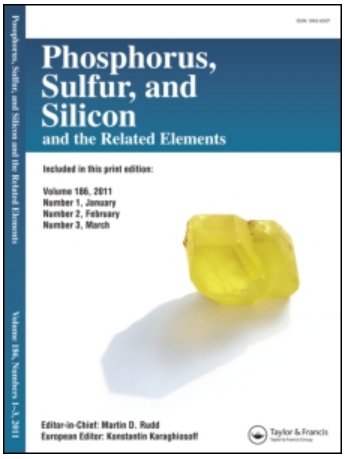


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

PREPARATION OF PRIMARY AND SECONDARY ALKYL PHOSPHINES FROM ELEMENTAL PHOSPHORUS OR PHOSPHORUS TRICHLORIDE IN ORGANIC SOLVENTS

M. C. J. M. Van Hooijdonk[a]; G. Gerritsen[a]; L. Brandsma[a]
[a] Department of Preparative Organic Chemistry, Utrecht, Netherlands

To cite this Article Van Hooijdonk, M. C. J. M. , Gerritsen, G. and Brandsma, L.(2000) 'PREPARATION OF PRIMARY AND SECONDARY ALKYL PHOSPHINES FROM ELEMENTAL PHOSPHORUS OR PHOSPHORUS TRICHLORIDE IN ORGANIC SOLVENTS', Phosphorus, Sulfur, and Silicon and the Related Elements, 162: 1, 39 — 49
To link to this Article: DOI: 10.1080/10426500008045218
URL: http://dx.doi.org/10.1080/10426500008045218

Phosphorus, Sulfur and Silicon, 2000, Vol. 162, pp. 39-49
Reprints available directly from the publisher
Photocopying permitted by license only

PREPARATION OF PRIMARY AND SECONDARY ALKYL PHOSPHINES FROM ELEMENTAL PHOSPHORUS OR PHOSPHORUS TRICHLORIDE IN ORGANIC SOLVENTS

M.C.J.M. VAN HOOIJDONK, G. GERRITSEN and L. BRANDSMA*

Department of Preparative Organic Chemistry, Padualaan 8, 3584-CH Utrecht, Netherlands

(Received February 01, 2000)

A number of volatile and non-volatile primary and secondary alkyl phosphines have been prepared by one-pot procedures from elemental phosphorus or from phosphorus trichloride. The element or chloride was first converted into trisodium phosphide by reaction with sodium in the presence of naphthalene or another solubilisation reagent. Subsequent addition of two equivalents of *t*-butyl alcohol and an alkyl halide gave monoalkyl phosphines in fair to good yields. *In situ* conversion of the primary phosphine into a dialkyl phosphine was achieved by metallation with BuLi or sodium and subsequent alkylation.

Keywords: naphthalene-sodium; phenanthrene-sodium; trisodium phosphide; monosodium phosphide

INTRODUCTION

Monoalkyl phosphines have been obtained by deprotonation of phosphane PH_3 with a strongly basic reagent and subsequent alkylation. If the base is present in excess, secondary or tertiary phosphines may be formed by alternation of metallation and alkylation[1]. Phosphane is not cheaply available, but it can be generated from elemental phosphorus and aqueous alkali. However, its low boiling point (-88°C) and low solubility in the various solvents make it difficult to determine the required amount for some synthesis. There are some indirect methods for primary and second-

* Corresponding Author.
Dedicated to Prof Dr H. Gunther (University of Siegen) on the occasion of his 65th Birthday in July 2000.

ary phosphines in which a mono- or dichlorophosphine is synthesised and subsequently converted into the desired phosphine by reduction with lithium alanate, sodium tetrahydroborate or sodium[2]. Unfortunately, only a few mono- and dichlorophosphines are readily available by reaction of $PCl_3$with Grignard reagents[3]. Recently, our group showed that alkali metal phosphides MPH_2 can be generated by *t*-butyl alcohol-assisted fission of the P-P bonds in elemental phosphorus with alkali metals in liquid ammonia[4]. This finding led to the development of efficient procedures for of a number of primary and secondary phosphines. However, liquid ammonia is thought to be less attractive as a solvent because more elaborate equipment is required and more advanced manipulative techniques are involved than for working in the usual organic solvents. Moreover, for the preparation of volatile phosphines in liquid ammonia laborious absorption techniques have to be applied to avoid losses due to evaporation along with the ammonia[1a,5]. The preparation of trialkali metal phosphides in organic solvents from elemental phosphorus and alkali metals has been reported[6]. The best results were obtained with the system sodium-naphthalene in tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) using ordinary mixing techniques and apparatus:[6g]

$$P + 3\,Na \xrightarrow[\text{Naphthalene}]{\text{THF or DME}} Na_3P$$

The resulting trisodium phosphide has been used for the preparation of phosphonium halides $R_4P^+X^-$ and for the tertiary phosphines $P(COOR)_3$ $P(SiMe_3)_3$.[6h,i]

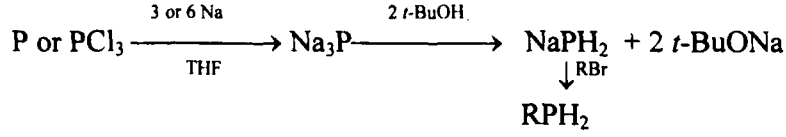
We felt that, with some adaptations, the naphthalene-assisted reaction between phosphorus and alkali metal could serve as a basis for developing preparative procedures for a number of primary and secondary phosphines.

RESULTS AND DISCUSSION

A. Preparation of non-volatile phosphines

In order to prepare alkyl phosphines with b.p. >125°C at atmospheric presssure we chose THF as the solvent; in one case DME was used. White

or red phosphorus was first stirred at about 50°C with three equivalents of sodium in the presence of a certain amount of naphthalene, which serves to solubilise the metal. As expected from its better solubility in THF, white phosphorus reacted much faster than did the red modification. In a few cases phenanthrene was used. The use of this compound is recommended if the b.p. of the phosphine to be prepared and that of naphthalene are comparable. Phosphorus trichloride proved to be a relatively convenient source of phosphorus. In order to generate monosodium phosphide, two mol equivalents of *t*-butyl alcohol were added dropwise to the suspension, which was supposed to contain Na_3P:



$$P \text{ or } PCl_3 \xrightarrow[THF]{3 \text{ or } 6\ Na} Na_3P \xrightarrow{2\ t\text{-BuOH}} NaPH_2 + 2\ t\text{-BuONa}$$

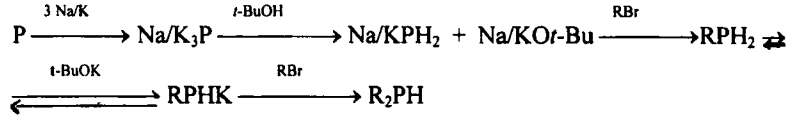
$$NaPH_2 \xrightarrow{RBr} RPH_2$$

A number of primary phosphines were prepared with fair to good yields by addition of alkyl halides to the reaction mixtures obtained by protonation with *t*-butyl alcohol.

The reason for preferring this alcohol as a proton donor to primary alcohols such as methanol is the much better solubility of sodium *t*-butoxide in THF giving a better possibility for complete conversion of Na_3P. Protonation with more acidic reagents may lead to irreversible formation of PH_3 which can escape from the reaction mixture so that less $NaPH_2$ will be available for the subsequent alkylation. In one experiment with methanol as proton donor we observed evolution of gas, possibly PH_3, from the reaction mixture. The product obtained from subsequent alkylation with heptyl bromide was contaminated with ca. 10% of this halide, although a short measure of this had been used.

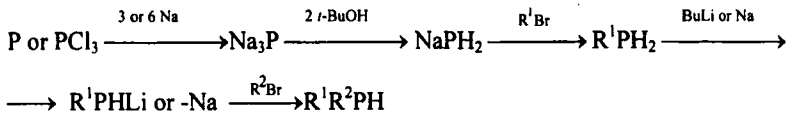
Another method of preparing trialkali phosphide consists of heating white phosphorus with the liquid alloy of sodium and potassium in DME[2a,b]. In this method no naphthalene is used, which makes the purification of the phosphorus compounds formed in subsequent reactions much easier. However, reaction with *t*-butyl alcohol not only affords the sodium, but also the *potassium* alkoxide. Interaction between primary phosphines and *t*-BuOK will give rise to significant equilibrium concentrations of the potassium phosphide, which with alkyl halides affords secondary phosphines[7]. With *sodium t*-butoxide the concentration of phosphide

RPHNa in the equilibrium is extremely small (for the influence of the alkali metal ion on the position of a deprotonation equilibrium see ref. 8).



In accordance with the expectation appreciable amounts of dialkyl phosphines were found after alkylation.

The absence of dialkyl phosphines when applying the Na/naphthalene/*t*-BuOH method for generating $NaPH_2$ enabled us to develop the following one-pot synthesis of non-symmetrical secondary phosphines:



Thus, the primary phosphines prepared from reaction of elemental P or PCl_3 with sodium/naphthalene and subsequent alkylation with R^1Hal were *in situ* converted into secondary phosphines R^1R^2PH by metallation with sodium or BuLi followed by addition of another alkyl halide R^2Hal.

B. Preparation of volatile phosphines

The preparation of most of the volatile (b.p. <110°C at atmospheric pressure) was carried out in the high-boiling ether $C_2H_5OCH_2CH_2OCH_2CH_2OC_2H_5$ from which the phosphines could be isolated by simple distillation *in vacuo* and condensation in strongly cooled receivers. The conditions for the generation of trisodium phosphide from elemental phosphorus or from phosphorus trichloride were similar to those applied for the preparation of less volatile phosphines. The BuLi used for the metallation of the *in situ* prepared primary phosphines was added as a solution in dodecane (obtained by evaporation of the hexane under reduced pressure from a BuLi solution and subsequently adding dodecane). In one case (diethyl phosphine) the preparation of the phos-

phine was carried out in DME, which in the work-up was removed by repeated washing with water.

EXPERIMENTAL

General information

^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded on a Bruker AC-300 spectrometer (^{1}H: 300 MHz, ^{13}C: 75 MHz, ^{31}P: 121.5 MHz) at 298°K, using $CDCl_3$ as a solvent and internal standard. In ^{1}H- and ^{13}C-NMR spectra, chemical shifts are given in ppm downfield from TMS, in ^{31}P-NMR spectra in ppm relative to 85% H_3PO_4 such that a downfield shift is positive. Coupling constants J are given in Herz. Gas liquid chromatography was performed on a Varian 3400 gas chromatograph using a capillary column (DB-0.5, 15 m). The solvents used for the syntheses were dried over machine-powdered KOH and, after filtration, distilled under nitrogen (THF, DME) or *in vacuo* (ethyleneglycol ether) from lithium alanate. The solvents were stored under nitrogen. The water used during the work-up was freed from dissolved oxygen by alternative evacuation and admission of nitrogen. White phosphorus was cut under water into 0.1–1.5 g pieces, which were dried by successive rinsing with acetone and diethyl ether. Red P was purified by successive treatment (for 10 min) with a hot (70°) 1 molar aqueous solution of potassium carbonate, filtration on G-3 sintered glass, rinsing with acetone (3 times) and diethyl ether (3 times). The solvents were removed under reduced pressure after which the powder was stored under nitrogen. All reactions and operations during the work-up were scrupulously carried out under nitrogen.

Temperatures are given in °C.

The purity of the characterised products was at least 95 % (by GC and NMR).

1. Preparation of monosodium phosphide in organic solvents

A. using elemental phosphorus

In a 500-ml round-bottomed, three-necked flask (vertical necks) was placed 180 ml of THF or DME or 150 ml of the glycol ether. The flask

was equipped with a mechanical stirrer and a combination of a nitrogen inlet and a thermometer. A vigorous flow (about 1 l/min) of nitrogen was introduced while 0.1 to 0.3-g pieces of sodium (freshly cut, 6.9 g, 0.30 mol) and 0.7 mmol of naphthalene or phenanthrene were successively introduced. The outlet was placed on the flask and stirring was started at a low rate (to avoid bumping caused by clustering of the sodium pieces). The flow of nitrogen was decreased to about 300 ml/min and after a few min the characteristic colour of the radical-anion appeared. A slurry of 3.1 g (0.10 mol) of red P and 10 ml of the solvent or 3.1 g of white P (cut into pieces of different size) was introduced (temporary removal of the outlet and increase of the flow of nitrogen). The flow of nitrogen was adjusted at 100 to 150 ml/min and maintained throughout the period of the reaction (any losses of volatile solvent due to evaporation were compensated for regularly).The mixture was brought at about 50°. After about 1 h (white P) or 4 h (red P) the greater part of the sodium had dissolved and a very dark suspension had formed. The rate of stirring could be gradually increased. After a further 4 h (white P) or 20 h (red P) the outlet was replaced with a dropping funnel containing a mixture of 14.8 g (0.20 mol) of dry (distilled from potassium) *t*-butyl alcohol and 20 ml of the solvent. The reaction mixture was cooled to −5° (temporary increase of the nitrogen flow) and the alcohol was added drop wise over 15 min to the efficiently stirred suspension. During this addition the temperature was maintained between −5 and −15°. After stirring for an additional 15 min, the flask was equipped for the reaction with alkyl halide.

B. Using phosphorus trichloride

In these experiments 0.60 mol (13.8 g) of sodium was used. After appearance of the dark colour freshly distilled PCl_3 (13.8 g, 0.10 mol) was added drop wise over a few min resulting in a weakly exothermic reaction. The mixture was then heated at 50° and the further operations were carried out as described above. The time required for complete conversion of the sodium varied from 4 to 10 h.

2. Preparation of non-volatile primary phosphines

After the addition of the *t*-butyl alcohol-THF mixture (exp. 1) the suspension was cooled to between −5 and −15° and the alkyl halide RHal (0.08 mol) or $Br(CH_2)_nBr$ (0.04 mol) was added in one portion causing the

temperature to rise to 25° or higher. After stirring for an additional 1 h at this temperature a solution of 20 g of ammonium chloride in 200 ml of water was slowly added with cooling and vigorous stirring. After separation of the layers, the aqueous phase was extracted twice with 75-ml portions of pentane. The combined organic solutions were washed at least 5 times with 100-ml portions of water in order to remove the greater part of THF and the *t*-butyl alcohol. After drying over magnesium sulfate, the greater part of the solvent was distilled off at normal pressure using a 20-cm Vigreux column or a Widmer column (in the case of cyclopentyl phosphine). The remaining liquids were distilled at atmospheric pressure (cyclopentyl phosphine) or *in vacuo*.

The following phosphines were prepared.

Cyclopentyl phosphine, b.p. 120° /760 mm Hg, in 45 % yield from red P, Na/naphthalene, *t*-BuOH and cyclopentyl chloride. The compound was isolated by careful distillation through a 30-cm Vigreux column.

^{31}P-NMR: $\delta = -118.5$.

$H_2P(CH_2)_4PH_2$, b.p. 75° /20 mm Hg, in 60% yield from white P, Na/naphthalene *t*-BuOH and $Br(CH_2)_4Br$.

^{1}H-NMR: $\delta = 1.4–1.7$ (m, 8H); 2.7 (broad signal, 4H); ^{13}C-NMR: $\delta = 13.3$ (d, J = 12.2), 33.7; ^{31}P-NMR: $\delta = -137.0$ (lit.[9] −138).

$H_2P(CH_2)_5PH_2$, b.p. 90° /27 mm Hg, in 40% yield from PCl_3, Na/naphthalene, *t*-BuOH and $Br(CH_2)_5Br$.

^{1}H-NMR: $\delta = 1.3–1.6$ (m); 2.3 (broad signal, 2H); 3.0 (broad signal, 2H); ^{13}C-NMR: $\delta = 13.6$ (d, 2C); 31.4 (t, 1C); 32.4 (d, 2C); ^{31}P-NMR: $\delta = -136.8$ (t, J = 191.0) (lit.[10] 136.5, J = − 191).

n-$C_{12}H_{25}PH_2$, b.p. 110° /2 mm Hg, in 56 % yield from red P, Na/phenanthrene, *t*-BuOH and dodecyl bromide.

^{1}H-NMR: $\delta = 0.9$ (t, 3H); 1.2 (m, 20H); 1.4 (m, 2H); ^{13}C-NMR; $\delta = 13.7$ (d, J = 7.2); 14.1; 20.8; 22.7; 29.2; 29.4; 29.6; 29.7 (two signals); 30.5 (d, J= 5.6); 31.9; 32.9 (d, J = 3.0); ^{31}P-NMR: $\delta = -136.9$ (t, J = 174.0) (lit.[11] −139.0)

3. Preparation of non-symmetrical secondary phosphines

Suspensions of $NaPH_2$ were prepared as described in procedures 1a and 1b using the amounts mentioned.The first alkyl bromide R^1Br (0.09 mol) was added in one portion at 0°. The light-coloured suspension was stirred for an additional 1 h or 2 h at 30° in the case of the primary alkyl bromide and

isopropyl bromide, respectively. The reaction mixture was then cooled to −60° and 56 ml (0.09 mol) of a 1.6 molar solution of BuLi in hexane was added over 2 min by syringe while keeping the temperature below −40°. The colour changed to orange-yellow. After the temperature had been allowed to rise to −5°, the second alkyl bromide R^2Br (0.09 mol) was added in one portion. After an additional 1h or 2h in the case of primary or secondary bromides, respectively, the product was isolated as described in exp. 1.

In one case sodium was used as metallation agent. After addition of the first alkyl bromide small pieces of sodium (2.1 g, 0.09 mol) were added and the mixture was stirred for 20 h at 50°. It was then cooled to 0° and the second alkyl halide (0.09 mol) was added in one portion. After stirring for an additional 1 h at 35°, the product was isolated as described in exp. 1.

The following phosphines were prepared.

$(i\text{-}C_3H_7)_2PH$, b.p. 120–25° /760 mm Hg, in 50% yield from white P, Na/naphthalene, $i\text{-}C_3H_7Br$, BuLi and $i\text{-}C_3H_7Br$.

^{1}H-NMR: δ = 0.9 (t, J = 7.0, 6H); 1.1 (dd, J = 7.0 and 13.3, 12H); 2.8 (broad signal, 1H); ^{13}C-NMR: δ = 20.1 (d, J = 7.7); 22.0 (d, J = 12.5); ^{31}P-NMR: δ =-15.4 (d, J = 197).

$n\text{-}C_6H_{13}PH\text{-}c$-pentyl, b.p. 90° /1.5 mm Hg, in 77% yield from white P, Na/phenanthrene, hexyl bromide, BuLi and *c*-pentyl bromide.

^{1}H-NMR: δ = 0.9 (t, J = 6.8, 3H); 1.1–1.4 (m, 8H); 1.9 (m, 2H); 2.1 (m, 1H); 2.7 and 3.4 (broad signal, 1H); ^{13}C-NMR: δ = 14.0; 20.2; (d, J = 8.4); 22.5; 26.2 (d, J = 6.2); 28.4 (d, J = 8.5); 30.7 (d, J = 12.9); 30.8; 31.5; 32.4 (d, J = 13.3); ^{31}P-NMR: δ = −50.8.

$n\text{-}C_6H_{13}PH\text{-}C_2H_5$, b.p. 85° /23 mm Hg, in 66% yield from red P, Na/phenanthrene, hexyl bromide, Na and ethyl bromide.

^{1}H-NMR: δ = 0.7–0.9(m, 3H); 0.9–1.2 (m, 3H); 1.2–1.6 (m, 12H); 3.0 (broad signal, 1H); ^{31}P-NMR: δ = −61.3.

4. Preparation of volatile primary phosphines

The primary phosphine RPH_2 was prepared in solution from red P (3.1 g, 0.10 mol), naphthalene (4.7 g, 37 mmol), sodium (6.9 g, 0.30 mol) and *t*-BuOH (14.8 g, 0.20 mol) as described in exp. 1 using diethyleneglycol diethyl ether as a solvent. The period of additional stirring (at 30°) was 2 h. The stirrer was then replaced with a 30-cm Vigreux column and stoppers were placed on the outer necks of the reaction flask. The column was con-

nected with a condenser and single receiver cooled in a bath with liquid nitrogen. The system was evacuated (water aspirator) and the reaction mixture heated. The distillation was stopped as soon as the solvent began to reflux in the upper part of the column. Nitrogen was then admitted and the contents of the receiver were subjected to the same operation.

The following products were prepared.

$C_2H_5PH_2$ (b.p. not determined), in 56 % yield from red P, Na/naphthalene, *t*-BuOH and ethyl bromide.

^{1}H-NMR: $\delta = 1.2$ (m, 3H); 1.5 (m, 2H); 2.4 (broad signal, 1H); 3.0 (broad signal, 1H): ^{13}C-NMR: $\delta = 7.4$ (d, $J = 6.0$); 17.6 (d, $J = 2.8$); ^{31}P-NMR: $\delta = -126.1$ (t, $J = 194$) (lit[12]. −128).

i-$C_3H_7PH_2$ (b.p. not determined), in 70 % yield from red P, Na/naphthalene, *t*-BuOH and isopropyl bromide.

^{1}H-NMR: $\delta = 1.2$ (dd, 6H); 2.0 (m, 1H); 2.4 (broad signal, 1H); 3.0 (broad signal, 1H); ^{13}C-NMR: $\delta = 17.3$ (d, $J = 3.3$); 25.3 (d, $J = 8.3$); ^{31}P-NMR: δ =-102.6 (t, J= 195).

n-$C_3H_7PH_2$ (b.p. not determined), in 84 % yield from red P, Na/naphthalene, *t*-BuOH and propyl bromide.

^{1}H-NMR: $\delta = 0.9$ (t, $J = 7.0$, 3H); 1.5 (m, 4H); 2.3 (t, $J = 7.1$, 1H); 2.9 (t, $J = 7.1$, 1H); ^{31}P-NMR $\delta = -138$ (t, $J = 195$).

n-$C_4H_9PH_2$, b.p. 85–90° /760 mm Hg, in 85 % yield from PCl_3, Na/naphthalene, *t*-BuOH and butyl bromide.

^{1}H-NMR: $\delta = 0.9$ (t, 3H); 1.3 (s, 2H); 1.5 (m, 4H); 2.3 (t, 1H); 3.0 (t, 1H); ^{13}C-NMR: $\delta = 13.4$ (d, $J = 13.6$); 23.5 (d, $J = 6.2$); 31.1; 34.9 (d, $J = 2.9$); ^{31}P-NMR: $\delta = -137.2$ (t, $J = 194$) (lit[13]. −135).

5. Preparation of diethyl phosphine

In a 2-L round-bottomed, three-necked flask equipped with a combination of gas inlet and dropping funnel, a mechanical stirrer and a combination of a thermometer and outlet was placed 200 ml of DME, 18.8 g (0.148 mol) of naphthalene and 27.6 g (1.20 mol) of 0.1 to 0.2 g pieces of sodium. A slurry of 12.4 g (0.40 mol) of red P and 50 ml of DME was added. In order to avoid bumping, the mixture was stirred at a low rate. The mixture was heated at 50°. After 2 h, when the greater part of the sodium had dissolved, the rate of stirring was increased. After a further 15 to 20 h the very dark reaction mixture was cooled to −5° and a mixture of 50 ml of DME and 59.2 g (0.80 mol) of *t*-BuOH was added over 15 min while keeping the

temperature between 0 and 5°. Ethyl bromide (39.2 g, 0.36 mol) was added in one portion causing the temperature to rise above 30°. The colour of the reaction mixture changed to grey or white. After an additional 15 min the mixture was cooled again to −10° and 100 ml of a solution of 0.36 mol of butyllithium in 120 ml of dodecane (decane also may be used) was added by syringe while keeping the temperature below 10°. This solution was made by removal of the hexane from a solution of BuLi under reduced pressure (the last traces at < 1 mm Hg) and subsequent addition of dodecane. After this addition the reaction mixture was cooled to ~ 0° and a second amount of 0.36 mol of ethyl bromide was added portion wise while keeping the temperature below 35°. After an additional 1 h a solution of 50 g of ammonium chloride in 500 ml of water was added. The upper layer was washed five times with 300-ml portions of water. The remaining upper layer was dried over magnesium sulfate. The product was isolated from the decane solution in the same way as described for the volatile primary phosphines (exp. 4). Redistillation at normal pressure through a short Vigreux column afforded pure diethyl phosphine, b.p. 83–85°, in 64 % yield.

^{1}H-NMR: $\delta = 0.9$–1.2 (m, 10H); 2.7 and 3.1 (broad signals, 1H); ^{13}C-NMR: $\delta = 12.4$ (d, $J = 9.0$); 12.8 (d, $J = 9.0$); 12.8 (d, $J = 8.0$); ^{31}P-NMR: $\delta = -54.1$ (lit[12,14].-55.5; –57).

Acknowledgements

This investigation was financially supported by Shell.

References

1. a. E.C. Evers, E.H. Street jr., S.L. Jung, J. Amer. Chem. Soc., **73**, 5088, (1951);
   b. R.I. Wagner, A.B. Burg, J. Amer. Chem. Soc., **75**, 3869, (1953);
   c. H. Albers, W. Schuler, Chem. Ber., **76**, 23, (1943);
   d. N. Kreuzkamp, Chem. Ber., **87**, 919, (1954);
   e. G.W. Watt, R.C. Thompson jr, J. Amer. Chem. Soc., **70**, 2295, (1948);
   f. E. Pass, E. Steininger, H. Schindlbauer, Monatsh. Chem., **90**, 792, (1959);
   g. P.R. Bloomfield, K. Parvin, Chem. and Ind., **1959**, 541;
   h. F.G. Mann, I.T. Millar, H.R. Watson, J. Chem. Soc., 1958, 2516;
   i. C.H.S. Hitchcock, F.G. Mann, J. Chem. Soc., **1958**, 2081;
   j. W. Kuchen, H. Buchwald, Angew. Chem., **69**, 307, (1957);
   k. F.G. Mann, I.T. Millar, F.H.C. Stewart, J. Chem. Soc., **1954**, 2832.
2. a. F. Pass, H. Schindlbauer, Monatsh. Chem., **90**, 148, (1959);
   b. W. Kuchen, H. Buchwald, Chem. Ber., **91**, 2871, (1958) and Angew. Chem., **68**, 791, (1956);
   c. H. Hoffmann, P. Schellenbeck, Chem. Ber., **99**, 1134, (1966);
   d. H.R. Hays, T.J. Logan, J. Org. Chem., **31**, 3391, (1966);
   e. O. Stelzer, N. Weferling, Z. Naturforsch., **35B**, 74, (1980).

3. W. Voskuil, J.F. Arens, Recl. Trav. Chim. Pays-Bas, **82**, 302, (1963).
4. a. L. Brandsma, N.K. Gusarova, A.V. Gusarov, H.D. Verkruijsse, B.A. Trofimov, Synth. Commun., 1994, **24**, 3219;
b. L. Brandsma, J.A. van Doorn, R.-J. de Lang, N.K. Gusarova, B.A. Trofimov, Mendeleev Commun., 1995, 14;
c. L. Brandsma, N.K. Gusarova, S.N. Arbuzova, B.A. Trofimov, Phosphorus, Silicon and Sulfur, **111**, 175, (1996);
d. S.N. Arbuzova, L. Brandsma, N.K. Gusarova, B.A. Trofimov, Recl. Trav. Chim. Pays-Bas, **113**, 575, (1994).
5. R.D. Stewart, R.I. Wagner, U.S. Patent, 1959, 2,900,416.
6. a. A. Cahours, Liebigs Ann. Chem., **122** 329, (1862);
b. E.A. Letts, N. Collie, Proc. Roy. Soc., Edinburgh, **11**, 46, (1881);
c. D.J. Peterson, T.J. Logan, J. Inorg. Nucl. Chem., **28**, 53, (1966);
d. G. Becher, W. Hölderich, Chem. Ber., **108**, 2584, (1975);
e. G. Brauer, E. Zintl, Z. Phys. Chem., **B37**, 323, (1937);
f. L. Horner, P. Beck, H. Hoffmann, Chem. Ber., **92**, 2088, (1959);
g. D.J. Peterson, U.S. Patent 3,397,039 (Aug. 13, 1968);
h. A.W. Frank G.L. Drake, jr., J. Org. Chem., **36**, 3461, (1971);
i. F. Uhlig, M. Dargatz, M. Scheer, E. Hermann, Z. Anorg. Allg. Chem., **606**, 105, (1991).
7. L. Brandsma, unpublished observation.
8. M. Schlosser, Polare Organometalle. p. 102, Springer-Verlag, Berlin, 1973.
9. E. Fluck, K. Issleib, Chem. Ber., **98**, 2674, (1965); H. Goldwhite, R.N. Hazeldine, D.G. Rowsell, J. Chem. Soc., **1965**, 6815; L. Maier, Helv. Chim. Acta, **49**, 842, (1966).
10. L. Maier, Helv. Chim. Acta, **53**, 1940, (1979).
11. L. Maier, Helv. Chim. Acta, **49**, 1718, (1966); H.R. Hays, J. Org. Chem., **31**, 3817, (1966).
12. V. Mark, C.H. Dungan, M.M. Crutchfield, J.R. van Wazer, Top. Phosphorus Chem., 5 (**1967**), 227.
13. G.M. Kosolapof, L. Maier, Org. Phosphorus Comp., vol. *1*, 1, (1972).
14. S.O. Grim, W McFarlane, Nature, **208**, 995, (1965).