Hydrogenation of A and B was run over 10 mg of platinum(IV) oxide in 3 mL of ethanol. After hydrogen was bubbled through the solution for 1 h, approximately 10 mg (0.07 mmol) of the alcohol in 1.0 mL of ethanol was added. After another hour of hydrogen addition under stirring, the reaction mixture was filtered and ethanol evaporated under reduced pressure. The yield of hydrogenated product was 6 mg. Mass spectra for both compounds are the same with peaks at m/e 136, 121, 107, 94, 81, 67, 55: IR (A) 3350, 2920, 2855, 1445, 1040, 975, 965, 930 cm^{-1}; IR (B) 3360, 2920, 2855, 1710, 1460, 1445, 1040, 975, 965, 930 cm^{-1}.

Photostimulated Reaction of Diphenylarsenide and Diphenylstibide Ions with Haloaromatic Compounds by the S$_{RN}$1 Mechanism. Electron Transfer vs. Bond Breaking of the Radical Anion Intermediate[1]
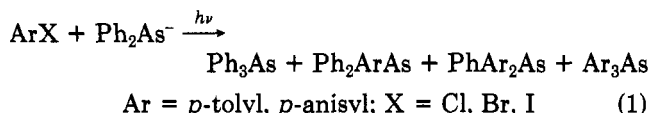
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Photostimulated reactions of haloaromatic compounds with potassium diphenylarsenide and potassium diphenylstibide were studied in liquid ammonia. 1-Bromonaphthalene and 9-bromophenanthrene reacted with diphenylarsenide ion to give four products: triphenylarsine, diphenylarylarsine, phenyldiarylarsine, and triarylarsine (aryl = 1-naphthyl and 9-phenanthryl); with 2-chloroquinoline as substrate only the straightforward substitution product 2-quinolyldiphenylarsine was formed. *p*-Bromoanisole and 4-chlorobenzophenone reacted with potassium diphenylstibide to give four stibines: triphenylstibine, diphenylarylstibine, phenyldiarylstibine, and triarylstibine (aryl = *p*-anisyl and 4-benzoylphenyl). These reactions are believed to occur by the S$_{RN}$1 mechanism with an extra feature of reversible coupling of aryl radicals with arsenide and stibide ions, which causes the scrambling of aryl rings. It is suggested that the low-lying π* MO of the quinolyl moiety prevents C–As bond breaking of the radical anion intermediate.

The photostimulated reaction of potassium diphenylarsenide with *p*-halotoluenes and *p*-haloanisoles (chloro, bromo, iodo) in liquid ammonia gave four arsines as products: triphenylarsine, diphenylarylarsine, phenyldiarylarsine, and triarylarsine (aryl = *p*-tolyl, *p*-anisyl) (eq 1).[2]

$$ArX + Ph_2As^- \xrightarrow{h\nu}$$

$$Ph_3As + Ph_2ArAs + PhAr_2As + Ar_3As$$

$$Ar = p\text{-tolyl}, p\text{-anisyl}; X = Cl, Br, I \qquad (1)$$

These results were explained in terms of the S$_{RN}$1 mechanism,[3] where the radical anion formed from the coupling of an aryl radical with the nucleophile suffers competitive reactions: reversion to starting materials, bond fragmentation leading to scrambling of aryl rings, and electron transfer leading to the substitution products. Scheme I is a representation of the intermediate involved and the products obtained.

On the other hand, the photostimulated reaction of diphenylarsenide ion with 4-chlorobenzophenone gave only one arsine, namely, the straightforward substitution product. There is evidence that this reaction also occurred by the S$_{RN}$1 mechanism,[2] but the radical anion intermediate formed does not fragment, and the only reaction observed is the electron transfer leading to the substitution product (eq 2).
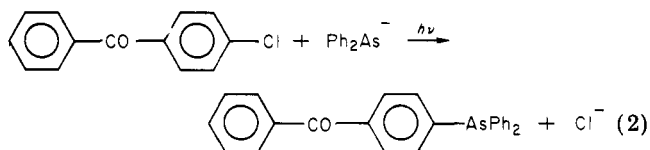
It was suggested that the predominance of the bond-fragmentation or electron-transfer pathways depends on the relative energies of the σ* and π* molecular orbitals (MO's). The low-lying MO's of the radical anion intermediate when *p*-tolyl or *p*-anisyl radicals couple with diphenylarsenide ion are the σ* of the C–As bond, and lead to bond fragmentation of any of the three C–As bonds (eq 3).[2,4]
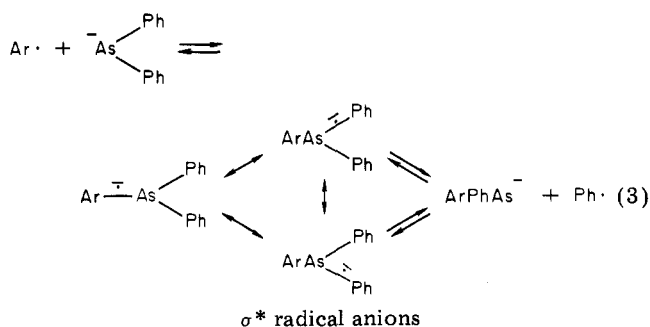
σ* radical anions

On the other hand, in the coupling reaction of 4-benzoylphenyl radical with diphenylarsenide ion, the low-lying MO of the radical anion intermediate is the π* MO of the 4-benzoylphenyl moiety, and the only process

(1) Presented in part at the 5th IUPAC Conference on Physical Organic Chemistry, Santa Cruz, CA, 1980, p 97. Based in part on the Ph.D. Thesis of Ruben A. Alonso, Universidad Nacional de Córdoba, Argentina, Aug 1981.

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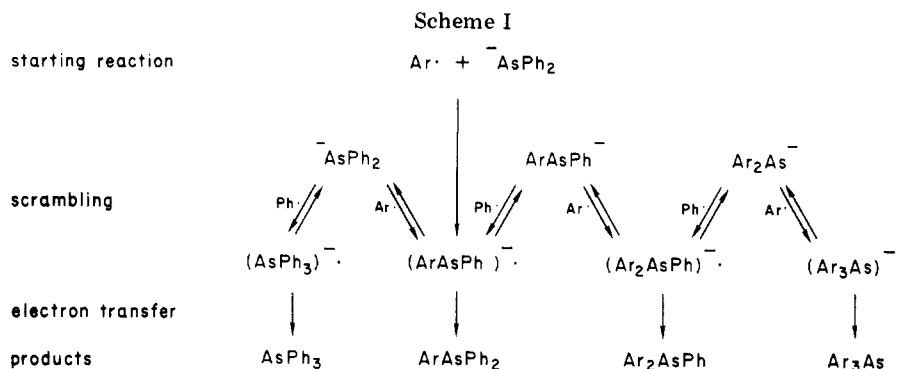(4) Rossi, R. A. *J. Chem. Educ.*, in press.

Scheme I

Table I. Photostimulated Reactions of Diphenylarsenide and Diphenylstibide Ions
with Haloaromatic Compounds in Liquid Ammonia[a]

ArX	mmol	Ph$_2$M$^-$, M	mmol	hν, min	% yield[b]			
					Ph$_3$M	Ph$_2$ArM	PhAr$_2$M	Ar$_3$M
1-bromonaphthalene	3.34	As	2.23	10	33	40	21	c
9-bromophenanthrene	4.36	As	2.94	60	20	60	15	c
2-chloroquinoline	5.98	As	3.99	5	0	60	0	c
p-bromoanisole	2.31	Sb	2.30	30	30[d]	45[d]	19[d]	2[d]
4-chlorobenzophenone	3.66	Sb	2.44	30	30	33	15	c

[a] Reactions carried out in 250–300 mL of liquid ammonia. [b] Isolated yield, unless otherwise indicated. [c] Not quantified. [d] Determined by GC with internal standard considering equal molar response of the stibines.

observed is the electron-transfer reaction, which gives the substitution product (eq 4).

π* radical anion
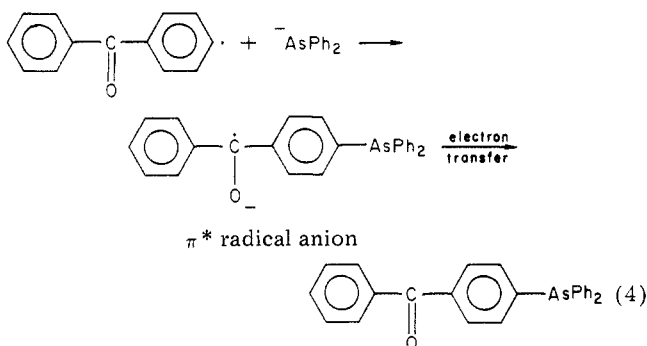
We describe here the photostimulated reaction of several haloaromatic substrates (changes in π* MO of the aryl moiety) with diphenylarsenide and diphenylstibide ions (changes in the values of the σ* MO of the carbon–metal bond), which give more insight into the factors that determine the competition between bond fragmentation and electron-transfer reactions.
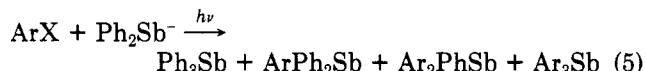
Results and Discussion

The reactions were carried out as described earlier.[2] In the photostimulated reaction of 1-bromonaphthalene and 9-bromophenanthrene as substrates, with diphenylarsenide ion as nucleophile, four arsines were formed as products (eq 1, Ar = 1-naphthyl, 9-phenanthryl), which would suggest that the radical anion intermediate in these reactions is of σ* nature, and the scrambling process occurred as described in Scheme I (Ar = 1-naphthyl, 9-phenanthryl; Table I).

However, the same nucleophile reacting with 2-chloroquinoline under similar conditions gave only the straightforward substitution product 2-quinolyldiphenylarsine, suggesting that in this case the radical anion intermediate is of π* nature.

It was reported before that diphenylarsenide ion reacted with 8-chloroquinoline in liquid ammonia to give, after 12 h of reaction, 8-quinolyldiphenylarsine.[5] This work was

published 2 years before the photostimulated S$_{RN}$1 reactions were discovered.[6] The fact that 2-chloroquinoline reacts under irradiation in 5 min may indicate that the dark reaction of the 8-isomer also occurred by the S$_{RN}$1 mechanism.

The photostimulated reaction of diphenylstibide ion, prepared in situ by the same method used for diphenylarsenide ion in liquid ammonia,[2,7] with p-bromoanisole and 4-chlorobenzophenone as substrates, leads to four stibines (Table I, eq 5).

$$\text{ArX} + \text{Ph}_2\text{Sb}^- \xrightarrow{h\nu}$$
$$\text{Ph}_3\text{Sb} + \text{ArPh}_2\text{Sb} + \text{Ar}_2\text{PhSb} + \text{Ar}_3\text{Sb} \quad (5)$$

Ar = p-anisyl, 4-benzoylphenyl; X = Cl, Br

Previous studies using diaryl or dialkyl stibide ions as nucleophiles for aromatic substitutions have shown that they failed to react with o-dichlorobenzene to give o-phenylenebis(diphenylstibine).[8] Dimethylstibide ion reacts with o-bromoiodobenzene, giving only 9% yield of the disubstitution product and even less with o-dibromo- or o-dichlorobenzenes.[9] On the other hand diphenyl- and dialkylstibide ions gave ditertiary stibines in good yields when reacting with dichloroalkanes in liquid ammonia.[10]

Although with 4-chlorobenzophenone there is a dark reaction with diphenylstibide ion, the mechanism is probably S$_{RN}$1, because the scrambling of aryl rings in the products is hard to explain by other known ionic mechanisms of nucleophilic aromatic substitution.[2,11] The S$_{RN}$1 mechanism, which involves the formation of stibine radical anions intermediates that react in part by electron transfer and in part by aryl–Sb bond breaking (the mechanism resembles that of diphenylarsenide ion, Scheme I), gives a good account of the observations. There are precedents

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in the literature of reactions occurring by this mechanism in the dark.[2,3,12,13]

It is known that diphenylphosphide ion reacts with p-iodoanisole, giving the straightforward substitution product p-anisyldiphenylphosphine by the $S_{RN}1$ mechanism.[13] On the other hand, diphenylarsenide ion gave scrambling of aryl rings with p-halotoluenes, p-halo-anisoles, 1-bromonaphthalene, and 9-bromopheneanthrene but the straightforward substitution product with 4-chlorobenzophenone and 2-chloroquinoline. Besides, diphenylstibide ion gave only scrambling of aryl rings with p-bromoanisole and 4-chlorobenzophenone.

All these contrasting results can be explained by the $S_{RN}1$ mechanism that involves two competing reactions, namely, electron transfer vs. bond breaking. It was suggested that the bond fragmentation of radical anions occurs from σ^* radical anions.[4,14]

In the process of coupling of an aryl radical with a nucleophile, and in this particular case with a Ph_2M^- as nucleophile (M = P, As, and Sb), σ and σ^* MO's are formed, and two situations can be found where the σ^* MO's of the aryl–metal bonds are the lowest energy of the system, and in this case scrambling of aryl rings is found.

On the other hand, if the π^* MO of the aryl moiety is lower in energy than the σ^* MO's of the aryl–metal bonds, as the aryl radical couples with the nucleophile, a σ^* MO is formed with the odd electron, and by intramolecular electron transfer to the π^* MO, a π^* radical anion is formed, and only the straightforward substitution product is obtained.

The reduction potential of unsubstituted aromatic compounds is related to their π^* MO, i.e., the more negative the reduction potential, the higher the π^* MO.[15] On the other hand, the phenyl-M (M = P, As, and Sb) bond strength[16] gives a measure of the σ MO energy, which in turn may be related to the σ^* MO energy[17] and probably is not very much affected by the nature of the aromatic moiety in the series studied.

Figure 1 is a schematic representation of the relative energies involved in these reactions and their relation to the reaction pathway. In the left-hand side are the reduction potentials of the aryl moiety that couples with the nucleophile Ph_2M^- ion as a measure of the π^* MO's energies, and in the right-hand side are the phenyl–metal bond strengths. In Figure 1 the phenyl–P bond energy is set above the reduction potential of benzene, and the phenyl–Sb bond energy is set below the reduction potential of benzophenone, because the reaction of phenyl radical with diphenylphosphide ion gave only electron transfer, and the reaction of 4-benzoylphenyl radical with diphenylstibide ion gave bond-fragmentation reaction.

Although the reduction potential of anisole and toluene are not known in DMF vs. SCE, they are more negative than the discharge of the supporting electrolyte (more negative than –3.0 V).[18]

When the bond strength is higher than the reduction potential in this relative energy scale, the radical anion intermediate has the low-lying antibonding π^* MO, and the intramolecular electron transfer to the σ^* MO's is unfavorable, thus no scrambling of aryl rings is observed.
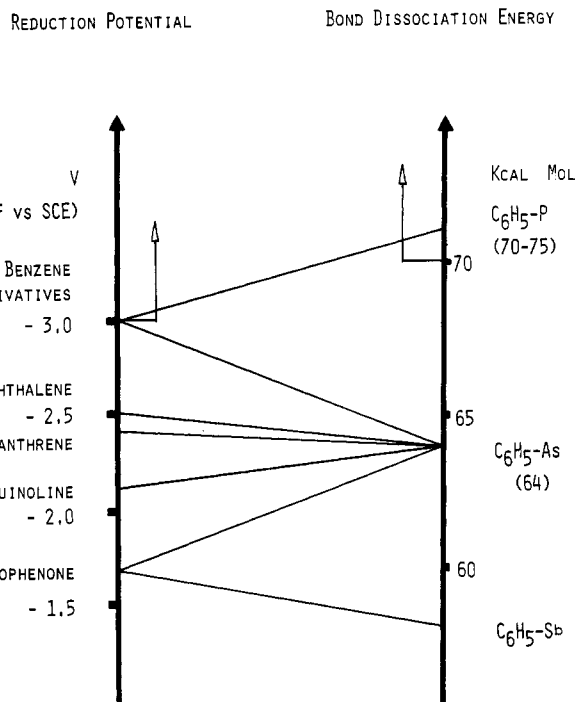

Figure 1. Reduction potential of arenes (left) represented in a relative scale with respect to the bond dissociation energy of Ph–M (M = P, As, Sb).

If the bond strength is lower in energy than the reduction potential of the aryl moiety, the radical anion may be π^* or σ^*, but the difference in energy between them is small, and bond fragmentation occurs, leading to scrambling of aryl rings.

From Figure 1 it can be seen that if the phenyl–P bond dissociation energy is higher than the reduction potential of benzene (and derivatives), then straightforward substitution products are obtained. On the other hand, when phenyl–Sb bond dissociation energy is lower than the reduction potential of benzophenone, scrambling of aryl rings is observed accordingly. The phenyl–As bond dissociation energy lies between the reduction potential of phenanthrene (–2.4 V) and quinoline (–2.1 V), thus scrambling is found with the first substrate, as well as with all the others with more negative reduction potential, but is not observed with 2-chloroquinoline and 4-chlorobenzophenone.

We conclude that in the photostimulated reaction in liquid ammonia, diphenylphosphide ion will give the straightforward substitution product with every substrate having a reduction potential more positive than –3.0 V, whereas diphenylstibide ion will give scrambling of aryl rings with substrates having more negative reduction potential than –1.6 V. With this nucleophile the value of the reduction potential of the aromatic moiety required to avoid scrambling is not yet known.

Diphenylarsenide ion give the straightforward substitution product with any substrate of more positive reduction potential than –2.1 V and scrambling of aryl rings when the reduction potential is more negative than –2.4 V.

Experimental Section

General Methods. The instruments and procedures were as previously reported.[2]

Photostimulated Reaction of Diphenylarsenide Ion with 1-Bromonaphthalene. After the photostimulation, 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 100

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mL of diethyl ether. The water was analyzed for bromide ion (99.6% yield). The ether was dried and distilled. The residue was submitted to column chromatography on neutral aluminum oxide (Merck) and eluted with petroleum ether; triphenylarsine (33% yield) was isolated and identified by comparison with an authentic sample; (1-naphthyl)diphenylarsine (40% yield) was then isolated as a white solid and recrystallized from benzene: mp 105.5–106.5 °C; mass spectrum, m/e (relative intensity) 356 (42), 278 (12), 277 (31), 227 (14), 204 (100), 203 (48), 202 (86), 201 (28), 152 (88); di(1-naphthyl)phenylarsine (21% yield) was eluted by acetone and recrystallized from benzene: mp 191.5–192.5 °C; mass spectrum, m/e (relative intensity) 406 (66), 329 (4), 327 (11), 279 (10), 277 (35), 254 (86), 252 (28), 202 (100), 152 (20), 127 (6), 126 (10).

Photostimulated Reaction of Diphenylarsenide Ion with 9-Bromophenanthrene. The procedure was as described above. The water was analyzed for bromide ion. The residue was submitted to column chromatography on neutral aluminum oxide (Merck) and eluted with petroleum ether. Triphenylarsine (20% yield) was isolated and characterized. (9-Phenanthryl)diphenylarsine (60% yield) was isolated and recrystallized from benzene: mp 137–138 °C; mass spectrum, m/e (relative intensity) 406 (74), 328 (10), 327 (20), 255 (68), 254 (100), 253 (87), 252 (98), 227 (16), 176 (16), 152 (25). Di(9-phenanthryl)phenylarsine (15% yield) was isolated and recrystallized from benzene: mp 164–165 °C; mass spectrum, m/e (relative intensity) 329 (10), 327 (74), 252 (100), 177 (26), 176 (63), 152 (50).

Photostimulated Reaction of Diphenylarsenide Ion with 2-Chloroquinoline. The procedure was as described above. 2-Quinolyldiphenylarsine was isolated as the only reaction product from column chromatography and recrystallized from benzene (60% yield): mp 101–102 °C; mass spectrum, m/e (relative intensity) 357 (100), 356 (63), 281 (10), 280 (61), 279 (60), 227 (18). The water was analyzed for chloride ion (97% yield).

Photostimulated Reaction of Diphenylstibide Ion with *p*-Bromoanisole. The procedure was as described above. The water was analyzed for bromide ion (99% yield). The GC tracing of the ether extract showed four peaks, the first one with the same retention time as authentic triphenylstibine. With a sample of the ether extract, the products were quantified on the assumption that all the stibines had the same molar response as triphenylstibine (Table I). After distillation of the ether extract, the residue was submitted to column chromatography on aluminum oxide and eluted with petroleum ether, but it was not possible to isolate the constituents in pure form. By GC/MS analysis[19] the first peak showed the same mass spectrum as authentic triphenylstibine; the three other peaks showed a mass spectra that can be attributed to *p*-anisyldiphenylstibine, di(*p*-anisyl)phenylstibine, and tri(*p*-anisyl)stibine. Triphenylstibine: mass spectrum, m/e (relative

intensity) 352.8 (0.6), 275.4 (2.8), 200.2 (32.6), 199.3 (6.0), 198.3 (38.1), 154.4 (41.4), 153.3 (20.9), 152.4 (12.3), 128.3 (2.6), 121.1 (6.5), 77.1 (78.7), 51.1 (100). (*p*-Anisyl)diphenylstibine: mass spectrum, m/e (relative intensity) 382.8 (1.1), 305.5 (2.2), 230.4 (5.0), 200.3 (31.8), 198.3 (39.4), 184.4 (74.3), 169.4 (33.1), 154.3 (10.9), 141.4 (31.4), 139.3 (8.1), 115.3 (23.5), 92.3 (10.0), 77.2 (81.2), 63.2 (21.4), 51.2 (100). Di(*p*-anisyl)phenylstibine: mass spectrum, m/e (relative intensity) 412.8 (1.2), 230.4 (18.1), 228.4 (22.3), 214.5 (100), 199.4 (35.5), 171.5 (12.8), 169.9 (13.3), 141.4 (17.3), 128.4 (10.2), 115.5 (12.8), 77.2 (24.7), 51.2 (12.4). Tri(*p*-anisyl)stibine: mass spectrum, m/e (relative intensity) 442.8 (3.0), 355.7 (3.0), 335.6 (3.2), 281.5 (3.9), 230.4 (74.0), 228.4 (100), 214.6 (67.7), 199.5 (58.7), 185.3 (6.4), 171.5 (31.7), 156.4 (11.0), 139.4 (7.5), 128.4 (27.2), 107.3 (7.5), 92.3 (15.0), 79.2 (25.1), 77.2 (31.9), 63.2 (20.8).

Photostimulated Reaction of Diphenylstibide Ion with 4-Chlorobenzophenone. The procedure was as described above. The water was analyzed for chloride ion (100% yield). The residue was submitted to column chromatography on neutral aluminum oxide (Merck) and eluted with petroleum ether. Triphenylstibine (30% yield) was isolated and identified by comparison with an authentic sample. 4-Benzoylphenyldiphenylstibine (33% yield) was eluted with petroleum ether/benzene (20:80) and recrystallized from benzene: mp 123–125 °C; mass spectrum,[19] m/e (relative intensity) 456 (9), 454 (11), 381 (2), 379 (2), 304 (14), 302 (18), 277 (5), 275 (9), 200 (74), 198 (100), 181 (19), 154 (60), 152 (25). Di(*p*-benzoylphenyl)phenylstibine (15%) was eluted by benzene and recrystallized from benzene: mp 139–141 °C; mass spectrum, m/e (relative intensity) 562 (3), 560 (2), 458 (3), 457 (17), 456 (3), 455 (22), 303 (30), 301 (44), 200 (67), 198 (89), 181 (22), 105 (100), 77 (72).

Dark Reaction of Diphenylstibide Ion with 4-Chlorobenzophenone. The procedure was as described above, except that the reaction mixture was kept in the dark for 40 min and then quenched by ammonium nitrate, and the reaction was worked up as before. The chloride ion was quantified (67% yield), and the same products were formed as in the photostimulated reaction, but they could not be isolated in pure form by column chromatography due to the overlaping of the products with 4-chlorobenzophenone.

Registry No. 1-Bromonaphthalene, 90-11-9; 9-bromophenanthrene, 573-17-1; 2-chloroquinoline, 612-62-4; *p*-bromoanisole, 104-92-7; 4-chlorobenzophenone, 134-85-0; diphenylarsenide ion, 14971-22-3; diphenylstibide ion, 14971-21-2.

(19) All the mass spectra of the compounds described showed the characteristic pattern of the different isotopes of Sb.