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ONE POT SYNTHESIS FROM THE ELEMENTS OF SYMMETRICAL AND UNSYMMETRICAL TRIARYL-PHOSPINES, -ARSINES AND -STIBINES BY THE $S_{RN}1$ MECHANISM

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Summary

The reactions of elemental phosphorus, arsenic and antimony with sodium metal in liquid ammonia form "M^{-3}" species that react with haloarenes under irradiation to form symmetrical triaryl derivatives of these metals by the $S_{RN}1$ mechanism in fair to good yields. Further reaction with sodium metal gives a derivative nucleophile (diarylphosphide and diarylarsenide ions) that reacts with another haloarene under irradiation to form unsymmetrical phosphines and arsines.

Introduction

The $S_{RN}1$ mechanism of aromatic nucleophilic substitution has proved to be very effective in organometallic chemistry [1]. Several nucleophiles derived from sulfur [2], selenium [3], tellurium [4], phosphorus [5], arsenic [6] and antimony [7] react with haloarenes under irradiation to give the substitution product in good yields, although in some systems scrambling of aryl rings occur [1,8].

We have recently reported that several organoselenium and organotellurium compounds can be prepared from the elements in a one pot reaction in liquid ammonia by the $S_{RN}1$ mechanism [9]. Not only can aromatic derivatives of selenium or tellurium be prepared but also found that 1-adamantyl derivatives can be obtained by this method [10].

We decided to study the synthesis of symmetrical and unsymmetrical triaryl-phosphines, -arsines and -stibines by a one pot reaction from the elements under condition favoring an $S_{RN}1$ mechanism.

Results and discussion

It is known that elemental phosphorus reacts with sodium in liquid ammonia to produce a "$^{-2}P\text{–}P^{2-}$" ion which can be trapped with alkyl halides. If the species

TABLE 1
FORMATION AND PHOTOSTIMULATED REACTIONS OF "M^{-3}" IONS WITH HALOARENES IN LIQUID AMMONIA[a]

Exp. no.	Metal (mmol)	ArX (mmol)	Irradiation time (min)	Ar′X (mmol)	Irradiation time (min)	Product, Yield (%)[b]
1[c]	P (13.5)	PhI (47)	120	–	–	Ph_3PO[d], 75
2[e]	P (15.2)	PhI (60)	120	–	–	Ph_3PO[d], 70
3	P (2.28)	PhCl	60	*p*-BrAn[f]	60	*p*-$AnPh_2PO$[d,f] 55
4	As (4.0)	PhBr (16)	60			Ph_3As, 75
5	As (2.14)	PhCl (8.6)	30	2-ClQ[g] (3.2)	60	2-QPh_2As[g], 90
6[h]	As (1.97)	PhI (5.91)	60			Ph_3As, 0
7	Sb (1.00)	PhCl (4.02)	60			Ph_3Sb, 40
8[i]	Sb (2.0)	PhCl (8.0)	60			Ph_3Sb, 45

[a] Liquid ammonia in ca. 250–300 ml. The alkali metal used was Na metal, unless otherwise indicated. [b] Based on the metal used [c] Method A (see Experimental). [d] After oxidation, isolation yield [e] Method B (see Experimental); [f] An = anisyl. [g] Q = quinolyl [h] Dark reaction [i] The alkali metal used was K

"$^{-2}P{-}P^{2-}$" is protonated by an acid, and more sodium is added, the P–P bond also fragments to give a PH_n^{-3+n} nucleophile ("P^{3-} synthon") [11] (eqs. 1–4).

$$P_{red} + Na \xrightarrow{NH_3} \text{"}^{-2}P{-}P^{2-}\text{"} + 4Na \tag{1}$$

$$\text{"}^{-2}P{-}P^{2-}\text{"} \xrightarrow{NH_4^+} H_2P{-}PH_2 \tag{2}$$

$$H_2P{-}PH_2 + Na \rightarrow \text{"}P^{3-}\text{"} \tag{3}$$

$$P^{3-} + nNH_3 \leftrightharpoons PH_n^{-3+n} + n\,^{-}NH_2 \tag{4}$$

Elemental phosporus (red) reacts with sodium metal to give the "$^{-2}P{-}P^{2-}$" nucleophile in liquid ammonia. Ammonium chloride is added to neutralize it. By adding more sodium, the blue solution of solvated electrons (from sodium metal in excess in liquid ammonia) thus obtained persisted after 20 min. To this solution t-butyl alcohol was added to neutralize any amide ion that might be formed (eq. 5). Iodobenzene was added and after 120 min of irradiation, the reaction was quenched with ammonium chloride. After oxidation, triphenylphosphine oxide (75% based on elemental phosphorus) was obtained (Exp. no. 1) (eqs. 5–7).

$$P \xrightarrow[\text{(c) Na, (d) t-BuOH}]{\text{(a) Na, (b) }NH_4Cl} \text{"}P^{3-}\text{synthon"} \tag{5}$$

$$3\,PhI + \text{"}P^{3-}\text{"} \xrightarrow[S_{RN}1]{h\nu} Ph_3P + 3\,I^- \tag{6}$$

$$Ph_3P \overset{[O]}{\rightarrow} Ph_3PO \tag{7}$$

We tried to trap the “$^{-2}P\text{–}P^{2-}$” species formed (eq. 1). Reaction of red phosphorus with sodium metal, followed by reaction with t-butyl alcohol and iodobenzene, and irradiation of the reaction mixture gave only triphenylphosphine oxide (70% isolated yield, exp. no. 2).

This result suggests that either the species “$^{-2}P\text{–}P^{2-}$” was not formed, or if it was formed fragmentation occurred in the presence of phenyl radicals. Therefore we prepared the nucleophile under the same experimental conditions and tried to trap it by reaction with n-butyl bromide. However tri-(n-butyl) phosphine oxide was the major product instead of tetrabutyldiphosphine (GLC, mass spectrum).

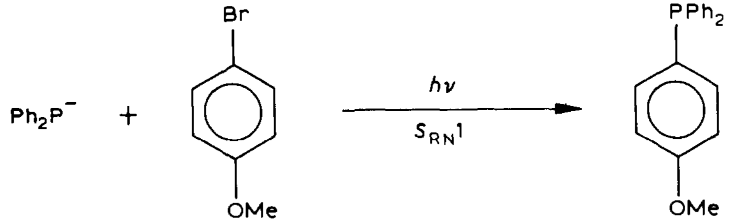
As diphenylphosphide ion can be formed by reaction of triphenylphosphine and sodium metal in liquid ammonia [12], we tried to synthesize in a one pot reaction an unsymmetrical triaryl phosphine from elemental phosphorus.

We performed a reaction under the same experimental conditions used to synthesize triphenylphosphine (from elemental phosphorus and chlorobenzene) (eq. 8, 9). We then added sodium metal to form the diphenylphosphide ion (eq. 10) and destroy the excess chlorobenzene. After completing this procedure, we added *p*-bromoanisole, and after 60 min of irradiation the reaction was quenched. After air oxidation, *p*-anisyldiphenylphosphine oxide was obtained (55% yield based on elemental phosphorus) (Exp. no. 3).

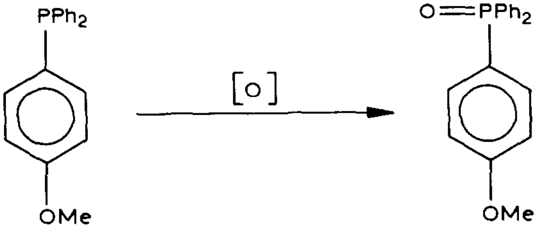
$$P \xrightarrow[\text{(b) t-BuOH}]{\text{(a) Na}} \text{“}P^{3-}\text{”} \tag{8}$$

$$\text{“}P^{3-}\text{”} + PhCl \xrightarrow[S_{RN}1]{h\nu} Ph_3P \tag{9}$$

$$Ph_3P \xrightarrow[\text{(b) t-BuOH}]{\text{(a) Na}} Ph_2P^- \tag{10}$$



(11)



(12)

We prepared the “As^{3-} synthon” from arsenic and sodium metal in liquid ammonia (eq. 13), and by a photostimulated reaction with bromobenzene, triphenylarsine was obtained in good yields (eq. 14) (Exp. no. 4).

$$\mathrm{As} \xrightarrow[\text{(b) t-BuOH}]{\text{(a) Na}} \text{“}\mathrm{As}^{3-}\text{ synthon”} \qquad (13)$$

$$\text{“}\mathrm{As}^{3-}\text{”} + \mathrm{PhBr} \xrightarrow[S_{\mathrm{RN}}1]{h\nu} \mathrm{Ph_3As} + \mathrm{Br}^- \qquad (14)$$

Diphenylarsenide ion reacts with some haloarenes by the $S_{\mathrm{RN}}1$ mechanism giving products of the type $\mathrm{As{-}R_{3-n}R'_n}$ ($n = 0, 1, 2, 3$) [8] (eq. 15).

$$\mathrm{ArX} + \mathrm{Ph_2As}^- \xrightarrow{h\nu} \mathrm{Ph_3As} + \mathrm{Ph_2AsAr} + \mathrm{PhAsAr_2} + \mathrm{AsAr_3} \qquad (15)$$

(ArX = p-haloanisole, p-halotoluenes, 1-chloronaphthalene)

Only the straightforward substitution product is formed with other haloarenes under the same reaction conditions [8] (eq. 16).

$$\mathrm{Ar'X} + \mathrm{Ph_2As}^- \xrightarrow{h\nu} \mathrm{Ar'{-}As{-}Ph_2} + \mathrm{X}^- \qquad (16)$$

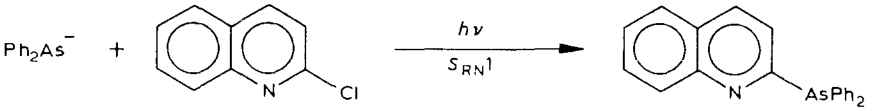
(Ar'X = 4-chlorobenzophenone, 2-chloroquinoline)

Diphenylarsenide ion can be prepared in liquid ammonia from triphenyl arsine and sodium metal [6,12]. We studied the possibility of synthesizing unsymmetrical triarylarsines from elemental arsenic in a one pot reaction. However, in order to avoid difficulties with scrambled products [8], we used 2-chloroquinoline as a second aromatic substrate.

In the photostimulated reaction of the “As^{3-}” ion (eq. 13) with chlorobenzene to form triphenylarsine (eq. 17), sodium metal was added to destroy residual chlorobenzene and to form the diphenylarsenide ion (eq. 18). By adding 2-chloroquinoline, and after irradiation of the solution, we obtained 2-quinolyldiphenylarsine in excellent yield (90% yield based on the elemental arsenic used) (eq. 19).

$$\text{“}\mathrm{As}^{3-}\text{”} + \mathrm{PhCl} \xrightarrow[S_{\mathrm{RN}}1]{h\nu} \mathrm{Ph_3As} \qquad (17)$$

$$\mathrm{Ph_3As} \xrightarrow[\text{(b) t-BuOH}]{\text{(a) Na}} \mathrm{Ph_2As}^- \qquad (18)$$



(19)

We tried to prepare the “Sb^{3-} synthon” by the same method as the other metals, but the reactions of antimony with sodium or potassium elements are slower compared to elemental phosphorus or arsenic. Besides, some antimony metal was always recovered. Nevertheless, we prepared the “Sb^{3-}” species by the same method (eq. 20) and chlorobenzene was added. After 60 min of irradiation (longer irradiation times do not improve the yield) triphenylstibine was obtained in 45% yield (eq.

21) (Expt. no. 7, 8).

$$\mathrm{Sb} \xrightarrow[\text{(b) t-BuOH}]{\text{(a) Na (K)}} \text{“}\mathrm{Sb}^{3-}\text{ synthon”} \tag{20}$$

$$\text{“}\mathrm{Sb}^{3-}\text{”} + 3\mathrm{PhCl} \xrightarrow[S_{\mathrm{RN}}1]{h\nu} \mathrm{Ph_3Sb} + 3\mathrm{Cl}^- \tag{21}$$

Experimental

Melting points have not been corrected. NMR spectra were performed on a Varian T-60 nuclear magnetic resonance spectrometer, using CCl_4 as solvent. The spectra are reported in ppm relative to Me_4Si (δ). Mass spectral measurements were obtained with a Finnigan Model 3300 mass spectrometer. Gas chromatographic analyses were performed on a Varian Aerograph, Series 2400 with a flame ionization detector equipped with a Data processor Chromatopac C-R1A, Shimadzu. Analyses were performed using a 1.5% OV-101 on 80–100 mesh Chromosorb P, 1.52 mm × 3.2 mm column. All the metals and haloaromatic compounds were analytic grade, commercially available products and used as received.

Photostimulated reactions. These reactions were carried out in a photochemical reactor equipped with four 250 W lamps with maximum emission at 350 nm (Philips, model HPT, water refrigerated).

Photostimulated reaction with "P^{3-}" ions

Method A. Ammonia (250 ml), previously dried over Na metal, was distilled into a 500 ml three-neck, round-bottom flask equipped with a cold finger, nitrogen inlet and magnetic stirrer. To the ammonia elemental P (red, recently cleaned and dried at 110 °C, 13.5 mmol) was added. Na metal (26.9 mmol) was added bit by bit; the fast reaction forms an orange solution while all the elemental phosphorus is consumed. Ammonium chloride (27 mmol) was added, and then elemental sodium was added in excess until the dark blue solution persisted for 20 min. The solution was decolorized with t-butyl alcohol. Once it was decolorized, t-butyl alcohol (27.0 mmol) was added followed by iodobenzene (47 mmol). After 120 min of irradiation, the reaction was quenched by water (50 ml) and the ammonia was allowed to evaporate. Water (30 ml) was added to the residue. The resulting mixture was then extracted three times with diethyl ether. The presence of Ph_3P and Ph_3PO was indicated by GLC by comparing their retention times with authentic samples. The ether was distilled. The residue was then dissolved in dichloromethane. The solution was washed twice with a solution of hydrogen peroxide (20 vol.%, 50 ml each), twice with a solution of sodium hydroxide (3 *M*, 50 ml each) and once with distilled water. After drying with anhydrous magnesium sulphate, the solvent was removed by distillation. The residue of Ph_3PO (75% yield) was recrystallized from petroleum ether/diethyl ether (1/9); mp. 154–155 °C (Lit. 13 156–157 °C). Mass spectrum: 278, 201, 199, 185, 183, 152, 77 (similar to those reported [14]).

Method B. To 250 ml of ammonia, elemental phosphorus (15.2 mmol) was added, followed by Na metal in excess until the blue solution persisted for 20–30 min (ca. 82 mmol). The resulting solution was decolorized with t-butyl alcohol. After the color was destroyed, additional t-butyl alcohol (30.4 mmol) was added followed by iodobenzene (60 mmol). After 120 min of irradiation the reaction was quenched and worked-up as in method A. Ph_3PO was isolated in 70% yield.

Photostimulated reaction with diphenylphosphide ion prepared "in situ"

Following method B, Ph_3P was prepared from elemental phosphorus (2.28 mmol) and chlorobenzene (11.36 mmol) during 60 min of irradiation. Then Na metal was added in excess until the blue solution persisted for 20 min. Then the resulting solution was decolorized with t-butyl alcohol. After the color was destroyed, additional t-butyl alcohol (2.82 mmol) was added followed by *p*-bromoanisole (4.23 mmol) and the solution was irradiated for 60 min. The reaction was quenched with ammonium chloride and the ammonia was allowed to evaporate. The residue was extracted with dichloromethane and it was oxidized as in method A. *p*-Anisyldiphenylphosphine oxide was isolated in 55% yield. Recrystallized from petroleum ether/diethyl ether (1/9), white crystals, m.p. 100–103°C (Lit. 15 112–113°C). NMR, 3.80 (5, 3H), 7.0–7.8 (nm, 14H).

Photostimulated reaction with "As^{3-}" ions

Arsenic (powder, 4.0 mmol) was added to 250 ml of ammonia. After addition of excess Na metal (23.7 mmol) until the blue solution persisted for 45 min, the solution was decolorized with t-butyl alcohol. After the color was destroyed, additional t-butyl alcohol (7.92 mmol) was added. A red solution was formed, with consumption of all the As. Bromobenzene was added (16 mmol) and after 60 min of irradiation, the reaction was quenched (ammonium chloride) and the ammonia allowed to evaporate. The residue was extracted with ether. The only organic product containing arsenic was found to be Ph_3As by comparing it with an authentic sample. Analysis by GLC indicated 75% yield.

Photostimulated reaction with diphenylarsenide ion prepared "in situ"

Ph_3As was prepared from As (2.14 mmol) and chlorobenzene (8.6 mmol) during 30 min of irradiation according to the above described method. To this solution Na metal was added in excess until the blue solution persisted for 25 min, the solution was decolorized with t-butyl alcohol. After the color was destroyed, additional t-butyl alcohol (2.14 mmol) was added, and then 2-chloroquinoline (3.21 mmol). The solution was irradiated during 60 min, and then it was worked-up as before. 2-Quinolyldiphenylarsine was determined by GLC (90% yield). The ether was distilled and the residue recrystallized from benzene, m.p. 101–102°C (Lit. 7 101–102°C).

Photostimulated reaction with "Sb^{3-}" ions

Sb (powder, 1.0 mmol) was added to 250 ml of dried and distilled ammonia, and then Na metal in excess until the blue solution persisted for 45 min. However, when t-butyl alcohol was added, some Sb did not react (in other experiments more Na metal and more time did not increase the yield, the same results were obtained with potassium metal), chlorobenzene (4.02 mmol) was added, and after 60 min of irradiation the reaction was quenched and worked-up as before. Ph_3Sb was determined by GLC (40% yield). The ether extract was distilled, and the residue recrystallized from petroleum ether, mp. 52–53°C (Lit. 16 53.5°C).

Dark reaction with "As^{3-}" ion and iodobenzene

The reaction of "As^{3-}" ions prepared from As (1.97 mmol) by the procedure described before, with iodobenzene in the dark (60 min) did not give any reaction. No Ph_3As was found (GLC) and the iodide ion liberated was ~ 2% yield (determined potentiometrically from the water extract).

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