appear in connection with a report of the crystal structure of *syn*-(H,Cl)B.[14] The unusually strong C–H stretching vibration which appears in the stage III IR spectrum is probably due to intermolecular hydrogen bonding, with a C—H···O=C bond between bimanes in the same plane.[14]

It is interesting to note that Seki and Itoh[15] have proposed that rearrangement of anthracene in ultrathin films from random order to "dimers" is responsible for the spectroscopic shifts in the UV–vis spectra appearing after annealation over the range from 6 to 240 K. We have created "ultrathin" films of *syn*-(H,Cl)B on Corning glass 7930; such films show UV–vis absorption spectra like those obtained for glassy films or solutions.[16]

The orange color of *syn*-(H,Cl)B crystals is clearly deeper than might have been expected from the light yellow solutions of the compound. The present results demonstrate that the spectroscopic properties of the crystal are different from those of the molecules in solution and that modification of the electronic transitions of the molecule rather than new absorption due to complex formation is involved.

In summary, we have shown that solid-state spectroscopic properties of the *syn*-bimanes are easily studied and have a variety of interesting features. Both kinetic and equilibrium changes should be accessible to study. The apparatus we use is convenient and simple compared to the usual ones for thin films.[15] Its use opens the field of physical and chemical investigation on thin films of organic materials in glassy and crystalline states to those without elaborate cryoscopic equipment.

Acknowledgment. We are grateful to the European Research Office, United States Army, for support.

Registry No. 1, 78763-68-5; 2, 68654-26-2.

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[15] Seki, H.; Itoh, U. *J. Chem. Phys.* **1980**, *72*, 2166–2178.

[16] The special experimental conditions required for deposition of material on optical windows of Corning glass 7930 ("thirsty glass") are as follows: A copper ring is used to attach the 7930 optical window to the inner liquid N_2-cooled sapphire window of the thin-film spectroscopic apparatus (see ref 8). Deposition is carried out slowly, but the spectra observed are characteristic of stage II organization. However, annealing at ca. 90 °C produces a film with a stage I spectrum, indicating that the *syn*-(H,Cl)B had penetrated the pores of the porous glass and formed a thin film. Whether the stage I spectrum is simply the result of the diminished intermolecular interaction (like that in a glassy film) in an ultrathin film and the consequent lack of long-range organization or the result of interaction of the *syn*-(H,Cl)B in a moderately organized state (local groups of no more than five to seven molecules could be stacked in the 40-Å-diameter pores) with the surface of the 7930 glass cannot now be ascertained.

Direct (One Pot) Synthesis of Organoselenium and Organotellurium Compounds from the Metals[1]

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Received March 2, 1981

The chemistry of organoselenium compounds has been growing in recent years, because of the many synthetic applications of organoselenium compounds.[2]

Table I. Photostimulated Reaction of Iodobenzene with Selenide and Telluride Ions in Liquid Ammonia[a]

PhI, mmol	XNa_2,[b] mmol	method[c]	product[m] (yield, %)
		For X = Se	
9.96	4.97	A	PhSePh (12),[d] PhSeSePh (78)[d]
9.87	4.94	B	
9.96	4.98	C,[e] A	PhSeSePh (76)[f]
17.10	8.55	C, A	PhSeSePh (92)[f]
10.14	5.06	C, D	PhSeMe (67)[g]
9.90	4.95	C, E	(1-Naph)SePh (67),[d] PhSeSePh (29)[d]
10.14	5.07	C, F	(1-Naph)SePh (98)[f]
9.99[h]	5.00	C, D	(o-MeC_6H_4)SeMe (87)[f]
		For X = Te	
10.76	5.29	A	PhTePh (17),[i] PhTeTePh (17)[i]
9.96	4.99	B	
10.00	5.01	D	PhTePh (21),[i] PhTeMe (29)[i]
10.05[j]	5.02	A	$(1\text{-Naph})_2Te$ (35),[k] $(1\text{-Naph})_2Te_2$ [l]

[a] Reactions were carried out in 250–300 mL of dry liquid ammonia and were irradiated 4 h with four 250-W UV lamps (Philips, Model HPT, water refrigerated). [b] Prepared in situ by 1 mol of selenium or tellurium metals and 2 mol of sodium metal. [c] A, the reaction mixture was air oxidized: B, dark reaction; C, after the irradiation sodium metal was added until a blue solution was obtained; D, the reaction was quenched by methyl iodide; E, 1-iodonaphthalene (5.0 mmol) was added, and the reaction was irradiated for 50 min; F, 1-iodonaphthalene (5.1 mmol) was added, and the reaction was irradiated for 160 min. [d] Determined by GC with phenanthrene as an internal standard. [e] One-hour irradiation. [f] Isolated yield. [g] Isolated as the dibromide. [h] *o*-Iodotoluene. [i] Determined by GC with 9-bromophenanthrene as an internal standard. [j] 1-Iodonaphthalene. [k] Determined by GC with 9,10-dibromophenanthrene as an internal standard. [l] Not quantified. [m] Naph = naphthyl.

One convenient method for the synthesis of symmetrical and unsymmetrical diaryl selenides is the photostimulated reaction of phenyl selenide ion and aryl halides in liquid ammonia by the $S_{RN}1$ mechanism.[3,4]

We now describe the photostimulated reaction of iodobenzene with selenide ion as the nucleophile, which can be used as a "one pot" method to prepare arylselenols, diaryl diselenides, aryl alkyl selenides, and symmetrical and unsymmetrical diaryl selenides in excellent yields.

Results and Discussion

Selenide ion can be formed from the reaction of selenium and sodium metals in liquid ammonia (eq 1).[5]

$$Se + 2Na \xrightarrow{NH_3} Se^{2-} + 2Na^+ \qquad (1)$$

When a solution of selenide ion thus prepared and iodobenzene was irradiated and the resulting solution was air oxidized,[6] diphenyl selenide and diphenyl diselenide were obtained (Table I). In the dark there is no reaction, thus ruling out benzyne or other alternative mechanisms.

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

[2] For a review on functional-group manipulations using organoselenium compounds, see: Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22.

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

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[5] Bogolyubov, G. M.; Shlyk, Y. N.; Petrov, A. A. *Zh. Obshch. Khim.* **1969**, *39*, 1804.

[6] Sharpless, K. B.; Yound, M. W. *J. Org. Chem.* **1975**, *40*, 947.

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Scheme I

$$PhI + Se^{2-} \xrightarrow{h\nu} (PhI)^{-}\cdot + \text{residue} \tag{2}$$

$$(PhI)^{-}\cdot \rightarrow Ph\cdot + I^{-} \tag{3}$$

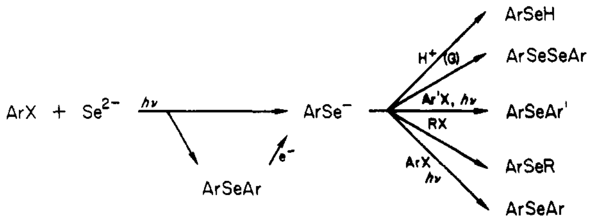
$$Ph\cdot + Se^{2-} \rightarrow (PhSe^{-})^{-}\cdot \tag{4}$$

$$(PhSe^{-})^{-}\cdot + PhI \rightarrow PhSe^{-} + (PhI)^{-}\cdot \tag{5}$$

$$Ph\cdot + PhSe^{-} \rightarrow (PhSePh)^{-}\cdot \tag{6}$$

$$(PhSePh)^{-}\cdot + PhI \rightarrow PhSePh + (PhI)^{-}\cdot \tag{7}$$

Scheme II



These reactions are believed to occur by the $S_{RN}1$ mechanism, as sketched in Scheme I.

This is the usual scheme for $S_{RN}1$ reactions that comprise a photostimulated initiation step (eq 2) and propagation steps (eq 3–5).[4] Some of the phenyl selenide ion formed in eq 5 can react with phenyl radical to give ultimately diphenyl selenide (eq 6, 7).[3] The remainder was isolated as diphenyldiselenide.[6]

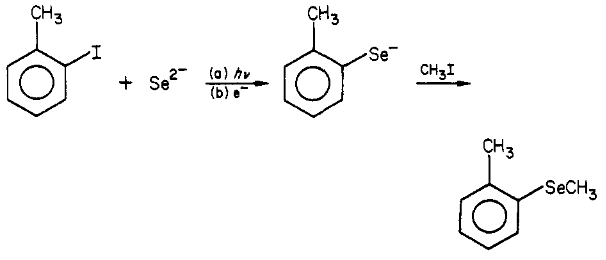
This reaction leads to a mixture of two products, namely, phenyl selenide ion and diphenyl selenide; however, the latter can be easily converted into the former by reduction of the reaction mixture with solvated electrons (eq 8).[7]

$$PhSePh + 2e^{-} \xrightarrow{NH_3} PhSe^{-} + PhH \tag{8}$$

The whole procedure leads to a nearly quantitative yield of phenyl selenide ion based on the amount of selenium metal used.

Phenyl selenide ion can be protonated and isolated as benzeneselenol, but in this case care must be taken to exclude oxygen because it is easily oxidized by air to diphenyl diselenide. In fact air oxidation of the reaction mixture is a very convenient way of formation of diphenyl diselenide, which was isolated in 92% yield (Table I).

The aryl selenide ion can also be trapped by alkyl halides to form aryl alkyl selenides. For instances phenyl methyl selenide (isolated as the dibromide) was obtained in 67% yield by the reaction of phenyl selenide ion and methyl iodide, and *o*-methylphenyl selenide ion, obtained by the method reported here, reacted with methyl iodide to form *o*-methylphenyl methyl selenide in 87% yield (eq 9).



(9)

Besides, when 1-iodonaphthalene was added to a solution of phenyl selenide ion freshly prepared in liquid ammonia and the mixture was submitted to the usual method of photostimulation,[3] a 98% yield of 1-naphthyl phenyl selenide was obtained. Scheme II summarize all these possible transformations.

Although no efforts have been made to optimize these reactions, they clearly show the versatility of the method to obtain several organoselenium compounds.

There are other alternative methods to obtain some of these compounds; for instance, benzeneselenol can be prepared from phenylmagnesium bromide and selenium[8] or diphenyl diselenide by bromine oxidation of (phenylseleno)magnesium bromide,[9] but the method reported here appears to us to be the most advantageous for preparation of diaryl selenides or alkyl aryl selenides.

Sulfide ion prepared as selenide ion in liquid ammonia did not react with iodobenzene after 4 h of irradiation. This result is not fully understood, because thiophenoxide ion is about 20 times as reactive as phenyl selenide ion in photostimulated reactions with iodobenzene in liquid ammonia.[10]

Telluride ion, prepared as was the selenide ion in liquid ammonia, also reacts with iodobenzene under photostimulation, but the yields are somewhat lower than with selenide ion (Table I). Besides, this nucleophile does not offer the synthetic possibilities described in Scheme II for selenide ion. In the photostimulated reaction of telluride ion with iodobenzene, a mixture of phenyl telluride ion and diphenyl telluride is formed, and the reduction of the reaction mixture with solvated electrons leads ultimately to benzene.[11] Moreover, the photostimulated reaction of aryl halides with phenyl telluride ion gives a mixture of products derived from fragmentation of the radical anion intermediate.[3]

Experimental Section

General Methods. The instruments and procedures were as previously reported.[3]

Preparation of Phenyl Selenide Ion in Liquid Ammonia. The preparation of phenyl selenide ion is representative. Dry ammonia (250–300 mL) was condensed into a three-necked, 500-mL, round-bottomed flask fitted with a cold-finger condenser, nitrogen inlet, and magnetic stirrer. Selenium metal (675.2 mg, 8.55 mmol) and sodium metal (395 mg, 17.2 mmol) were added, and after about 60 min a clear solution was formed. Iodobenzene (3.5 g, 17.1 mmol) was added, and after 4 h of irradiation, sodium metal was added in excess in small pieces until a blue solution persisted (10 min).

Synthesis of Diphenyl Diselenide. To the solution of phenyl selenide ion thus prepared was added water (50 mL), and the ammonia was allowed to evaporate. To the residue were added ethyl ether (100 mL) and water (100 mL), and air was bubbled into the mixture; the ether solution was separated, dried, and evaporated, yielding diphenyl diselenide: 1.22 g (3.92 mmol, 92% yield); mp 55–56 °C; after recrystallization from ethyl alcohol, mp 62–63 °C (lit.[6] mp 63 °C).

Synthesis of 1-Naphthyl Phenyl Selenide. To a solution of phenyl selenide ion prepared from 10.14 mmol of iodobenzene and 5.07 mmol of selenide ion was added 5.1 mmol of 1-iodonaphthalene, after 160 min of irradiation, the reaction was quenched by addition of water (50 mL), and the ammonia was allowed to evaporate. To the residue were added ethyl ether (100 mL) and water (100 mL). The ether solution was separated, dried, and evaporated, and 1-naphthyl phenyl selenide was isolated in 98% yield and identified by comparison with an authentic sample.[3]

Synthesis of Phenyl Methyl Selenide Dibromide. To a solution of phenyl selenide ion prepared from 10.14 mmol of iodobenzene and 5.06 mmol of selenide ion was added 5.21 mmol of methyl iodide. The reaction was quenched by adding water

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(50 mL), and the ammonia was allowed to evaporate. To the residue were added ethyl ether (100 mL) and water (100 mL). The ether solution was extracted, dried, and evaporated, and phenyl methyl selenide was isolated (778 mg, 4.55 mmol, 90% yield) and then oxidized with Br_2 in CCl_4, giving a precipitate of phenyl methyl selenide dibromide: 1.115 g (3.3 mmol, 67% yield); after recrystallization from CCl_4, mp 141–143 °C (lit.[3] mp 143–144 °C).

Synthesis of *o*-Methylphenyl Methyl Selenide. *o*-Methylphenyl selenide ion was prepared as described above from 9.99 mmol of *o*-iodotoluene and 5.00 mmol of selenide ion with 4 h of irradiation, and then sodium metal was added in excess, followed by methyl iodide (5.2 mmol). Water (50 mL) was added and the ammonia was allowed to evaporated. To the residue were added ethyl ether (100 mL) and water (100 mL). The ether solution was separated, dried, and evaporated, and *o*-methylphenyl methyl selenide was isolated in 87% yield and purified by column chromatography.[12]

Acknowledgment. A.B.P. gratefully acknowledges receipt of a fellowship from the Consejo Universitario de Investigaciones, Universidad Nacional de Córdoba.

Registry No. Phenyl selenide ion, 14971-39-2; selenium, 7782-49-2; iodobenzene, 591-50-4; diphenyl diselenide, 1666-13-3; 1-iodonaphthalene, 90-14-2; 1-naphthyl phenyl selenide, 65490-21-3; phenyl methyl selenide, 4346-64-9; phenyl methyl selenide dibromide, 78763-69-6; *o*-methylphenyl selenide ion, 78763-70-9; *o*-iodotoluene, 615-37-2; (*o*-methylphenyl)methyl selenide, 1528-88-7; diphenyl selenide, 1132-39-4; diphenyl telluride, 1202-36-4; diphenyl ditelluride, 32294-60-3; phenyl methyl telluride, 872-89-9; bis(1-naphthyl) telluride, 4537-22-8; bis(1-naphthyl) ditelluride, 32294-58-9; $SeNa_2$, 1313-85-5; $TeNa_2$, 12034-41-2; Te, 13494-80-9.

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7-Amino-5-(Methylamino)heptanoic Acid: A Potential Putrescine Hapten

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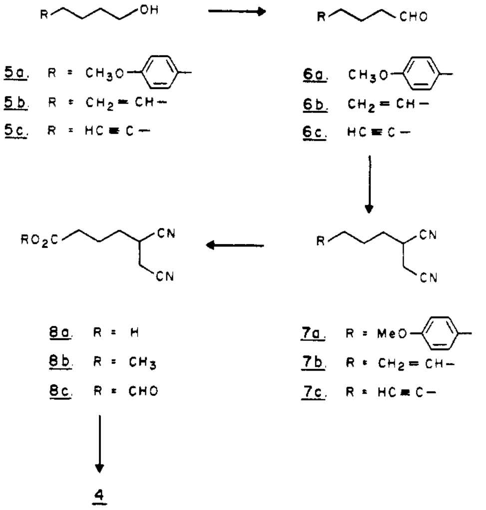
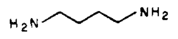
Received May 8, 1981

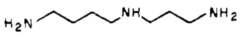
There is currently a significant interest in the development of specific and highly sensitive technqiues for analysis of the biologically ubiquitous di- and polyamines putrescine, spermidine, and spermine (1–3), respectively.[2-5] Radioimmunoassay techniques, currently available for spermidine[6] (2) and spermine[7,8] (3) but not putrescine (1), are of particular interest in view of their high sensitivity and specificity, low cost and convenience in clinical settings.[2,3] We have considered the structural requirements for a hapten suitable for developing a specific radioimmunoassay for the diamine putrescine (1). 7-Amino-5-(aminomethyl)heptanoic acid (4) was selected for initial study; this report describes an efficient synthesis of 4 which permits facile introduction of a ^{14}C label at the 5-aminomethyl carbon.

Scheme I





1



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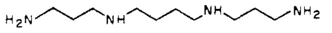
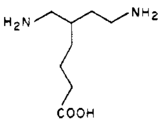


3



4

A number of criteria were employed in the design of 4 as a hapten for preparation of antiputrescine antibodies. The aliphatic chain containing the terminal carboxylic acid function to be used for attachment of the hapten to a protein carrier via amide linkage was placed β to the amine group of the putrescine moiety to minimize steric factors detrimental to antiputrescine antibody development. The length of the chain separating the carboxyl and amine functional groups was chosen to minimize intramolecular lactamization during coupling of the hapten to protein.[9]

The synthetic route used for construction of 4 is shown in Scheme I. In an initial synthesis, commercially available 4-(4-methoxyphenyl)butanol (**5a**) was oxidized to the corresponding aldehyde **6a** in 89% yield, using a procedure developed by Swern and co-workers.[10] Elaboration of a succinonitrile moiety with **6a** was accomplished by a one-step method reported by Whitely and Marianelli.[11] A dimethyl sulfoxide solution of aldehyde **6a**, potassium cyanide, and ethyl cyanoacetate was allowed to react at room temperature for 16 h and then acidified and heated to afford, after chromatographic purification, a 72% yield of dinitrile **7a**.

The selective oxidation of the aromatic ring of **7a** by ruthenium tetraoxide was used to construct the carboxyl group.[12] Treatment of **7a** with ruthenium tetraoxide resulted in an exothermic reaction with evolution of carbon dioxide and formation of carboxylic acid **8a**, which was methylated with diazomethane and purified by chroma-

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(1) (a) Department of Chemistry, Lehigh University, Bethlehem, PA 18015. (b) Recipient of a Career Development Award, 1978–1983, from the National Cancer Institute of the National Institutes of Health (CA 00486).

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