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To the 80th Anniversary of B.I. Ionin

Synthesis of Phosphiranes

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Abstract—Phosphiranes, three-membered phosphorus-containing heterocycles, have been prepared via reaction of tertiary phosphines dilithium derivatives with carbon tetrachloride. The elaborated method can be applied for preparation of some phosphiranes which are not easily accessible.

Keywords: phosphirane, tertiary phosphine, dicarbanion, *P*-chloro ylide, bis(alkylidene)phosphorane

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Phosphiranes (three-membered phosphorus-containing heterocycles) are of practical and fundamental interest. Phosphiranes were described for the first time in 1963 [1, 2], and their formation was unambiguously confirmed later in [3, 4]. Compounds derived from phosphiranes can act as ligands for transition metals complexes; some of the latter revealed valuable catalytic properties [5, 6]. In general, phosphiranes are not enough stable; however, their complexes with transition metals are less reactive and can be isolated in pure form [3]. Overall, this class of compounds has been scarcely studied so far; therefore, development of new methods of phosphiranes preparation is of apparent interest.

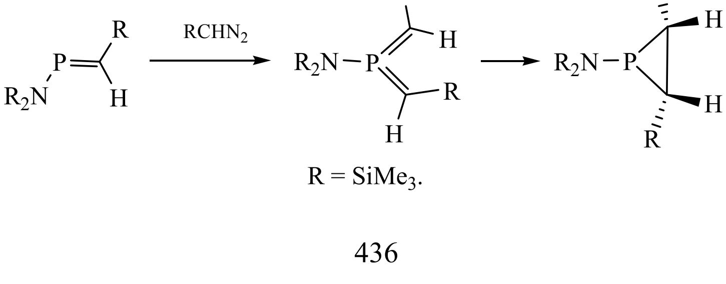
To date, several convenient methods of phosphiranes synthesis have been proposed. In particular, their preparation via reaction of phosphaalkenes or phosphaalkynes with different carbenes has been described [7, 8] (Scheme 1).

A multi-step preparation route has been discussed, using diazoalkanes as a source of carbene. The 4π-electrocyclic closing of bis(methylene)phosphorane a into three-membered ring is a conrotator process following the Woodward–Hoffman rule [9, 10]. Similarly, alkylidendiazophosphols were used for preparation of alkylidenephosphiranes. Other carbene sources for preparation of phosphiranes include organometallic carbenoids and bis-ylides [11–15].

In the present work we describe synthesis of phosphiranes via the intermediate formation of tertiary phosphines dilithium derivatives followed by their reaction with carbon tetrachloride. The starting tertiary phosphines **II** were prepared in high yield (70–90%) via the phosphorus(III) chlorides **I** interaction with the Grignard reagents (Scheme 2).

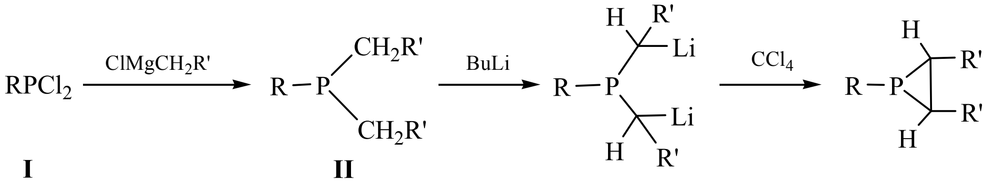
Tertiary dibenzylphosphines **IIa**–**IIc** could be metalated with *n*-butyllithium in the presence of tetramethylethylenediamine (TMEDA) with formation of

Scheme 1.

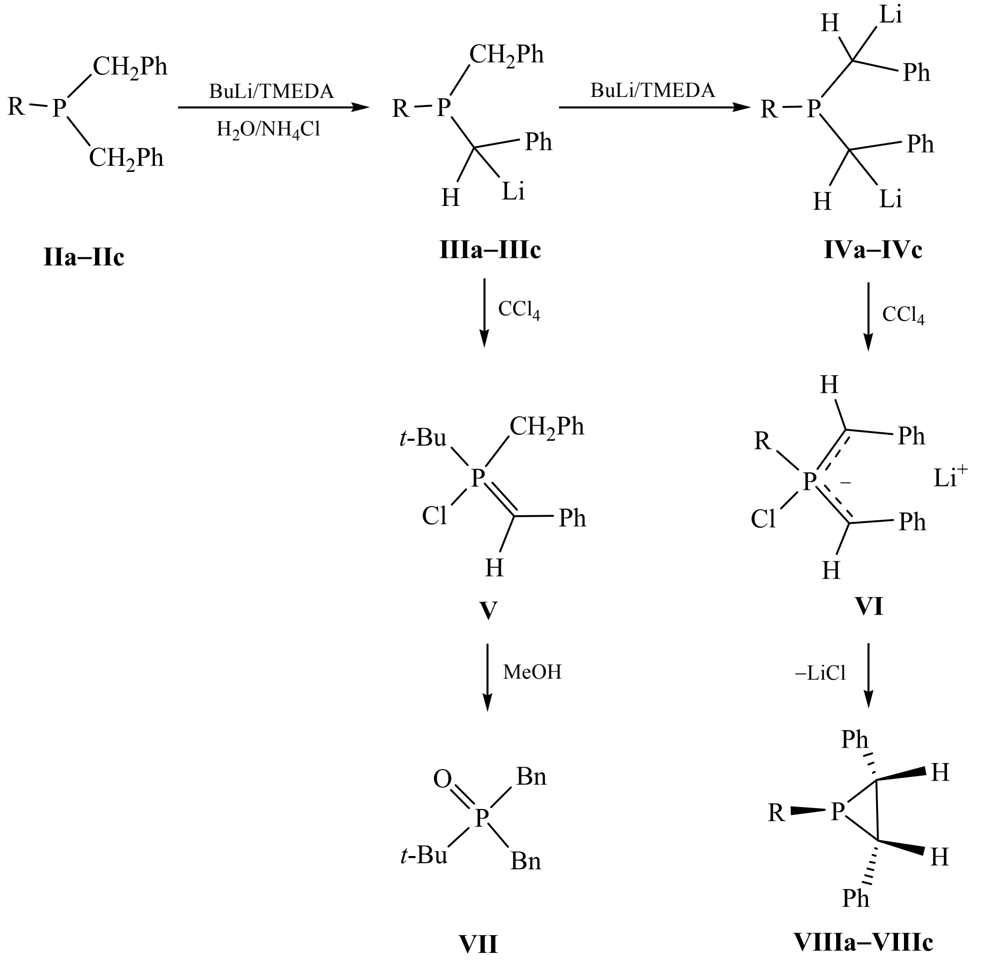


R = SiMe$_3$.

Scheme 2.



Scheme 3.

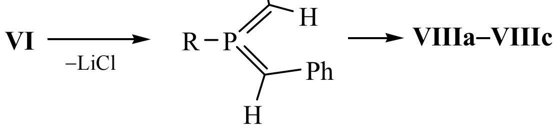


R = *t*-Bu (**a**), Et$_2$N (**b**), Bn (**c**).

colored solutions of mono- or dilithium derivatives of tertiary phosphines. Interaction of tertiary phosphines **IIa**–**IIc** with equivalent amount of *n*-butyllithium provided monolithium derivatives **IIIa**–**IIIc**. The reaction with twofold excess of *n*-butyllithium in the presence of TMEDA upon prolonged refluxing in hexane led to dilithium derivatives **IVa**–**IVc** (Scheme 3).

Formation of lithium derivatives of tertiary dibenzylphosphines **IIa**–**IIc** was accompanied by deep-red coloration of the reaction mixture. Generally, lithium derivatives of benzyl-containing compounds are red-colored due conjugation of the phenyl ring with the negative charge of carbanion localized at the CH-group. On top of that, the upfield shift of the ^{31}P NMR spectra signals was observed in the cases of lithium derivatives **III** (by 13–15 ppm) and dilithium derivatives **IV** (by 35–40 ppm) as compared to the starting tertiary phosphines **II**. In particular, treatment of (*tert*-butyl)dibenzylphosphine **IIa** (δ_P 11.3 ppm) with one equivalent of *n*-butyllithium yielded monolithium derivative of tertiary phosphine **IIIa** (δ_P –1.5 ppm); refluxing of tertiary phosphine **IIa** with twofold excess of *n*-butyllithium in the presence of TMEDA in hexane provided dilithium derivative **IVa** (δ_P –25 ppm). Similarly, lithiation of tribenzylphosphine **IIc** (δ_P –12 ppm) led to formation of dicarbanion **IVc** (δ_P –51 ppm). Treatment of the lithium derivatives with aqueous solution of ammonium chloride allowed regeneration of the starting tertiary phosphines.

Monolithium derivative **IIIa** reacted with carbon tetrachloride to form the P-chloro ylide **V**, the phosphorus chemical shift (δ_P 73 ppm) being typical of such compounds [16, 17]. Reaction of the P-chloro ylide **V** with methanol afforded the corresponding tertiary phosphine oxide **VII** in quantitative yield. Halogenating of dilithium derivatives **IVa**–**IVc** with carbon tetrachloride at –70°C gave phosphiranes **VIIIa**–**VIIIc**. The solution color changed from red to yellow in the course of the reaction; simultaneously, signals of the starting lithium derivatives **IVa**–**IVc** disappeared and the strong-field signals characteristic of phosphiranes (from –100 to –180 ppm) appeared in the reaction mixture ^{31}P NMR spectrum. Likely, the reaction proceeded via formation of P-chloro ylides **VIa**–**VIc**, similarly to the reaction of monolithium derivatives **III** with carbon tetrachloride. The subsequent elimination of lithium chloride resulted in conversion of P-chloro ylides **VI** into bis(alkylidene) phosphoranes **IX** undergoing further cyclization to yield the phosphiranes. Bis(alkylidene)phosphoranes **IX** could not be detected by means of NMR method. Those compounds are known to be stable their molecules contain bulky substituents (*tert*-Bu, TMS, 2,4,6-*tert*-$\mathrm{BuC_6H_3}$, etc.) at the carbon or phosphorus, suppressing the intramolecular cyclization [7, 8]. In the case of bis(benzylidene)phosphiranes, the phenyl group could not provide sufficient steric stabilization, and the compounds easily underwent cyclization to form phosphiranes **VIIIa**–**VIIIc**.



IX

Phosphiranes **VIIIa**–**VIIIc** could be isolated in individual form and stored in a refrigerator at –20ºC. Phosphirane **VIIIa** containing a P-bound *tert*-butyl group was isolated via vacuum distillation; phosphiranes **VIIIb** and **VIIIc** were less stable and partially decomposed during distillation. Nevertheless, those compounds could be isolated via column chromatography on oxygen-free silica gel under inert atmosphere.

Structures of phosphiranes **VIIIa**–**VIIIc** were confirmed by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy as well as by mass spectrometry. The ^{1}H NMR spectra contained doublet signals of endocyclic CH-protons at 3.0 ppm with the coupling constant of 2–3 Hz. The ^{13}C NMR spectra showed doublet signals of carbon atoms in three-membered ring directly bound to phosphorus, at 35–40 ppm with $^{1}J_{CP} \approx 80$ Hz. The chemical shift in ^{31}P NMR spectra ranged from –150 to –180 ppm, being typical of P(III) atom in a three-membered phosphirane ring.

Even though phosphirane **VIIIa**–**VIIIc** molecules contained three asymmetric centers, a single set of signals in the NMR spectra indicated formation of the only one stereoisomer; NMR data allowed elucidation of phosphiranes **VIIIa**–**VIIIc** stereochemistry. In detail, parameters of ^{1}H and ^{13}C NMR spectra indicated symmetric structure of the phosphirane molecule with respect to the plane passing through the phosphorus atom and a midpoint of the CH–CH bond perpen-dicularly to the phosphirane ring plane. A single signal of the endocyclic CH-groups and a very small constant $^{2}J_{HP}$ of 1–3 Hz in the ^{1}H NMR spectra was assigned to the *cis*-configuration of the hydrogen atoms in the groups with respect to lone-electron pair of trivalent phosphorus atom and *trans*-configuration with respect to the substituent at the phosphorus atom. High stereoselectivity of the reaction of dilithium derivatives **IVa**–**IVc** with carbon tetrachloride coincided with intermediate formation of bis(alkylidene)phosphoranes **IX** and conrotator mechanism of their cyclization following the rules of orbital symmetry retention in concerted reactions (the Woodward–Hoffman rule).

The spectral parameters of the phosphiranes (extremely low chemical shift of the phosphorus nucleus, up-field shift of the signals of endocyclic CH-groups, and low spin-spin coupling constants $^{1}J_{PC}$ and $^{2}J_{HP}$) were typical of the three-membered rings and could be explained by significant difference between HOMO and LUMO levels and by *p*-character of the lone-electron pair of the phosphorus [3].

To conclude, a convenient method to prepare phosphiranes has been elaborated.

EXPERIMENTAL

In this experimental work chemicals, silica gel, and TLC plates (Poligram SIL G/UV$_{254}$) from Fluka and Acros were used. The solvents were distilled under inert atmosphere before use.

NMR spectra were registered using a Varian VXR-300 instrument [300 MHz (^{1}H), 75 MHz (^{13}C), and 126.16 MHz (^{31}P)] relative to internal Me_4Si (^{1}H and ^{13}C) or external 85% H_3PO_4 (^{31}P) references.

***tert*-Butyldibenzylphosphine (IIa)**. A solution of 0.22 mol of benzylmagnesium chloride in diethyl ether was added to a solution of 0.1 mol of *tert*-butyldichlorophosphine in 100 mL of diethyl ether upon stirring and cooling to 0°C. The reaction mixture was stirred during 1 h at room temperature, and then refluxed during 2 h. The formed precipitate was centrifuged off, the solvent was distilled off, and the product was extracted from the residue with hot hexane. The extract was evaporated, and the residue was distilled in vacuum. Yield 60%, bp 130–140°C (0.1 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.1 d (9H, CH_3, J 8 Hz), 2.9 d (4H, CH_2Ph, J 4 Hz), 7.1–7.5 m (10H, Ph). ^{31}P NMR spectrum ($CDCl_3$): δ_P 11.3 ppm. Found, %: C 79.45; H 8.68; P 11.71. $C_{18}H_{23}P$. Calculated, %: C 79.97; H 8.58; P 11.46.

***N*,*N*-Diethylaminodibenzylphosphine (IIb)** was prepared similarly from diethylaminodichlorophosphine. Yield 60%, bp 145°C (0.1 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.95 t (6H, CH_3, J 7 Hz), 2.9 m (4H, CH_2Ph), 3.1 m (4H, CH_2CH_3), 7.1–7.5 m (10H, Ph). ^{31}P NMR spectrum ($CDCl_3$): δ_P 66.0 ppm. Found, %: N 4.91; P 10.85. $C_{18}H_{24}NP$. Calculated, %: N 4.91; P 10.85.

Tribenzylphosphine (IIc) was prepared similarly from phosphorus trichloride [18]. Yield 85%. ^{1}H NMR spectrum (C_6D_6), δ, ppm: 2.95 d (6H, CH_2, J 2 Hz), 6.8–7.3 m (15H, C_6H_5). ^{31}P NMR spectrum ($CDCl_3$): δ_P 12.0 ppm. Found P, %: 10.25. $C_{21}H_{21}P$. Calculated P, %: 10.18.

***tert*-Butyldibenzylphosphine oxide (VII)**. 0.015 mol of tetramethylethylenediamine and a solution of 0.012 mol of *n*-butyllithium in hexane were sequentially added to a solution of 0.01 mol of *tert*-butyldibenzylphosphine **IIa** in 10 mL of hexane. The reaction mixture was stirred at 50°C during 1 h and then cooled to –60°C; 0.015 mol of carbon tetrachloride was added. The formed precipitate was centrifuged off, and the solvent was evaporated in vacuum. The signal of P-chloro ylide **V** at 73.0 ppm was observed in ^{31}P NMR spectrum of the residue (yellow liquid). 0.015 mol of methanol was added to a solution of ylide **V** in 5 ml of diethyl ether cooled to 0°C. The reaction mixture was incubated during 0.5 h at 0°C, and then evaporated. The residue was yellowish crystalline product. Yield 80%, mp 156–158°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.04 d (9H, CH_3C, J_{HP} 14.4 Hz), 3.01 d q (4H, PCH_2, J 15, J 12 Hz), 7.21 m (10H, C_6H_5). ^{31}P NMR spectrum ($CDCl_3$): δ_P 53.0 ppm. Found, %: C 75.41; H 8.08; P 10.76. $C_{18}H_{23}OP$. Calculated, %: C 75.50; H 8.10; P10.82.

1-*tert*-Butyl-2,3-diphenylphosphirane (VIIIa). 0.025 mol of tetramethylethylenediamine and a solution of 0.025 mol of *n*-butyllithium in hexane were sequentially added to a solution of 0.01 mol of *tert*-butyldibenzylphosphine (**IIa**) in 10 mL of hexane. The reaction mixture was heated at 50°C during 3 h. After the complete conversion, the only signal at –25.5 ppm was observed in ^{31}P NMR spectrum of the reaction mixture, assigned to dilithium derivative of *tert*-butyldibenzylphosphine **IVa**. Next, 0.03 mol of carbon tetrachloride was added to a solution of the dilithium derivative in hexane at –60°C. The reaction mixture turned yellow. Precipitate of lithium chloride was filtered off, the solvent was evaporated, and the residue was distilled in vacuum. Yield 50%, bp 130°C (0.05 mmHg), mp 46–47°C [19]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.18 d (9H, CH_3C, J_{HP} 12.6 Hz), 3.13 d (2H, PCH, J_{HP} 2.6 Hz), 7.05–7.45 m (10H, C_6H_5). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 16.0, 17.8, 33.5, 38.6, 35.7, 125.9, 128.0, 130.2, 130.3, 137.0, 137.1. ^{31}P NMR spectrum ($CDCl_3$): δ_P 151 ppm. Mass spectrum (70 eV): m/e 268 [M^+]. Found P, %: 11.65. $C_{18}H_{21}P$. Calculated P, %: 11.54.

1-Diethylamino-2,3-diphenylphosphirane (VIIIb) was prepared similarly. The product was isolated by column chromatography eluting with the 1 : 1 toluene–hexane mixture. Yield 35%, yellow oily substance. ^{1}H NMR spectrum (C_6D_6), δ, ppm: 0.93 t (6H, CH_3, J_{HH} 7.0 Hz), 2.8 m (4H, NCH_2), 3.9 d (2H, PCH, $J_{PH} \approx$ 2 Hz), 7.0 m (10H, Ar). ^{13}C NMR spectrum (C_6D_6), δ_C, ppm: 16.0, 39.0 d (J_{CP} 44.3 Hz), 45.6, 45.8, 125.9, 128.0, 130.2, 130.3, 137.0, 137.1. ^{31}P NMR spectrum (C_6D_6): δ_P –95 ppm. Mass spectrum (70 eV): m/e 283 [M^+]. Found, %: N 4.91; P 11.05. $C_{18}H_{22}NP$. Calculated, %: N 4.94; P 10.93.

1-Benzyl-2,3-diphenylphosphirane (VIIIc) was prepared similarly. The product was isolated by column chromatography eluting with the 1 : 1 toluene–hexane mixture, followed by recrystallization from hexane. Yield 25%, mp 80°C. ^{1}H NMR spectrum (C_6D_6), δ, ppm: 2.30 d (PCH_2, J_{PH} 4.0 Hz), 2.90 d (2H, PCH, J_{PH} 2.0 Hz), 6.5–7.8 m (15H, Ph). ^{13}C NMR spectrum (C_6D_6), δ_C, ppm: 35.0, 36.0, 36.5 d (J_{PC} 45 Hz), 123.6, 123.7, 125.5, 125.7, 126.9, 128.0, 130.8, 130.9, 137.2, 137.6. ^{31}P NMR spectrum ($CDCl_3$): δ_P –180 ppm. Mass spectrum (70 eV): *m*/*e* 302 [M^+]. Found, %: C 83.42; H 6.33; P 10.35. $C_{21}H_{19}P$. Calculated, %: C 84.0; H 6.38; P 10.24.

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