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Mendeleev Commun., 2007, **17**, 197–198
Mendeleev Communications

Direct formation of P–C and P–H bonds by reactions of organozinc reagents with white phosphorus

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DOI: 10.1016/j.mencom.2007.06.002

The reactions of the organozinc reagents [R_2Zn] (R = Ph, Mes; Mes = 2,4,6-trimethylphenyl) with white phosphorus followed by hydrolysis lead to selective formation of organophosphorus products with P–C and P–H bonds.

The search for new highly effective synthetic methods and procedures is a key strategic direction in the development of science and technology.[1] In this context, the creation of new processes of selective chemical bond formation and cleavage is an important goal of modern organoelement chemistry.[2,3]

Special attention is devoted to the creation of highly effective synthetic methods for the preparation of organophosphorus compounds directly from elemental (white) phosphorus.† It was shown that, under electrocatalytic conditions operated in the presence of transition metal complexes based on nickel and cobalt, which are electrocatalytically regenerated in the reaction mixture, the cleavage of P–P bonds in a white phosphorus tetrahedron leads to the selective formation of new compounds with phosphorus–carbon and phosphorus–hydrogen bonds.[4,5] Moreover, the use of a single electrochemical cell supplied with a sacrificial zinc anode strongly increases the yield of organophosphorus products.[6] The presence of transition phosphides as the intermediates of the process has been proposed. It is known[7] that only alkali metal and zinc phosphides can react with organic halides (RX) with the formation of organophosphorus compounds with P–C bonds. Note that, in an electrochemical process, the formation of organozinc intermediates from organonickel σ-bonded complexes takes place as a result of transmetallation.[8] Probably, organozinc derivatives generated in the reaction mixture can react with white phosphorus to form organophosphorus products due to the known high reactivity of organozinc derivatives in coupling processes.[9,10] For this reason, the investigation of the reactivity of organozinc derivatives in relation to white phosphorus is of considerable interest.

The model organozinc compounds were synthesised according to a published procedure[11] (Scheme 1).‡

$$Mg + PhBr \xrightarrow{Et_2O} [PhMgBr]$$
$$[PhMgBr] + ZnBr_2 \longrightarrow [PhZnBr] + MgBr_2$$
$$2[PhZnBr] \rightleftharpoons [Ph_2Zn] + [ZnBr_2]$$

Scheme 1

The ^{31}P NMR monitoring† of the reaction mixture containing white phosphorus and an organozinc reagent in THF showed that, immediately after the addition of [Ph_2Zn] to the solution containing white phosphorus in THF, only one signal of white phosphorus was observed [^{31}P NMR, 40.48 MHz, THF (C_6D_6-capillary), 25 °C: δ –525.5 (s)]. After two days at room temperature, the colour of the mixture turned to saturated orange and in the ^{31}P NMR spectra very broad signals in the range δ_P –20 to –150 ppm appeared. Note that the signals observed in this region correspond to phosphine and phosphorus hydride derivatives. After acidic hydrolysis of the reaction mixture using a 2 N solution of hydrochloric acid only two signals corre-

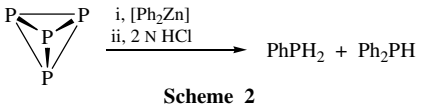
† White phosphorus, phosphines and organometallic reagents mentioned in this communication are hazardous compounds. White phosphorus is highly toxic and burns spontaneously when warmed in air. In an emergency, white phosphorus can be treated with an aqueous copper sulfate solution or sand. Getting on the skin, white phosphorus gives strong painful a long time not healing burns. Continuous breathing of white phosphorus vapour results in disease of the bone tissue, loss of the teeth and necrosis of the parts of jaw. White phosphorus should be stored under water in well airing dark place. In case of the skin burn, to wash out by a dilute aqueous solution of $KMnO_4$ or $CuSO_4$. An aqueous copper sulfate solution (2%) can be used as the antidote at a poisoning. All of the reactions and handing of phosphines and white phosphorus should be carried out under an inert atmosphere in a well-ventilated hood.

All operations were performed under an atmosphere of purified argon or using high-vacuum and standard Schlenk techniques. The ^{31}P NMR spectra were recorded using CXP-100 (40.48 MHz) and Varian-300 (121.4 MHz) spectrometers (Bruker). ^1H NMR spectra were recorded on a Varian-300 spectrometer.

Diethyl ether, tetrahydrofuran and toluene were dried by distillation over sodium. The white phosphorus was purified according to a described procedure[6] and was consecutively cleaned by absolute acetone, ethanol and diethyl ether followed by drying in a vacuum (0.18 Torr) during 10 min before reaction. The reagents used as the substrates (organic halides, magnesium and zinc bromide) were commercial products. The organic halides were purified by distillation. The zinc bromide was dried in a vacuum and stored in an atmosphere of dry argon.

‡ *Preparation of organomagnesium reagents [RMgX].* 2.55 g (105 mmol) of magnesium shavings were placed to a 250 ml round-bottom flask and kept in a vacuum (0.18 Torr) at 350 °C for an hour. After the cooling of the flask to room temperature, 10 ml of diethyl ether, a small crystal of I_2 and 28.5 mmol of organic halide RX (3.0 ml PhBr or 4.4 ml MesBr) were consistently added to the flask. After the reaction has been started, a solution of 66.5 mmol of organic halide (7.0 ml PhBr or 10.2 ml MesBr) in 50 ml of diethyl ether was added dropwise for 30 min. After that, the reaction mixture was refluxed for 2 h. The resulting mixture was cooled to room temperature and filtered. The solutions of [PhMgBr] and [MesMgBr] with concentrations of 1.3 and 1.4 mol dm^{-3} were obtained in 75 and 63% yields, respectively.

Preparation of organozinc reagents [R_2Zn].[11] A solution containing 19.3 mmol of an organomagnesium reagent (14.8 ml of a solution of [PhMgBr] or 13.8 ml of a solution of [MesMgBr]) was added to a suspension of 2.18 g (9.67 mmol) of zinc bromide in 5 ml of toluene with stirring at room temperature. After that, precipitated magnesium bromide was filtered off. The obtained 0.5 M solution of [R_2Zn] of pale-yellow colour was used in reaction with white phosphorus without additional purification.[11]



Scheme 2

sponding to $PhPH_2$ and Ph_2PH are observed in the ^{31}P NMR spectrum (Scheme 2).§

The strong coordination interaction of a metal centre in organozinc compounds with oxygen-containing solvent molecules (like THF and dioxane) strongly decreases the reactivity of organozinc reagents.[12] To determine this influence, toluene was used as the solvent to investigate the reaction of organozinc reagents with white phosphorus. Note that P_4 is readily soluble in toluene, and organozinc compounds are not associated and coordinated with the solvent molecule.[9,10]

Thus, the addition of a diphenylzinc [Ph_2Zn] solution in toluene to a suspension of white phosphorus in this solvent immediately leads to the formation of a yellow very viscous mixture. In the ^{31}P NMR spectra of this mixture, a very broad signal in the region of δ_P –20 to –150 ppm is observed. The complete disappearance of the signal of starting P_4 suggests the total conversion of P_4 in reaction with organozinc reagent. It is known that broadness of the signals in ^{31}P NMR spectra can result from exchange processes in the coordination sphere of the metal at room temperature.[13] After the complete hydrolysis of obtained mixture by a 2 N solution of hydrochloric acid followed by the distillation of the formed mixture, phenyl phosphine and diphenyl phosphine were isolated in a pure state.

Note that the use of dimesitylzinc derivative [Mes_2Zn] in this process leads to the formation of the primary phosphine $MesPH_2$ as a single organophosphorus product. Leaving the reaction mixture for one day leads to the formation of MesP(O)(OH)H {^{31}P NMR [121.42 MHz, toluene (C_6D_6-capillary), 25 °C] δ: 16.2 (d, $^1J_{PH}$ 549 Hz)} as the result of oxidation of primary formed $MesPH_2$. The selective formation of the primary phosphine $MesPH_2$ could result from the presence of *ortho* substituents in the aromatic fragment that creates some hindrances for the second addition of organic (mesityl) group to the phosphorus atom bearing Mes group.

§ *Reaction of organozinc reagents [R_2Zn] with white phosphorus.* A solution containing 9.67 mmol of an organozinc reagent (19.3 ml) was added dropwise to a solution containing 0.81 mmol (0.1 g) of white phosphorus in 5 ml of toluene at room temperature. After the reaction has been started, the system was cooled to room temperature. After the exothermic stage of the reaction, the reaction mixture was stirred for 10 h and 10 ml of a 2 N solution of HCl was added dropwise to the resulting mixture. The organophosphorus products were extracted with diethyl ether from the organic phase. The solvent was evaporated from the extracts, and the viscous rest was distilled in a vacuum. The characteristics of the synthesised compounds are in agreement with the literature data.[15–18]

For $PhPH_2$:[15–18] bp 40 °C (10 Torr), 0.17 g (48%). ^{31}P NMR (121.4 MHz, C_6D_6, 25 °C) δ: –122.1 (t/m, $^1J_{PH}$ 197 Hz). ^1H NMR (300.0 MHz, C_6D_6, 25 °C) δ: 7.0–7.4 (m, 5H, Ph), 3.82 (d, 2H, PH, $^1J_{PH}$ 197 Hz).

For Ph_2PH:[17] bp 75 °C (0.18 Torr), 0.14 g (23%). ^{31}P NMR (121.4 MHz, C_6D_6, 25 °C) δ: –41.2 (d, $^1J_{PH}$ 208 Hz). ^1H NMR (300.0 MHz, C_6D_6, 25 °C) δ: 6.5–7.2 (m, 10H, Ph), 5.13 (d, 1H, PH, $^1J_{PH}$ 208 Hz).

For $MesPH_2$:[18] bp 50 °C (0.001 Torr), 0.17 g (36%). ^{31}P NMR (121.4 MHz, C_6D_6, 25 °C) δ: –154.8 (t, $^1J_{PH}$ 203 Hz). ^1H NMR (300.0 MHz, C_6D_6, 25 °C) δ: 6.63 (s, 2H, *meta*-H), 3.53, (d, 2H, PH, $^1J_{PH}$ 203 Hz), 2.18 (s, 6H, *ortho*-Me), 2.11 (s, 3H, *para*-Me).

Some attempts of arylation and alkylation of elemental (white) phosphorus using organometallic reagents have been already performed on the basis of magnesium and lithium reagents.[14] The relatively high yield of phenyl phosphine (25–40%) was obtained in reactions of white phosphorus with phenylmagnesium and phenyllithium.[14]

Thus, the interaction of white phosphorus with organozinc reagents followed by acidic hydrolysis of the reaction mixture leads to the selective formation of organophosphorus compounds bearing phosphorus–carbon and phosphorus–hydrogen chemical bonds: primary and secondary phosphines.

This work was supported by the Russian Foundation for Basic Research (grant no. 06-03-32247-a), the Complex Programme of the Russian Academy of Sciences 'Theoretical and Experimental Investigation of the Chemical Bond Nature and the Mechanisms of Important Chemical Reactions and Processes', INTAS (grant no. 03-55-2050) and the Research and Educational Centre of the Kazan State University – REC 007 (Y1-C-07-06). We are grateful to Dr. Vasili Miluykov for invaluable scientific consultations and suggestions concerning some topics of this research.

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Received: 25th December 2006; Com. 06/2850