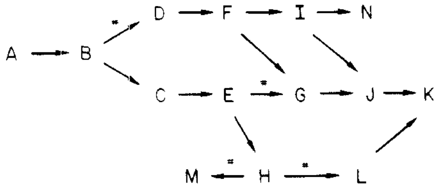
the hypothetical set of reactions



where the rate-limiting step for each path is marked #. Using X → Y as the representation of a step which converts X to Y

A → B; #,1:B → D; D → F; 2:F → I; 3:I → N;
1:B → C; C → E; #,4:E → G:5;
G → J:6; J → K;
4:E → H; #,7:H → L; L → K;
#,7:H → M;
2:F → G:5;
3:I → J:6;

The numbering of intermediates at the confluence of paths (G,J) is not strictly necessary but helps to indicate that products arrived at by both paths are the same and that they are not the final products.

(3) Examples of the Application of the Notation to Known Reactions (See Table I). The applicability of this scheme has been illustrated by notating a number of reaction mechanisms with the suggested rules. The first section consists of some of the commoner "Ingold-type" mnemonics for particular processes. A simple one-to-one translation of the Ingold-type symbols is not possible, and situations occur where either several symbols refer to essentially identical mechanisms or one symbol encompasses a variety of situations where there are differences in the mechanism or, at least, the rate-limiting step. A somewhat random selection of other reactions follows. Reference numbers prefaced by M refer to the relevant pages in ref 15. The general symbols used are X or Y for leaving groups or reagents of nucleophilic type, M or N for electrophilic types (including H^+), and J for a substituent subject to radical displacement; the molecule A–B is assumed capable of giving rise to radicals A and B. The minimal structures of reagents are listed before the representation of these mechanisms, with H replacing any unimportant groups. Optional information is included in some examples.

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Photostimulated $S_{RN}1$ Reactions of Phenyl Selenide and Phenyl Telluride Ions with Halo- and Dihaloarenes in Liquid Ammonia[1]

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The photostimulated reactions of haloarenes with phenyl selenide **2** and phenyl telluride **6** ions were studied in liquid ammonia. In the reactions of **2** with chloro- and bromobenzene, the yields were low, but with iodobenzene and halogen derivatives of naphthalene, phenanthrene, and quinoline, the yields of substitution products were good. With **6** and iodobenzene, a very good yield of diphenyl telluride was obtained, but with 1-chloro- or 1-bromonaphthalene, besides the unsymmetrical 1-naphthyl phenyl telluride, the symmetrical diphenyl telluride and bis(1-naphthyl) telluride were formed. In the photostimulated reaction of **6** and *p*-iodoanisole, both the unsymmetrical and the symmetrical substitution products were obtained. A reversible coupling of aryl radicals with aryl telluride ion is suggested in terms of the $S_{RN}1$ mechanism. There is no dark reaction with either nucleophile. **2** and **6** also react with dihaloarenes under photostimulation to give disubstitution products in fair to good yields.

Unactivated aromatic substrates bearing suitable leaving groups react under photostimulation with several nucleophiles by the $S_{RN}1$ mechanism.[3] The steps comprising a typical photostimulated $S_{RN}1$ reaction are outlined in Scheme I.

Scheme I

$$\mathrm{ArX} + \mathrm{Nu}^- \xrightarrow{h\nu} (\mathrm{ArX})^{-}\cdot + \text{residue} \tag{1}$$

$$(\mathrm{ArX})^{-}\cdot \longrightarrow \mathrm{Ar}\cdot + \mathrm{X}^- \tag{2}$$

$$\mathrm{Ar}\cdot + \mathrm{Nu}^- \longrightarrow (\mathrm{ArNu})^{-}\cdot \tag{3}$$

$$(\mathrm{ArNu})^{-}\cdot + \mathrm{ArX} \longrightarrow \mathrm{ArNu} + (\mathrm{ArX})^{-}\cdot \tag{4}$$

Photons probably stimulate electron transfer from the nucleophile to the substrate, forming a radical anion and a residue (step 1). This radical anion decomposes into an aryl radical and the leaving group (step 2). The radical then reacts with the nucleophile to give a new radical anion (step 3). This radical anion can transfer its extra electron to the substrate (step 4), but in some systems it can decompose in other ways, depending on the identities of the aromatic moiety and the nucleophile.[3] Steps 2–4 are the propagation steps of a chain mechanism.

Phenoxide ion does not react under photostimulation by this mechanism in liquid ammonia, although it has been

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reported that phenoxide ion reacts with halobenzenes in aqueous *tert*-butyl alcohol with sodium amalgam to promote the substitution process.[4] Its sulfur analogue, the thiophenoxide ion, reacts in liquid ammonia under photostimulation with iodobenzene[5] and dihalobenzenes[6] to give substitution products in high yields.

Alkoxide ions are also unreactive as nucleophiles for this mechanism, but alkanethiolate ions react slowly with iodobenzene to give alkyl phenyl sulfides in modest yields, together with products from the decomposition of the radical anions formed in step 3, Scheme I, namely diphenyl sulfide and benzenethiol.[7] On the other hand, alkyl 1-naphthyl sulfides are formed in high yields from the photostimulated reactions of alkanethiolate ions with 1-chloronaphthalene.[8]

The facts that oxygen and sulfur belong to group 6A of the elements and that derivatives of the first are unreactive, whereas derivatives of the second are good nucleophiles for photostimulated $S_{RN}1$ reactions, prompted us to study the behavior of the corresponding selenium and tellurium functionalities as nucleophiles in photostimulated reactions with haloarenes. The nucleophiles studied were phenyl selenide and phenyl telluride ions.

Results and Discussion

Preparation of the Nucleophiles. Phenyl selenide ion 2 was prepared in liquid ammonia by either of two methods.[9] Method A involved Se–Se bond cleavage in diphenyl diselenide (1) by sodium metal in liquid ammonia.

$$\underset{1}{\text{PhSeSePh}} + 2\text{Na} \rightarrow \underset{2}{2\text{PhSe}^-\text{Na}^+} \qquad (5)$$

Previously, 2 was prepared by reaction of 1 with sodium borohydride in ethyl alcohol.[10] Simultaneously with our work, reports appeared describing preparation of this ion by cleavage of 1 with sodium metal in THF[11] and in liquid ammonia.[12] Method B involved acid–base reaction of sodium *tert*-butoxide with benzeneselenol in ammonia.

Phenyl telluride ion was prepared only by method A. As discussed previously,[13] an excess of sodium metal cleaves the phenyl–tellurium bond, giving ultimately benzene (88% yield), but with 2 g-atoms of sodium metal per mol of diphenyl ditelluride, we obtained a high yield of phenyl telluride ion. This anion has been prepared previously by the reaction of diphenyl ditelluride with lithium metal in THF[14] or with sodium borohydride in ethanol.[15]

Photostimulated Reactions with the Phenyl Selenide Ion. Mixtures of 2, prepared by method A or B, and a halobenzene were irradiated with Pyrex filtered UV light in liquid ammonia. Chlorobenzene did not react, and bromobenzene gave a small yield of bromide ion. With iodobenzene, iodide ion was formed in 66–73% yield, and the substitution product, diphenyl selenide (3), was isolated as the dibromide adduct in 55% yield.

$$\text{PhI} + 2 \xrightarrow{h\nu} \underset{3}{\text{PhSePh}} + \text{I}^- \qquad (6)$$

1-Chloronaphthalene reacted with 2 prepared by method B giving 68% of chloride ion after 165 min of irradiation. With 220 min of irradiation, the chloride yield increased to 80%, and the substitution product, 1-naphthyl phenyl selenide (4), was isolated as such in 69% yield. A slight increase in yield was obtained with 2 prepared by method A under otherwise similar conditions, but with 2 prepared by method A and with a ratio of 1-chloronaphthalene to 2 of 1:2, the yield of chloride ion was 88% after 170 min of irradiation. In these reactions, 4 was isolated in 70 and 73% yields, respectively. In the dark there was no reaction.

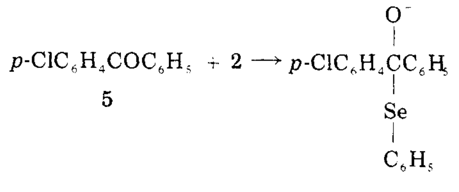
With 4-chlorobiphenyl and 2 prepared by method B, 18% of the chloride ion was released during 180 min of irradiation. With 2 prepared by method A, and after 240 min of irradiation, the yield of chloride ion was 59%, and the substitution product, 4-biphenylyl phenyl selenide, was isolated in 37% yield (by GLC the yield was 52%).

From these results we can see that 2 prepared by method A is a little more reactive than when it is prepared by method B. Probably this decrease in reactivity is due to the small amount of ferric chloride added to catalyze the formation of sodium *tert*-butoxide from sodium metal and *tert*-butyl alcohol in liquid ammonia.[16]

With 9-bromophenanthrene as substrate, the substitution product, 9-phenanthryl phenyl selenide, was obtained in 72% yield.

Previously it was reported that 4-chlorobenzophenone (5) reacts by photostimulation with the cyanomethyl anion in liquid ammonia by the $S_{RN}1$ mechanism, giving good yield of the substitution product,[17] and that the reaction of 4-bromobenzophenone with the thiophenoxide anion catalyzed by electrons from a cathode also gives the substitution product in good yield.[18] However, the photostimulated reaction of 2 with 5 gave only 5% yield of chloride ion during 180 min of irradiation. When we added 5 to the nucleophile in ammonia, a violet color appeared in the solution.

It occurred to us that there may have been some interference with the $S_{RN}1$ process owing to nucleophilic addition of 2 to the carbonyl group of 5.



$$\underset{5}{p\text{-ClC}_6\text{H}_4\text{COC}_6\text{H}_5} + 2 \longrightarrow p\text{-ClC}_6\text{H}_4\overset{\text{O}^-}{\underset{\text{SeC}_6\text{H}_5}{\text{C}}}\text{C}_6\text{H}_5 \qquad (7)$$

It is known that 2 reacts with carbonyl groups.[19] We tried to isolate the product of this reaction, but after the addition of water and evaporation of the ammonia, it rapidly decomposed to 5 and benzeneselenol of characteristic odor. In an attempt to isolate the product from the dark reaction, we took samples at 60, 120, and 360 min, dropped them into water, and extracted them with carbon tetrachloride. The UV and NMR spectra of these samples

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[19] W. Dumont and A. Krief, *Angew. Chem., Int. Ed. Engl.*, **16**, 540 (1977); W. Dumont, M. Sevrin, and A. Krief, *ibid.*, **16**, 541 (1977); D. Liotta and H. Santiesteban, *Tetrahedron Lett.*, 4369 (1977).

were identical with those of starting materials.

In the photostimulated reaction of 4-chloroquinoline with **2**, chloride ion was released in 54% yield, and the substitution product, 4-quinolyl phenyl selenide, was formed in 46% yield.

We sought to determine how much diphenyl diselenide (**1**) was formed in this reaction. It was found as a component of all product mixtures. However, since **1** can be formed from **2** by air oxidation during workup, a special experiment was devised to avoid ambiguity from that source. A solution of iodobenzene and **2**, prepared by method A, was irradiated for 220 min. Excess methyl iodide was then added to trap unreacted **2** as methyl phenyl selenide. GLC analysis of the resulting product mixture revealed 23% of unreacted iodobenzene, 26% of methyl phenyl selenide, 73% of **3**, and 2.5% of **1**. Thus relatively little **1** is actually formed. Moreover, 2.5% may be an overestimate because traces of **1** may have eluded the original sodium metal reduction of **1** to **2**, for example, by lodging on the wall of the flask above the solution surface.

Photostimulated Reactions of Phenyl Telluride Ion. Bromobenzene reacts with phenyl telluride ion **6**, giving bromide ion in 24% yield and diphenyl telluride **7** in 20% yield after 220 min of irradiation. Iodobenzene gave 100% of the iodide ion and **7** in 90% yield (isolated as the dibromide).

$$\mathrm{PhI} + \underset{\mathbf{6}}{\mathrm{PhTe^-}} \xrightarrow{h\nu} \underset{\mathbf{7}}{\mathrm{PhTePh}} + \mathrm{I^-} \qquad (8)$$

The photostimulated reactions of 1-chloronaphthalene and 1-bromonaphthalene gave 60 and 80% yields of halide ion, respectively, as well as the substitution product, 1-naphthyl phenyl telluride (**8**), in 37 and 50% isolated yields.

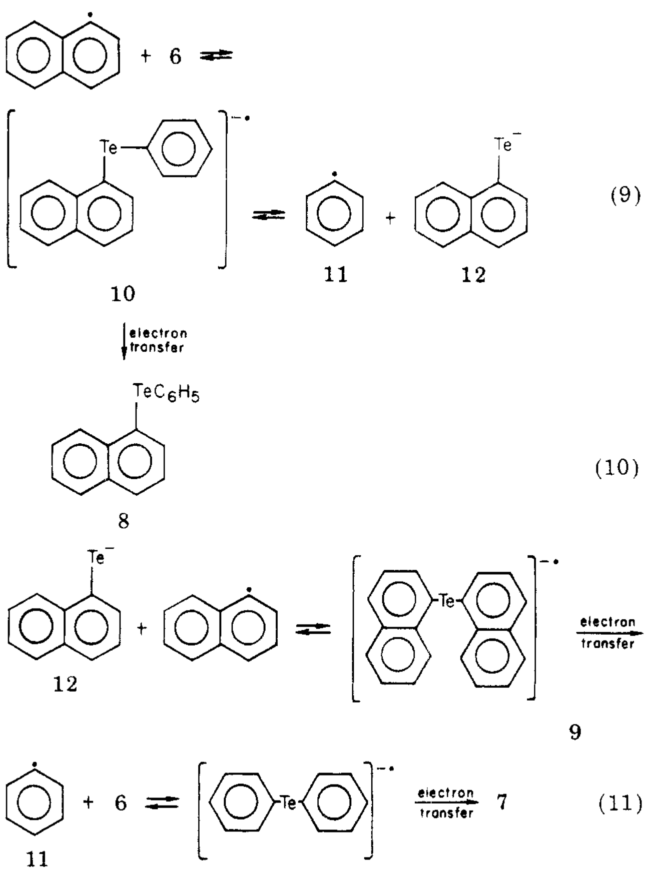
GLC analysis indicates the presence of two unexpected products, one with the same retention time as authentic **7**. By GC-MS analysis, these two products were identified as **7** and bis(1-naphthyl) telluride (**9**). These products were formed in reactions with both 1-bromo- and 1-chloronaphthalene. In the dark reaction with 1-bromonaphthalene after 60 min, there was no substitution product, whereas after 60 min of irradiation, **8** was formed in 35% yield and **7** in 10% yield. Thus photostimulation is necessary for this reaction.

The formation of **7** and **9** cannot be explained by the steps sketched in Scheme I ($Nu^- = PhTe^-$). Possible reaction steps are shown in Scheme II. The 1-naphthyl phenyl telluride radical anion **10** formed in step 3 of Scheme I undergoes three competitive reactions: namely, reversion to starting materials, electron transfer to the substrate (eq 4, Scheme I), and decomposition into phenyl radical **11** and 1-naphthyl telluride ion **12** (eq 9, Scheme II).

In eq 9 Scheme II, two new intermediates are formed, phenyl radical and 1-naphthyl telluride ion. 1-Naphthyl telluride ion competes as the nucleophile with **6** for reaction with naphthyl radicals to give **9** (eq 10), whereas phenyl radicals can be trapped by **6** to give **7** (eq 11, Scheme II).

According to Scheme II, the symmetrical tellurides **7** and **9** come from the decomposition of radical anion **10** to form **11** and **12** in competition with electron transfer to the substrate. This behavior is not observed with thiophenoxide or phenyl selenide ion as nucleophiles. Presumably that means that their radical anions are more stable and survive long enough to transfer their "extra" electrons in a bimolecular step, giving the straightforward substitution product.

Scheme II



It is known that other radical anions formed by coupling of an aromatic radical and a nucleophile decompose in competition with electron transfer, giving not only the substitution product, but also fragmentation products, such as in eq 12[20] and 13.[7]

$$\mathrm{Ph\cdot} + {}^-\mathrm{CH_2CN} \rightarrow (\mathrm{PhCH_2CN})^{-\cdot} \rightarrow \mathrm{PhCH_2\cdot} + \mathrm{CN^-} \qquad (12)$$

$$\mathrm{Ph\cdot} + {}^-\mathrm{SEt} \rightarrow (\mathrm{PhSEt})^{-\cdot} \rightarrow \mathrm{PhS^-} + \mathrm{Et\cdot} \qquad (13)$$

In order to check if the pattern of Scheme II is also established with phenyl rings, we conducted an experiment with *p*-iodoanisole as substrate and **6** as nucleophile. After 220 min of irradiation, methyl iodide was added to trap any unreacted aryl telluride anion forming the methyl derivative. In this reaction, we isolated by column chromatography **7** (15% yield), *p*-anisylphenyl telluride (73% yield), and bis(*p*-anisyl) telluride (11% yield). These results suggest that the *p*-anisylphenyl telluride radical anion intermediate formed in this reaction decomposes in a fashion analogous to that sketched in Scheme II. These results can be compared with those obtained in the reaction of *p*-iodoanisole and the thiophenoxide ion where no decomposition of the radical anion intermediate was found.[7]

Photostimulated Reactions of Phenyl Selenide and Phenyl Telluride Ions with Dihaloarenes. The synthesis of compounds with two atoms of selenium or tellurium was attempted by photostimulated reactions of phenyl selenide or phenyl telluride ions with dihaloarenes in liquid ammonia.

In the photostimulated reaction of thiophenoxide ion with *p*-dibromobenzene, the disubstitution product was formed in 64% yield after 300 min of irradiation.[5] In the photostimulated reaction with **2** as the nucleophile, we got

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[20] J. F. Bunnett and B. F. Gloor, *J. Org. Chem.*, **38**, 4156 (1973).

only 23% of bromide ion elimination (average of two reactions), and the disubstitution product, *p*-bis(phenylselenyl)benzene, was isolated in 13% yield.

Using *p*-bromoiodobenzene, a substrate with a better leaving group for photostimulated $S_{RN}1$ reactions,[3,21] we obtained an 86% yield of iodide ion and an 83% yield of bromide ion. The disubstitution product was isolated in 70% yield.

The facts that the yield of iodide is similar to that of bromide ion, despite the fact that iodine is a better leaving group and the substrate *p*-bromoiodobenzene was to some extent (12%) recovered unchanged and that a mere trace of monosubstituted product was found suggest that the radical anion intermediate formed in step 16, Scheme III, decomposes to a *p*-(phenylselenyl)phenyl radical and a bromide ion (step 17) before the electron transfer reaction to the substrate (step 18), which would give the monosubstituted product (Scheme III). The same behavior has been found previously in reactions of dihaloarenes with thiophenoxide ion in ammonia.[5]

With the substrate 4,4'-dibromobiphenyl (a substrate quite insoluble in ammonia), the yield of bromide ion was modest (23%) after 220 min of irradiation. Isolation of the product was not attempted.

In the photostimulated reaction of *p*-bromoiodobenzene with **6** in ammonia, iodide ion was liberated in 69% yield and bromide ion in 53% yield. The disubstitution product, *p*-bis(phenyltelluryl)benzene, was isolated in 30% yield, but *p*-bromophenyl phenyl telluride (7% yield) and **7** (20% yield) were also formed. The formation of these last two products suggests that electron transfer occurred in part in the sense of eq 18 and that in part the radical anion intermediate decomposes in the sense of eq 9, Scheme II. In this reaction, the substrate *p*-bromoiodobenzene was recovered in 26% yield.

Mechanism of Reaction. Salient experimental facts are (a) that the reaction requires photostimulation, (b) that the reactivity order of the nucleofugal groups is I > Br > Cl, and (c) that the reactivity order of aromatic moieties with the same leaving group is phenantrene ≃ naphthalene > benzene. These suggest that these reactions occur by the $S_{RN}1$ mechanism, as depicted in Scheme I, with Nu^- being **2** or **6**.

The formation of **7** and **9** in the reaction of **6** with 1-chloro- and 1-bromonaphthalene and **7** and bis(*p*-anisyl) telluride in the reaction of *p*-iodoanisole with **6** is difficult to explain by other mechanisms. However, these products are easily interpreted by the $S_{RN}1$ mechanism, in which the reactions described by eq 9 give the intermediates that ultimately produce the observed products.

Potentialities in Synthesis. Unsymmetrical aromatic diorganoselenides and tellurides are well-known compounds. Among useful and general methods of preparation, we can cite those involving the reaction of an aryltellurium trichloride with an arylmercuric chloride followed by reduction of the resulting diorganotellurium dichloride,[22] that involving the reaction of an arylselenium monobromide with a diaryl mercuric compound,[23] and the direct reaction of aryl selenocyanates with aryllithium derivatives or Grignard reagents.[24] Diaryl diselenides or arylselenium halides,[23] as well as diaryl ditellurides or arenetellurenyl halides,[25] also react with Grignard reagents

Scheme III

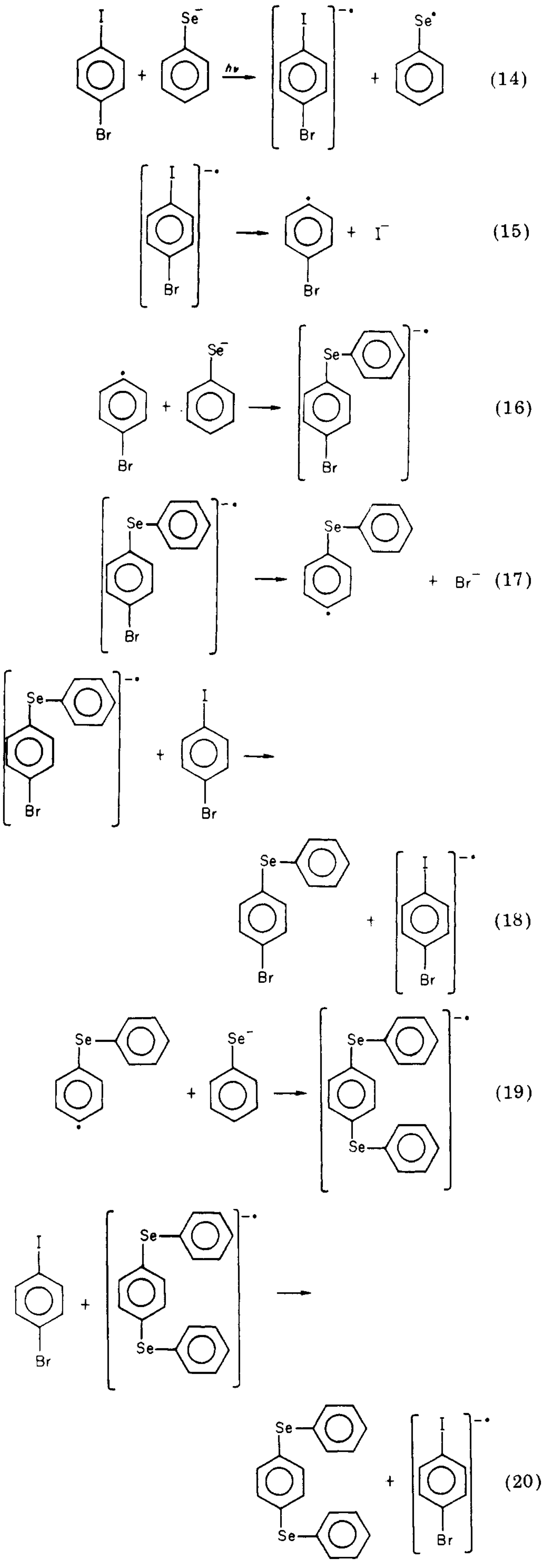

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Table I. Photostimulated Reactions of Phenyl Selenide Ion in Liquid Ammonia

run no.	ArX	[ArX], M	[PhSeNa], M	method[a]	irradiation time, min	% yield	
						X^- [b]	ArSePh[c]
1	chlorobenzene	0.053	0.053	B	180	1	*d*
2	bromobenzene	0.045	0.045	B	120	5	*d*
2'	bromobenzene	0.018	0.016	A	100	4	1
3	iodobenzene	0.030	0.030	A	60[e]	1	*d*
4	iodobenzene	0.030	0.030	A	220	66	55[f]
5	iodobenzene[g]	0.029	0.029	A	220	*d*	73[h]
6	1-chloronaphthalene	0.045	0.045	B	165	68	*i*
7	1-chloronaphthalene	0.050	0.050	B	290	80	69
8	1-chloronaphthalene	0.037	0.037	A	220	84	70
9	1-chloronaphthalene	0.016	0.034	A	170	88	73
10	1-chloronaphthalene	0.037	0.037	A	120[e]	1	0[j]
11	4-chlorobiphenyl	0.050	0.050	B	180	18	*d*
12	4-chlorobiphenyl	0.027	0.027	A	240	59	37 (52)[k]
13	9-bromophenanthrene	0.019	0.020	A	220	85	72
14	2-chloroquinoline	0.025	0.025	A	220	54	46
15	4-chlorobenzophenone	0.050	0.050	B	180	5	*d*

[a] Method to prepare the PhSeNa, see text. [b] Determined potentiometrically. [c] Product isolated, unless otherwise quoted. [d] Not determined. [e] Dark reaction, wrapped with aluminum foil. [f] Isolated as the dibromide. [g] Reaction quenched with methyl iodide. [h] Determined by GLC, together with 23% of unreacted iodobenzene, 26% of methyl phenyl selenide, and a 2.5% yield of diphenyl diselenide. [i] 1-Naphthyl phenyl selenide was identified but not quantified. [j] Determined by TLC and GLC. [k] Determined by GLC, together with 40% of the unreacted 4-chlorobiphenyl.

to form unsymmetric diaryl compounds. It should be noted that these all involve highly reactive reagents that must be specially prepared.

The results reported in this paper suggest a novel, simple, and direct route of synthesis of unsymmetrical and symmetrical diaryl selenides and tellurides. Reaction occurs at low temperatures, giving moderate to good yields, depending on the aryl moiety and the leaving group. With tellurium compounds, there are some complications deriving from decomposition of the radical anion intermediate as discussed above.

Heretofore there has been no general method to obtain aromatic compounds bearing two arylselenyl or aryltelluryl substituents. The $S_{RN}1$ mechanism appears to provide the method of choice for synthesis of these compounds.

Experimental Section

General. NMR spectra were recorded on a Varian T 60 nuclear magnetic resonance spectrometer, and all spectra are reported in parts per million relative to Me_4Si (δ), using CCl_4 as solvent. Potentiometric titrations were carried out with a Seybold Digital pH Meter Model GTE, using a combined silver–calomel electrode. Mass spectral measurements were obtained with a Hitachi Perkin-Elmer Model RMU-6 E mass espectrometer, and the GC–MS were obtained with Varian MAT CH 7 A or Finnigan Model 4000 mass spectrometers. All of the mass spectra of the compounds described showed the characteristic pattern of the different isotopes of Se[26] and Te.[27] Thin-layer chromatography was performed on silica gel plates. Gas chromatographic analyses were performed on a Varian Aerograph Series 2400 with flame ionization detector, using a column packed with 4% Silicon Rubber SE 30 on Chromosorb G 80–100, 1.5 m × 3 mm, and 1.5% OV 101 on Chromosorb P, 1.5 m × 3 mm. Column chromatography was performed on neutral aluminum oxide (Merck) and eluted with petroleum ether. Microanalyses were performed on a Carbon Hydrogen Nitrogen Analyzer F&M, Model 185.

Melting points are uncorrected. Irradiation was conducted into a reactor equipped with two 250 W UV lamps emitting maximally at 350 nm, Philips, Model HPT, water refrigerated.

Materials. Reagents were all commercially available materials unless otherwise quoted and were purified by standard procedures. Liquid ammonia was dried over Na metal and distilled under nitrogen into the reaction flask. Na metal was cut into small pieces and washed free of oil with dried diethyl ether immediately before addition to the reaction flask. Benzeneselenol was prepared from phenylmagnesium bromide and selenium metal in diethyl ether,[28] yield 70%, bp 57–9 °C (8 torr), and stored under nitrogen in ampules. Diphenyl diselenide was prepared from benzeneselenol[29] (75% yield) or from phenyl selenocyanate with KOH in ethyl alcohol[23] (80% yield), recrystallized from ethyl alcohol, mp 62–3 °C (lit.[29] mp 63 °C). Diphenyl ditelluride was obtained according to the method described[30] (70% yield), recrystallized from ethyl alcohol, mp 64–5 °C (lit.[30] mp 66 °C).

Photostimulated Reactions of the Phenyl Selenide Ion. Method A. The photostimulated reaction of phenyl selenide ion 2 with 1-chloronaphthalene is representative: into a three-neck, 500-mL, round-bottom flask, equipped with a cold finger condenser charged with solid CO_2 and alcohol, nitrogen inlet, and magnetic stirrer, ~250 mL of ammonia was condensed. To the ammonia was added diphenyl diselenide (1.443 g, 4.64 mmol) and then small pieces of Na metal until the blue color persisted, ~20 min (~0.22 g). If it does not decolorize, a very small amount of diphenyl diselenide was added until the blue color of the solvated electrons disappeared. 1-Chloronaphthalene (2.428 g, 9.26 mmol) was added and then irradiated for 220 min. The reaction was quenched by adding distilled water (~10 mL), and then ammonia was allowed to evaporate. Water (100 mL) was added to the residue, and the mixture was extracted three times with 100 mL of diethyl ether. In the water, chloride ion was determined potentiometrically. The ether extract was dried over anhydrous Na_2SO_4 and distilled. The residue was treated with Zn dust and 10% methanolic sodium hydroxide to eliminate any diphenyl diselenide formed[24] and then sublimed to remove 1-chloronaphthalene. 1-Naphthyl phenyl selenide was isolated as an oil: 1.84 g (70% yield); NMR δ 6.6–7.4 (11 H, m) and 7.8–8.2 (1 H, m); MS, *m/e* (rel intensity) 284 (46), 282 (26), 204 (100), 127 (37), 126 (31), 115 (43), 101 (19), m* 146.5 (284 → 204). Anal. Calcd for $C_{16}H_{12}Se$: C, 67.85; H, 4.27. Found: C, 67.7; H, 4.10.

Method B. The photostimulated reaction of 2 with 1-chloronaphthalene is representative. To 250 mL of dry liquid ammonia prepared as method A, 0.288 g of Na metal, 0.925 g of *tert*-butyl alcohol, and a small amount of $FeCl_3$, as catalyst to form $t\text{-Bu-Na}^+$,[16] were added. Then 1.963 g of benzeneselenol was added, and after 5 min 3.28 g of 1-chloronaphthalene was added. The reaction mixture was irradiated during 290 min, and the extraction procedure was similar to that used in method A.

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Table II. Photostimulated Reactions of Phenyl Telluride Ion in Liquid Ammonia

run no.	ArX	[ArX], M	[PhTeNa], M	irradiation time, min	% yield X^- [a]	% yield products obtained[b]
1	bromobenzene	0.028	0.028	220	24	Ph_2Te, 20
2	iodobenzene	0.032	0.032	220	100	Ph_2Te, 90[c]
3	*p*-iodoanisole	0.018	0.018	220	*d*	Ph_2Te, 15[e] *p*-anisyl phenyl telluride, 73[e] bis(*p*-anisyl) telluride, 11[e] *p*-iodoanisole, 1
4	1-chloronaphthalene	0.032	0.032	220	60	Ph_2Te, 9 1-naphthyl phenyl telluride, 41 (37)[c] bis(1-naphthyl) telluride, 6 1-chloronaphthalene, 39
5	1-bromonaphthalene	0.026	0.027	60[f]	1	1-naphthyl phenyl telluride, 0[g]
6	1-bromonaphthalene	0.026	0.027	60	*d*	Ph_2Te, 10 1-naphthyl phenyl telluride, 35 bis(1-naphthyl) telluride[h] 1-bromonaphthalene, 45
7	1-bromonaphthalene	0.026	0.027	220	80	Ph_2Te, 16 1-naphthyl phenyl telluride, 53 (50)[e] bis(1-naphthyl) telluride, 10 1-bromonaphthalene, 15

[a] Determined potentiometrically. [b] Determined by GLC, assuming equal response by equal weight, unless otherwise quoted. [c] Yield of product isolated as dibromide. [d] Not determined. [e] Yield of product isolated. [f] Dark reaction wrapped with aluminum foil. [g] Determined by GLC and TLC. [h] Detected by GLC but not quantified.

Table III. Photostimulated Reactions of Phenyl Selenide and Phenyl Telluride Ions with Dihaloarenes in Liquid Ammonia[a]

run no.	ArX_2	$[ArX_2]$, M	PhZ^- [b]	$[PhZ^-]$, M	% yield X^- [c]	% yield PhZArZPh[d]
1	4,4′-dibromobiphenyl[e]	0.015	$PhSe^-$	0.035	23	*f*
2	*p*-dibromobenzene	0.019	$PhSe^-$	0.041	26	13
3	*p*-bromoiodobenzene	0.014	$PhSe^-$	0.028	I^-, 86 Br^-, 83	70[g]
4	*p*-bromoiodobenzene	0.017	$PhTe^-$	0.033	I^-, 69 Br^-, 63	30 (40)[h]

[a] Irradiation time of 220 min. [b] The nucleophiles were prepared according to method A, see text. [c] Determined potentiometrically. [d] Product isolated. [e] Very insoluble in liquid ammonia. [f] Not determined. [g] 12% of *p*-bromoiodobenzene isolated by sublimation. [h] Determined by GLC, together with diphenyl telluride (20%), *p*-bromophenyl phenyl telluride (7%), and *p*-bromoiodobenzene (26%), using 1-chloronaphthalene as internal standard.

Aryl Phenyl Selenides Obtained. Diphenyl Selenide. The residue of reaction 4, Table I, oxidized with Br_2 in CCl_4, giving a precipitate of Ph_2SeBr_2 in 55% yield: mp 135–140 °C; recrystallized from CCl_4, mp 143–144 °C (lit.[31] mp 144 °C).

***p*-Biphenylyl Phenyl Selenide.** The residue of reaction 12, Table I, was treated at 100 °C for 1 h with a mixture of Zn dust, methanolic sodium hydroxide (10%), and 1 mL of benzene. The mixture was added to 50 mL of water and extracted with benzene. After evaporation of the benzene extract, the residue was sublimed at 60 °C (0.2 torr) to remove the 4-chlorobiphenyl and then at 90 °C (0.2 torr) to obtain the pure product: mp 65.5–66.5 (lit.[24] mp 69–70 °C); MS, *m/e* (rel intensity) 310 (35), 308 (19), 230 (100), 152 (42), 77 (20), m* 170.6 (310 → 230). Anal. Calcd for $C_{18}H_{14}Se$: C, 69,90; H, 4.56. Found: C, 69.6; H, 4.4.

9-Phenanthryl Phenyl Selenide. The residue of reaction 13, Table I, was washed with diethyl ether (slightly soluble) and dried: mp 150–155 °C; recrystallized from CCl_4, mp 158–159 °C; MS, *m/e* (rel intensity) 334 (56), 332 (30), 254 (100), 253 (50), 252 (28), 176 (35), 165 (34), m* 193 (334 → 254). Anal. Calcd for $C_{20}H_{14}Se$: C, 72.07; H, 4.23. Found: C, 71.7; H, 4.15.

2-Quinolyl Phenyl Selenide. This compound was isolated by column chromatography: mp 46.5–47 °C; MS, *m/e* (rel intensity) 285 (66), 284 (81), 283 (40), 282 (51), 205 (6), 204 (19), 157 (6), 155 (3), 129 (15), 128 (64), 102 (34), 101 (87), 77 (99), 51 (100). Anal. Calcd for $C_{15}H_{11}NSe$: C, 63.39; H, 3.90; N, 4.92. Found: C, 62.9; H, 3.8; N, 4.8.

***p*-Bis(phenylselenyl)benzene.** This compound was isolated by column chromatography and purified by oxidation with Br_2 in CCl_4. The tetrabromide compound was reduced to *p*-bis(phenylselenyl)benzene in acetone–water:[23] mp 100–101 °C; MS, *m/e* (rel intensity) 390 (51), 388 (48), 386 (27), 310 (7), 308 (4), 233 (100), 231 (61), 230 (94), 157 (26), 155 (16), 152 (86), m* 246 (390 → 310), m* 170.6 (310 → 230), m* 139 (390 → 233), m* 135.7 (390 → 230). Anal. Calcd for $C_{18}H_{14}Se_2$: C, 55.68; H, 3.61. Found: C, 55.66; H, 3.59.

Photostimulated Reactions of the Phenyl Telluride Ion. This nucleophile was prepared as the phenyl selenide ion, method A, except that exactly 2 equiv of Na metal per mol of diphenyl ditelluride were added.[13] The procedure was similar to that previously described. The products were isolated as follows:

Diphenyl Telluride. The residue of reaction 2, Table II, was oxidized with Br_2 in cold diethyl ether, giving Ph_2TeBr_2 in 90% yield, mp 198 °C (lit.[32] mp 197 °C). Pure Ph_2Te was obtained by reduction of Ph_2TeBr_2 with $Na_2S{\cdot}9H_2O$:[33] MS, *m/e* (rel intensity) 284 (5), 282 (5), 280 (3), 279 (1), 206 (6), 204 (6), 202 (3), 201 (1), 154 (13), 153 (18), 152 (8), 151 (3), 130 (4), 128 (5), 126 (3), 125 (1), 77 (85), 51 (100).

1-Naphthyl Phenyl Telluride. The residue of reaction 7, Table II, was vacuum distilled, bp 145–148 °C (0.01 torr) (lit.[22a] bp 147–148 °C (0.01 torr)) with 50% yield. The dibromide derived was obtained by treatment of 1-naphthyl phenyl telluride with Br_2 in benzene–petroleum ether: mp 183 °C (lit.[22a] mp 180.5–182 °C); MS, *m/e* (rel intensity) 415 (1), 413 (2), 411 (2), 409 (1), 334 (42), 332 (40), 330 (25), 329 (9), 257 (11), 255 (10), 253 (13), 252 (6), 208 (4), 207 (7), 206 (4), 205 (18), 204 (100), 203 (69), 202 (26), 127 (94), 82 (30), 81 (12), 80 (33), 79 (12), 77 (53), 51 (25).

By GC there were two unknown peaks, the first one with the same retention time as Ph_2Te. By GC–MS the first one showed the same MS as authentic Ph_2Te, and the second one showed a

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MS that could be attributed to bis(1-naphthyl) telluride: MS, *m/e* (rel intensity) 384 (36), 382 (32), 380 (21), 379 (17), 257 (12), 255 (19), 254 (100), 253 (92), 252 (57), 127 (10).

***p*-Bis(phenyltelluryl)benzene.** The residue obtained in reaction 4, Table III, was column chromatographed, and the pure product was isolated in 30% yield: mp 88–90 °C; MS, *m/e* (rel intensity) 490 (25), 488 (47), 486 (49), 485 (17), 484 (35), 483 (14), 482 (21), 360 (10), 358 (12), 283 (42), 281 (40), 279 (26), 278 (18), 230 (100), 207 (44), 205 (43), 203 (23), 202 (11).

By GC–MS there were also Ph_2Te and *p*-bromophenyl phenyl telluride: MS, *m/e* (rel intensity) 364 (36), 362 (47), 360 (34), 358 (26), 287 (6), 285 (13), 283 (11), 234 (99), 232 (100), 207 (11), 205 (10), 203 (16), 202 (14), 77 (58).

Photostimulated Reaction of *p*-Iodoanisole with 7. The procedure was the same as that used before, except that the reaction was quenched with methyl iodide to avoid the oxidation products, diaryl ditellurides. By GC of the ether extract three peaks were detected, the first one with the same retention time as Ph_2Te. The diethyl ether was distilled and the residue column chromatographed, obtaining 15% yield of Ph_2Te, 73% yield of *p*-anisyl phenyl telluride, and 11% yield of bis(*p*-anisyl) telluride. *p*-Anisyl phenyl telluride: mp 59–60 °C (lit.[22a] mp 60.5–61.5 °C); NMR δ 3.70 (3 H, s), 6.6–6.8 (2 H, m), 7.04–7.20 (3 H, m), 7.40–7.77 (4 H, m); MS, *m/e* (rel intensity) 315 (2), 314 (13), 313 (3), 312 (12), 311 (3), 310 (7), 309 (3), 308 (2), 307 (1), 306 (1), 237 (3), 236 (4), 235 (3), 234 (4), 221 (8), 219 (7), 217 (4), 206 (4), 204 (4), 193 (6), 191 (6), 189 (4), 184 (28), 183 (45), 169 (10), 168 (18), 142 (9), 141 (65), 140 (4), 139 (8), 130 (6), 128 (5), 115 (33), 92 (23), 79 (5), 78 (11), 77 (94), 76 (17), 75 (10), 65 (8), 64 (32), 63 (41), 62 (10), 51 (100), 50 (48). Bis(*p*-anisyl) telluride: mp 52–54 °C (lit.[34] mp 56–57 °C), this compound gave NMR and MS spectra in agreement with those previously reported.[34,27]

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Registry No. 1, 1666-13-3; **2**, 14971-39-2; **3**, 1132-39-4; **4**, 65490-21-3; **5**, 134-85-0; **6**, 65081-67-6; **7**, 1202-36-4; **8**, 70838-54-9; **9**, 4537-22-8; 1-chloronaphthalene, 90-13-1; benzeneselenol, 645-96-5; Ph_2SeBr_2, 4190-46-9; *p*-biphenylyl phenyl selenide, 65490-22-4; 9-phenanthryl phenyl selenide, 65490-23-5; 2-quinolyl phenyl selenide, 71672-71-4; *p*-bis(phenylselenyl)benzene, 71672-72-5; diphenyl ditelluride, 32294-60-3; Ph_2TeBr_2, 29135-65-7; *p*-bis(phenyltelluryl)benzene, 71672-73-6; *p*-iodoanisole, 696-62-8; *p*-anisyl phenyl telluride, 56949-99-6; bis(*p*-anisyl) telluride, 4456-34-2; chlorobenzene, 108-90-7; bromobenzene, 108-86-1; iodobenzene, 591-50-4; 4-chlorobiphenyl, 2051-62-9; 9-bromophenanthrene, 573-17-1; 2-chloroquinoline, 612-62-4; 1-bromonaphthalene, 90-11-9; *p*-dibromobenzene, 106-37-6; *p*-bromoiodobenzene, 589-87-7.

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$S_{RN}1$ Reactions of Some Phosphorus Nucleophiles with Iodo- and Bromobenzene[1]

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Four phosphanion nucleophiles, $PhP(OBu)O^-$, Ph_2PO^-, $(EtO)_2PS^-$, and $(Me_2N)_2PO^-$, react with iodo- or bromobenzene in ammonia under brief irradiation to form substitution products $Ph_2PO(OBu)$, Ph_3PO, $PhPS(OEt)_2$, and $PhPO(NMe_2)_2$, respectively. Reactions of the first three nucleophiles with iodobenzene occur in nearly quantitative yield. Iodobenzene/bromobenzene reactivity ratios, measured in competition experiments, are 1×10^3 for $PhP(OBu)O^-$, 5×10^2 for $(Me_2N)_2PO^-$, and 45 for $(EtO)_2PS^-$. These reactions are believed to occur by the radical chain $S_{RN}1$ mechanism.

Dialkyl phosphite ions (eq 1) and diphenylphosphide ion (eq 2) react with halobenzenes and like substrates to re-

$$(RO)_2PO^- + PhX \rightarrow PhPO(OR)_2 + X^- \qquad (1)$$

$$Ph_2P^- + ArX \rightarrow ArPPh_2 + X^- \qquad (2)$$

place the halogen atom by a phosphorus moiety.[2,3] The former reaction requires photostimulation.[2] The latter occurs in the dark at room temperature or below but more rapidly under irradiation.[3] Both reactions are much faster with iodobenzene than with bromobenzene.

These reactions are believed on good evidence to occur by the radical chain $S_{RN}1$ mechanism.[4]

Both these reactions occur in high yield and serve to establish aryl carbon–phosphorus bonds. Inasmuch as other methods for attaching phosphorus to aromatic sites, including Friedel–Crafts, Grignard, and diazonium salt reactions,[5] are subject to limitations of various kinds,[5] these $S_{RN}1$ reactions have actual or potential value for synthetic purposes.

Furthermore, there is the possibility that additional types of phosphanion nucleophiles may react similarly with aryl halides, so as to install various types of phosphorus functionality on aromatic rings. It is this possibility that we now explore.

Results

Descriptive Studies. Our principal experiments are summarized in Table I. They concern four phosphanion nucleophiles not previously involved in $S_{RN}1$ reactions, namely, $PhP(OBu)O^-$, Ph_2PO^-, $(EtO)_2PS^-$, and $(Me_2N)_2PO^-$. These can be regarded as analogues of the much-studied[2,5-11] $(EtO)_2PO^-$. Whereas diethyl phosphite

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