period, GC was used to determine the weight percent of **6** present and the percent reduction reported above was calculated as 100 − [weight percent of **6** (from plot) with the trap present] × 100/[weight percent of **6** (plot) in the absence of the trap]. The maximal concentration of **8** was 0.3–0.4 mol % rather than the usual 1 mol %; some variation in results is attributable to crystallization from the (still supersaturated) solution prepared by dissolving **8**, allowing the solution to cool briefly, and decanting from solid **8**.

Insertion of Monoatomic Sulfur into Methyl 2-Acetamido-3-mercapto-3-methylbutanoate (8) and Isolation of Methyl 2-Acetamido-3-[(2,4-dinitrophenyl)dithio]-3-methylbutanoate (14a). A solution of 1.00 g of **8** prepared at ca. 85 °C in 100 mL of cyclohexane (containing dodecane) was allowed to cool briefly until **8** that crystallized had settled, and the solution then was decanted from the **8**; ca. 80% (ca. 0.8 g, 4 mmol, 0.4 mol %) remained in solution. COS was bubbled into the solution in a quartz flask as usual for 5 min, and the solution then was irradiated for 6 h (UV intensity measure, 8.4 μW × 100/cm^2). Since a previous experiment showed that standing after photolysis for 1–2 days led to polysulfides corresponding to **8** (R_f 0.4, EtOAc), a characteristic of the hydrodisulfide **11a**,[8] cyclohexane was removed under reduced pressure without heat, and the residue was dissolved in 12 mL of MeOH containing 100 μL of Et$_3$N and 100 mg of **12**. After 30 min, 2 drops of HCl were added to neutralize the amine (light yellow crystals appeared), and the mixture was concentrated to dryness under reduced pressure. The residue was dissolved in a minimum of EtOAc (a little precipitate appeared to be sulfur), and the solution was filtered and subjected to preparative TLC using 6:4 acetone–petroleum ether. The band of **14a**, identified by its previously established position as the middle of three bands, was removed and extracted with EtOAc. Removal of the EtOAc yielded a yellow-orange oil, which was suspended in Et$_2$O at 0 °C overnight. Yellow crystals that appeared were recrystallized (twice) to constant melting point from EtOAc to give 12 mg of **14a** (also 12 mg, with the same properties, in a confirming experiment). In comparisons of this **14a** with authentic **14a**,[8] IR spectra were congruent, melting points and mixture melting points were identical (161–163 °C, Köfler; lit.[8] mp 161–163 °C), and R_f values (Eastman 13181) were the same in either EtOAc (R_f 0.63) or CHCl$_3$ (R_f 0.28). In a control experiment where UV only was omitted, no **14a** whatever could be detected.

Insertion of Monoatomic Sulfur into Cyclohexane and Isolation of 1-(Cyclohexyldithio)-2,4-dinitrobenzene (14b). After photolysis of 25 mL of standard cyclohexane (dodecane) with COS as usual, except that the solution from the trapping experiment with **10** is referred to (**10** having been shown to have a negligible effect), cyclohexane was removed under reduced pressure. The residual oil was dissolved in MeOH, and **12** (100 mg) was added, followed by 50 μL of Et$_3$N. After 1 h, TLC (1:9 EtOAc–pentane) showed a spot with R_f 0.55, the same as that of authentic **14b**. Cyclohexane was removed under reduced pressure, and the residue was separated by preparative TLC to give 8 mg of **14b**. This **14b** had the same R_f value and mp (109–112 °C) as authentic **14b** (mp 113.5–114.5 °C), which was prepared from cyclohexanethiol and the sulfenyl chloride **13** (lit.[9] mp 114.5–115.5 °C).[9] The melting point of this **14b** was undepressed by the authentic **14b**, and IR spectra of the two were congruent (CHCl$_3$, 1-mm cell).

Acknowledgment. This investigation was supported by PHS Grant ES 00267 to the Center in Environmental Toxicology in the School of Medicine, Vanderbilt University, awarded by the National Institute of Environmental Health Sciences, DHHS, and in the latter phases by PHS Grant CA 30321, awarded by the National Cancer Institute, DHHS. We thank D. E. Pearson, J. B. Tellinghuisen, and E. Dawson for helpful conversations.

Registry No. **6**, 1569-69-3; **7**, 688-73-3; **8**, 39239-85-5; **9**, 998-30-1; **10**, 617-86-7; **11a**, 83151-19-3; **11b**, 83115-77-9; **12**, 97-00-7; **14a**, 76480-13-2; **14b**, 51245-66-0; C$_6$H$_{12}$, 110-82-7; COS, 463-58-1; monoatomic sulfur, 7704-34-9.

Reaction of 1-Bromoadamantane with Diphenylphosphide and Diphenylarsenide Ions by the S$_{RN}$1 Mechanism. Facile Nucleophilic Substitution at the Bridgehead Position[1]

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The photostimulated reaction of 1-bromoadamantane (**1**) with diphenylphosphide (**2**) and diphenylarsenide (**6**) ions in liquid ammonia afforded good yields of the substitution products, together with small amounts of adamantane (**4**) and 1,1′-biadamantyl (**5**) as byproducts. The reaction of **1** with **2** in the dark did not occur, but stimulation with solvated electrons gives a small amount of the substitution product and **5**, with a large amount of **4**. The photostimulated reaction of **1** with **2** is inhibited by *p*-dinitrobenzene and di-*tert*-butyl nitroxide. All these results suggest that these reactions occur by the S$_{RN}$1 mechanism of substitution, where radical and radical anions are intermediates.

It is well-known that 1-halosubstituted bridgehead compounds are very unreactive toward nucleophilic substitution reactions. The low reactivity shown in S$_N$1 reactions was attributed to the strain arising from the formation of a carbonium ion at the bridgehead position. The structure of the bicyclic system precludes adoption of a planar geometry around the cationic carbon and requires a great activation energy for the ionization step. The S$_N$2 mechanism is also precluded because the direct displacement of the halogen atom with inversion of configuration is impossible.[2]

Different adamantyl intermediates have been suggested in nucleophilic substitution reactions such as ion pairs,[3] radical anions,[4] or simply radicals.[5] There is also a report

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[1] Research supported in part by the Consejo Nacional de Investigaciones Cientificas y Tēcnicas and the Subsecretaria de Ciencia y Tecnologia, Argentina. Presented in part at the Segunda Reuniōn Argentina de Fisico Quimica Orgânica, Villa Giardino, 1981.

[2] See, for example: Barlett, P. B.; Knox, L. H. *J. Am. Chem. Soc.* **1939**, *61*, 3184. Schleyer, P. v. R.; Nicholas, R. D. *Ibid.* **1961**, *83*, 2700.

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0022-3263/82/1947-4654$01.25/0

in which the nitro group of 1-nitroadamantane can be replaced by a thiol group in a reaction with dry "$Na_2S_{1.5}$" in Me_2SO at 125–130 °C, which in 16 h of reaction gives a 38% yield of 1-adamantanethiol, and it was suggested that probably an $S_{RN}1$-type substitution occurred.[6]

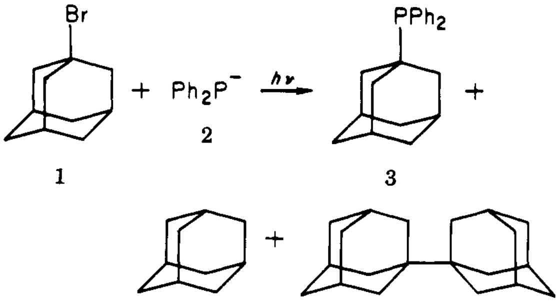
On the other hand, other classes of compounds such as unactivated haloarenes and vinyl halides, that are very unreactive toward nucleophilic substitution reactions, have been found to suffer a facile nucleophilic displacement through a radical nucleophilic mechanism ($S_{RN}1$).[7,8]

The reactivity pattern of unactivated aryl and vinyl halides resembles that of 1-halosubstituted bridgehead compounds in many respects. We thought it of interest to investigate the behavior of 1-halobridgehead compounds under usual $S_{RN}1$ conditions to see if they could be suitable substrates for this mechanism, since this question is important not only from a mechanistic point of view but also for the synthetic utility of the method.

Results

1-Bromoadamantane (**1**) was chosen as a model to study the behavior of 1-halo-substituted bridgehead compounds. These reactions were carried out under photostimulation, since light is one of the most frequently used catalysts in $S_{RN}1$ reactions,[7] and with diphenylphosphide ion (**2**) as the nucleophile, which is one of the most reactive nucleophiles toward phenyl radicals.[9,10]

The photostimulated reaction of **1** with **2** in liquid ammonia afforded 100% of bromide ion in 20 min of irradiation (although the time required for completion is not known, it is less than the 20 min for these reactions). (1-Adamantyl)diphenylphosphine (**3**) was found as the major product, together with adamantane (**4**) and 1,1′-biadamantyl (**5**, eq 1).



1 2 3

4 5

(1)

The substitution product **3** was not isolated as such, because of its ease of oxidation to (1-adamantyl)diphenylphosphine oxide.

This reaction does not occur in the dark. The photostimulated reaction is inhibited by *p*-dinitrobenzene (from 100% to 10% of bromide ion elimination in the same period of time) and by di-*tert*-butyl nitroxide (from 100% to 37% of bromide ion elimination in the same period of time; see Table I).

Another example of stimulated $S_{RN}1$ reactions is the reaction of an aromatic substrate with an appropriate leaving group with solvated electrons from the dissolution of alkali metals in liquid ammonia.[11] In the reaction of **1** with **2** in the dark, and after addition of potassium metal to the reaction mixture, **3** was formed, but in modest yields, together with substantial amounts of **4** and small amount of **5** (Table I).

Similar behavior was found with diphenylarsenide ion (**6**) as the nucleophile: there is a photostimulated reaction to give (1-adamantyl)diphenylarsine (**7**) with **4** and **5** (eq 2), but there is no dark reaction.

$$1 + \underset{6}{Ph_2As^-} \xrightarrow{h\nu} \underset{7}{1\text{-}AdPh_2As} + 4 + 5 \qquad (2)$$

$$Ad = adamantyl$$

The reaction catalyzed by potassium metal failed to give the substitution product **7** (Table I).

It is known that diphenylarsenide ion (**6**) reacts by photostimulation by the $S_{RN}1$ mechanism with haloaromatic compounds, giving in some cases scrambling of aryl rings but in other cases only the straightforward substitution product.[12,13] In the photostimulated reaction of **6** with **1**, despite of a careful search, an indication of scrambling products was not found; the only substitution product formed was **7**.

Discussion

The facts that **1** does not react with diphenylphosphide and diphenylarsenide ions in the dark, that the reactions are catalyzed by light and by solvated electrons (although less satisfactorily), and that *p*-dinitrobenzene and di-*tert*-butyl nitroxide inhibited the photostimulated reaction indicated that radical and radical anion intermediates are involved in these reactions.

The formation of adamantane and 1,1′-biadamantyl is another piece of evidence, and we suggest that these reactions occur by the $S_{RN}1$ mechanism of nucleophilic substitution. This is a radical chain mechanism, and comprises initiation, propagation, and termination steps as sketched in Scheme I.

Scheme I

Initiation Step

(a) Solvated Electron Stimulation

$$1\text{-}BrAd + e^- \rightarrow (1\text{-}BrAd)^{-}\cdot \qquad (3a)$$

(b) Photostimulated Reaction

$$1\text{-}BrAd + Ph_2Z^- \xrightarrow{h\nu} (1\text{-}BrAd)^{-}\cdot + Ph_2Z\cdot \qquad (3b)$$

Propagation Steps

$$(1\text{-}BrAd)^{-}\cdot \rightarrow 1\text{-}Ad\cdot + Br^- \qquad (4)$$

$$1\text{-}Ad\cdot + Ph_2Z^- \rightarrow (1\text{-}AdPh_2Z)^{-}\cdot \qquad (5)$$

$$(1\text{-}AdPh_2Z)^{-}\cdot + 1\text{-}BrAd \rightarrow 1\text{-}AdPh_2Z + (1\text{-}BrAd)^{-}\cdot \qquad (6)$$

Termination Steps

$$1\text{-}Ad\cdot + \text{"}e^-\text{"} \rightarrow 1\text{-}Ad^- \qquad (7)$$

$$1\text{-}Ad\cdot + Ph_2Z^- \rightarrow 1\text{-}Ad^- + Ph_2Z\cdot \qquad (8)$$

$$1\text{-}Ad^- \xrightarrow{NH_3} AdH \qquad (9)$$

$$1\text{-}Ad\cdot + SH \rightarrow AdH + S\cdot \qquad (10)$$

$$2\ 1\text{-}Ad\cdot \rightarrow (1\text{-}Ad)_2 \qquad (11)$$

$$Ad = adamantyl;\ Z = P, As$$

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Table I. Reactions of 1-Bromoadamantane with Diphenylphosphide and Diphenylarsenide Ions in Liquid Ammonia[a]

expt.	Ph_2Z^- [b] (concn, M × 10^3)	catalyst	yield,[c] % Br$^-$	1-AdZPh_2 [d]	4	5
1[e]	**2** (5.8)	*hν* (20 min)	100	70[f] (**3**)	16	*g*
2	**2** (6.0)	dark (20 min)	0	0 (**3**)	0	0
3	**2** (7.2)	*hν* (20 min)[h]	10	*g* (**3**)	*g*	*g*
4	**2** (6.3)	*hν* (20 min)[i]	37	30 (**3**)	5	*g*
5[e]	**2** (5.9)	K (7.2 × 10^{-3} M)[j]	83	6[f] (**3**)	67	4
6[e]	**6** (4.5)	*hν* (60 min)	90	65[k] (**7**)	5	7
7	**6** (5.1)	dark (60 min)	0	0 (**7**)	0	0
8	**6** (5.8)	K (7.2 × 10^{-3})[j]	52	0 (**7**)	23	16
9		*hν* (120 min)[l]	0		0	0

[a] 1-Bromoadamantane, 7.2 × 10^{-3} M. [b] Obtained by bond cleavage of Ph_3Z [Z = P (**2**) and Z = As (**6**)] with 2 equiv of K metal (see ref 12). [c] Yields are based on the nucleophile concentration; bromide ion was determined potentiometrically, and the organic products were determined by GC with an internal standard (naphthalene for adamantane and 1-bromoadamantane; 9-bromophenanthrene for 1,1′-biadamantyl) unless otherwise indicated. [d] Ad = adamantyl, Z = P (**3**), Z = As (**7**). [e] Duplicate runs. [f] Isolated yield by column chromatography as the oxide. [g] Not quantified. [h] *p*-Dinitrobenzene (20 mol %) was added. [i] Di-*tert*-butyl nitroxiee (10 mol%) was added. [j] K metal was added in small pieces in the dark. [k] Isolated yield by column chromatography as the oxide. [l] Toluene (140 mol %) was added.

It is known that 1-adamantyl radicals are formed by reaction of sodium metal with 1-bromoadamantane.[14] In the reaction stimulated by solvated electrons, the initiation step may occur by **1** accepting a solvated electron to form a radical anion, which then breaks up as in eq 4.

That 1-adamantyl radicals are intermediates in these reactions is supported by the formation of adamantane and 1,1′-biadamantyl, which probably arise from eq 7–11. In these reactions eq 7 predominates over the coupling reaction (eq 5) with **2** as the nucleophile and even more so with **6** as the nucleophile, in which no substitution product is found. The solvated electron-stimulated reactions are not very efficient as compared with those with haloarenes[7] but resemble the behavior of haloazines[15] and 2-halothiophenes[16] under similar experimental conditions. On the other hand, in photostimulated reactions, the main reaction of 1-adamantyl radicals appears to be the coupling with the nucleophiles (eq 5).

The nature of the initiation step in the photostimulated $S_{RN}1$ reactions is not very clear, and several possibilities, such as photoassisted homolysis of the C–halogen bond or electron transfer from the nucleophile to the substrate, have been suggested. In this case the homolysis of the C–Br bond is considered unlikely, because in an experiment where **1** was subjected to a long irradiation time (2 h) in liquid ammonia in the presence of toluene as the hydrogen donor to trap any 1-adamantyl radical formed, no adamantane or 1,1′-biadamantyl was obtained (less than 0.1%; expt 9, Table I).

We suggest that 1-bromoadamantane radical anion is formed from the transfer of an electron of the nucleophile stimulated by light (eq 3b).

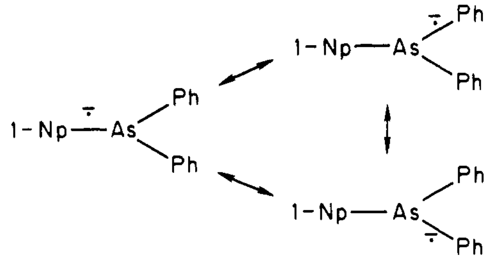
The formation of **4** and **5** is probably the result of termination steps. Dimerization of 1-adamantyl radicals affords **5** (eq 11), and **4** is probably formed through eq 7–10, which represent reduction of 1-adamantyl radicals by the electron donors present in the solution (solvated electrons or radical anions) or by hydrogen atom abstraction (eq 10). Since ammonia is a very poor hydrogen atom donor, this reaction can be neglected.

The formation of **7** as the only substitution product of the reaction of **1** with **6** (eq 2) contrasts with results previously reported regarding the reaction of **6** with some haloarenes.[12,13] For instance, the photostimulated reaction of 1-bromonaphthalene with **6** affords four arsines (eq 12).

$$\text{1-BrNp} + \mathbf{6} \xrightarrow{h\nu} Ph_3As + \text{1-NpPh}_2As + (\text{1-Np})_2PhAs + (\text{1-Np})_3As \quad (12)$$

$$\text{Np} = \text{naphthyl}$$

The scrambling of aryl rings was ascribed to the formation of a σ* radical anion, **8**, when the 1-naphthyl radical couples with **6**, which then fragments at any of the C–As bonds. The scrambling was avoided with aryl radicals having a low-lying π* MO, such as 4-benzoilphenyl radical. The formation of π* radical anion **9** prevents bond fragmentation, and only the straightforward substitution product is obtained.[17,18]



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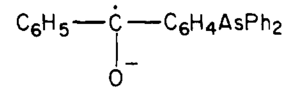
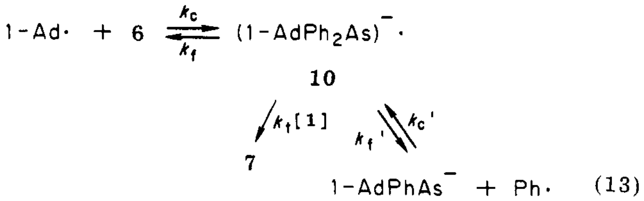


$$C_6H_5-\underset{\underset{O^-}{|}}{\dot{C}}-C_6H_4AsPh_2$$

9

A similar interpretation cannot be given to the lack of scrambling in the reaction now reported since it is very unlikely that the (1-adamantyl)diphenylarsine radical anion is of π* nature. The formation of scrambled or straightforward substitution products depends on the competition between the electron-transfer rate (k_t[1]) and the bond fragmentation rate (k_f'; eq 13). Either of the



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conditions $k_t[1] \gg k_f'$ or $k_f \gg k_f'$ should lead to the formation of the straightforward substitution product.

In the reaction of **7** with potassium metal in liquid ammonia, 100% of adamantane is formed. Since under these conditions radical anion **10** is probably formed, this result indicates that $k_f \gg k_f'$, otherwise benzene would be formed.[19]

Incidentally, the formation of 6% of 1-adamantylamine in the later reaction (see Experimental Section) gives further support to the mechanism since it is well-known that amide ion is a good nucleophile for $S_{RN}1$ reactions.[7]

All these results suggest that **1** reacts under photostimulation probably by the $S_{RN}1$ mechanism with the nucleophiles **2** and **6** in liquid ammonia, and it is concluded that substrates of low reactivity in S_N1 or S_N2 reactions (such as unactivated haloarenes, vinyl halides and haloadamantanes) are suitable substrates for the $S_{RN}1$ mechanism of substitution. Although the bridgehead position is at an aliphatic site, it is clearly different from the other aliphatic substrates that react by the $S_{RN}1$ mechanism such as the *p*-nitrobenzylic systems or other substrates with electron-withdrawing groups.[20]

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 by using a column packed with 1.5% OV-101 on Chromosorb P (1.5 m × 3 mm). Irradiation was conducted in a reactor equipped with three 250-W UV lamps emitting maximally at 350 nm (Philips 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 was cut into small pieces and washed free of oil with dried diethyl ether immediately before addition to the reaction flask. 1-Bromoadamantane (Aldrich) was sublimated twice before used. Diphenylphosphide and diphenylarsenide ions were prepared from triphenylphosphine (Fluka) and triphenylarsine (Aldrich) and 2 equiv of potassium metal in liquid ammonia, and the amide ion formed was neutralized with *tert*-butyl alcohol.[12] 1,1′-Biadamantyl was prepared from 1-bromoadamantane and sodium metal in xylene as reported.[21] Di-*tert*-butyl nitroxide was kindly provided by Professor James F. Wolfe.

Photostimulated Reaction of 1-Bromoadamantane with Diphenylphosphide Ion. The photostimulated reaction of diphenylphosphide ion with 1-bromoadamantane is representative. Into a three-necked, 500-mL, round-bottomed flask, equipped with a cold finger condenser charged with solid CO_2 and ethanol, a nitrogen inlet, and a magnetic stirrer, was condensed ~250 mL of ammonia. To the ammonia were added triphenylphosphine (1.5 mmol) and potassium metal (3 mmol) to form the diphenylphosphide ion, and then *tert*-butyl alcohol (1.5 mmol) was added. To this solution was added 1-bromoadamantane (1.8 mmol), and the solution was irradiated for 20 min. The reaction was quenched by adding ammonium nitrate in excess, and the ammonia was allowed to evaporate. Water (100 mL) was added to the residue, and the mixture was extracted three times with 50 mL of diethyl ether. To a sample of the ether extract were added naphthalene as an internal standard to quantify adamantane and 1-bromoadamantane and 9-bromophenanthrene to quantify 1,1′-biadamantyl. The ether extracts were dried and distilled. In the water layer bromide ion was determined potentiometrically. The residue was column chromatographied on silica gel and eluted with diethyl ether. The product isolated was (1-adamantyl)diphenylphosphine oxide, which comes from the self-oxidation of (1-adamantyl)diphenylphosphine during the workup. No attempts were made to isolate (1-adamantyl)diphenylphosphine as such. (1-Adamantyl)diphenylphosphine oxide is a white solid and was recrystallized from benzene: mp 216–220 °C (lit.[22] mp 219–222 °C); NMR (C_3D_6O) δ 1.8–2.1 (br, 15 H), 7.2–8.2 (br, 10 H); MS, *m/e* (relative intensity) 336 (18), 335 (8), 202 (8), 201 (8), 136 (13), 135 (100), 105 (6), 93 (12), 79 (12).

Photostimulated Reaction of Diphenylphosphide Ion with 1-Bromoadamantane in the Presence of Inhibitors. The procedure was similar to that for the previous reactions, except that in expt 3 (Table I) 20 mol % of *p*-dinitrobenzene was added and in expt 4 (Table I) 10 mol % of di-*tert*-butyl nitroxide was added.

Photostimulated Reaction of 1-Bromoadamantane with Diphenylarsenide Ion. The procedure was similar to that for the previous reaction, except that the irradiation time was 60 min. The residue of the ether extract was column chromatographed on silica gel and eluted with methanol. The product isolated was (1-adamantyl)diphenylarsine oxide, which comes from the self-oxidation of (1-adamantyl)diphenylarsine during the workup. No attempts were made to isolate (1-adamantyl)diphenylarsine as such. (1-Adamantyl)diphenylarsine oxide was recrystallized from benzene: mp 153–156 °C; NMR (Cl_3CD) δ 1.6–2.0 (br, 15 H), 7.4–7.8 (br, 10 H); MS, *m/e* (relative intensity) 380 (2), 320 (1), 245 (2), 229 (24), 227 (12), 152 (18), 135 (100), 92 (21), 90 (20).

Reaction of Diphenylphosphide Ion with 1-Bromoadamantane Stimulated by Solvated Electrons. The reaction was carried out as before, except that the reaction flask was wrapped with aluminum foil, and K metal was added in small pieces.

Reaction of (1-Adamantyl)diphenylarsine with Solvated Electrons in Liquid Ammonia. We attempted to prepare (1-adamantyl)diphenylarsine pure, but it always was contaminated with the oxide. We decided to prepare it in liquid ammonia by the procedure described before and do the reaction with potassium metal in situ. (1-Adamantyl)diphenylarsine was synthesized from 1.78 mmol of 1-bromoadamantane and 1.45 mmol of diphenylarsenide ion in liquid ammonia. To this solution was added potassium metal bit by bit until a blue solution was obtained, the reaction was quenched by methyl iodide[12] to trap any arsenide ion formed, and the ammonia was allowed to evaporate. To the residue was added water, and the mixture was extracted with diethyl ether. The ether extract was dried and distilled. The residue was column chromatographed on silica gel and eluted with petroleum ether, and diphenylmethylarsine (70% yield), adamantane and 1,1′-biadamantyl (73%), and 1-adamantylamine (6% yield) were isolated.

Acknowledgment. S.M.P. gratefully acknowledges receipt of a fellowship from the Consejo Nacional de Investigaciones Cientificas y Tēcnicas, Argentina. Professor James F. Wolfe is thanked for the gift of a sample of di-*tert*-butyl nitroxide.

Registry No. 1, 768-90-1; **2**, 34676-89-6; **6**, 14971-22-3; **7**, 83135-27-7; 1-adamantyldiphenylarsine oxide, 83135-26-6; triphenylphosphine, 603-35-0; 1-adamantyldiphenylphosphine oxide, 60509-83-3; K, 7440-09-7.

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(19) The reaction of (1-naphthyl)diphenylarsine with potassium metal in liquid ammonia afforded benzene (80%) and naphthalene (20%) in a distribution similar to the statistical distribution of the C–As bonds, which suggests the formation of σ^* radical anion **8**. Alonso, R. A., Ph.D. Thesis, Universidad Nacional de Cōrdoba, 1981.

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