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92284-87-2; **43**, 13566-43-3; 2,6,7-tris[(2-(methoxycarbonyl)ethyl]-β,4-[(β-(methoxycarbonyl)ethylene]-1,3,5,8-tetramethylporphrin, 62786-79-2; methyl acrylate, 96-33-3; diethyl malonate, 105-53-3; ethyl oximinoacetoacetate, 5447-76-7; pentane-2,4-dione, 123-54-6; ethyl 3,5-dimethylpyrrole-2-carboxylate, 2199-44-2; 3,5-dimethylpyrrole-2-carboxylic acid, 4513-93-3; 2-(*tert*-butoxycarbonyl)-3-ethyl-4-methylpyrrole-5-carboxylic acid, 52459-88-8.

Photostimulated Reaction of 1-Haloadamantane and 9-Bromotriptycene with Nucleophiles. A Nucleophilic Substitution by $S_{RN}1$ at the Bridgehead Position

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1-Haloadamantanes and 9-bromotriptycene react under irradiation with diphenylphosphide and diphenylarsenide ions to give the substitution product in good yields. 1-Iodoadamantane (**8**) also reacts with disodium telluride and disodium selenide under irradiation to give di-1-adamantyl ditelluride and di-1-adamantyl diselenide, respectively. 9,10-Dibromotriptycene with diphenylphosphide gives a good yield of the disubstitution product. It seems that all these reactions occur by the $S_{RN}1$ mechanism. Substrate **8** reacts under irradiation with carbanionic nucleophiles and diethyl phosphite ion, but the products are adamantane and 1,1′-biadamantyl rather than substitution products. These nucleophiles transfer an electron to **8** to form radical anions which fragment to 1-adamantyl radicals. The radicals are reduced or dimerized. In contrast, amide ions do not react with **8**. The ease of the halogen nucleofugality is I > Br > Cl, the same as in the aromatic system.

It is well-known that 1-halo-substituted bridgehead compounds are very unreactive toward nucleophilic substitution reactions (S_N1 or S_N2 type mechanism),[1] but we have recently reported that 1-bromoadamantane reacts with nucleophiles by the $S_{RN}1$ mechanism.[2]

$$\underset{\mathbf{1}}{\text{1-BrAd}} + \underset{\substack{\mathbf{2},\ M = P\\ \mathbf{3},\ M = As}}{Ph_2M^-} \xrightarrow{h\nu} \underset{\mathbf{4}}{\text{1-AdMPh}_2} + \underset{\mathbf{5}}{\text{AdH}} + \underset{\mathbf{6}}{(\text{1-Ad})_2} \tag{1}$$

Ad = adamantyl

This novel nucleophilic substitution on a bridgehead position opens an interesting field, not only from the mechanistic point of view but also as a synthetic route for this type of compounds.

We report here the photostimulated reaction of 1-X-adamantane (X = Cl, Br, I) with several nucleophiles as well as the photostimulated reactions of 9-bromo- and 9,10-dibromotriptycene with nucleophiles in order to determine the scope of this novel nucleophilic substitution at bridgehead carbon.

Results and Discussion

Reactions of 1-Haloadamantanes with Amide Ions. In the photostimulated reaction of **1** with **3** in liquid ammonia, we found a small amount of 1-aminoadamantane (**7**).[2] But when we performed a photostimulated reaction of **1** with amide ions, no reaction occurred. This result might suggest that amide ions failed to initiate the reaction (eq 2), but would propagate it (eq 3–5). However, when 1-adamantyl radicals were formed by reaction of **1** with sodium metal in liquid ammonia[3] or by photostimulation with carbanionic nucleophiles (see below) together with amide ions, no **7** was found, but only **5** and **6** were formed (Table I, expt 2, 5, 6).

$$\mathbf{1} + NH_2^- \overset{h\nu}{\nrightarrow} (\text{1-BrAd})^{-\cdot} + NH_2\cdot \tag{2}$$

$$(\text{1-BrAd})^{-\cdot} \rightarrow \text{1-Ad}\cdot + Br^- \tag{3}$$

$$\text{1-Ad}\cdot + NH_2^- \rightarrow (\text{1-NH}_2\text{Ad})^{-\cdot} \tag{4}$$

$$(\text{1-NH}_2\text{Ad})^{-\cdot} + \mathbf{1} \rightarrow (\text{1-BrAd})^{-\cdot} + \underset{\mathbf{7}}{\text{1-NH}_2\text{Ad}} \tag{5}$$

These results suggest that amide ions do not react either with 1-adamantyl radicals or with **1**, but **7** is formed in the reaction of **1** with **2** or **3** in the presence of amide ions (Table I, expt 3, 4). Then, **7** might be formed by the reaction of amide ions with the substitution product **4** in a consecutive reaction (eq 6 and 7).

$$\mathbf{1} + Ph_2M^- \xrightarrow[S_{RN}1]{h\nu} \underset{\mathbf{4}}{\text{1-AdMPh}_2} \tag{6}$$

$$\mathbf{4} + NH_2^- \rightarrow \underset{\mathbf{7}}{\text{1-NH}_2\text{Ad}} \tag{7}$$

4 reacted with amide ions (M = As) to give **7** (Table I, expt 7, 8) in photostimulated as well as in dark conditions, thus suggesting that the formation of **7** is derived from the attack of amide ions on **4**.

Reaction of 1-Haloadamantane with Carbanionic Nucleophiles. Carbanionic nucleophiles, such as ketone enolated ions, cyanomethyl anion, etc., react with aryl radicals to give good yields of substitution products by the $S_{RN}1$ mechanism.[3]

In the photostimulated reaction of 1-iodoadamantane with several carbanionic nucleophiles, the only products formed were the reduction product adamantane and the dimeric product **6**. No coupling products were formed (eq 8) (Table II).

$$\underset{\mathbf{8}}{\text{1-IAd}} + {}^-CH_2Z \xrightarrow{h\nu} \underset{\mathbf{5}}{\text{AdH}} + \underset{\mathbf{6}}{(\text{1-Ad})_2} \tag{8}$$

Because there was no dark reaction, and because **5** and **6** were the only products formed from **8** in the photostimulated reactions, carbanionic nucleophiles probably

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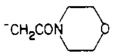
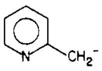
Table I. Reaction of 1-Bromoadamantane with Amide Ions in Liquid Ammonia

expt	1-BrAd, 10^3 M	NH_2^-, 10^3 M	conditions	yield, % Br$^-$	yield, % 1-AdNH$_2$	yield, % other products
1	7.8	7.2	*hν*, 120 min	0	0	
2	14.0	41	Na (18×10^{-3} M)	55	0	AdH, 47; $(1\text{-Ad})_2$, 8
3	12.0	18	*hν*, 120 min, **3** (6×10^{-3} M)	50	27	1-AdAsPh$_2$, 26
4	12.0	11	*hν*, 120 min, **2** (6×10^{-3} M)	55	10	1-AdPPh$_2$, 40
5	6.0[a]	40	*hν*, 240 min, $^-CH_2COCH_3$ (10×10^{-3} M)	44	0	AdH, 22; $(1\text{-Ad})_2$, 15
6	5.8[a]	12	*hν*, 180 min, $^-CH_2CN$ (12×10^{-3} M)	79	0	AdH, 23; $(1\text{-Ad})_2$, 24
7	6.2[b]	40	*hν*, 120 min		44	*c*
8	5.9[b]	40	dark; 120 min		42	*d*

[a] 1-Iodoadamantane. [b] 1-Adamantyldiphenylarsine. [c] 43% of recovered substrate. [d] 35% of recovered substrate.

Table II. Photostimulated Reactions of 1-Iodoadamantane with Carbanion Nucleophiles in Liquid Ammonia[a]

expt	carbanion nucleophile	10^3 M	irradn, time min	yield,[b] % I$^-$	yield,[b] % AdH	yield,[b] % $(1\text{-Ad})_2$
1	$^-CH_2COCH_3$	40	240	70	5	34
2	$^-CH_2CO\bar{C}HCOCH_3$	10	180	45	7	21
3		20	180	71	*c*	*c*
4	$^-CH_2CN$	12	180	63	27	38
5		8	210	2	*c*	*c*

[a] 1-Iodoadamantane, 6×10^{-3} M. The carbanions were prepared from the acid–base reaction with amide ion, except acetone enolate ion which was from an excess of *t*-BuONa. [b] Iodide ion was determined potentiometrically, and adamantane and 1,1′-biadamantyl by GLC. [c] Not quantified.

Table III. Photostimulated Reaction of 1-Iodoadamantane with Disodium Selenide and Telluride Ions[a]

substrate, M	nucleophile	M	yield of I$^-$, %	isolated product, yield, %
0.012	Se^{2-}	0.013	70	$(1\text{-AdSe})_2$; 46 adamantane; 23
0.023	Te^{2-}	0.020	69	$(1\text{-AdTe})_2$; 47 adamantane; 20

[a] Irradiation time 120 min.

transferred one electron to **8** in the photostimulated reaction (eq 9) and the radical anion **9** fragmented to give 1-adamantyl radicals (eq 10), which did not couple with the carbanionic nucleophiles but were reduced to adamantane or formed the dimer **6** (eq 11 and 12).

$$\mathbf{8} + {}^-CH_2Z \xrightarrow{h\nu} \underset{\mathbf{9}}{(1\text{-IAd})^{-\cdot}} \quad (9)$$

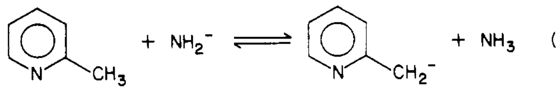
$$\mathbf{9} \rightarrow 1\text{-Ad}\cdot + I^- \quad (10)$$

$$1\text{-Ad}\cdot \rightarrow \underset{\mathbf{5}}{1\text{-AdH}} \quad (11)$$

$$1\text{-Ad}\cdot \rightarrow \underset{\mathbf{6}}{(1\text{-Ad})_2} \quad (12)$$

2- And 4-picolyl anions reacted with haloaromatic compounds[4,5] under conditions conducive to the $S_{RN}1$ mechanism. In the photostimulated reaction of **8** with 2-picolyl anion in liquid ammonia and after 3.5 h of irradiation, only 2% yield of iodide ion was eliminated (Table II, expt 5). These results are in contrast with the other carbanionic nucleophiles studied.

The approximate pK_a's of 2- and 4-picoline are about 31 and 29,[6] similar to the pK_a of ammonia (pK_a = 32.5),[7] probably amide ion and 2-picolyl anion are in equilibrium in liquid ammonia (eq 13), and the actual concentration of 2-picolyl anion is not enough for the photostimulated electron transfer to the substrate.


(13)

Diethyl Phosphite Ion. Diethyl phosphite ion is reactive with aryl radicals.[8-10] However, a solution of diethyl phosphite ion (4.5×10^{-2} M) and 1-iodoadamantane (1.2×10^{-2} M) after 3 h of irradiation gave only 14% yield of iodide ion elimination, and the only product formed was adamantane (13.5%). These results establish that diethyl phosphite ion transfers an electron to the substrate but that 1-adamantyl radical does not couple with this nucleophile.

Disodium Telluride and Disodium Selenide as Nucleophiles. Disodium telluride and disodium selenide were prepared from tellurium and selenium metals by reaction with sodium metal in liquid ammonia and they reacted under irradiation with haloarenes by the $S_{RN}1$ mechanism to give the substitution product.[11]

In the photostimulated reaction of disodium selenide and disodium telluride ions with 1-iodoadamantane, iodide ion was eliminated in 70% yield, and after air oxidation, di-1-adamantyl diselenide and di-1-adamantylditelluride were obtained (eq 14–16) (Table III).

$$Z + 2Na \xrightarrow{NH_3} Z^{2-} + 2Na^+ \quad (14)$$

$$1\text{-IAd} + Z^{2-} \xrightarrow[S_{RN}1]{h\nu} 1\text{-AdZ}^- + I^- \quad (15)$$

$$1\text{-AdZ}^- \xrightarrow{[O]} (1\text{-AdZ})_2 \quad (16)$$

$$Z = Se, Te$$

Halogen Nucleofugality in Adamantanes. The halogen nucleofugality found in photostimulated reactions of several nucleophiles with aromatic compounds is I > Br > Cl > F.[3]

Although 1-haloadamantanes (X = Cl, Br, I) are not completely soluble in liquid ammonia and their quantitative reactivities cannot be determined, we studied their photostimulated reaction in order to know qualitatively if the same trend is obtained.

1-Chloroadamantane with **2** gave 40% yield of chloride elimination in 105 min of irradiation. The yield of bromide in the reaction of 1-bromoadamantane with **2** as nucleophile was 16% in 5 min, 50% in 10 min, and 100% in 20 min of irradiation (Table IV). 1-Iodoadamantane is quite insoluble in liquid ammonia and its reaction with **2** as

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(4) Bunnett, J. F.; Gloor, B. F. *J. Org. Chem.* **1974**, *39*, 382.

(5) Moon, M. P.; Komin, A. P.; Wolfe, J. F.; Morris, G. F. *J. Org. Chem.* **1983**, *48*, 2393.

(6) Zoltewicz, J. A.; Helmick, L. S. *J. Org. Chem.* **1973**, *38*, 658.

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(10) Bunnett, J. F.; Shoper, S. J. *J. Org. Chem.* **1978**, *43*, 1873.

(11) Rossi, R. A.; Peñeñory, A. B. *J. Org. Chem.* **1981**, *46*, 4580.

Table IV. Reactivity of 1-Haloadamantanes in Photostimulated Reaction with 2 and Acetone Enolate Ions

expt	1-halo-adamantane, X (M × 10^3)	nucleophile (M × 10^3)	irradn time, min	X^-, %
1	Cl (7.4)	**2** (6.0)	105	40
2	Br (7,12)	**2** (6.4)	5	16
3	Br (7.12)	**2** (6.4)	10	50
4	Br (6.9)	**2** (5.8)	20	100
5	I (7.08)	**2** (5.80)	20	42
6	I[a] (8.4)	**2** (6.0)	20	76
7	Br (24)	$^-CH_2COCH_3$ (48)	200	16
8	I (5.8)	$^-CH_2COCH_3$ (16.8)	180	42
9	I (8.02)	$^-CH_2COCH_3$ (40)	240	70

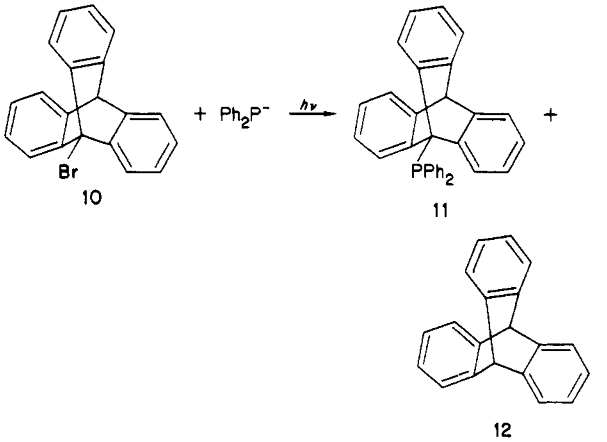
[a] The substrate was solubilized in 2 mL of diethyl ether.

nucleophile gave 42% yield of iodide in 20 min of irradiation. On the other hand, if 1-iodoadamantane is dissolved in 2 mL of anhydrous diethyl ether, the yield increases up to 76% in the same period of time. Thus, the observed reactivity of 1-iodoadamantane seems to be determined by the rate of solubilization in liquid ammonia rather than by its intrinsic reactivity.

In the photostimulated reaction with acetone enolate ion which is a slow reaction because there are no chain-propagation steps, 1-bromoadamantane gave 16% yield of bromide elimination after 200 min, but 1-iodoadamantane yielded 42% of iodide in 180 min and 70% in 240 min.

We conclude that the halogen nucleofugality for 1-haloadamantanes is I > Br > Cl, the same order as in the aromatic series.

Reaction of 9-Bromotriptycene. We have previously determined $S_{RN}1$ substitution in bridgehead haloadamantanes. In the presente study we have investigated the $S_{RN}1$ mechanism in another bridgehead molecule such as 9-bromotriptycene (**10**). In the photostimulated reaction of **10** with **2** in liquid ammonia, there was 71% yield of 9-triptycyldiphenylphosphine (**11**) and 10% yield of the reduction product triptycene (**12**) (eq 17) during 350 min of irradiation, but no dimeric product was observed.



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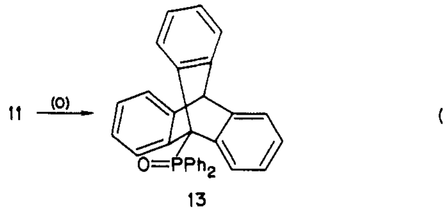

(18)

The substitution product **11** was not isolated as such because of its easy oxidation to 9-triptycyldiphenylphosphine oxide (**13**) (eq 18).

There was a slow dark reaction in the same period of time with 14% yield of bromide and 10% yield of **13** and 3.5% of **12**. This dark reaction was completely inhibited by 10 mol % of di-*tert*-butyl nitroxide (0% yield of bromide elimination) which is a well-known inhibitor of $S_{RN}1$ reactions (Table V).[3] Another inhibitor of $S_{RN}1$ reactions is *p*-dinitrobenzene,[3] but the dark reaction in the presence of *p*-dinitrobenzene (20 mol %) was slightly accelerated (37% of bromide elimination). There are precedents in $S_{RN}1$ reactions in which added substances inhibited the reaction in some systems but catalyzed it in others.[3b]

Table V. Reaction of 10 with 2 in Liquid Ammonia

expt	**10**, 10^3 M	**2**, 10^3 M	irradn time, min	Br^-	9-triptycyl-Ph_2PO yield,[a] %	triptycene
1[b]	6.7	6.7	350	77	71	9
2[c]	2.1	2.1	350[d]	14	10	3.5
3	1.8	1.9	350[d,e]	0	0	0
4	1.1	1.2	350[d,f]	37	g	g
5[h]	2.5	2.5	60	76	41[i]	34
6[j]	3.3	8.4	300	94[k]	49[l]	g

[a] Bromide ion determined potentiometrically; 9-Triptycyldiphenylphosphine oxide and triptycene as isolated yield. [b] **10** recovered 20%. [c] **10** recovered 82%. [d] Dark condition. [e] Di-*tert*-butyl nitroxide (10 mol %) added. [f] *p*-Dinitrobenzene (20 mol %) added. [g] Not quantified. [h] Diphenylarsenide ion. [i] 9-Triptycyldiphenylarsine. [j] 9,10-Dibromotriptycene. [k] Considering two bromine atom by molecule. [l] 9,10-Bis(diphenylphosphinyl)triptycene (recrystallized yield).

The strong catalysis of the reaction of **10** with **2** by light, the complete inhibition by di-*tert*-butyl nitroxide and the formation of the byproduct **12** constitute a strong evidence that **10** reacts with **2** by the $S_{RN}1$ mechanism of nucleophilic substitution (eq 19–23). A similar behavior was found with diphenylarsenide ion as nucleophile. The photostimulated reaction of **10** with **3** gave after 60 min of irradiation the substitution product **15** (41% yield) with 34% of tryptycene (eq 24).

$$\underset{\mathbf{10}}{\text{9-Br-Tript}} + \mathbf{2} \xrightarrow{h\nu} \underset{\mathbf{14}}{(\text{9-BrTript})^{-}\cdot} \quad (19)$$

$$(\text{9-Br-Tript})^{-}\cdot \rightarrow \text{9-Tript}\cdot + Br^- \quad (20)$$

$$\text{9-Tript}\cdot + \mathbf{2} \rightarrow [(\text{9-Tript})PPh_2]^{-}\cdot \quad (21)$$

$$[(\text{9-Tript})PPh_2]^{-}\cdot + \mathbf{10} \rightarrow \mathbf{11} + \mathbf{14} \quad (22)$$

$$\text{9-Tript}\cdot \rightarrow\ \rightarrow \mathbf{12} \quad (23)$$

Tript = triptycyl

$$\mathbf{10} + \underset{\mathbf{3}}{Ph_2As^-} \xrightarrow{h\nu} \underset{\mathbf{15}}{(\text{9-Tript})AsPh_2} + \mathbf{12} \quad (24)$$

There was much more reduction product **12** with **3** as nucleophile compared with **2** as nucleophile. Several aryl radicals coupled with **3** in a reversible reaction[12,13] and so probably did 1-adamantyl radical.[2] The fact that **12** is formed in higher yields might suggest a slow coupling of 9-triptycyl radical with **3** or reversible coupling between them (eq 25). In any case, there is an increased amount of 9-triptycyl radicals which lead ultimately to **12** (eq 23).

$$\text{9-Tript}\cdot + \mathbf{3} \rightleftharpoons [(\text{9-Tript})AsPh_2]^{-}\cdot \quad (25)$$

In contrast with the reactions of the 1-haloadamantanes, no dimeric product 9,9′-bitriptycyl was found. In other reactions such as the reaction of **10** with sodium metal in mineral oil[14] or the thermal decomposition of ditriptoyl

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[12] Rossi, R. A.; Alonso, R. A.; Palacios, S. M. *J. Org. Chem.* **1981**, *46*, 2498.

[13] Alonso, R. A.; Rossi, R. A.; *J. Org. Chem.* **1982**, *47*, 77.

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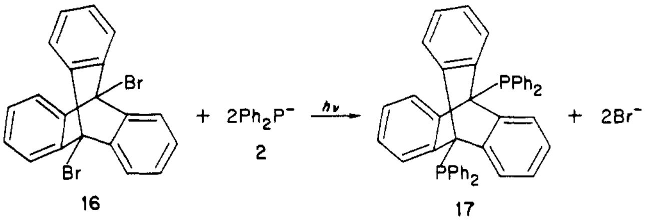
peroxide the dimeric product was not found either.[15]

Reaction of 9,10-Dibromotriptycene with Diphenylphosphide Ion. The reaction of dihaloarenes with nucleophiles by the $S_{RN}1$ mechanism gave either the monosubstitution or disubstitution product depending on the aromatic moiety, the nucleofugal group, or the nucleophile.[16] The monosubstitution product was not an intermediate in the formation of the disubstitution product.

9,10-Dibromotriptycene (**16**) was used as a model compound to see if it was possible to perform a disubstitution in both bridgehead positions. In the photostimulated reaction of **16** with **2** as nucleophile (eq 26), we found 94% yield of bromide elimination (considering two bromine atoms per molecule) and the disubstitution product was obtained in 49% yield of isolated product. The disubstituted **17** was not isolated as such, but as its dioxide **18** (eq 27). Due to the fact that **16** is slightly soluble in liquid NH_3, it is not possible to know if the monosubstitution is an intermediate in this reaction. But we suggest that when 10-bromo-9-triptycyl radical **19** reacts with the nucleophile **2**, it forms a radical anion **20** which would fragment faster (eq 29) than the intermolecular electron transfer to **16**.



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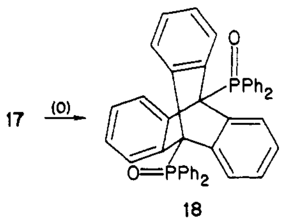

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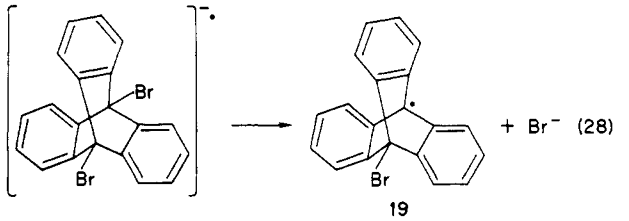

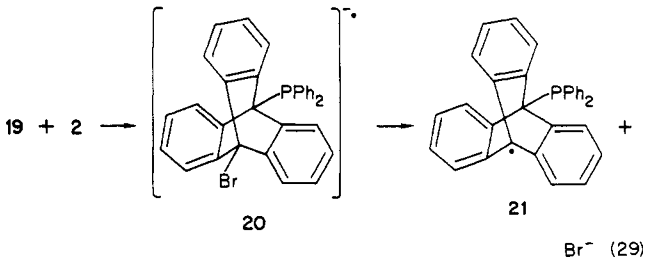

$$\mathbf{21} + \mathbf{2} \longrightarrow \mathbf{17}^{-\cdot} \xrightarrow{-e^-} \mathbf{17} \qquad (30)$$

These results show that a nucleophilic substitution is possible not only on a bridgehead position but also on two or more bridgehead positions by the $S_{RN}1$ mechanism.

Experimental Section

General Methods. The general method was as described before.[2]

Materials. Reagents were commercially available materials unless otherwise indicated and were purified by standard procedures. 1-Bromoadamantane (Fluka) was sublimed twice before use. 1-Chloroadamantane and 1-iodoadamantane were prepared as described before.[17] 9-Bromotriptycene (mp 253–254 °C) was prepared from isoamyl nitrite, 9-bromoanthracene, bis(2-methoxyethyl) ether (diglyme), and anthranilic acid as described in the literature,[18] purified by column chromatography on silica gel, and eluted with petroleum ether. 9,10-Dibromotryptycene was prepared from isoamyl nitrite, 9,10-dibromoanthracene, bis(2-methoxyethyl) ether, and anthranilic acid as described in the literature,[19] purified by column chromatography on aluminum oxide, and eluted with petroleum ether.

Photostimulated Reaction of 1-Haloadamantane with Carbanionic Nucleophiles. The photostimulated reaction of acetone enolate ion with 1-iodoadamantane 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 *tert*-butyl alcohol (10 mmol) and sodium metal (10 mmol) to form sodium *tert*-butoxide. Then, acetone (0.74 mL) was added and by acid–base reaction, acetone enolate ion was formed. To this solution was added 1-iodoadamantane (2.01 mmol), and the solution was irradiated for 240 min with four 250-W lamps with maximum emission at 350 nm. 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 3 times with 50 mL of diethyl ether. The ether extract was chromatographed on silica gel to quantify adamantane and 1,1′-biadamantyl. Iodide ion was determined potentiometrically in the water layer.

Photostimulated Reaction with Disodium Telluride and Disodium Selenide. One equivalent of disodium telluride and disodium selenide was prepared with tellurium and selenium metal, respectively, and sodium metal as reported.[11] Then, 2 equiv of 1-iodoadamantane were added and the solution was irradiated for 210 min. The reaction mixture was then extracted as described above. The ether extract was allowed to evaporate. Di-1-adamantyl ditelluride was recrystallized from ethanol/acetone (1:1): 170–171 °C; NMR δ 1.68–2.2 (br peak); mass spectrum, m/e (relative intensity) 528 (0.6), 526 (0.6), 524 (0.4), 135 (100), 107 (8), 93 (15), 79 (15). Di-1-adamantyl diselenide was recrystallized from petroleum ether: mp 149–152 °C; NMR δ 1.50–2.05 (br peak); mass spectrum, m/e (relative intensity) 430 (7.2), 428 (3.6), 215 (3), 136 (11), 135 (100), 107 (3), 93 (2), 79 (2).

Photostimulated Reaction of 1-Adamantyldiphenylarsine with Amide Ion. 1-Adamantyldiphenylarsine was prepared in situ by an $S_{RN}1$ reaction with diphenylarsenide ion and 1-bromoadamantane. Then, a solution of amide was added (10 mmol in 100 mL of ammonia). This solution was illuminated during 2 h. The dark reaction was done with the same procedure. The reaction was extracted and the residue was chromatographed by column chromatography on silica gel and eluted with diethyl ether. The products isolated were 1-aminoadamantane and 1-adamantyldiphenylarsine oxide, which comes from oxidation of 1-adamantyldiphenylarsine. They were identified by NMR and mass spectra[2] and compared with authentic samples on GC.

Photostimulated Reaction of 9-Bromotriptycene with Diphenylphosphide Ion. Diphenylphosphide ion (1 mmol) was prepared with triphenylphosphine (1 mmol) and sodium metal (2 mmol). Then, *tert*-butyl alcohol (1 mmol) and 9-bromotriptycene (1 mmol) were added and the solution was irradiated for 350 min. The reaction mixture was extracted with ether and the residue was purified by column chromatography on silica gel and eluted with petroleum ether.

The product isolated was 9-triptycyldiphenylphosphine oxide, which comes from the self-oxidation of 9-triptycyldiphenylphosphine during the workup. 9-Triptycyldiphenylphosphine

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oxide is a white solid and was recrystallized from $Cl_4C/MeOH$ (90:10): mp 180–186 °C; NMR δ (Cl_4C/Me_4Si) 5.3 (s, 1 H) 6.4–7.6 (m, 22 H); MS, *m/e* (relative intensity) 454 (23), 453 (13), 252 (15), 216 (100), 201 (51), 124 (23), 77 (52), 51 (15).

Photostimulated Reaction of Diphenylphosphide Ion with 9-Bromotriptycene in the Presence of Inhibitors. The procedure was similar to that for the previous reactions, except that in expt 4 (Table I) 20 mol % of *p*-dinitrobenzene was added and in expt 3 (Table I) 10 mol % of di-*tert*-butyl nitroxide was added.

Photostimulated Reaction of 9-Bromotriptycene 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 petroleum ether.

The product isolated was 9-triptycyldiphenylarsine, recrystallized from benzene: mp 242–246 °C; NMR (Cl_4C/Me_4Si) 5.4 (s, 1 H), 6.5–7.6 (m, 22 H); MS, *m/e* (relative intensity) 483 (10), 482 (80), 320 (28), 253.4 (100), 227 (43), 152 (20), 77 (5), 51 (5).

Photostimulated Reaction of 9,10-Dibromotriptycene with Diphenylphosphide Ion. The procedure was similar to that for the previous reaction. The reaction mixture was extracted as was described. The ethereal extract was oxidized with hydrogen peroxide, and the 9,10-bis(diphenylphosphinyl)triptycene produced was recrystallized from chloroform/petroleum ether (50:50): mp 325 °C; NMR δ 7–7.4 (m); MS, *m/e* (relative intensity) 655 (35), 454 (11), 453 (45), 252 (42), 202 (16), 201 (100), 185 (14).

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Registry No. **1**, 768-90-1; **2**, 34676-89-6; **3**, 14971-22-3; **4** (M = As), 83135-27-7; **8**, 768-93-4; **10**, 15364-55-3; **11**, 92012-49-2; **13**, 92012-53-8; **15**, 92012-50-5; **16**, 795-42-6; **18**, 92012-51-6; 1-AdCl, 935-56-8; Na_2Te, 12034-41-2; Na_2Se, 1313-85-5; NH_2^-, 17655-31-1; $CH_3C(O)CH_2^-$, 71695-00-6; 1-AdTeTe-1-Ad, 92012-47-0; 1-AdSeSe-1-Ad, 92012-48-1; $CH_3C(O)\bar{C}HC(O)CH_2^-$, 54210-56-9; $O(CH_2CH_2)_2NC(O)CH_2^-$, 92012-52-7; $NCCH_2^-$, 21438-99-3; 2-picolyl anion, 18860-16-7.

Radical Intermediates in the Photoreaction between Disulfides and Acylsilanes

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Photolysis of cyclopropane solutions of a number of disulfides RSSR (R = Me, *n*-Bu, CF_3) in the presence of acylsilanes $R'C(O)SiMe_3$ led to radicals of general structure $R'\dot{C}(OSiMe_3)SR$ which have been detected by EPR spectroscopy. The structure of the observed paramagnetic species has been ascertained by producing $Ph\dot{C}(OSiMe_3)SMe$ via an alternative route, i.e., by reacting $Me_3\dot{S}i$ radicals with the thio ester PhC(O)SMe. The lifetime of these radicals varies considerably with the bulkiness of the substituents in the neighborhood of the radical center. The decay rates as a function of temperature, together with the corresponding activation parameters, have been determined for the hindered $t\text{-}Bu\dot{C}(OSiMe_3)SCF_3$ radical; it is suggested that the decay process involves an equilibrium with a dimeric species. A number of possible reaction sequences leading to these radicals have been examined, although the actual mechanism is as yet unclear.

Ethylenic and aromatic carbon–carbon double bonds readily undergo addition by a variety of organic and organometallic free radicals, including silicon, germanium, tin, phosphorus, and sulfur centered species;[1-3] in many cases the resulting spin adducts have been observed by EPR spectroscopy.[4-9] Group IVB organometallic and phosphorus centered radicals also add to the carbonylic and thiocarbonylic functions by attacking the more electronegative oxygen and sulfur atoms.[7,10-16] On the other hand, although detection of the radical derived from addition of MeS to thiocamphor has been reported[17] and formation of diadamant-2-yl disulfide upon photoreaction of adamantanethione with the corresponding thiol has been rationalized with the attack to C═S by adamantane-2-thiyl radical,[18] addition to thiocarbonyl compounds does not

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