ORGANOMAGNESIUM SYNTHESIS OF SOME ORGANOPHOSPHORUS COMPOUNDS IN AN ETHER-FREE MEDIUM*

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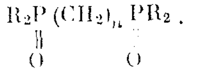
In our previous papers [1-2] we described a simple method of preparing organomagnesium compounds in the complete absence of ethers or of any other catalysts for the Grignard reaction. The alkylmagnesium halides prepared in this way were used for the synthesis of various simple heteroorganic compounds. In some of the cases studied our proposed method of work was found to be more convenient than the usual organomagnesium synthesis in presence of ether or other solvating substances.

In the present work we studied the possibility of using noncatalyzed organomagnesium synthesis for the preparation of dialkylphosphinous ester, dialkylphosphinic acids, and alkylenebis(dialkylphosphine) P, P'-dioxides,  $R_2\underset{O}{\underset{\|}{P}}(CH_2)_n\underset{O}{\underset{\|}{P}}R_2$. For the preparation of dialkylphosphinous esters we used the readily accessible alkyl phosphorodichloridites:

$$2RMgX + Cl_2POR' \xrightarrow[-60^\circ]{4C_5H_5N} R_2POR' + 2\,[MgXCl \cdot 2C_5H_5N]$$
$$R = n\text{-}C_4H_9,\ C_6H_5;\ R' = C_4H_9;\ X = Cl.$$

Kabachnik and Tsvetkov [3] described a synthesis of this kind in which the usual Grignard reagents were used at low temperature (in ether). We found that for this purpose solid organomagnesium compounds prepared in absence of solvent are just as successful. Subsequent treatment of the reaction mixture with pyridine, which binds magnesium halides, raises the yields of the desired products substantially. On the whole, the yields of the latter were not greater than the yields attainable when working with ether and were 50-60%. It must be pointed out that we obtained butyl diphenylphosphinite in 50% yield, whereas attempts to carry out the reaction in ether were unsuccessful and a satisfactory yield (42%) was attained only in tetrahydrofuran [4]. The order in which the reactants are mixed does not seem to affect the yields substantially: butyl dipentylphosphinite was obtained in 61.8% yield when addition was in the reverse order (butyl phosphorodichloridite was added to a suspension of pentylmagnesium chloride at − 65°). Kosolapoff's synthesis of dialkylphosphinic acids from dialkyl hydrogen phosphites [5] can also be improved by the use of nonsolvated organomagnesium compounds:

$$(C_2H_5O)_2POH + 3RMgX \rightarrow R_2POMgX$$
$$R_2POMgX \xrightarrow[H+]{H_2O_2} R_2POOH$$
$$R = n\text{-}C_4H_9,\ n\text{-}C_6H_{13},\ n\text{-}C_7H_{15},\ n\text{-}C_8H_{17},\ n\text{-}C_{12}H_{25};\ C_6H_5;$$
$$X = Cl,\ Br.$$

The reaction was carried out by the addition of diethyl hydrogen phosphite to a suspension of the organomagnesium compound in heptane at room temperature with subsequent heating to 100°; the oxidation was effected by means of hydrogen peroxide. The yields of dialkylphosphinic acids were about 75%, i.e. not less than the yields obtained

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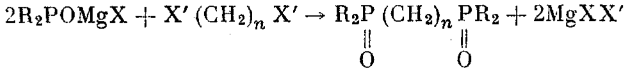
when the reaction is carried out in ether. Alkylenebis(dialkylphosphine) P,P'-dioxides were prepared in accordance with the following scheme:

$$(C_2H_5O)_2POH + 3RMgX \rightarrow R_2POMgX$$



$$2R_2POMgX + X'(CH_2)_nX' \rightarrow \underset{O}{\underset{\|}{R_2P}}(CH_2)_n\underset{O}{\underset{\|}{PR_2}} + 2MgXX'$$

$$R = n\text{-}C_6H_{13},\ n\text{-}C_7H_{15};\ X = Cl;\ n = 3,4;\ X' = Br.$$

The yields of the dioxides depend substantially on the time of heating in the second stage of the process (rearrangement). Thus, when the reaction mixture is heated with the dihalide at 100° for six hours the main reaction products are dialkylphosphinic acids (yields more than 70%). When the time of heating is increased to 18 hours, the yield of dioxides is about 30%. It is quite possible that the dioxides can be obtained in still higher yields at a higher temperature and with increase in the reaction time.

EXPERIMENTAL

Butyl Dibutylphosphinite. Butylmagnesium chloride powder, prepared from 13.4 g of magnesium and 46.3 g of butyl chloride, was added gradually at −60 ± 3° to a solution of 28 g of butyl phosphorodichloridite in 200 ml of heptane with vigorous stirring. When the addition was complete, the mixture was left overnight. 100 ml of pyridine was then added, and the mixture was stirred for two hours, after which the precipitate was filtered off and washed carefully with heptane. Solvents were removed in a vacuum, and the residue was distilled. We obtained 19.5 g (56%) of butyl dibutylphosphinite; b.p. 83° (2 mm); n_D^{20} 1.4518; d_4^{20} 0.8480. The literature [3] gives: b.p. 68-69° (1.5 mm); n_D^{20} 1.4520; d_4^{20} 0.8479. Found: C 65.94, 66.39; H 12.38, 12.52; P 13.72, 13.83%. $C_{12}H_{27}PO$. Calculated: C 66.01; H 12.47; P 14.19%.

Butyl Diphenylphosphinite. Phenylmagnesium chloride powder, prepared from 13.4 g of magnesium and 56.3 g of chlorobenzene, was added gradually at − 60° to a solution of 28 g of butyl phosphorodichloridite in 200 ml of heptane with vigorous stirring. On the next day 100 ml of pyridine was added, and the mixture was stirred for two hours, after which the precipitate was filtered off and carefully washed with heptane; solvents were removed in a vacuum, and the residue was distilled. We obtained 20.8 g (50%) of butyl diphenylphosphinite; b.p. 142-143° (1 mm); n_D^{20} 1.5750; d_4^{20} 1.0389. The literature [3] gives: b.p. 127-128° (2 mm); n_D^{20} 1.5733; d_4^{20} 1.0387. Found: C 74.15, 73.13; H 7.49, 7.42; P 12.00, 12.17%. $C_{16}H_{19}PO$. Calculated: C 74.40; H 7.41; P 11.99%.

Butyl Dipentylphosphinite. A solution of 31.5 g of butyl phosphorodichloridite in 200 ml of heptane was added gradually with vigorous stirring to a suspension, cooled to - 65°, of pentylmagnesium chloride, prepared from 13.4 g of magnesium and 42.6 g of pentyl chloride. The mixture was gradually warmed to room temperature and then left overnight. After the addition of pyridine (100 ml) and stirring for two hours, the precipitate was filtered off and carefully washed with heptane. Solvents were removed in a vacuum, and the residue was distilled.

We obtained 27.4 g (62%) of butyl dipentylphosphinite; b.p. 84.5-85.5° (1 mm); n_D^{20} 1.4500, d_4^{20} 0.8482. The literature [3] gives: b.p. 84-85° (1 mm); n_D^{20} 1.4520; d_4^{20} 0.8475. On hydrolysis of the ester and oxidation with hydrogen peroxide we obtained 24.6 g of dipentylphosphinic acid, m.p. 68-69°. The literature [6] gives m.p. 68-69°.

Dihexylphosphinic Acid. With vigorous stirring in a stream of nitrogen a solution of 60.3 g of hexyl chloride in 100 ml of heptane was added gradually at 100° to 13.4 g of magnesium powder activated with iodine. When the whole of the solution had been added, the reaction mixture was heated at 100° for one hour. The mixture was cooled to room temperature, 13.8 g of diethyl hydrogen phosphite was added dropwise, and the reaction mixture was again heated at 100° for two hours. The resulting mixture was poured carefully onto ice, and 100 ml of concentrated sulfuric acid was added, after which the mixture was treated with 30% hydrogen peroxide. The organic layer was separated, and the aqueous layer was washed with five 150-ml portions of benzene. The organic layers were combined, solvent was driven off, and the dihexylphosphinic acid was crystallized from heptane. We obtained 15.5 g (66%) of dihexylphosphinic acid, m.p. 77.5-78.5° (from hexane). The literature [8] gives m.p. 77-78.5°.

Dibutylphosphinic Acid. This was prepared analogously to dihexylphosphinic acid. We took 13.4 g of magnesium powder, 46.3 g of butyl chloride, 13.8 g of diethyl hydrogen phosphite, and 100 ml of heptane. We obtained 12.5 g (70%) of dibutylphosphinic acid, m.p. 65-66°. The literature [4] gives m.p. 66-67°.

Diheptylphosphinic Acid. This was prepared analogously to dihexylphosphinic acid. We took 13.4 g of magnesium powder, 67.3 g of heptyl chloride, 13.8 g of diethyl hydrogen phosphite, and 100 ml of heptane. We obtained 18.5 g (71%) of diheptylphosphinic acid, m.p. 77-78.5°. The literature [6] gives m.p. 77-78°.

Dioctylphosphinic Acid. This was prepared analogously to dihexylphosphinic acid. We took 13.4 g of magnesium powder, 96.6 g of octyl bromide, 13.8 g of diethyl hydrogen phosphite, and 100 ml of heptane. We obtained 21.8 g (75%) of dioctylphosphinic acid, m.p. 84.4-85.2°. The literature [6] gives m.p. 85°. Found: H 12.19, 12.24; C 66.29, 66.11; P 10.30, 10.42%. $C_{16}H_{35}PO_2$. Calculated: H 12.15; C 66.17; P 10.67%.

Didodecylphosphinic Acid. This was prepared analogously to dihexylphosphinic acid. We took 13.4 g of magnesium powder, 124.6 g of dodecyl bromide, 13.8 g of diethyl hydrogen phosphite, and 100 ml of heptane. We obtained 29.5 g (73%) of didodecylphosphinic acid, m.p. 92.4-94°. The literature [6] gives m.p. 93.8-94.8°. Found: H 12.85, 12.70; C 71.61, 71.47; P 7.58, 7.80%. $C_{24}H_{51}PO_2$. Calculated: H 12.76; C 71.59; P 7.69%.

Diphenylphosphinic Acid. This was prepared analogously to dihexylphosphinic acid. We took 13.4 g of magnesium powder, 56.3 g of chlorobenzene, 13.8 g of diethyl hydrogen phosphite, and 100 ml of heptane. We obtained 15.9 g (71%) of diphenylphosphinic acid, m.p. 190°, undepressed by admixture of a known sample. The literature [8] gives m.p. 190-192°.

Trimethylenebis(dihexylphosphine) P,P'-Dioxide. A solution of 60.3 g of hexyl chloride in 100 ml of heptane was added gradually at 100° with vigorous stirring in a stream of nitrogen to 13.4 g of magnesium powder activated with iodine. When the whole of the solution had been added, the reaction mixture was heated at 100° for one hour. The mixture was allowed to cool to room temperature, and then 13.8 g of diethyl hydrogen phosphite was added gradually. The mixture was heated at 100° for two hours, and then 8.1 g of 1,3-dibromopropane was added. Heating of the mixture at 100° was continued for 18 hours. The cooled reaction mixture was then poured onto ice, and the precipitate was treated with a solution of potassium hydroxide (20 g) in ethanol (200 ml). Magnesium hydroxide was filtered off, and the pH of the filtrate was brought to 6 by the addition of hydrochloric acid. The precipitated magnesium hydroxide was again filtered off, and the solution was vacuum-evaporated to dryness. The residue was ground with 10% aqueous potassium hydroxide solution. The oily layer was separated, and the aqueous layer was extracted several times with benzene. The organic layers were combined and vacuum-evaporated. The residue was crystallized from heptane. We obtained 5.1 g (26.7%) of trimethylenebis(dihexylphosphine) P,P'-dioxide, m.p. 105.5-107.5°. Found: H 12,10, 12.10; C 67.95, 67.96; P 13.19, 12.93%. $C_{27}H_{58}P_2O_2$. Calculated: H 12.26; C 68.03; P 13.00%.

Tetramethylenebis(diheptylphosphine) P,P'-Dioxide. This was prepared analogously to trimethylenebis(dihexylphosphine) P,P'-dioxide. From 13.4 g of magnesium powder, 67.3 g of heptyl chloride, 13.8 g of diethyl hydrogen phosphite, and 8.6 g of 1,4-dibromobutane in 100 ml of heptane we obtained 6.6 g (30%) of tetramethylenebis-(diheptylphosphine) P,P'-dioxide, m.p. 98-99°. Found: H 12.66, 12.45; C 70.25, 70.21; P 11.31, 11.45%. $C_{22}H_{68}P_2O_2$. Calculated: H 12.53; C 70.28; P 11.33%.

SUMMARY

Some dialkylphosphinic acids, dialkylphosphinous esters, and alkylenebis(dialkylphosphine) P,P'-dioxides were synthesized via organomagnesium compounds prepared in absence of ether and other catalysts for the Grignard reaction.

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