.

Photostimulated Reaction of 1-Iodoadamantane with Benzeneselenate Ion.

The photostimulated reaction of 1-iodoadamantane with benzeneselenate ion is representative. Into a three-necked 500 ml, round-bottomed flask, equipped with a cold finger condenser charged with solid CO₂ and ethanol, a nitrogen inlet and a magnetic stirrer, was condensed 250 ml of ammonia, to the ammonia were added 362 mg. of diphenyldiselenide (1.16 mmol) and 55 mg. of sodium metal (2.40 mmol) to form the benzeneselenate ion. 626 mg. of 1-iodoadamantane (2.30 mmol) was added to this solution and then the solution irradiated for 3 hs.

The solution was quenched by addition of ammonium nitrate in excess, and ammonia was allowed to evaporate, water (100 ml) was added to the residue, and the mixture was extracted 3 times with 10 ml of diethyl ether. Diphenyldisulfide was added as an internal standard to a sample of the ether extract to quantify 1-adamantylphenyl selenide, diphenylselenide and di(1-adamantyl) selenide.

In the water layer, iodide ion was determined potentiometrically (92% yield based on the nucleophile concentration).

The ether extract was evaporated until all ether was removed, and the residue was column chromatographed on silica gel and eluted with petroleum ether the products isolated were 1-adamantylphenyl selenide (yield 62%); yellow solid; m. p. 35°C; NMR (δ) 1.58-2.05 (m, 15 H); 7-7.8 (m, 5H); mass spectrum, m/e (relative intensity) = 292 (7), 290 (3,5), 288 (2), 157 (9), 155 (7), 135 (100), 107 (4), 93 (9), 77 (4). Di(1-adamantyl) selenide (yield, 14%); solid; m.p. 155-160°C; recrystallized from acetone; NMR (δ) = 1.66-2.22 (m); mass spectrum, m/e (relative intensity) 350 (18), 348 (11), 346 (5), 215 (3.5), 135 (100), 93 (18).

Diphenylselenide (yield, 13%), after being isolated, was identified by oxidation with Br₂ in CCl₄ giving a precipitate of Ph₂SeBr₂ this product recrystallized from CCl₄, m.p. 143-144°C (Lit.¹² 144°C).

Photostimulated Reaction of 1-Iodoadamantane with Benzenethiolate Ion.

The procedure was similar to that for the previous reaction. In the water layer, iodide ion was determined potentiometrically (60% yield based on the nucleophile concentration). The ether extract was evaporated, and the residue was column chromatographed on silica gel and eluted with petroleum ether. The product isolated was 1-adamantyl phenylsulfide; solid; m.p. = 71,5-72°C; recrystallized from methanol; NMR (δ) 1.62-2.2 (m, 15H), 7.0-7.6 (m, 5H); mass spectrum, m/e, (relative intensity) = 244 (7.5), 135 (100), 108 (15), 93 (20), 77(15). The amount of product isolated was 250 mg. (45% yield based on the iodide).

Photostimulated Reaction of 1-Iodoadamantane with Benzenetellurate Ion.

The procedure was similar to that for the previous reactions. All the attempts to isolate the products failed because they always decomposed. As it was not possible to obtain the isolated yield, we quantified them by gc immediately after the ammonia evaporated and only the relative yields were obtained considering equal molar response. By column chromatography on silica gel and eluted with petroleum ether, only a pure sample of 1-adamantylphenyltelluride was isolated in low yields, orange solid m.p. = 113-115°C, recrystallized from petroleum ether; mass spectrum, m/e (relative intensity) 342 (3.5), 340 (3.5), 338 (1.6), 207 (14), 205 (14), 135 (100), 107 (8), 93 (18), 77 (16).

Reaction of 1-AdZPh (Z = S, and Te) with Sodium Metal in Ammonia.

To 250 ml of distilled ammonia was added 1-AdZPh (1 to 2 mmol) and then sodium metal was added in small pieces until the blue solution of sodium metal in excess persisted for 10 min. the reaction was quenched by methyl iodide in excess (1.5 to 2.5 mmol), 100 ml of diethyl ether was added, and toluene was added as internal standard to quantify benzene and naphthalene was added to quantify adamantane. In some reactions the selenides were also quantified (PhSeCH₃ and 1-AdSeCH₃) and the relationship PhSeCH₃/1-AdSeCH₃ was similar to AdH/PhH.

TABLE I: Photostimulated Reactions of 1-Iodoadamantane and Iodobenzene with Thiolate, Selenate and Tellurate ions in liquid Ammonia^a.

#	RX(mmole)	RZ ⁻ (mmole)	X ⁻	Ph ₂ Z	1-AdZPh	1-Ad ₂ Z
Yield,% ^b (relative Yields)						
1	1-I-Ad(3.90)	PhS ⁻ (4.01)	58	0 (0)	45 ^c (100)	0 (0)
2	1-I-Ad(2.34)	Ph-Se ⁻ (1.91)	d	5 (6)	72 (86)	7 (8)
3	1-I-Ad(2.60)	Ph-Se ⁻ (2.47)	d	3 (7)	30 (70)	10 (23)
4	1-I-Ad(2.20)	Ph-Se ⁻ (2.00)	d	6 (13)	32 (70)	8 (17)
5	1-I-Ad(2.39)	Ph-Se ⁻ (2.32)	92	13 ^c (15)	62 ^c (69)	14 ^c (16)
	Average	# 2-5		(10 ± 5)	(74 ± 12)	(16 ± 8)
6	Ph-I (0.37)	1-Ad-Se ⁻ (0.30)	100	(33)	(36)	(31)
7	Ph-I (1.07)	1-Ad-Se (0.76)	d	(35)	(33)	(32)
	Average	# 6-7		(34 ± 1)	(35 ± 3)	(32 ± 1)
8	1-I-Ad(5.08)	Ph-Te ⁻ (5.07)	46	(31)	(69)	(0)
9 ^e	Ph-I (1.38)	Ad-Te ⁻ (1.38)	d	66 ^c (84)	13 ^c (16)	0 (0)
10 ^f	1-I-Ad(1.00)	Ad-Te ⁻ (0.96)	98	--	--	0
11	1-I-Ad(1.90)	1-Naph-Se ⁻ (1.60)	80	0 (0)	50 ^c (100)	0 (0)

a) The reactions were carried out in 250 ml of liquid ammonia and irradiated during 3 ns. Ad = 1-adamantyl.

b) Iodide ions were determined potentiometrically and the substitution products by GC, unless otherwise indicated and based on the nucleophile concentration.

c) Isolated yields. d) Not quantified. e) The reaction was quenched adding methyl iodide, and 1-adamantyl methyl telluride was found in 5.4% yield, together with 7% yield of unreacted iodobenzene, AdH and (1-Ad)₂ were also formed.

f) The only products found were adamantane and 1,1'-diadamantyl.

REFERENCES AND NOTES

- ¹ For reviews see: a) Kornblum, N., *Angew. Chem. Int. Ed. Engl.*, **14**, 734 (1975); Kornblum, N., "The Chemistry of the Functional Groups", Supplements F (Ed. S. Patai and Z. Rappoport) Ch. 10 (John Wiley, Chichester) (1982); Norris, R. K. *idem*, Supplement D Ch. 16, (1983).
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