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Communication

Red Phosphorus

Superbase-Assisted Selective Synthesis of Triarylphosphines from Aryl Halides and Red Phosphorus: Three Consecutive Different S_NAr Reactions in One Pot

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Abstract: Aryl halides, ArX (Ar = Ph, 2-, 3- and 4-Tol, 1- and 2-Np, 4-$C_6H_4CONH_2$; X = F, Cl, Br), rapidly and exothermically (100–180 °C, 0.5–2 h) react with red phosphorus in superbase systems KOH/L, where L is a polar nonhydroxylic complexing solvent (ligand), such as NMP, DMSO, HMPA, to afford the corresponding triarylphosphines (Ar_3P) in up to 74 % yield (for X = F). Thus, three consecutive reactions of S_NAr (aromatic nucleophilic substitution) to form the three C(sp^2)–P bonds are realized in one pot. The synthesis is mostly chemoselective (with rare exception): neither mono- nor diphosphines have been isolated. The best results were attained when aryl fluorides were treated with red phosphorus (P_n) in the KOH/NMP superbase system. This environmentally friendly, PCl_3-free synthesis of Ar_3P from available starting materials opens an easy and straightforward access to triarylphosphines, which are important ligands, synthetic auxiliaries, and components of high-tech- and medicinally oriented complexes.

Introduction

Triarylphosphines, especially triphenylphosphine (Ph_3P), are most widespread organic phosphines, which represent a paramount interest for synthetic chemistry,[1] catalysis,[2] biomedicines[3] and high-tech materials,[4] optoelectronics,[5] solar cells,[6] organometallopolymers,[7] *etc*.

Industrial synthesis of triphenylphosphine includes interaction of PCl_3 with melted sodium and phenyl halides at 200 °C.[8] Another route to triphenylphosphine is the reaction of PCl_3[9] or $(PhO)_3P$[10] with phenylmagnesium halides in Et_2O or THF.[11]Also known is a method based on reaction of PCl_3 with lithiated benzenes (phenyl halides + *n*BuLi).[12] The reaction of PCl_3 with $AlCl_3$ (or Al powder) and PhCl at 180–200 °C was claimed to give to triphenylphosphine in 91 %.[13]

Now, all these PCl_3 based syntheses of triphenylphosphine are perceived as environmentally unfriendly,[14] which are strongly desirable to be substituted by greener approaches, particularly, using elemental phosphorus. Sinyashin et al. had shown that triphenylphosphine can be synthesized electrochemically in 20–60 % yield from white phosphorus (P_4) and PhBr or PhI at 25–50 °C in the presence of Ni complexes applying soluble metallic (Zn, Al, Mg) anodes and DMF or MeCN as solvents.[15] According to Mezailles et al.,[16] triphenylphosphine was synthesized in good yield from P_4, nanosized potassium metal/graphite composite and PhI in PhMe. White phosphorus was also employed for the synthesis of triphenylphosphine using phenyl halides and sophisticated Ti complexes, {Ti[NAr(*t*Bu)]$_3$, 3–5 equiv.}.[17]

However, until now red phosphorus (P_n) remained almost ignored as a starting platform for the synthesis of triarylphosphines. In 1984 Bornancini prepared triphenylphosphine (80 % yield) from PhI in the system P_n/Na/*t*BuOH/NH_3(liq.) under UV irradiation (350 nm),[18] but further this finding was not developed. It was reported that the heating (230 °C, 16 h) of PhI with red phosphorus in the presence of $NiBr_2$ and iron filings led to triphenylphosphine (the yield was not given).[19] Functionalized fluorobenzenes possessing strong EWG (electron-withdrawing groups) reacted with red phosphorus in the system Li/*t*BuOH/NH_3(liq.) to give the corresponding functionalized Ar_3P in 37–60 %.[20]

In the last decades, we were systematically developing the synthesis of organophosphorus compounds (phosphines, phosphine oxides, phosphinic and phosphonic acids) using red phosphorus and various electrophiles in the multiphase superbase systems of the type KOH/H_2O/DMSO (or HMPA) or under phase-transfer conditions (KOH/H_2O/organic solvent/phase-transfer catalyst).[21] Among electrophiles, acetylenes,[21] alkenes,[22] different organic halides,[21a,21c,23] heterocyclic halides (2-halopyridines)[24] and some condensed aromatic halides were employed.[21c] However, phenyl halides[23a] turned out to be entirely inert towards polyphosphide anions generated from red phosphorus in the superbase systems under conditions suitable for the synthesis of aforementioned organophosphorus compounds.

We report that the longstanding problem, namely the synthesis of triarylphosphines using red phosphorus and aryl hal-

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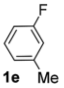
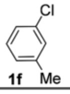
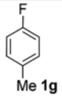
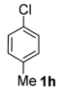
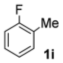
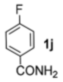
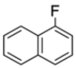
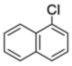
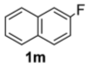
Table 1. Optimization of the reaction conditions.[a]

$$\underset{\mathbf{1}}{ArX} + P_n \xrightarrow[\substack{100\text{-}180\,^{\circ}C \\ 0.5\text{-}2\ h}]{KOH/L} \underset{\mathbf{2}}{Ar_3P} + KX + K_2HPO_3\ (KH_2PO_2,\ H_2/PH_3)$$

Ar = Ph; 2-, 3-, 4-Tol; 1-, 2-Np; 4-$C_6H_4CONH_2$
X = F, Cl, Br, I
L = DMF, NMP, DMSO, Sulfolane, HMPA

Entry	ArX	L	T [°C][b]	t [h]	Conv. [%]	Product	Yield [%][c]
1	PhF **1a**	DMF	100-120 (130)	1	99	{$PhPH_2$, Ph_2PH}	traces
2		NMP	100-120 (128)	1	99	Ph_3P **2a**	74
3		DMSO	100-120 (130)	0.75	99		41[d]
4		Sulfolane	100-120	0.75	99		34
5		HMPA	100-120 (150)	0.5	99		69
6	PhCl **1b**	NMP	100-120 (130)	1	66	Ph_3P **2a**	24 (36)
7		DMSO	105-115 (126)	0.75	49		20[e] (40)
8[f]		DMSO	100[g]	2	70		18[e] (42)
9[h]		DMSO	100[g]	1	37		13[e] (36)
10		HMPA	100-115 (145)	0.75	69		43 (62)
11[h]		HMPA	100[g]	0.5	67		38 (71)
12[f]		HMPA	100[g]	2	30		3 (11)
13	PhBr **1c**	NMP	100-115 (140)	1	96	Ph_3P **2a**	9[i]
14		DMSO	100-117 (129)	1	98		7[j]
15		HMPA	97-110 (160)	1	76		28 (37)
16	PhI **1d**	HMPA	100-120 (134)	1	60	**2a**	none
17	 **1e**	NMP	100-118 (134)	1	86	3-Tol_3P **2b**	51(59)
18		HMPA	100-105 (145)	1	74		40(54)
19	 **1f**	NMP	100-120 (131)	1	57		17(31)
20	 **1g**	NMP	100-110 (126)	1	66	4-Tol_3P **2c**	34(51)
21		HMPA	107-110 (132)	1	68		38(55)
22	 **1h**	NMP	100-112 (125)	1	23		15(20)
23[k]	 **1i**	NMP	100-120 (131)	1	88	2-Tol_3P **2d**	15[l] (19)
24		HMPA	100-115 (135)	1	-		none
25	 **1j**	NMP	100-115 (120)	1	93	4-Bza_3P **2e**	27(30)
26[k]	 **1k**	NMP	110-120 (126)	1	99	1-Np_3P **2f**	67
27[k]		HMPA	100-110 (150)	1	99		70
28		HMPA	100-120 (140)	1	99		23
29[k]	 **1l**	HMPA	110-120 (125)	1	66		24(40)
30[k]	 **1m**	NMP	110-120 (126)	1.0	99	2-Np_3P **2g**	60
31[k]		HMPA	100-110 (180)	1.0	99		54

[a] Reaction conditions: molar ratio of ArX (75 mmol)/P_n/KOH•0.5H_2O as 1:1.3:5.13; L (40 mL), argon (Tol = tolyl, Np = naphthyl, Bza = benzamide, DMF = dimethylformamide, NMP = *N*-methyl-2-pyrrolidone, DMSO = dimethyl sulfoxide, HMPA = hexamethylphosphorus triamide). [b] In brackets exothermic peaks are given. [c] Yield of isolated product. (in brackets yield basing on reacted ArX). [d] Also, Ph_2PMe (10 %) and PhSMe (≈ 1 %) were isolated. [e] Also, Ph_2PMe (≈ 9 %) and PhSMe (≈ 1 %) were isolated. [f] Molar ratio of ArX (75 mmol)/P_n/KOH•0.5H_2O as 1:1:3.85. [g] Fix temperature. [h] Molar ratio of ArX (75 mmol)/P_n/KOH•0.5H_2O as 1:1.5:3.85. [i] Also, Ph_2PMe (≈ 3 %) and Ph_2PEt (≈ 2 %) were isolated. [j] Also, Ph_2PSMe (5.3 %), Ph_2PMe (≈ 1 %) were formed. [k] Molar ratio of ArX/P_n/KOH•0.5H_2O as 1: 2.8: 8.7. [l] Also 2-Tol_2PH was formed in ≈ 1:1 molar ratio (isolated as phosphine oxide in 15 % yield).

ides has now been solved, and the synthetic details are presented in this communication. This goal was achieved due to the following two essential amendments to the previous methodology: i) the basicity enhancement of the multiphase superbase systems (which disassemble P_n 3D molecules to supernucleophilic polyphosphide anions) by exclusion of water from their composition, and ii) the rapid heating of the reaction mixture (up to 100–115 °C) to initiate short exothermic process thereby allowing completion of the synthesis within 0.5–1 h. Representative data concerning the influence of the reaction conditions and structure of the ArX on the yield of triarylphosphines are shown in Table 1.

Results and Discussion

The syntheses were implemented by immersing the reaction mixture (P_n, ArX, KOH/L) into the preliminarily heated (115 °C) glycerol bath upon stirring. After the short exothermic effect (2–5 min, 120–180 °C, depending on the L nature), the temperature of the reaction mixture drops to 100 °C during 0.5–1 h, and triarylphosphines thus obtained are isolated by conventional workup (see the Supporting Information for details). If the exothermic effect is quenched by outer cooling, the yield of triarylphosphines is remarkably decreased (sometimes, twice as less). Some amounts of the PH_3 mixture[14] formed in the process are oxidized by the H_2O/DMSO/$CuSO_4$ solution (see the Supporting Information), or can be used as synthetic reagent, e.g. for preparation of organic phosphines.[25]

The overall redox process is accompanied by formation of oxidized phosphorus molecules, mostly potassium phosphite (^{31}P NMR monitoring), which, if necessary, can be isolated as a product.

As seen from Table 1, the major factors which influence the triarylphosphines yield are the nature of polar complexing solvent (L) as a ligand of a superbase system (KOH/L) and the structure of aryl halides, mainly the nature of halogen. The best yields of triphenyl- (**2a**), tritolyl- (**2b**, **2c**), and trinaphthylphosphines (**2f, 2g**), which span 51–74 % were attained when the reaction was conducted in the KOH/NMP superbase system with corresponding aryl fluorides (entries 2, 17, 20, 26, 30). The close results for the same aryl fluorides were obtained when the reaction was implemented in the KOH/HMPA superbase system, the yield ranging 54–70 % (entries 5, 18, 21, 27, 31). In view of adverse physiological properties of HMPA as a solvent,[26] the KOH/NMP should be considered as a system of choice. It is worthwhile to note that in the KOH/HMPA system the most significant exothermic effect (132–180 °C) have been observed. That could have a negative effect on scaling up this protocol. Surprisingly, the KOH/DMSO system which previously most often was used for the P_n-based syntheses of phosphines and phosphine oxides,[21] in this case proved to be inferior: the yield of Ph_3P from PhF was 41 % only, i.e. by 33 % lower than in KOH/NMP system (entry 2 vs. 3). Besides, this reaction was complicated by the side-methylation of the intermediate diphenylpolyphosphide species (entry 3), resulting in formation of Ph_2PMe (yield ≈ 10 %). In the experiments with PhCl and PhBr the same methylation was observed, the yield of Ph_2PMe being 9 % and 1 % respectively (entries 7, 14). In some experiments, methyl phenyl sulfide, MeSPh, was also detectable in ≈ 1 % yield (entries 3, 7–9), that (together with above methylation) indicates an insignificant reductive destruction of DMSO. This is also confirmed by the detection of Ph_2PSMe (yield ≈ 5 %) in the synthesis of Ph_3P from PhBr (entry 14).

Under the same conditions, in sulfolane, the process proceeded without an exothermic effect (100–120 °C) resulting only in 34 % yield of Ph_3P though free of any contaminants (entry 4). This experiment shows again that a rapid preheating is indeed necessary to get a good yield of Ph_3P. Note that DMF appeared to be absolutely insufficient ligand of KOH to promote the synthesis of triphenylphosphine: only traces of primary phenyl- and secondary diphenylphosphines were detected in the reaction mixture (entry 1). Obviously, the deep alkaline solvolysis of DMF as aliphatic amide occurs in this case. The key role in activation of red phosphorus in this redox reaction and polyphosphide anions generated from P_n belongs to a metal cation of the superbase media that follows from the drastic reduction of the triphenylphosphine yield from 69 to 6 % when the KOH/HMPA system was replaced by NaOH-tailored its analog.

A very strong influence on the yield of triphenylphosphine exerts the nature of halogen atom in the benzene ring. Under the best conditions (KOH/NMP), the highest yield was reached in the case of fluorobenzene (74 %), while for chloro-, bromo- and iodo-analogs the yield of Ph_3P dramatically drops: 36, 9 and 0 %, correspondingly (entries 6, 13, 16). This fact is in good agreement with a general regularity of the aromatic nucleophilic displacement (S_NAr) that the fluorine atom in an aromatic ring undergoes nucleophilic aromatic substitution much faster than other halogens.[27]

From the practical point, the most attractive substrates are chloroarenes as available and inexpensive, however our attempts to improve the yields of corresponding triarylphosphines using chloroarenes have not been successful enough (Table 1, entries 6–12, 19, 22 and 29).

Next, the effect of aromatic moiety of aryl fluorides on the yield of Ar_3P has been examined. The aryl fluorides were chosen because PhF provided the best yields of triphenylphosphine.

As follows from Table 1, methyl substituents in the benzene ring decrease the yields of tri(tolyl)phosphines, which with 3- and 4-tolyl fluorides (in the KOH/NMP system) are 59 % and 51 % (entries 17, 20). In the case of *2*-tolyl fluoride the corresponding tri(*2*-tolyl)phosphine was isolated just in 19 % yield (entry 23) along with di(*2*-tolyl)phosphine (yield 15 %). The latter result is the only example of the secondary phosphine synthesis in this reaction, which is usually resulted in formation of exclusively tertiary phosphines. The observed depression of the triarylphosphines yield compared to Ph_3P is the expected outcome of negative influence of the electron-donating methyl substituent on the aromatic nucleophilic substitution that is additionally aggravated by the steric shielding for *2*-tolyl fluoride. A similar regularity takes place also for the KOH/HMPA system wherein *2*-tolyl fluoride gave no tritolylphosphine **2d** at all (entry 24).

In accordance with the assumed reaction mechanism as aromatic nucleophilic substitution were the negative results for such π-electron-donating substituents as amino-(3-, 4-), methoxy-(3-, 4-), *4*-chloro-, and *3*-bromo- in the benzene ring: only traces of secondary phosphines were detected (^{31}P NMR) in the reaction mixture for these fluoroaromatics.

A modest yield of the tertiary phosphine, obtained from 4-fluorobenzamide, despite the electron-withdrawing substituent (H_2NCO) in the benzene ring (30 %), is likely caused by a partial decomposition of the amide function under the action of active hydroxide and polyphosphide anions to give the corresponding benzoic acid derivative (entry 25).[28]

Surprisingly good yields of corresponding tertiary phosphines **2f**, **2g** have been obtained from 1- and 2-fluoronaphthalenes (67 and 60 % in KOH/NMP or 70 and 54 % in KOH/HMPA system), despite their obvious steric encumbrance, so in these cases the loadings of P_n and KOH were necessary to be increased about twice as much (entries 27 vs. 28). Notably that 1-fluoronaphthalene wherein the fluoride atom is more sterically shielded than in its 2-isomer provides a higher yield of the target phosphine **2f**.

It should be underlined that most of the syntheses were performed on the gram (up to 5 g) scale thereby demonstrating good prospects for a larger scale application of the developed methods.

Overall, the best practically result of this investigation is the efficient (74 % yield) straightforward synthesis of triphenylphosphine (most widely used organic phosphine), from red phosphorus and fluorobenzene in the KOH/NMP superbase system. Despite that fluorobenzene is 1.5–2.5 times more expensive than chlorobenzene (depending on purity and supplier), the yield of triphenylphosphine (in NMP) from the former is three times higher than from chlorobenzene (74 % and 24 %, respectively). Although, in HMPA, the best yield of Ph_3P from chlorobenzene reached 43 % (Table 1, entry 10), the practical application of this solvent has no future due to its toxicity (carcinogenicity) and much higher cost compare to NMP. On the contrary, the latter is a readily available, industrially produced, biologically friendly, non-toxic solvent,[29] applied as a penetration enhancer for topically administrated drugs, and as a vehicle for cosmetics.

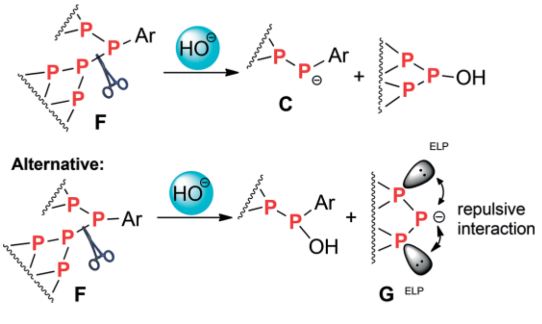
An intriguing feature of the reaction studied is the selective formation of triarylphosphines: neither corresponding primary no secondary phosphines are usually detectable in the reaction mixtures. Formally the synthesis proceeds as consecutive nucleophilic displacement of halogen in the aromatic moiety by the anions P^{3-}, ArP^{2-}, Ar_2P^-, resulted from disassembling of the P_n 3D-network under the action of active OH-anion.

Such poorly solvated hydroxide anions in the frustrated ion pairs K^+OH^-, wherein the potassium cations are specifically coordinated with the complexing strongly polar solvent (L), represent the most reactive species in the superbasic media used in this case. In view of the known low activity of arylhalides in the reaction S_NAr (usually activation by strongly EWG-substitution or metal-catalysis is required), the observed rapid and exhaustive synthesis of Ar_3P via the three different in nature phosphorus-centered nucleophiles should be rated as abnormal phenomenon. Obviously, this is caused by the mechanistic specificity of the process under investigation which progresses in multiphase superbasic media.

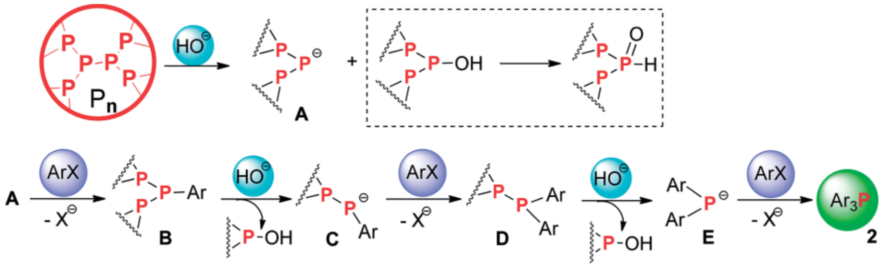
Apparently, the process starts with P–P bond cleavage by hydroxide anion to form polyphosphides **A**, as a part of P_n network, and the oxidized counterpart of the cleaved P_n network terminated by HP=O-groups (Scheme 1). The polyphosphide anion species, undergoing in time the further disassembling, react with aryl halides to form aryl polyphosphide intermediates **B** (the first S_NAr act). The consequent cleavage of the P–P bond adjacent to the P–Ar moiety by the OH-anion leads to the P-centered intermediate anions **C**. This polymeric anions **C**, after the reaction with the next molecule of ArX, gives the diarylpolyphosphide intermediates **D** (the second S_NAr act), which still remains in the polyphosphide aggregates, probably nanosized and, hence, cannot be released into the solution. Finally, the hydroxide-assisted cleavage of the P–P bond neighboring PAr_2 terminal group followed by the arylation of the diarylphosphide anion **E** thus formed (the third S_NAr act) affords triarylphosphine **2** (Scheme 1).

The polyphosphide P-centered anions **A**, **C** should have an enhanced nucleophilicity, i.e. they should be supernucleophiles, due to the α-effect of adjacent phosphorus atoms that is expressed in a lower ionization potential and higher polarizability. The possible existence of the polyphosphides species as micro-, submicro- and nanosized particles with a higher surface energy may also contribute to the easiness of the nucleophilic displacement under question. In the superbase media with their lower proton activity, the above supernucleophiles are poorly solvated and therefore should have even a higher reactivity. All these should facilitate the nucleophilic displacement of halogen atoms in aromatic rings by the polyphosphide P-centered anions.

In fact, the real nucleophiles are oligophosphide and aryl-terminated oligophosphide anions. The preferred further formation of phosphides bearing two or three aryl groups is likely due to the higher nucleophilicity of P atom adjacent to the organic moiety, compared to the P-centered anion bound with two other P atoms. Indeed, the cleavage of the P–P bond by hydroxide anion in the intermediate aryl-oligophosphides **F** (Scheme 2), should be preferably occur, so that the negative charge, thus formed, could be distributed over the arene moiety (a benzylic type anion). The alternative cleavage of the same P–P bond seems to be less preferred because anionic center in this case (**G**) is affected by the repulsive interaction with the electron lone pairs (ELP) of the two neighboring phosphorus atoms. Consequently the next molecules of aryl halides will preferable interact with intermediate **C** to locate another aryl substituent at the same P atom. The final formation of triarylphosphines should be even more favorable since it will involve the P-centered anion stabilized by 2 neighboring aryl substituents. Correspondingly the consecutive attacks of hydroxide anion should be directed at the P-atoms which already bear hydroxide substituents owing to the progressively increasing positive charge on the P atom. The approximated rationalization, here presented, helps to understand the high selectivity of the reaction i.e. the predominant formation of triarylphosphines and potassium phosphite and hypophosphite.



Scheme 2. Two ways of polyphosphide intermediate formation.



Scheme 1. Plausible mechanism for the formation of Ar_3P.

The short thermal jump in the beginning of the process (the temperature/time curves, see the Supporting Information) can be roughly estimated in terms of the bond breaking/bond forming during the disassembling of the P_n 3D network under the action of the hydroxide anions (P_n → **A**, **B** → **C**, **D** → **E**, Scheme 1). Indeed, according to,[30] the energy of P–P bonds, which are broken, is ≈ 200 kJ/mol while the energies of forming P=O and P–H bonds are ≈ 640 and ≈ 300 kJ/mol that corresponds to the approximated energy balance as ≈ +700 kJ/mol, i.e. the process is to be actually exothermic.

Conclusion

Triarylphosphines, top requested ligands, synthetic intermediates and components of high-tech and bioactive metal complexes, have become much more easily accessible owing to their selective synthesis from red phosphorus (P_n) and aryl fluorides in the superbasic media KOH/polar non-hydroxylic complexing solvent-ligand (L) developed here. The process is realized via three consecutive different S_NAr reactions involving polyphosphide supernucleophilic species generated from the disassembling of the P_n molecule under the action of hydroxide anion. The synthesis is readily scalable and avoids toxic, irritative and ecologically malignant phosphorus chlorides, organometallics, and harsh conditions inherent in previous methods.

Acknowledgments

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Keywords: Red phosphorus · Phosphines · Aromatic substitution · Synthetic methods · Superbase systems

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