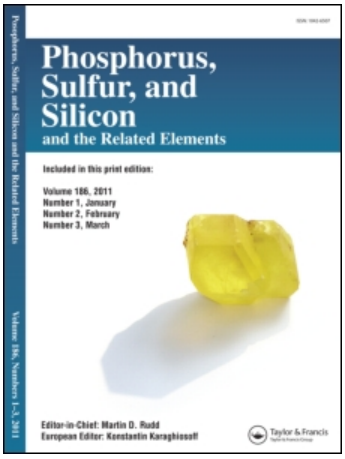

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REDUCTIVE CLEAVAGE OF THE HALOGEN-PHOSPHORUS, OXYGEN-PHOSPHORUS AND PHOSPHORUS-PHOSPHORUS BONDS WITH ALKALI METALS

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The reduction of phosphorus acid chlorides as well as hypophosphates, pyrophosphates and mixed P(III)-P(V) anhydrides with alkali metals (Li, Na, K) in NH_3 liq. / THF solution and potassium naphthalenide was investigated. It was found that this type of phosphorus compounds easily undergo reduction: a) >P(O)Cl to >P(O)H; b) >P(O)P(O)< to >P(O)H; c) >P(O)-O-P(O)< to >P(O)OH and >P(O)H; d) >P(O)-O-P< to >P(O)O^- and >P^-. The results of our experiments strongly suggest that the mixed P(III)-P(V) anhydride is reduced by potassium naphthalenide in THF with the cleavage of the P(III) – oxygen bond.

INTRODUCTION

The first application of the Wurtz-Fittig type synthesis for the P-P bond formation was the coupling of PI_3 with mercury to diphosphorus tetraiodide as early as the end of the last century[1]. This procedure was also successfully used for the synthesis of several other biphosphines. The reaction probably proceeds via an intermediate phosphorus-mercury compound[2]. Other metals such as lithium[3], sodium[4], potassium[4d,e] and magnesium[5] in organic solvents have been successfully used for the coupling of the less reactive but more accessible phosphinous halogenides. N-substituted aminoorganochlorophosphines undergo also this reductive coupling,

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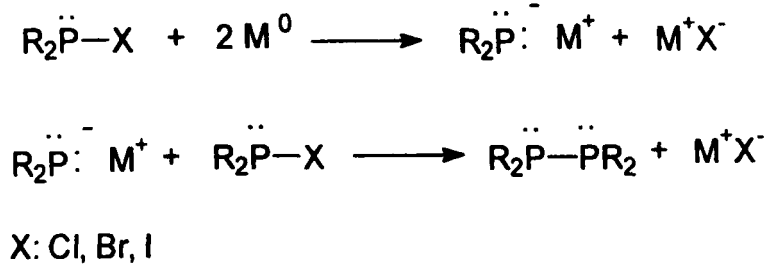
producing aminoorganobiphosphine[6]. Recently P. Knochel[7] was able to demonstrate that the reaction of bis(diethylamino)chlorophosphine borane complex with lithium naphtalenide affords the lithiated derivative which undergoes nucleophilic substitution with primary and secondary alkyl halides.

This alkali metal coupling probably proceeds via the alkali metal phosphide intermediate[4b, 8], since biphosphines have been produced from the second step of the above reaction (Scheme 1).



SCHEME 1

On the other hand it was presented that 1,3,1′,3′-tetraethyl-bis(2,2′-imidazolidene), an electron-rich olefin, is a mild homogeneous reducing agent which reduces the P-Cl bond in phosphinous chlorides to give compounds with phosphorus-phosphorus bonds[9]. Since the reduction of the hindered phosphinous chlorides by this bis-imidazolidenes leads to phosphinyl radicals[10], it seems likely that the presented reactions also proceed via phosphinyl radicals, which dimerize to yield biphosphines.

The reaction of the >P(O)Cl compounds (dialkylphosphoric acid chlorides, phosphonic acid chlorides, phosphinic acid chlorides) with alkali metals is much more complex and the data presented in the literature are often incompatible. M. Baudler[11] reported that the treatment of dialkyl chlorophosphate with sodium in an inert solvent such as xylene, toluene, or ether, at room temperature followed by gentle warming, results in a mixture of products consisting, in the main, of hypophosphoric acid esters together with considerable amounts of pyrophosphoric acid esters. It is interesting enough that the reaction of sodium dialkylphosphite with chlorides of dialkylphosphoric acids produces: tetraalkylhypophosphates,

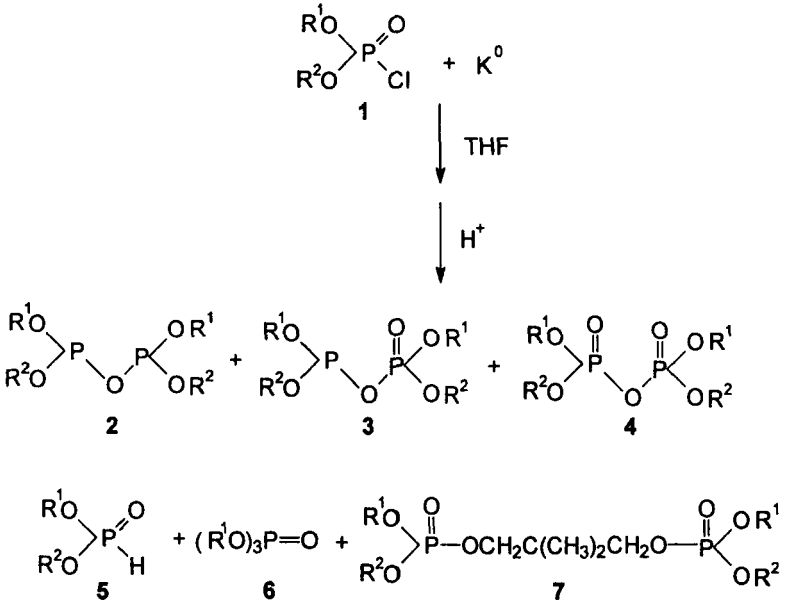
tetraalkylpyrophosphates and mixed P(III)-O-P(V) anhydrides in low yield[12].

L. Horner[13b] isolated, in a poor yield, tertraphenylbiphosphine dioxide from the reaction mixture of diphenylphosphinyl chloride and Li/Hg. On the other hand, in the reaction of diphenylphosphinyl chloride with sodium in toluene he observed the formation of sodium diphenylphosphinite or diphenylphosphide depending on the amount of sodium used in this reaction[13c]. N. Inamoto and coworkers[14] carried out several experiments using diphenylphosphinic acid chloride and alkali metals and metal salts in THF. He reported for example, that the reaction of diphenylphosphinic acid chloride with lithium in THF at 150°C gave 29% of diphenylphosphine oxide, 3% of tetraphenylbiphosphine dioxide, and a trace amount of 1,4-bis(diphenylphosphino)butane-1,4-dioxide.

The reductive cleavage of P-C as well as P-O bonds is a subject of current interest[15] from the theoretical as well as the synthetic point of view. The presented evidence indicates that cleavage of aryl phosphates with electron donors may occur either by one-electron or two-electron pathways. Thus, high concentrations and greater reducing power of the electron donor favor production of arene (C-O cleavage product) while low concentrations and/or lower reducing power of the electron donor favor production of phenol (P-O cleavage) from aryl phosphates. Moreover it was demonstrated that the reductive cleavage reaction of functionalised triphenylphosphines depends strongly on the nature of the functionality and on the reducing agent.

In contrast to that, the reductive cleavage of the P-Cl bond in the compounds of the >P(O)Cl type, particularly under homogenous conditions, was not the subject of systematic studies. In connection with our interest in the reactivity of the acids of trivalent phosphorus we took up the studies of the reaction between >P(O)Cl type compounds and electron donors (alkali metals, alkali metals in liquid ammonia, naphthalene anion radical).

In our experiments we observed that the treatment of chlorophosphates in THF with one equivalent of potassium metal (with or without the catalysts: naphthalene, 4,4′-ditertbutylbiphenyl) as well as potassium naphthalenide resulted in a complex mixture of products. On the basis of ^{31}P NMR analysis we identified in this reaction mixture (comparison of the chemical shifts with authentic samples): chlorophosphates **1**, pyrophosphites **2**, phosphorous phosphoric anhydrides **3**, pyrophosphates **4**, H-phosphonates **5**, and phosphates **6** and **7** (Scheme 2).

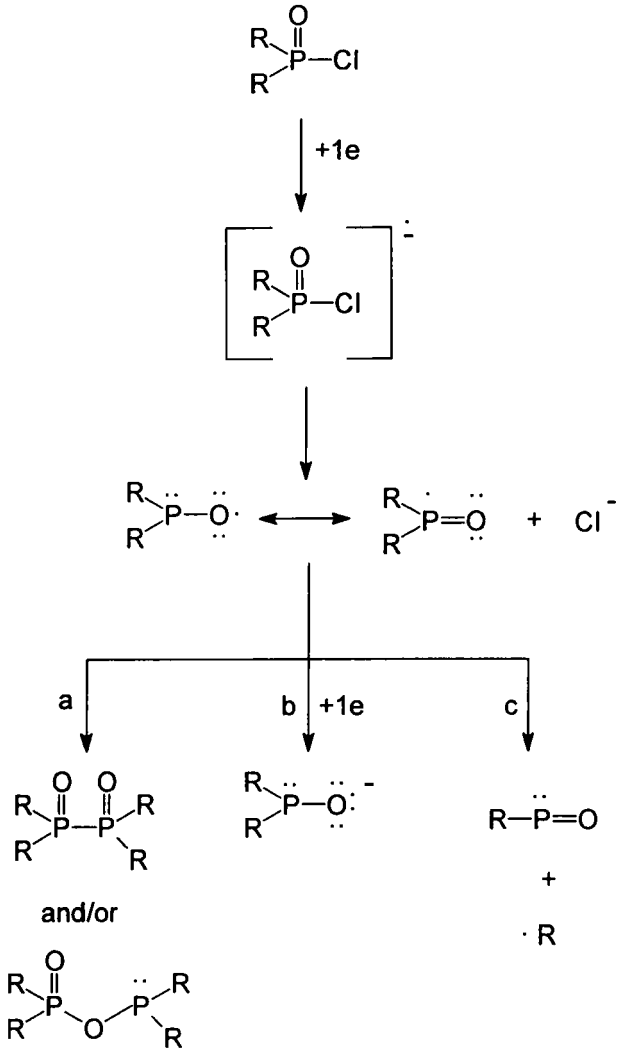


	1a	1b	2a	2b	3a	3b	4a	4b	5a	5b	6	7
R^1	Ph	CH_2 CMe_2 CH_2	Ph	CH_2 CMe_2 CH_2	Ph	CH_2 CMe_2 CH_2	Ph	CH_2 CMe_2 CH_2	Ph	CH_2 CMe_2 CH_2	Ph	CH_2 CMe_2 CH_2
R^2	Ph		Ph		Ph		Ph		Ph			

SCHEME 2

From the theoretical point of view the >P(O)Cl electrophile can accept an electron to form an anion radical, which should collapse into a phosphonyl radical and a chlorine anion. The phosphonyl radical, as a very reactive species, may, according to the substituents on the phosphorus and the reaction conditions: a) dimerize; b) subsequently accept an electron, being reduced to an >P-O$^-$ anion; c) undergo further fragmentation, (Scheme 3).

At this point it is worth to add that the reagents of the electrophilic, nucleophilic as well as radical character can exist in such a reaction mixture. Additionally P. Tordo[16] was able to demonstrate that diarylphosphonyl radical can be reduced into diarylphosphinite anion by the electron-rich olefin.



SCHEME 3

In this paper we would like to present the preliminary results of our experiments.

RESULTS AND DISCUSSION

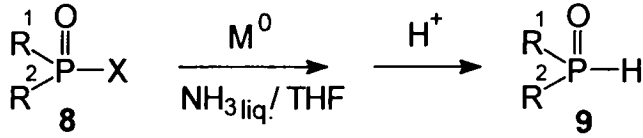
For our study we chose: dialkylchlorophosphates, 2-chloro-5,5-dimethyl-2-oxo-2λ^5-1,3,2-dioxaphosphinane, diphenylphosphinic acid chloride, t-butylphenylphosphinic acid chloride and isopropyl phenylchlorophosphonate as a phosphorus electrophilic reagents.

In order to compare the reactivity of the various >P(O)X (X = Cl, Br) **8** compounds we have performed the reactions under standardized conditions with alkali metal/NH_3 / THF solution at −78°C. One equv. of the >P(O)Cl type compound was added into the blue solution of two equv. of alkali metals (Li, Na, K) dissolved in the mixture of liquid NH_3: THF = 1:1. The blue color of the solution disappears in a few minutes after the addition of the last drop of phosphorus electrophile. The reaction was quenched by NH_4Cl, and after the removal of the solvents the products were isolated by radial chromatography (or distilled). These reactions were carried out under argon. The results of this set of experiments are presented in Scheme 4 and Table I.

TABLE I Reduction of the >P(O)X type compounds with alkali metals in liquid ammonia

Run	R^1	R^2	*X*	*M*	*Ratio M / >P(O)X*	*Isolated Yield %*	
						8	***9***
1	t-Bu	Ph	Cl	Li	2		70
2	t-Bu	Ph	Cl	Na	1	58	37
3	t-Bu	Ph	Cl	Na	2		70
4	t-Bu	Ph	Br	Na	2		96
5	t-Bu	Ph	Cl	K	2		80
6	EtO	EtO	Cl	Na	2		72
7	iPrO	iPrO	Cl	Na	2		84
8	$OCH_2C(CH_3)_2CH_2O$		Cl	Na	2		80

As one can see from the data collected in Table I all the used >P(O)X electrophiles were reduced with two equiv. of alkali metal into secondary phosphine oxide and dialkyl phosphite respectively. We do not find in the reaction mixture compounds with P-P bond (hypophosphonates or biphosphine dioxide). Potassium gives a somewhat higher yield of the reduction

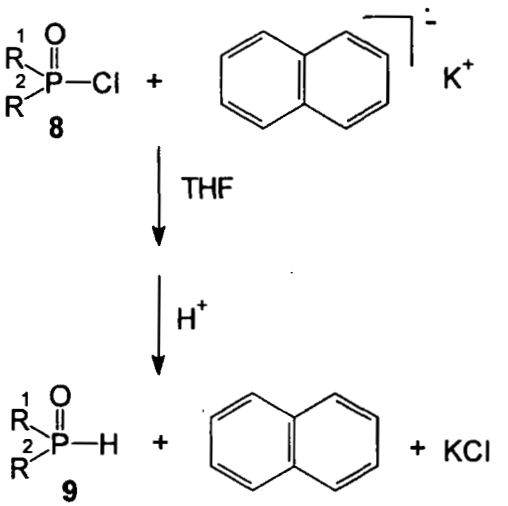


SCHEME 4

product than lithium and sodium (Table I, run 5 vs. 1 and 3), also in case of t-butylphenylphosphinic acid bromide we obtained the highest yield of the reduction product (Table I, run 4). The treatment of 1 equv. of t-butylphenylphosphinic acid chloride with 1 equiv. of sodium in NH_3/THF produced a low yield of phosphine oxide **9** (R^1= t-Bu, R^2= Ph), from this reaction mixture we isolated t-butylphenylphosphine oxide (37%) and starting material (58%). The starting material recovery from this reaction mixture strongly suggests, that the phosphonyl radical undergoes much faster a one electron reduction process (producing >P-O^- anion) than the >P(O)Cl electrophile.

We also performed reduction experiments with potassium naphthalenide in THF. In the standard procedure we added into the THF solution of potassium naphthalenide at −78°C the >P(O)Cl electrophile. The blue color of the solution disappears in one hour after the addition of the last drop of the phosphorus electrophile. The reaction was quenched at −78°C by $KHSO_4$ solution (or by methyl iodide in excess), and after the removal of the solvents the products were isolated by radial chromatography. These reactions were carried out under argon. The results of this set of experiments are presented in Scheme 5 and Table II.

As one can see from the data collected in Table II all the used >P(O)Cl electrophiles were reduced with two equiv. of potassium naphthalenide into secondary phosphine oxide, phenylphosphinite and dialkyl phosphite respectively. We do not find in the reaction mixture compounds with a P-P bond (hypophosphates or biphosphine dioxides). The treatment of 1 equv. of t-butylphenylphosphinic acid chloride with 1 equiv. of potassium naphtalenide (Table II, run 1) produced a low yield of phosphine oxide **9** (R^1= t-Bu, R^2= Ph), from this reaction mixture we isolated t-butylphenylphosphine oxide (44%) and starting material (45%). The starting material recovery from the reaction mixture of t-butylphenylphosphinic acid chlo-



SCHEME 5

ride and potassium naphthalenide (in the ratio 1:1) strongly suggests, that also under these conditions the phosphinyl radical undergoes a much faster one electron reduction process (producing >P-O$^-$ anion) than the >P(O)Cl electrophile.

TABLE II Reduction of the >P(O)Cl type compounds with potassium naphthalenide

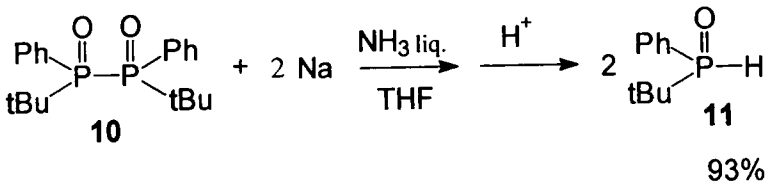
Run	R^1	R^2	*Ratio Nph$^-$ / >P(O)Cl*	*Isolated Yield %*	
				1	*2*
1	t-Bu	Ph	1	45	44
2	t-Bu	Ph	2	4	88
3	Ph	Ph	2		62
4	iPrO	Ph	2		93
5	EtO	EtO	2		94
6	iPrO	iPrO	2		59
7	$OCH_2C(CH_3)_2CH_2O$		2		68
8 2	PhO	PhO			62[a]

a. Isolated after quenching by CH_3I as a diphenyl methylphosphonate; futhermore from this reaction mixture 10% of triphenylphosphate was isolated.

The confrontation of the data collected in Table I and II shows that the reduction procedure of the >P(O)Cl electrophiles by potassium naphthalenide in THF is superior to the alkali metal / liquid ammonia procedure. In case of potassium naphthalenide as a reduction agent we got better yields of the isolated >P(O)H products, furthermore, produced in such a way, the >P-O$^-$ type anion solution can be used for other reactions (for instance Michaelis – Becker reaction).

Because in our first set of experiments (Scheme 2) we observed in the reaction mixture: pyrophosphonates **4**, pyrophosphites **2** as well as the phosphorous phosphoric anhydrides **3**; in the present work, reduction has been extended to this class of compounds.

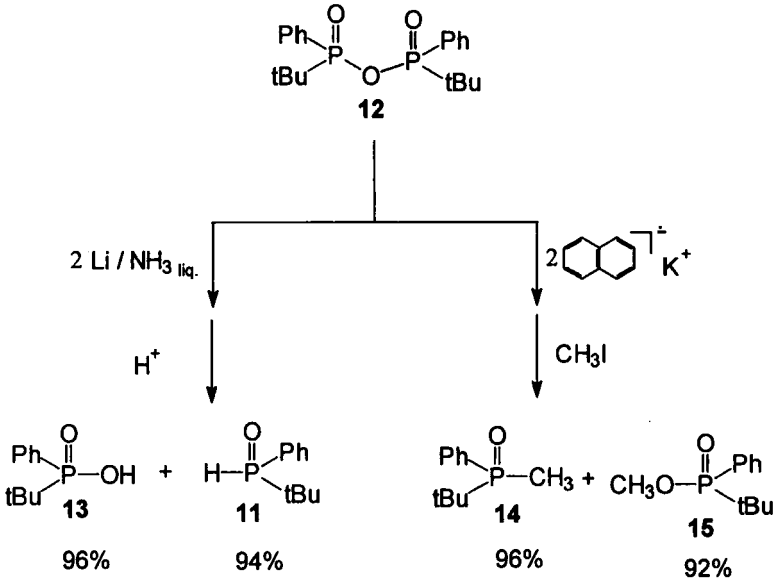
When 1,2-dit-butyl-1,2-diphenyldiphosphane 1,2-dioxide **10** was treated with two equiv. of sodium in NH_3 liq / THF at –78°C, after subsequent protonation, t-butylphenylphosphine oxide **11** was isolated in 93% yield (Scheme 6).



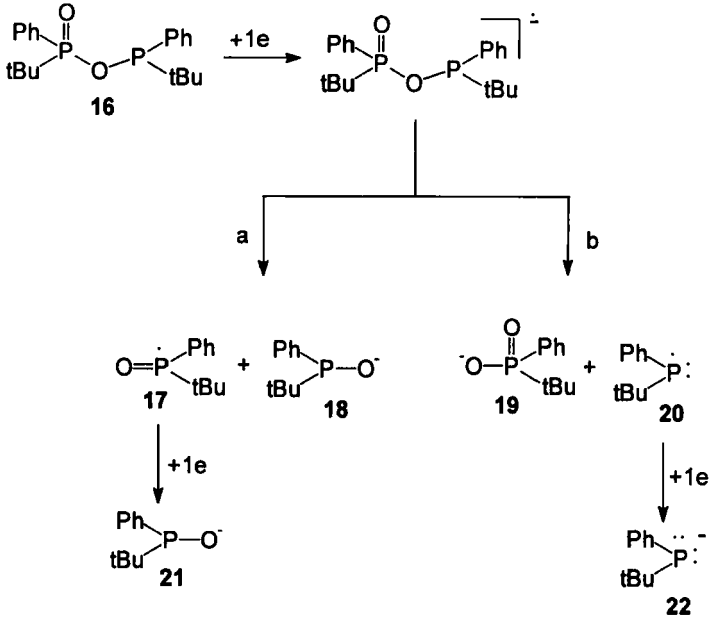
SCHEME 6

We also found that t-butylphenylphosphinic anhydride **12** easily undergoes reduction with lithium in NH_3 liq / THF as well as potassium naphthalenide in THF to produce after subsequent protonation, t-butylphenylphosphine oxide **11** and t-butylphenylphosphinic acid **13** or after the methylation t-butylmethylphenylphospine oxide **14** and methyl t-butylphenylphosphinate **15** respectively in quantitative yield (Scheme 7).

We also were interested in the behavior of the mixed anhydride namely bis[(t-butylphenyl)phosphino]phosphinic anhydride **16** toward potassium naphthalenide. From the theoretical point of view a radical anion derived from this mixed anhydride **16** can undergo dissociative cleavage in two possible ways (Scheme 8) to form: >P-O radical **17** and >P-O$^-$ anion **18** (pathway a) or phosphinic acid anion **19** and phosphino radical **20** (pathway b). Both phosphorus radicals can be reduced in the reaction mixture into suitable (appropriate) phosphinite **21** or phosphide **22** anions respectively.

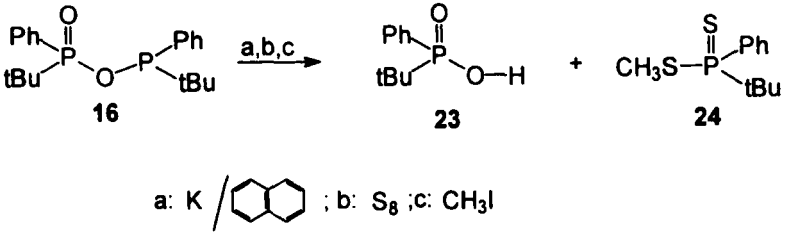


SCHEME 7



SCHEME 8

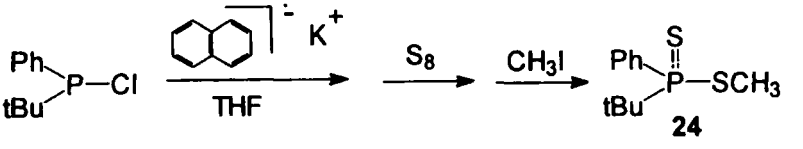
To distinguish between these two possibilities we treated bis[(t-butylphenyl)phosphino]phosphinic anhydride **16** with two eqiv of potassium naphthalenide in THF, then into this reaction mixture sulfur and methyl iodide was added subsequently. From this reaction mixture we isolated: methyl t-butylphenylphosphinate **23** and S-methyl t-butylphenyldithiophosphinate **24** (Scheme 9).



SCHEME 9

If in this reaction bis[(t-butylphenyl)phosphino]phosphinic anhydride were cleaved according to the pathway **a** we should isolate from the reaction mixture S-methyl t-butylphenylthiophosphinate; on the other hand if the cleavage follows the pathway **b** we should observe in the reaction mixture two esters namely: methyl t-butylphenylphosphinate and S-methyl tertbutylphenyldithiophosphinate.

In a separate experiment we treated t-butylphenylchlorophosphine with potassium naphthalenide and into this reaction mixture, sulfur and methyl iodide was added subsequently. We isolated from this reaction mixture S-methyl t-butylphenyldithiophosphinate (Scheme 10).



SCHEME 10

The results of this experiment shows that potassium t-butylphenylphosphide adds sulfur in THF to yield potassium t-butylphenylthiophosphinate.

By considering all the above pieces of evidence one can find that bis[(t-butylphenyl)phosphino]phosphinic anhydride is reduced by potassium naphthalenide with the cleavage of P(III) – oxygen bond (Scheme 8, pathway b).

EXPERIMENTAL

Dialkyl phosphites were purchased from Aldrich and distilled before use. Tetrahydrofuran and toluene were dried with sodium-potassium alloy. Isopropanol was dried with calcium hydride. Melting points were uncorrected. ^{31}P NMR and ^{1}H NMR spectra were recorded with a Varian apparatus at 60, 200 or 500 MHz.

Potassium naphthalenide was prepared from K and naphthalene in dry THF under argon and protection from oxygen before its use.

Reactions of chlorophosphates with potassium in THF

Into the suspension of potassium sand (0.390 g, 10 mmol) in 25 mL of THF 10 mMol of chlorophosphate (diphenylchlorophosphate, 2-chloro-5,5-dimethyl-(1,3,2)-dioxaphosphinane 2-oxide) in 5 mL of THF were added. The reaction mixture was stirred at room temperature overnight.

The above experiment was repeated in the presence of 1 and 10 mmol of naphthalene and 4,4′-di-t-butylbiphenyl. Progress of the reaction was followed by ^{31}P NMR. The results are presented in Scheme 2.

The reference compounds **1** – **7**, which have been used for the identification of some of the reaction products, were produced as follows. Diphenyl chlorophosphate **1a** was produced from $POCl_3$ and phenol[17], [^{31}P NMR ($CDCl_3$) $\delta = -5.4$ ppm];

2-chloro-5,5-dimethyl-(1,3,2)-dioxaphosphinane 2-oxide **1b**, was produced from $POCl_3$ and 2,2-dimethyl-1,3-propandiol[18], [^{31}P NMR ($CDCl_3$) $\delta = -4.15$ ppm]; tetraphenyl pyrophosphite **2a**[19], [^{31}P NMR (THF / C_6D_6) $\delta = 124.9$ ppm];

5,5,5′,5′-tetramethyl-2,2′-oxy-bis-(1,3,2)-dioxaphosphinane **2b**[20], [^{31}P NMR (THF/C_6D_6) $\delta = 110.2$ ppm]; 5,5,5′,5′-tetramethyl-2,2′-oxy-bis-(1,3,2)-dioxaphosphinane 2-oxide **3b**[21], [^{31}P NMR (C_6H_6/C_6D_6) $\delta_1 = 109.5$ ppm, $J_{POP} = 25$ Hz, $\delta_2 = -17.14$ ppm, $J_{POP} = 25$ Hz]; tetraphenyl pyrophosphate **4a**[17], [^{31}P NMR ($CDCl_3$) $\delta = -24,6$ ppm];

5,5,5′,5′-tetramethyl-2,2′-oxy-bis-(1,3,2)-dioxaphosphinane 2,2′-dioxide **4b**[22], [^{31}P NMR ($CDCl_3$) $\delta = -20,7$ ppm]; diphenylphosphite **5a** [^{31}P NMR ($CDCl_3$) $\delta = 0.88$ ppm]; 5,5-dimethyl-1,3,2-dioxaphosphinane-2-oxide **5b**[23], [^{31}P NMR ($CDCl_3$) $\delta = 3.45$ ppm]; triphenylphosphate **6** [^{31}P NMR ($CDCl_3$) $\delta = -16,9$ ppm]; **7** [^{31}P NMR (THF/C_6D_6) $\delta = -7,9$ ppm] was prepared from 2-chloro-5,5-dimethyl-(1,3,2)-dioxaphosphinane-2-oxide and 2,2-dimethyl-1,3-propanediol.

The reduction of >P(O)X (X = Cl, Br) compounds with NH_3 liq. / THF alkali metals solution. General procedure

Alkali metal was added into the mixture composed from liquid ammonia (25 mL) and THF (25 mL). The reaction mixture was stirred up to the complete dissolution of metal, than cooled to -78°C and 5 mmol of the chlorophosphorus compound (t-butylphenylphosphinic acid chloride, izopropyl phenylchlorophosphonate, diethyl chlorophosphate, diisopropyl chlorophosphate, 2-chloro-5,5-dimethyl-(1,3,2)-dioxaphosphinane 2-oxide) in 5 mL of THF were added. The reaction mixture was stirred at –78°C for 30 minutes, than 1.5 g of NH_4Cl were added and the ammonia was evaporated at 10 mm Hg. The residue was poured into the mixture of toluene and $KHSO_4$ solution. The water layer was extracted with toluene and the combined organic phase was dried over $MgSO_4$. The solvent was removed in vacuum and the products were separated by radial chromatography or distilled. The yields and conditions for the reactions carried out are summarized in Table I.

Run 1

t-butylphenylphosphine oxide (eluated with chloroform: metanol = 50:1), 0.643g (3.5 mmol, 70%), ^{1}H NMR ($CDCl_3$) $\delta = 1.13$ (d, $^2J_{P\text{-}H} = 15$ Hz, t-Bu, 9H), 6.70 (d, $J_{P\text{-}H} = 440$ Hz, PH, 1H), 6.83–7.67 (m, aromat, 5H); ^{31}P NMR ($CDCl_3$) $\delta = 46.0$ ppm.

Run 2

t-butylphenylphosphinic acid chloride, (eluated with chloroform), 1.255 g (5.8 mmol, 58%), ^{1}H NMR ($CDCl_3$) $\delta = 1.15$ (d, $^2J_{P\text{-}H} = 19$ Hz, t-Bu, 9H), 7.10–7.77 (m, aromat, 5H), ^{31}P NMR ($CDCl_3$) $\delta = 72.20$ ppm.

t-butylphenylphosphine oxide, (eluated with chloroform: metanol = 50:1), 0.673 g (3.7 mmol, 37%), ^{1}H NMR ($CDCl_3$) δ = 1.13 (d, $^2J_{P\text{-}H}$= 15 Hz, t-Bu, 9H), 6.70 (d, $J_{P\text{-}H}$ = 440 Hz, PH, 1H), 6.83–7.67 (m, aromat, 5H); ^{31}P NMR ($CDCl_3$) δ = 46.0 ppm.

Run 3

t-butylphenylphosphine oxide (eluated with chloroform: metanol = 50:1), 0.637g (3.5 mmol, 70%), ^{1}H NMR ($CDCl_3$) δ = 1.13 (d, $^2J_{P\text{-}H}$ = 15 Hz, t-Bu, 9H), 6.70 (d, $J_{P\text{-}H}$ = 440 Hz, PH, 1H), 6.83–7.67 (m, aromat, 5H); ^{31}P NMR ($CDCl_3$) δ = 46.0 ppm.

Run 4

t-butylphenylphosphine oxide (eluated with chloroform: metanol = 50:1), 0.883g (4.8 mmol, 96%), ^{1}H NMR ($CDCl_3$) δ = 1.13 (d, $^2J_{P\text{-}H}$ = 15 Hz, t-Bu, 9H), 6.70 (d, $J_{P\text{-}H}$ = 440 Hz, PH, 1H), 6.83–7.67 (m, aromat, 5H); ^{31}P NMR ($CDCl_3$) δ = 46.0 ppm.

Run 5

t-butylphenylphosphine oxide (eluated with chloroform: metanol = 50:1), 0.728g (4.0 mmol, 80%), ^{1}H NMR ($CDCl_3$) δ = 1.13 (d, $^2J_{P\text{-}H}$ = 15 Hz, t-Bu, 9H), 6.70 (d, $J_{P\text{-}H}$ = 440 Hz, PH, 1H), 6.83–7.67 (m, aromat, 5H); ^{31}P NMR ($CDCl_3$) δ = 46.0 ppm.

Run 6

diethyl phosphite (kugelrohr bp. 87°C/20 mm Hg), 0.494g (3.6 mmol, 72%), ^{1}H NMR ($CDCl_3$) δ = 1.27 (t, $^2J_{H\text{-}H}$= 7 Hz, $^3J_{P\text{-}H}$ =2 Hz, CH_3, 6H), 3.9 (dq, $^2J_{H\text{-}H}$ = 7 Hz, $^3J_{P\text{-}H}$= 2 Hz, CH_2, 4H), 6.68 (d, $J_{P\text{-}H}$ = 690 Hz, PH, 1H); ^{31}P NMR ($CDCl_3$) δ = 8.39 ppm.

Run 7

diisopropyl phosphite (kugelrohr bp. 86°C/17 mm Hg), 0.701g (4.2 mmol, 84%), ^{1}H NMR ($CDCl_3$) δ = 1.33 (d, $^2J_{H\text{-}H}$ = 7 Hz, CH_3, 12H), 4.17–4.77 (m, CH, 2H), 6,46 (d, $J_{P\text{-}H}$ = 656 Hz, PH, 1H); ^{31}P NMR ($CDCl_3$) δ = 5.47 ppm.

Run 8

5,5-dimethyl-(1,3,2)-dioxaphosphinane 2-oxide (eluated with diethyl ether), 0.606 g (4.0 mmol, 80%), ^{1}H NMR ($CDCl_3$) δ = 0.96 (s, CH_3, 3H), 1.28 (s, CH_3, 3H), 2.83–2.93 (m, CH_2, 4H), 6.43 (d, J_{P-H} = 660 Hz, PH, 1H); ^{31}P NMR ($CDCl_3$) δ = 3.5 ppm.

The reduction of > P(O)Cl compounds with potassium naphthalenide in THF

General procedure

Into the fresh prepared potassium naphthalenide in 25 mL of THF at –78°C, 5 mmol of chlorophosphorus compound (t-butylphenylphosphinic acid chloride, isopropyl phenylchlorophosphonate, diethyl chlorophosphate, diisopropyl chlorophosphate, diphenyl chlorophosphate, 2-chloro-5,5-dimethyl-(1,3,2)-dioxaphosphinane-2-oxide) in 5 mL of THF were added. The reaction mixture was stirred up to the disappearance of the blue color (Table II runs 1–3, 30 min.; run 4–7, 60 min.; run 8, 15 min.) then partitioned (toluene: $KHSO_4$ solution = 60: 1). The aqueous layer was extracted with toluene and the combined organic phase was dried ($MgSO_4$). The solvent was removed in vacuum and the products were separated by radial chromatography. Naphthalene was eluated with hexane, the reduction products with $CHCl_3$: MeOH = 50:1 (runs 1 – 3) or ether (runs 4 – 8).

The yields and conditions for the reactions carried out are summarized in Table II.

Run 1

naphthalen 1.293g (10 mmol, 92%), t-butylphenylphosphinic acid chloride 0.951 g (4.4 mmol, 44%), ^{1}H NMR ($CDCl_3$) δ = 1.15 (d, $^2J_{P-H}$= 19 Hz, t-Bu, 9H), 7.10–7.77 (m, aromat, 5H); ^{31}P NMR ($CDCl_3$) δ = 72.20 ppm t-butylphenylphosphine oxide 0.811 g (4.5 mmol, 45 %), ^{1}H NMR ($CDCl_3$) δ = 1.13 (d, $^2J_{P-H}$ = 15 Hz, t-Bu, 9H), 6.70 (d, J_{P-H} = 440 Hz, PH, 1H), 6.83–7.67 (m, aromat, 5H); ^{31}P NMR ($CDCl_3$) δ = 46.0 ppm.

Run 2

naphthalen 1.293g (10 mmol, 92%), t-butylphenylphosphinic acid chloride 0.037 g (0.2 mmol, 4%), ^{1}H NMR ($CDCl_3$) δ = 1.15 (d, $^2J_{P-H}$= 19 Hz,

t-Bu, 9H), 7.10–7.77 (m, aromat, 5H); ^{31}P NMR ($CDCl_3$) δ = 72.20 ppm, t-butylphenylphosphine oxide 0.800 g (4.4 mmol, 88%), ^{1}H NMR ($CDCl_3$) δ = 1.13 (d, $^2J_{P\text{-}H}$ = 15 Hz, t-Bu, 9H), 6.70 (d, $J_{P\text{-}H}$ = 440 Hz, PH, 1H), 6.83–7.67 (m, aromat, 5H); ^{31}P NMR ($CDCl_3$) δ = 46.0 ppm.

Run 3

naphthalen 1.214g (9.5 mmol, 86%), diphenylphosphine oxide 0.626 g (3.1 mmol, 88%), ^{1}H NMR ($CDCl_3$) δ = 6.57–7.57 (m, aromat, 10 H), 7.83 (d, $J_{P\text{-}H}$ = 480 Hz, PH, 1H); ^{31}P NMR ($CDCl_3$) δ = 22.6 ppm.

Run 4

naphthalen 1.258 g (9.8 mmol, 89%), isopropyl phenylphosphinate 0.852 g (4.6 mmol, 93%), ^{1}H NMR ($CDCl_3$) δ = 1.20 (d, $J_{H\text{-}H}$ = 6 Hz, CH_3, 3H), 1.27 (d, $J_{H\text{-}H}$ = 6 Hz, CH_3, 3H), 4.17–4.70 (m, CH, 1 H), 6.87–7.60 (m, aromat, 5 H), 7.16 (d, $J_{P\text{-}H}$ = 559 Hz, PH, 1H); ^{31}P NMR ($CDCl_3$) δ = 23.3 ppm.

Run 5

naphthalen 1.249 g (9.8 mmol, 89%), diethylphosphite 0.639 g (4.7 mmol, 94%), ^{1}H NMR ($CDCl_3$) δ = 1.27 (t, $^2J_{H\text{-}H}$= 7 Hz, $^3J_{P\text{-}H}$ = 2 Hz, CH_3, 6H), 3.9 (dq, $^2J_{H\text{-}H}$ = 7 Hz, $^3J_{P\text{-}H}$ = 2 Hz, CH_2, 4H), 6.68 (d, $J_{P\text{-}H}$ = 690 Hz, PH, 1H); ^{31}P NMR ($CDCl_3$) δ = 8.39 ppm.

Run 6

naphthalen 1.350 g (10.5 mmol, 96%), diisopropylphosphite 0.494g (2.9 mmol, 59%), ^{1}H NMR ($CDCl_3$) δ = 1.33 (d, $^2J_{H\text{-}H}$ = 7 Hz, CH_3, 12H), 4.17–4.77 (m, CH, 2H), 6,46 (d, $J_{P\text{-}H}$= 656 Hz, PH, 1H); ^{31}P NMR ($CDCl_3$) δ = 5.47 ppm.

Run 7

naphthalen 1.350 g (10.5 mmol, 96%), 5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide 0.502 g, (3.4 mmol, 68%), ^{1}H NMR ($CDCl_3$) δ = 0.96 (s, CH_3, 3H), 1.28 (s, CH_3, 3H), 3.00 – 4.00 (m, CH_2, CH_2, 4 H), 6.43 (d, $J_{P\text{-}H}$ = 660 Hz, PH, 1H); ^{31}P NMR ($CDCl_3$) δ = 3.5 ppm.

Run 8

naphthalen 1.350 g (10.5 mmol, 96%), triphenylphosphate 0.164 (0.5 mmol, 10%), ^{1}H NMR ($CDCl_3$) $\delta = 6.67 - 7.20$ (m, 15H); ^{31}P NMR ($CDCl_3$) $\delta = -16.26$ ppm diphenyl methylphosphonate 0.772 g (3.1 mmol, 62%), ^{1}H NMR ($CDCl_3$) $\delta = 1.58$ (d, $^2J_{P\text{-}H} = 18$ Hz, CH_3, 3H), 6.33–7.10 (m, aromat, 10H); ^{31}P NMR ($CDCl_3$) $\delta = 25.27$ ppm.

Reduction of 1,2-di-t-butyl-1,2-diphenyldiphosphane 1,2-dioxide with sodium in NH_3 liq / THF solution

Sodium (0.092 g, 4mMol) was dissolved in the mixture composed from liquid ammonia (25 mL) and THF (25 mL). This solution was cooled up to –78°C and 1,2-di-t-butyl-1,2-diphenyldiphosphane 1,2-dioxide (0.731 g, 2 mmol) in 9 mL of THF was added. The reaction mixture was stirred at –78°C for 15 minutes, then 1,5g NH_4Cl were added and poured into the mixture of toluene and $KHSO_4$ solution. The aqueous layer was extracted with toluene and the combined organic phase was dried over $MgSO_4$. The solvent was removed in vacuum and the product was separated by radial chromatography using $CHCl_3$:MeOH = 50:1 as an eluent system to yield 0.683 g (93%) of t-butylphenylphosphine oxide, ^{1}H NMR ($CDCl_3$) $\delta = 1.13$ (d, $^2J_{P\text{-}H} = 15$ Hz, t-Bu, 9H), 6.70 (d, $J_{P\text{-}H} = 440$ Hz, PH, 1H), 6.83–7.67 (m, aromat, 5 H); ^{31}P NMR ($CDCl_3$) $\delta = 46.0$ ppm.

Reduction of t-butylphenylphosphinic anhydride 12 with lithium in NH_3liq. / THF solution

Lithium (0.041 g, 5.7 mmol) was dissolved in the mixture composed from liquid ammonia (25 mL) and THF (25 mL). This solution was cooled up to –78°C and t-butylphenylphosphinic anhydride (diastereoisomer mixture) **12** (1.072 g, 2.8 mmol) in 20 mL of THF was added. The blue color of the solution changed into yellow in 30 minutes after the addition of the last drop of anhydride, than the reaction mixture was quenched with NH_4Cl (1.5 g, 28 mmol). Ammonia was removed under reduced pressure and the residue was poured in to the mixture of toluene and $KHSO_4$ solution. The aqueous layer was extracted with toluene and the combined organic phase was dried over $MgSO_4$. The solvent was removed in vacuum and the residue was dissolved in toluene, then extracted with K_2CO_3solution. The

aqueous layer was acidified with hydrochloric acid to yield 0.531g (96 %) of t-butylphenylphosphinic acid, m.p. 157°C; ^{1}H NMR ($CDCl_3$) δ = 0.93 (d, $^2J_{P-H}$ = 15 Hz, t-But, 9 H), 6.93 – 7.57 (m, aromat, 5 H), 11.0 (s, OH, 1 H); ^{31}P NMR ($CDCl_3$) δ = 52.0 ppm.

The toluene layer was dried over $MgSO_4$ and after removal of the solvent, the residue was separated on radial chromatography (chloroform: metanol = 50:1) to give 0.483 g (94%) of t-butylphenylphosphine oxide; ^{1}H NMR ($CDCl_3$) δ = 1.13 (d, $^2J_{P-H}$ = 15 Hz, t-Bu, 9 H), 6.70 (d, J_{P-H} = 440 Hz, PH, 1 H), 6.83–7.67 (m, aromat, 5 H); ^{31}P NMR ($CDCl_3$) δ = 46.0 ppm.

Reduction of t-butylphenylphosphinic anhydride 12 with potassium naphthalenide in THF

Into the fresh prepared potassium naphthalenide (from 0.390 g of K and 1.41g of naphthalene) in 50 mL of THF and cooled up to – 78°C t-butylphenylphosphinic anhydride **12** (diastereoisomers mixture) (1.892 g, 5.0 mmol) in 25 mL of THF was added. The reaction mixture was stirred for 1.5 hours at –78°C. Then methyl iodide (4 mL, 9.12 g, 64 mmol) was added and the mixture was stirred for 2 days. The reaction mixture was evaporated. The residue poured into the mixture of CH_2Cl_2 and $KHSO_4$ solution. The organic layer was dried over $MgSO_4$, the solvent was removed in vacuum and the products were separated by radial chromatography. The following compounds were obtained:

naphtalene 1.275 g (90%) methyl tertbutylphenylphosphinate 0.974 g (92%); ^{1}H NMR ($CDCl_3$) δ =1.00 (d, $^2J_{P-H}$ = 15 Hz, t-Bu, 9H), 3.40 (d, $^3J_{P-H}$ = 10 Hz, CH_3, 3H), 6.83–7.50 (m, aromat, 5 H); ^{31}P NMR ($CDCl_3$) δ = 54.04 ppm t-butylphenylmethylphosphine oxide 0.951g (96%), ^{1}H NMR ($CDCl_3$) δ = 1.03 (d, $^2J_{P-H}$ = 14 Hz, t-Bu, 9H), 1.58 (d, $^2J_{P-H}$ = 11 Hz, CH_3, 3H), 6.83–7.67 (m, aromat, 5 H); ^{31}P NMR ($CDCl_3$) δ = 48.52 ppm.

Reduction of bis[(t-butylphenyl)phosphino]phosphinic anhydride 16 with potassium naphthalenide in THF

Into the fresh prepared potassium naphthalenide (from 0.390 g of K and 1.41g of naphthalene) in 25 mL of THF and cooled up to – 78°C bis[(t-butylphenyl)phosphino]phosphinic anhydride **16** (1.811 g,

5.0 mmol) in 25 mL of THF was added. The reaction mixture was stirred for 2 hours at -78°C. A sample of the reaction mixture was taken off and after addition of $KHSO_4$, crown ether (18-Crown-6) and C_6D_6 ^{31}P NMR spectra were recorded. The ^{31}P NMR spectra of the crude reaction mixture showed two major resonance lines responsible for two phosphorus products in this reaction: t-butylphenylphosphinic acid anion ($\delta = 36.36$) and t-butylphenylphosphine ($\delta = -4.9$).

Next, sulfur (0.643 g, 20 mmol) in 25 mL of THF was added into the reaction mixture and the cool bath was removed. The solution was stirred for a further 14 hours, then methyl iodide (4 mL, 9.121 g, 64 mmol) was added and the mixture was stirred for 2 hours. The reaction mixture was evaporated. The residue was dissolved in toluene and extracted with K_2CO_3 solution. The aqueous layer was acidified with hydrochloric acid to give 0.777g (3.93 mmol, 79 %) of t-butylphenylphosphinic acid. The toluene layer was dried over $MgSO_4$, the solvent was removed in vacuum and the products were separated by radial chromatography. The following compounds were obtained:

naphtalene 1.318 g (94%);

S-methyl t-butylphenyldithiophosphinate 0.917 g (75 %), m.p. 72–75°C, ^1H NMR ($CDCl_3$) $\delta = 1.13$ (d, $^2J_{P\text{-}H} = 17$ Hz, t-Bu, 9 H), 2.03 (d, $^3J_{P\text{-}H} = 12$ Hz, CH_3, 3 H), 6.80–7.93 (m, aromat, 5 H); ^{31}P NMR ($CDCl_3$) $\delta = 95.95$ ppm methyl t-butylphenylphosphinate 0.052 g (5%), ^1H NMR ($CDCl_3$) $\delta = 1.00$ (d, $^2J_{P\text{-}H} = 15$ Hz, t-Bu, 9 H), 3.40 (d, $^3J_{P\text{-}H} = 10$ Hz, CH_3, 3 H), 6.83–7.50 (m, aromat, 5 H); ^{31}P NMR ($CDCl_3$) $\delta = 54.04$ ppm.

Thionation of potassium t-butylphenylphosphide

Into the fresh prepared potassium naphthalenide (from 0.392 g of K and 1.411g of naphthalene) in 25 mL of THF and cooled up to – 78°C t-butylphenylchlorophosphine (1.00 g, 5.0 mmol) was added. The reaction mixture was stirred for 2 hours at –78°C then sulfur (0.482 g, 20 mmol) in 25 mL of THF was added, the cool bath was removed and the mixture stirred for a further 14 hours. Next, methyl iodide (4 mL, 9.121 g, 64 mmol) was added and the mixture was stirred for 2 hours. The reaction mixture was evaporated and the products were separated by radial chromatography to give:

naphtalene (eluated with hexane) 1.210 g (9.4 mmol, 86%);

methyl t-butylphenyldithiophosphinate (eluated with hexane: chloroform =1:1) 0.754g (3.1 mmol, 62%), m.p. 72–75°C, ^{1}H NMR ($CDCl_3$) δ =1.13 (d, $^2J_{P-H}$ = 17 Hz, t-Bu, 9 H), 2.03 (d, $^3J_{P-H}$ = 12 Hz, CH_3, 3 H), 6.80–7.93 (m, aromat, 5 H); ^{31}P NMR ($CDCl_3$) δ = 95.95 ppm.

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