given in Table IV refer to **26**, i.e. complete conversion of **26** into **27** has been assumed. The product distributions obtained from **27** were corrected for the amount of **33**, which contaminated the solutions of **27** (see above). Consequently, the results obtained with **27** were less well reproducible than those from photolyses of **26**.

Authentic samples of **32**[42] and of **36**[43] were prepared according to published procedures; **29**, **33**, and **34** are commercially available (Aldrich). The hydroxy ethers **35** were isolated from the product mixtures by HPLC (silica gel, hexane–ether, 6:4) and/or prepared independently from 2-bromobenzyl ethers by reaction of the corresponding Grignard reagents with oxirane: ^{1}H NMR (CDCl$_3$) **35a** δ 1.60 (br s, 1 H), 2.94 (t, J = 6.5 Hz, 2 H), 3.83 (q, J = 8.7 Hz, 2 H), 3.86 (t, J = 6.5 Hz, 2 H), 4.72 (s, 2 H), 7.2–7.35 (m, 4 H); **35c**[44] δ 2.42 (br s, 1 H), 2.93 (t, J = 6.4 Hz, 2 H), 3.40 (s, 3 H), 3.85 (t, J = 6.4 Hz, 2 H), 4.48 (s, 2 H), 7.26 (br s, 4 H); **35d**[44] δ 1.25 (t J = 7.0 Hz, 3 H), 2.52 (br s, 1 H), 2.93 (t, J = 6.3 Hz, 2 H), 3.57 (q, J = 7.0 Hz, 2 H), 3.85 (t, J = 6.3 Hz, 2 H), 4.51 (s, 2 H), 7.2–7.35 (m, 4 H); **35e**[39] δ 1.33 (s, 9 H), 2.68 (br s, 1 H), 3.87 (t, J = 5.0 Hz, 2 H), 4.22 (t, J = 5.0 Hz, 2 H), 4.50 (s, 2 H), 6.8–7.4 (m, 4 H).

Acidolyses of 27. Solutions of p-toluenesulfonic acid in ROH and of **27** in ROH–THF were mixed at room temperature. The volumes were chosen to obtain solutions 0.025 M in **27** and 0.01 M in TsOH. For reaction in "neat" ROH, solutions of **27** in THF were concentrated in vacuo at 0 °C, and the residue was immediately dissolved in ROH. The formation of some **33** during this procedure cannot be excluded. The color of **27** faded within 5 min. The reaction mixture was shaken with powdered sodium carbonate, and the supernatant solution was analyzed directly by GC (Table V).

2-(2-Hydroxyethyl)benzylamine (28). The semiacetal **24** (1.35 g, 9 mmol), hydroxylamine hydrochloride (1.25 g, 18 mmol), barium carbonate (1.78 g, 9 mmol), and ethanol (20 mL) were heated at reflux for 8 h. The hot solution was filtered and concentrated in vacuo. The crude oxime (1.34 g, 90%, containing ca. 85% of **25**) was reduced with lithium aluminum hydride, as described for **8**, to give 0.67 g (44%) of **28**·HCl; mp 158–160 °C; ^{1}H NMR (CD$_3$SOCD$_3$) δ 1.82 (t, J = 6.2 Hz, 2 H), 2.63 (t, J = 6.2 Hz, 2 H), 3.07 (s, 2 H), 3.15 (br s, 1 H), 7.15–7.55 (m, 4 H), 8.50 (br s, 3 H). Anal. Calcd for C$_9$H$_{14}$ClNO: C, 57.60; H, 7.52; N, 7.46. Found: C, 57.73; H, 7.42; N, 7.53.

The nitrous acid deamination of **28** was carried out by the same procedure as described above for **8**. GC indicated the formation of **33** and **35b**[45] (15:85) in 25% yield.

Registry No. **2b**, 55479-94-2; **2b** (oxime), 125593-28-4; **3**, 125593-15-9; **6a**, 125593-16-0; **6b**, 612-14-6; **6c**, 62172-88-7; **6d**, 103386-05-6; **6e**, 125593-27-3; **7**, 496-14-0; **8**, 4152-92-5; **8**·HCl, 4152-84-5; **10**, 91-13-4; **12**, 1586-01-2; **13**, 125593-17-1; **14**, 125593-18-2; **15**, 100560-58-5; **16**, 125593-19-3; **18**, 7111-66-2; **20a**, 125593-20-6; **20c**, 125593-29-5; **20c** (tetrahydropyranol ether), 125593-31-9; **20d**, 125593-30-8; **21**, 17100-66-2; **22**, 125593-21-7; **23**, 4702-34-5; **24**, 95033-78-6; **25**, 125593-22-8; **26**, 125593-23-9; **26**·Na, 125593-35-3; **27**, 125593-24-0; **28**, 125593-25-1; **28**·HCl, 35050-30-7; **29**, 4254-29-9; **33**, 493-05-0; **35a**, 125593-26-2; **35b**, 6346-00-5; **35c**, 125593-32-0; **35d**, 125593-33-1; **35e**, 125593-34-2; p-MeC$_6$H$_4$SO$_2$NHNH$_2$, 1576-35-8; o-PhCOC$_6$H$_4$CO$_2$H, 85-52-9; phthalide, 87-41-2.

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Formation and Reactions of Diorganophosphinite Ions in Liquid Ammonia. Synthesis of Triorganophosphine Oxides by the $S_{RN}1$ Mechanism[1]

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The reaction of triphenyl- and tribenzylphosphine oxides with alkali metals in liquid ammonia gave diphenyl- and dibenzylphosphinite ions, respectively, in high yields and a small amount of deoxygenated products. These ions reacted under photostimulation with aryl halides by the $S_{RN}1$ mechanism to give aryldiphenyl- and aryldibenzylphosphine oxides in good yields. With tribenzylphosphine oxide, by consecutive debenzylation with alkali metals followed by photostimulated reaction with aryl halides, all the benzylic moieties could be replaced by aromatic moieties to finally obtain unsymmetrical triarylphosphine oxides.

The mechanism known as radical nucleophilic substitution or $S_{RN}1$ is well-known.[2] The three main steps of the propagation cycle are outlined in Scheme I. The addition of these three steps leads to eq 4, which is a nucleophilic substitution but with a radical and radical anions as intermediates. Many aromatic substrates react by this mechanism with different types of nucleophiles.

Scheme I

$$(\mathrm{RX})^{\bullet-} \rightarrow \mathrm{R}^{\bullet} + \mathrm{X}^- \qquad (1)$$

$$\mathrm{R}^{\bullet} + \mathrm{Nu}^- \rightarrow (\mathrm{RNu})^{\bullet-} \qquad (2)$$

$$(\mathrm{RNu})^{\bullet-} + \mathrm{RX} \rightarrow \mathrm{RNu} + (\mathrm{RX})^{\bullet-} \qquad (3)$$

$$\mathrm{RX} + \mathrm{Nu}^- \rightarrow \mathrm{RNu} + \mathrm{X}^- \qquad (4)$$

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Table I. Reactions of Diorganophosphinite Ions with Aryl Halides in Liquid Ammonia[a]

expt	R_3PO (mmol)	substrate (mmol)	$h\nu$ duratn, min	metal (mmol)	X^-	substitutn products (yield,[b] %)
1	Ph_3PO (2.56)	MeI (5.1)		Na[c]	*d*	$Ph_2P(O)Me$ (96)[e,f]
2	Ph_3PO (1.67)	*p*-IAn (1.99)	90	Li[c]	90	$Ph_2P(O)An$ (81); Ph_2PAn (6); Ph_3PO (6); Ph_3P (6)
3	Ph_3PO (2.96)	*p*-IAn (3.55)	90	Na (5.92)	72	$Ph_2P(O)An$ (58); Ph_2PAn (12); Ph_3PO (28); Ph_3P (1.3)
4	Ph_3PO (2.00)	*p*-IAn (2.40)	60	Na[c]	94	$Ph_2P(O)An$ (79); Ph_2PAn (14); Ph_3PO (1.0); Ph_3P (3)
5	Ph_3PO (1.84)	*p*-IAn (2.20)	60	Na[c]	94	$Ph_2P(O)An$ (92),[e] (81)[e,f]
6	Ph_3PO (1.73)	*p*-IAn (2.01)	60	K (3.46)	85	$Ph_2P(O)An$ (65); Ph_2PAn (19); Ph_3PO (6.0); Ph_3P (9.0)
7	$(PhCH_2)_3PO$ (0.69)	MeI (1.30)		Na[c]	*d*	$(PhCH_2)_2P(O)Me$ (90)[e]
8	$(PhCH_2)_3PO$ (0.99)	PhI (1.07)	60	Na (2.00)	62	$(PhCH_2)_2P(O)Ph$ (60); $(PhCH_2)_3PO$ (35)[e]
9	$(PhCH_2)_3PO$ (1.47)	PhI (1.44)	60	Na[c]	87	$(PhCH_2)_2P(O)Ph$ (85)[e,f]
10	$(PhCH_2)_3PO$ (1.30)	PhI (1.30)	60[g]	Na[c]	*d*	$(PhCH_2)_2P(O)Ph$ (<5%)
11	$(PhCH_2)_3PO$ (1.50)	PhBr (2.00)	60	Na[c]	97	$(PhCH_2)_2P(O)Ph$ (80)[e,f]
12	Ph_3PS (2.35)	*p*-BrAn (2.60)	90	Na (4.80)	71	Ph_3PS (15); Ph_3PO (10); *p*-$AnP(O)Ph_2$ (64)
13	Ph_3PS (2.02)	*p*-BrAn (3.20)	90	Na[c]	87	Ph_3PO (15);[e] *p*-$AnP(O)Ph_2$ (82)[e]
14	Ph_3AsO (2.03)	*p*-IAn (3.00)	60	Na (4.05)	45	Ph_3As (12); *p*-$AnAsPh_2$ (56); *p*-An_2AsPh (27); *p*-An_3As (5)[h]
15	Ph_3AsO (2.07)	2-ClQui (2.30)	60	Na[c]	80	2-$QuiAsPh_2$ (76)[e]
16	$(PhCH_2)Ph_2PO$ (1.17)	1-INaph (1.30)	60	Na[c]	83	1-$NaphP(O)Ph_2$ (79)[e]
17	$(PhCH_2)Ph_2PO$ (0.50)	*p*-BrAn (0.60)	120	Na[c]	89	*p*-$AnP(O)Ph_2$ (81)[e]
18	$(PhCH_2)Ph_2PO$ (0.90)	*p*-IAn (1.10)	60	Na[c]	90	*p*-$AnP(O)Ph_2$ (81)[e]

[a] All the reactions were carried out in ca. 250 mL of previously dried, freshly distilled NH_3, under N_2 stream; *p*-An = *p*-anisyl; Naph = naphthyl; 2-Qui = 2-quinolyl. [b] Yields were determined by GLC quantitative analysis, unless otherwise specified. [c] Metals were added in excess in keeping the blue color from the excess of solvated electrons for 30 min. [d] Not determined. [e] After H_2O_2 oxidation of the products (see Experimental Section). [f] Product isolated. [g] Reaction was carried out in the dark. [h] Relative yields.

Among them there are phosphanion nucleophiles such as P^{3-} ions formed by the reaction of phosphorus with sodium metal in liquid ammonia,[3] diphenylphosphide ions,[4] butyl phenylphosphonite,[5] *O,O*-diethyl thiophosphite,[5] and *N,N,N',N'*-tetramethylphosphonamide ions.[5]

It has been shown that the diphenylphosphinite ion (Ph_2PO^-) reacts under irradiation with iodobenzene in liquid ammonia to give good yields of triphenylphosphine oxide (eq 5).[5] This nucleophile was prepared by the reaction of diphenylphosphine oxide with potassium *tert*-butoxide in liquid ammonia.[5]

$$PhI + Ph_2PO^- \xrightarrow{h\nu} Ph_3PO + I^- \qquad (5)$$

On the other hand, phosphine oxides are important compounds in studies of the organophosphorus reaction mechanism and in the field of their possible applications.[6-9]

We therefore undertook the study of finding another alternative route to synthesize diorganophosphinite ions. One of the possibilities was to prepare these ions through the reaction of triorganophosphine oxides with alkali metals in liquid ammonia because they are more available and stable chemicals than diaryl- or dialkylphosphine oxides. We also studied the photostimulated reactions of *dialkylphosphinite ions* with aryl halides in order to know if they are suitable nucleophiles in $S_{RN}1$ reactions.

Results and Discussion

In the reaction of triphenylphosphine oxide with sodium metal in excess in liquid ammonia, the blue color from the excess of solvated electrons remained for about 30 min before the solution became orange-yellow. The reaction was quenched by methyl iodide in excess, and the main product formed was methyldiphenylphosphine oxide (≈ 90% yield). These reactions were carried out under nitrogen, and only small amounts of methyldiphenylphosphine, triphenylphosphine, and triphenylphosphine oxide were found. The phosphine oxides were not formed in the workup. In another experiment, the product mixture was oxidized with H_2O_2[10] and a 96% yield of methyldiphenylphosphine oxide was obtained (experiment 1, Table I).

We were also interested in the behavior of *aliphatic* phosphine oxides. With tribenzylphosphine oxide as substrate, dibenzylphosphinite ion was prepared by the same procedure and was also trapped with methyl iodide, to give methyldibenzylphosphine oxide in high yields (experiment 7, Table I).

The products obtained in these reactions can be explained by the reaction of methyl iodide with the diorganophosphinite ions formed by the reaction of the phosphine oxides with the solvated electrons in liquid ammonia (eqs 6–8), and the amide ions were neutralized by the addition of *tert*-butyl alcohol (eq 9).

$$R_3PO + 2e^- \rightarrow R_2PO^- + R^- \qquad (6)$$

$$R^- \xrightarrow{NH_3} RH + NH_2^- \qquad (7)$$

$$R_2PO^- + CH_3I \rightarrow R_2CH_3PO + I^- \qquad (8)$$

$$NH_2^- + t\text{-BuOH} \rightarrow NH_3 + t\text{-BuO}^- \qquad (9)$$

$$R = Ph, PhCH_2$$

The small amounts of triphenyl- and tribenzylphosphines show that the rate of C–P bond fragmentation (eq 6) is much more important than the reaction of deoxygenation of the phosphine oxide.

These results suggest that the reaction of triaryl- and trialkylphosphine oxides with sodium metal in liquid ammonia is a suitable method by which to prepare diorganophosphinite ions.

The same procedure as described above was followed to prepare diphenylphosphinite ions, and in the photosti-

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mulated reaction (60 min) with *p*-iodoanisole, we found the substitution product *p*-anisyldiphenylphosphine oxide in 79% yield together with *p*-anisyldiphenylphosphine (14% yield), triphenylphosphine (3% yield), and the starting material triphenylphosphine oxide (<1% yield) (experiment 4, Table I). (In this paper, anisyl is defined as methoxyphenyl.) The substitution product *p*-anisyldiphenylphosphine oxide was not formed from the oxidation of *p*-anisyldiphenylphosphine during the workup. These results can be explained according to eqs 10 and 11.

$$\mathrm{Ph_3PO} \xrightarrow[\text{b. } t\text{-BuOH}]{\text{a. Na}} \mathrm{Ph_2PO^-}\ (+\mathrm{Ph_2P^-}) + \mathrm{PhH} \tag{10}$$

$$\mathrm{Ph_2PO^-}\ (+\mathrm{Ph_2P^-}) + p\text{-IAn} \xrightarrow{h\nu\ (\mathrm{S_{RN}1})} p\text{-}\mathrm{AnPh_2PO}\ (+p\text{-}\mathrm{AnPh_2P}) \tag{11}$$

$$\mathrm{An} = \text{anisyl}$$

It is well-known that diphenylphosphide ions are also good nucleophiles in $S_{RN}1$ reactions, giving ultimately the product *p*-anisyldiphenylphosphine.[4] In another experiment, oxidation of the reaction mixture with H_2O_2 gave more than a 90% yield of the desired substitution product *p*-anisyldiphenylphosphine oxide (experiment 5, Table I). This result shows that it is a useful alternative method to prepare triarylphosphine oxides by the $S_{RN}1$ mechanism.

With only 2 equiv of sodium metal, 28% of triphenylphosphine oxide remained (experiment 3, Table I). Similar results were obtained with lithium metal in excess (experiment 2, Table I). With 2 equiv of potassium metal, we obtained less *p*-anisyldiphenylphosphine oxide and more product from the deoxygenation reaction (experiment 6, Table I).

Comparing the three alkali metals, it seems that there is more deoxygenation reaction with potassium metal (19%) than with sodium metal (12–14%) and with lithium metal (6%). As all the alkali metals afford solvated electrons by dissolution in liquid ammonia, the amount of deoxygenated products may depend on the rate of dissolution of the alkali metals, increasing the local concentration of solvated electrons, which is greater for potassium metal than for sodium or lithium metals. Nevertheless, as these products can be easily oxidized with H_2O_2, any of the alkali metals can be used in these reactions.

These reactions were also studied with triphenylarsine oxide and sodium metal in excess, but in this case deoxygenation of the arsine oxide and Ph–As bond fragmentation occurred, and in the photostimulated reaction with *p*-iodanisole, four arsines were obtained (experiment 14, Table I), this being a characteristic reaction of phenyl halides with diphenylarsenide ions by the $S_{RN}1$ mechanism (eqs 12 and 13).[11,12]

$$\mathrm{Ph_3AsO} \xrightarrow[\text{b. } t\text{-BuOH}]{\text{a. Na}} \mathrm{Ph_2As^-} \tag{12}$$

$$\mathrm{Ph_2As^-} + \mathrm{IAn} \xrightarrow[(\mathrm{S_{RN}1})]{h\nu} \mathrm{Ph_3As} + \mathrm{Ph_2AnAs} + \mathrm{PhAn_2As} + \mathrm{An_3As} \tag{13}$$

$$\mathrm{An} = p\text{-anisyl}$$

We prepared diphenylarsenide ions under the same experimental conditions (eq 12) and obtained a 76% yield of 2-quinolyldiphenylarsine in the photostimulated reaction with 2-chloroquinoline (experiment 15, Table I).

With triphenylphosphine sulfide and an excess of sodium metal in liquid ammonia, followed by the photostimulated reaction with *p*-bromoanisole, an 82% yield of *p*-anisyldiphenylphosphine oxide was obtained after oxidation. This result suggests that all the sulfur was lost in the reaction with solvated electrons, giving diphenylphosphide ions (eq 14), which react with *p*-bromoanisole under photostimulation, to give *p*-anisyldiphenylphosphine, which is oxidized in the workup (experiment 13, Table I).

$$\mathrm{Ph_3PS} + \mathrm{Na}\ (\text{excess}) \rightarrow \mathrm{Ph_2P^-} \tag{14}$$

In conclusion, the three systems studied showed that only the P–O bond did not fragment in the reaction with sodium metal in liquid ammonia except in a small amount, whereas the As–O and P–S bonds were completely cleaved.

As seen above, dibenzylphosphinite ions can be prepared by this method (eq 6). We prepared this nucleophile with 2 equiv of sodium metal, and after photostimulated reaction with iodobenzene followed by oxidation, we obtained dibenzylphenylphosphine oxide (60% yield) and the starting material tribenzylphosphine oxide (35% yield) (experiment 8, Table I). When the reaction sequence was performed with an excess of sodium metal, 85% of the substitution product dibenzylphenylphosphine oxide was isolated (eqs 15 and 16) (experiment 9, Table I).

$$\mathrm{(PhCH_2)_3PO} \xrightarrow[\text{b. } t\text{-BuOH}]{\text{a. Na excess}} \mathrm{(PhCH_2)_2PO^-} + \mathrm{PhCH_3} \tag{15}$$

$$\mathrm{(PhCH_2)_2PO^-} + \mathrm{PhI} \xrightarrow[\text{b. } \mathrm{H_2O_2}]{\text{a. } h\nu\ (\mathrm{S_{RN}1})} \mathrm{Ph(PhCH_2)_2PO} \tag{16}$$

Under the same experimental conditions but in the dark, there was less than a 5% yield of the substitution product (experiment 10, Table I). With bromobenzene as substrate, we obtained a very good yield of the substitution product (experiment 11, Table I). We suggest that dibenzylphosphinite ions react under photostimulation with aryl halides by the $S_{RN}1$ mechanism in a similar way to the aromatic diphenylphosphinite ions.

It is known from electrochemical determinations[13] that the benzyl–P bond is weaker than the aromatic–P bond in the reaction of a phosphine oxide that has aryl–P and benzyl–P bonds. Treatment of such a compound with sodium metal in liquid ammonia would fragment the benzyl–P bond to give a new nucleophile. It was of interest to see if all the benzylic moieties can be replaced by aromatic (or other aliphatic) moieties in consecutive reactions, as a general method of synthesis of *unsymmetrical* phosphine oxides.

The reaction of diphenylbenzylphosphine oxide (where two phenyl–P bonds compete with one benzyl–P bond) with an excess of sodium metal in liquid ammonia (eq 17) and 1-iodonaphthalene was carried out, and after 60 min of irradiation, a 79% yield of isolated substitution product 1-naphthyldiphenylphosphine oxide (eq 18) (experiment 16, Table I) was obtained. This result shows that the $PhCH_2$–P bond fragments faster than the Ph–P bond. No products derived from the fragmentation of the Ph–P bond were found.

$$\mathrm{Ph_2(PhCH_2)PO} \xrightarrow[\text{b. } t\text{-BuOH}]{\text{a. Na}} \mathrm{Ph_2PO^-} + \mathrm{PhCH_3} \tag{17}$$

$$\mathrm{Ph_2PO^-} + 1\text{-INaph} \xrightarrow[\text{b. [O]}]{\text{a. } h\nu} 1\text{-NaphPh_2PO} \tag{18}$$

$$\mathrm{Naph} = \text{naphthyl}$$

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A good yield of substitution product was obtained with diphenylphosphinite ions prepared as in eq 17, which reacted under irradiation with *p*-bromo- and *p*-iodoanisoles (experiments 17 and 18, Table I).

These results show that the formation of diorganophosphinite ions by the reaction of triorganophosphine oxides with alkali metals in liquid ammonia, followed by the $S_{RN}1$ reaction with haloarenes, is an excellent method by which to obtain triorganophosphine oxides. All the benzylic groups could be replaced by different aromatic moieties to give good yields of trisubstituted unsymmetrical phosphine oxides when tribenzylphosphine oxide is used as substrate.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded on a Varian T-60 nuclear magnetic resonance spectrophotometer, and all the values of $^2J_{P-H}$ for methyl and methylene groups are in the normal range of 13–15 Hz.[14] Infrared spectra were recorded on a Nicolet FTIR 5-SXC spectrophotometer. Mass spectral data were obtained with a Finnigan 3300 f-100 mass spectrometer, and gas chromatographic analyses were performed on Varian Aerograph series 1400 and Shimadzu GC-8A instruments, both with a flame-ionization detector and data system Shimadzu CR-3A or Spectra Physics SP-2400, using a stainless steel column packed with 3% SE 30 on Chromosorb G (0.5 m × 3 mm) or 5% OV 17 on Chromosorb G (1.5 m × 3 mm). Column chromatography was performed on silica gel (70–230 mesh, ASTM, Sigma). Irradiation was conducted in a reactor equipped with four 250-W lamps emitting maximally at 350 nm (Philips Model HPT, water refrigerated). Potentiometric titration of halide ions was performed in a pH meter (Seybold Wien) with a Ag/Ag$^+$ electrode (Metrohm Model 6.0404.100(IA) with internal reference) and $AgNO_3$ standard. The melting points were obtained with a Büchi 510 apparatus and are not corrected.

Materials. Triphenylphosphine oxide was obtained from Koch Light or by oxidation of triphenylphosphine (Aldrich) with H_2O_2 (15%).[10] Tribenzylphosphine oxide was obtained by oxidation of tribenzylphosphine (Strem) with H_2O_2 (15%)[10] or by reaction of benzylmagnesium chloride with Cl_3PO[15] (Carlo Erba). Triphenylphosphine sulfide (Strem), triphenylarsine oxide (Koch Light), iodobenzene (Aldrich), *p*-bromoanisole (Baker), *p*-iodoanisole (Fluka), 1-iodonaphthalene (Fluka), and methyl iodide (Fluka) were commercially available and used as received. Diphenylphosphinite ions were prepared from triphenylphosphine oxide and sodium metal in excess in liquid ammonia, and the amide ion formed was neutralized with 1 equiv of *tert*-butyl alcohol (Aldrich). Dibenzylphosphinite ions were prepared from tribenzylphosphine oxide and sodium metal by the same procedure. The paraffins used as internal standards were supplied by YPF (Yacimentos Petrolíferos Fiscales).

Reaction of Triphenylphosphine Oxide with Sodium Metal in Liquid Ammonia. The following procedure is representative of these reactions. Into a three-necked, 500-mL, round-bottomed flask equipped with a cold finger condenser charged with dry ice–ethanol, a nitrogen inlet, and a magnetic stirrer were condensed 250 mL of ammonia previously dried with sodium metal under nitrogen. To the ammonia were added triphenylphosphine oxide (2.56 mmol) and sodium metal in excess. The addition of sodium metal continued until the blue solution from solvated electrons in excess remained for 30 min before it became orange-yellow. To this solution was added *tert*-butyl alcohol (2.5 mmol) to neutralize the amide ion formed. Finally, methyl iodide in excess (5.1 mmol) was added to trap the phosphanion nucleophile. The ammonia was allowed to evaporate, and the residue was extracted twice with dichloromethane (50 mL each). The solution was oxidized with H_2O_2 by following a previously described procedure.[10] The solution was dried ($MgSO_4$), and the solvent was removed under reduced pressure. The solid was recrystallized from petroleum ether–diethyl ether (9:1), and a 96% yield of methyldiphenylphosphine oxide was obtained: mp 109–110 °C (lit. mp 111 °C,[16a] 108–109 °C,[16b]); ^{1}H NMR Cl_3CD (Me_4Si) δ 1.4–1.6 (d, 3 H, $J \approx 13.5$ Hz), 7.1–7.9 (m, 10 H); MS m/e (%) 217 (5), 216 (32), 215 (M$^+$, 100), 202 (13), 201 (88), 139 (10), 125 (2), 77 (13), 51 (5).

Photostimulated Reactions of *p*-Iodoanisole with Diphenylphosphinite Ions. To 250 mL of dry liquid ammonia were added triphenylphosphine oxide (1.84 mmol) and sodium metal in excess as described before, to form the diphenylphosphinite ions, and then *tert*-butyl alcohol (2.0 mmol) was added. The yellowish solution obtained was irradiated for 60 min after the addition of *p*-iodoanisole (2.20 mmol). The reaction was quenched by the addition of excess ammonium nitrate, and the ammonia was then allowed to evaporate. Water (50 mL) was added to the residue, and the mixture was extracted twice with dichloromethane. The iodide ions in the aqueous solutions were determined potentiometrically. The organic extract was analyzed by GLC and then oxidized with H_2O_2. The solvent was removed by distillation under reduced pressure, and the residue, after column chromatography on silica gel (eluted from hexane to diethyl ether), gave *p*-anisyldiphenylphosphine oxide in 81% yield: mp 110–111 °C (lit.[17] mp 112–113 °C); ^{1}H NMR (Cl_3CD) δ 3.80 (3 H, s), 7.0–7.8 (14 H, m); IR (KBr) 3085, 2950, 1186 cm^{-1}; MS m/e (%) 308 (100), 293 (3), 292 (2), 231 (33), 215 (35), 201 (14), 199 (18), 183 (21), 154 (5), 141 (8), 139 (5), 108 (7), 107 (5), 77 (25), 51 (11). In some experiments, the dichloromethane solution was not oxidized, and the products *p*-anisyldiphenylphosphine oxide (79% yield), *p*-anisyldiphenylphosphine (14% yield), triphenylphosphine oxide (<1%), and triphenylphosphine (3%) were quantified by GLC and compared with authentic samples. In other experiments, sodium metal was added in stoichiometric amounts, and then the same procedure was followed. In other experiments, we replaced sodium metal by potassium or lithium metals, following the same procedure.

Reaction of Tribenzylphosphine Oxide with Sodium Metal in Liquid Ammonia. To 250 mL of ammonia was added tribenzylphosphine oxide (0.69 mmol), followed by an excess of sodium metal. Then *t*-BuOH (1.0 mmol) was added to the yellowish solution obtained. The nucleophile was trapped with an excess of methyl iodide (1.3 mmol), and the ammonia was allowed to evaporate. The resulting solid residue was extracted with dichloromethane (twice, 50 mL each), and then the organic portion was oxidized as previously described. The column chromatography of the crude product of the reaction gave a white solid, which was recrystallized from benzene–petroleum ether (3:1): mp 130–132 °C (lit. mp 131–134 °C,[18] 133.5–134.0 °C[19]) corresponding to dibenzylmethylphosphine oxide (90% yield); ^{1}H NMR (Cl_3CD) δ (TMS) 1.5 (d, 3 H, J = 14–15 Hz), 2.9–3.2 (d, 4 H, $J \approx$ 13–14 Hz), 7.2–8.0 (m, 10 H); MS m/e (%) 244 (40), 229 (18), 228 (12), 167 (3), 153 (8), 139 (8), 91 (100), 77 (4), 65 (39), 51 (5).

Photostimulated Reaction of Dibenzylphosphinite Ions with Iodobenzene. The procedure was similar to that for the previous reaction. To 250 mL of dry liquid ammonia was added tribenzylphosphine oxide (0.99 mmol), followed by sodium metal (2.0 mmol). To the yellowish solution obtained was added *tert*-butyl alcohol (1.1 mmol), followed by iodobenzene (1.07 mmol). The reaction mixture was irradiated for 60 min and then quenched with an excess of ammonium nitrate. The workup was the same as the above described. After oxidation, tribenzylphosphine oxide (35% yield) and dibenzylphenylphosphine oxide (60% yield) were isolated by column chromatography on silica gel (eluted from benzene to ethanol). Dibenzylphenylphosphine oxide: mp 112–113 °C (lit.[6b] mp 113 °C); ^{1}H NMR (Cl_3CD) δ (TMS) 3.0–3.2 (d, 4 H, J = 14 Hz), 7.0–7.6 (m, 15 H); IR (KBr) 3030, 2939, 1566, 1175 cm^{-1}; MS m/e (%) 306 (40), 290 (10), 236 (8), 229 (13), 215 (8), 201 (100), 152 (6), 139 (40), 91 (40), 77 (75),

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65 (30), 63 (10), 51 (45). In another experiment, sodium metal was added in excess, the procedure was the same, the substitution product dibenzylphenylphosphine oxide was isolated in 85% yield, and tribenzylphosphine oxide was not found. With bromobenzene as substrate and with the same experimental conditions, dibenzylphenylphosphine oxide was isolated in 80% yield.

Reaction of Dibenzylphosphinite Ions with Iodobenzene in the Dark. The same procedure was followed as described before, except that the reaction flask was wrapped with aluminum foil, and the substitution product dibenzylphenylphosphine oxide was found in less than 5% yield after 60 min.

Photostimulated Reaction of *p*-Bromoanisole with Diphenylphosphinite Ions Generated from Diphenylbenzylphosphine Oxide and Sodium Metal. To 250 mL of liquid ammonia was added diphenylbenzylphosphine oxide (0.50 mmol), followed by an excess of sodium metal, giving an orange solution. Then *tert*-butyl alcohol (0.50 mmol) and *p*-bromoanisole (0.60 mmol) were added, and the solution was irradiated for 120 min. The reaction was quenched and worked up by the same procedure as previously described. The quantification by GLC (internal standard method with dotriacontane) after oxidation with H_2O_2 gave *p*-anisyldiphenylphosphine oxide (78%) as the only substitution product, compared with an authentic sample. With the same procedure, *p*-iodoanisole gave *p*-anisyldiphenylphosphine oxide with 81% yield in 60 min of irradiation. 1-Iodonaphthalene (1.30 mmol) and diphenylphosphinite ions (1.17 mmol) gave after 60 min of irradiation 1-naphthyldiphenylphosphine oxide (79% yield) by quantitative GLC analysis. 1-Naphthyldiphenylphosphine oxide: mp 178–179 °C (lit.[20] mp 178–179 °C); MS *m/e* (%) 328 (M^+, 100), 249 (22), 202 (12), 127 (5), 77 (10).

Reaction of Triphenylphosphine Sulfide with Sodium Metal in Liquid Ammonia. The same procedure being followed as previously described for the reactions of triphenylphosphine oxide, triphenylphosphine sulfide (2.35 mmol) was allowed to react with sodium metal (4.80 mmol) added in small pieces. Then *tert*-butyl alcohol (2.30 mmol) was added, followed by *p*-bromoanisole (2.60 mmol), and the reaction mixture was irradiated for 90 min. Finally, the reaction was quenched with ammonium nitrate and processed as previously described. After oxidation, quantitative GLC analysis using the internal standard method gave *p*-anisyldiphenylphosphine oxide (64% yield), triphenylphosphine sulfide (15% yield), and triphenylphosphine oxide (10% yield). In another experiment, triphenylphosphine sulfide (2.02 mmol) was allowed to react with an excess of sodium metal, *tert*-butyl alcohol (2.0 mmol) and *p*-bromoanisole (3.2 mmol) were added, and then the solution was irradiated for 90 min. After the workup, the reaction products were oxidized, and quantitative GLC analysis gave an 82% yield of *p*-anisyldiphenylphosphine oxide.

Reaction of Triphenylarsine Oxide with Sodium Metal in Liquid Ammonia. To 250 mL of liquid ammonia was added triphenylarsine oxide (2.03 mmol), followed by sodium metal (4.05 mmol) added in small pieces. Then *tert*-butyl alcohol (2.0 mmol) and *p*-iodoanisole (3.70 mmol) were added to the reddish solution. The reaction mixture was irradiated for 60 min and then quenched with an excess of ammonium nitrate. The extraction procedure was similar to the one previously described. GLC analysis of the organic portion showed the characteristic pattern of peaks resulting from the scrambling of the aromatic moieties,[11] and after comparison with authentic samples, the products were assigned as triphenylarsine, *p*-anisyldiphenylarsine, di-*p*-anisylphenylarsine, and tri-*p*-anisylarsine in a relative yield of 11:56:27:5. In another experiment, triphenylarsine oxide (2.07 mmol) was allowed to react with sodium metal in excess, then *tert*-butyl alcohol (2.1 mmol) and 2-chloroquinoline (2.3 mmol) were added to the solution and irradiated for 60 min, and the reaction was then quenched with an excess of ammonium nitrate. Finally, the GLC quantitative analysis using the internal standard method gave a 76% yield of 2-quinolyldiphenylarsine, and the potentiometric titration of the aqueous solution gave an 80% yield of chloride ions. 2-Quinolyldiphenylarsine: mp 100–102 °C (lit.[11b] mp 101–102 °C); MS *m/e* (%) 357 (100), 356 (65), 281 (12), 280 (65), 279 (50), 227 (18).

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Registry No. Ph_3PO, 791-28-6; *p*-IAn, 696-62-8; Ph_2CH_3PO, 2129-89-7; *p*-AnP(O)Ph_2, 795-44-8; *p*-AnPPh_2, 896-89-9; PPh_3, 603-35-0; $(PhCH_2)_3P(O)$, 4538-55-0; $(PhCH_2)_2P(O)CH_3$, 92556-44-0; PhI, 591-50-4; PhBr, 108-86-1; $(PhCH_2)_2P(O)Ph$, 24442-45-3; *p*-BrAn, 104-92-7; $(PhCH_2)P(O)Ph_2$, 2959-74-2; 1-INaph, 90-14-2; 1-NaphP(O)Ph_2, 3095-33-8; Ph_3PS, 3878-45-3; Ph_3AsO, 1153-05-5; Ph_3As, 603-32-7; *p*-AnAsPh_2, 24579-39-3; *p*-An_2AsP, 76917-08-3; 2-ClQui, 612-62-4; 2-QuiAsPh_2, 91239-44-0.

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