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Reactions of Elemental Phosphorus and Phosphine with Electrophiles in Superbasic Systems: XVI.[1] Phosphorylation of Benzyl Chloride with Elemental Phosphorus and Phosphine

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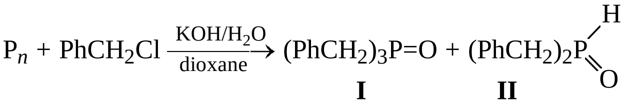
Abstract — The major product of the reaction of benzyl chloride with red phosphorus in the system concentrated aqueous KOH–dioxane–phase-transfer catalyst (43–95°C, Ar) is tribenzylphosphine oxide (yield up to 61%). Under similar conditions, phosphorylation of benzyl chloride with white phosphorus occurs differently, yielding dibenzylphosphine oxide as major product. Conditions are found for preparative synthesis of dibenzylphosphine from phosphine and benzyl chloride in the system KOH–DMSO.

It was reported previously that red phosphorus reacts with benzyl chloride in superbasic media of the type alkali metal hydroxide–nonhydroxyl solvent (DMSO) or under conditions of phase-transfer catalysis at elevated temperatures (75–100°C) to give as major product tribenzylphosphine oxide (yield up to 30%; here and hereinafter, yield based on the amount of benzyl chloride taken) and also minor amounts of tribenzylphosphine and tetrabenzylphosphonium chloride [2, 3]. Phosphorylation of benzyl chloride with the system PH_3–KOH–DMSO–H_2O at elevated pressure yields benzylphosphine [4], whereas the same reaction performed at atmospheric pressure gave dibenzylphosphine oxide in 50% yield, with dibenzylphosphine detected as intermediate by ^{31}P NMR [5].

To extend the possibilities of preparing organophosphorus compounds from elemental phosphorus and benzyl chloride and to obtain additional information on the comparative reactivity of red and white phosphorus in reactions with electrophiles (these reactions attract growing researchers’ attention as a new convenient route to organic phosphines and phosphine oxides [6–11]), we continued studying phosphorylation of benzyl chloride with elemental phosphorus and phosphine in the presence of a strong base.

We found that tribenzylphosphine oxide **I** can be prepared in a yield of up to 61% under relatively mild conditions (90–95°C, 3 h, molar ratio red phosphorus : benzyl chloride = 5 : 1, system concentrated aqueous KOH–dioxane–benzyltriethylammonium chloride). Dibenzylphosphine oxide **II** was isolated as by-product (yield 12%, see table, run no. 1). The conversion of red phosphorus in the process is quantitative.



$$P_n + PhCH_2Cl \xrightarrow[\text{dioxane}]{KOH/H_2O} \underset{\textbf{I}}{(PhCH_2)_3P{=}O} + \underset{\textbf{II}}{(PhCH_2)_2P(H){=}O} \qquad (1)$$

When benzyl chloride is phosphorylated with the same agents at a lower temperature (at 60–65°C and especially at 43–45°C), the conversion of red phosphorus noticeably decreases (to 63 and 37%, respectively); the yield of the reaction products decreased also. In these experiments, along with phosphine oxides **I** and **II**, we also isolated benzylphosphinic acid (by treatment of the aqueous layer with HCl; see table, run nos. 2 and 3).

With white phosphorus, as expected [10, 11], benzyl chloride reacts more actively than with red phosphorus: The conversion of white phosphorus and the total yield of phosphine oxides **I** and **II** and of potassium salts of benzylphosphonic and dibenzylphosphinic acids (identified in the form of the corresponding acids **III** and **IV**) are virtually quantitative, even at mild reaction conditions (43–45 and 60–65°C). The major product of phosphorylation of benzyl chloride with white phosphorus is secondary phosphine

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[1] For communication XV, see [1].

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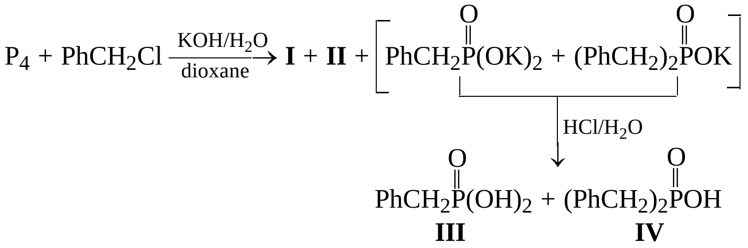
Phosphorylation of benzyl chloride with elemental phosphorus under the conditions of phase-transfer catalysis[a]

Run no.	Elemental phosphorus, mmol	$PhCH_2Cl$, mmol	Temperature, °C	Yield of compounds, %[b]				Phosphorus conversion, %
				I	**II**	**III**[c]	**IV**[c]	
1	P_n, 100	20	90–95	61	12	[d]	[d]	100
2	P_n, 33	6.6	60–65	46	12	11	[d]	63
3	P_n, 33	6.5	43–45	29	1	3	[d]	37
4[e]	P_4, 32.5	6.5	90–95	23	36	6	34	100
5[e]	P_4, 36	7.2	60–65	35	48	10	3	100
6[e]	P_4, 31.7	6.3	43–45	27	46	24	2	100
7[e,f]	P_4, 29	6.5	60–65	Traces	39	17	12	100

[a] In run no. 1, we took 625 mmol of KOH, 15 ml of H_2O, 0.5 g of benzyltriethylammonium chloride, and 40 ml of dioxane; in run nos. 2–7, 208 mmol of KOH, 5 ml of H_2O, 0.17 g of benzyltriethylammonium chloride, and 20 ml of dioxane; heating time 3 h. [b] Based on the amount of benzyl chloride taken. [c] Acids **III** and **IV** were isolated from the reaction mixture after acidification of the aqueous layer with HCl. [d] Is not formed. [e] In run nos. 4–7, the product yields were calculated from the ^{31}P NMR spectra. [f] Benzene (20 ml) was taken instead of dioxane.

oxide **II** (see table, run nos. 4–6). Similar results were obtained previously in a comparative study of the reactions of red and white phosphorus with 4-methoxybenzyl chloride [12].



$$P_4 + PhCH_2Cl \xrightarrow[\text{dioxane}]{KOH/H_2O} \mathbf{I} + \mathbf{II} + \left[PhCH_2\overset{O}{\overset{\|}{P}}(OK)_2 + (PhCH_2)_2\overset{O}{\overset{\|}{P}}OK\right] \xrightarrow{HCl/H_2O} \underset{\mathbf{III}}{PhCH_2\overset{O}{\overset{\|}{P}}(OH)_2} + \underset{\mathbf{IV}}{(PhCH_2)_2\overset{O}{\overset{\|}{P}}OH} \qquad (2)$$

When reaction (2) is performed in benzene (one of the best solvents for white phosphorus), the phosphorylation selectivity increases. Under these conditions, virtually no tertiary phosphine oxide **I** is formed, but the total yield of **II**–**IV** somewhat decreases (to 68%; see table, run no. 7, cf. run no. 5).

Despite the fact that all the steps of experiments on phosphorylation of benzyl chloride with elemental phosphorus were performed in an inert atmosphere (Ar), the major products were four-coordinate phosphorus compounds: phosphine oxides **I** and **II** and potassium salts of benzyl- and dibenzylphosphinic acids. The corresponding benzyl-, dibenzyl-, and tribenzylphosphines were detected in the reaction mixtures by ^{31}P NMR, but as minor products. This fact suggests that reactions (1) and (2) mainly involve not polyphosphide but polyphosphinite anions generated from elemental phosphorus in the presence of a base, by analogy with the previously reported schemes of phosphorylation of organyl halides [1, 2, 12] and weakly electrophilic alkenes [6, 8, 13].

The predominant formation of secondary phosphine oxide **II** in reaction (2) may be due to easier cleavage of the P–P bonds in a strained tetrahedral molecule of white phosphorus, compared to a macromolecule of red phosphorus, and hence to higher concentration of polyphosphinite and phosphinte ions in the case of phosphorylation of benzyl chloride with white phosphorus. This conclusion is also consistent with exclusive formation of the mono- and diphosphorylation products in the reaction of benzyl chloride with white phosphorus in benzene, i.e., a higher concentration of white phosphorus in this solvent also promotes faster cleavage of the P–P bonds and results in higher concentration of phosphinite anions.

Phosphine generated together with hydrogen from red phosphorus and KOH in the water–toluene solvent system does not noticeably react with benzyl chloride under the conditions of reactions (1) and (2). At the same time, phosphorylation of benzyl chloride with the system phosphine–KOH–DMSO in the presence of a small amount of water allows, under appropriate conditions, preparation of dibenzylphosphine **V** and dibenzylphosphine oxide **II** in 32 and 22% yields, respectively. The reaction is performed by vigorously passing phosphine through a heated (40–45°C) KOH–DMSO–H_2O suspension with simultaneous slow addition of benzyl chloride. Phosphine **V** was isolated from the reaction mixture by extraction with hexane followed by vacuum fractionation:

$$PH_3 \xrightarrow[\text{KOH/DMSO}]{PhCH_2Cl} \underset{\mathbf{V}}{(PhCH_2)_2PH} + \mathbf{II}. \qquad (3)$$

The key step of reaction (3) is, apparently, the formation of phosphide anions from phosphine under the action of a superstrong base (KOH–DMSO):

$$PH_3 \xrightarrow{\text{KOH/DMSO}} {}^{-}PH_2 \xrightarrow[\text{KOH/DMSO}]{PhCH_2Cl} \mathbf{V}. \qquad (4)$$

The subsequent oxidation of **V** in the presence of DMSO or traces of air yields phosphine oxide **II**, which is prone to further oxidation and readily transforms into dibenzylphosphinic acid **IV** in air.

Thus, direct reactions of benzyl chloride with elemental phosphorus and phosphine in the presence of strong bases allow easy formation of the C–P bond and preparation of promising organophosphorus compounds. In particular, tribenzylphosphine oxide was successfully used in the Horner–Wittig reaction for the synthesis of substituted alkenes of various structures [10, 14–17]. This phosphine oxide also proved to be an effective fireproofing agent for polyvinyl chloride plastisols [18, 19].

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 device. The ^1H and ^{31}P NMR spectra were taken on a Bruker DPX-400 spectrometer, internal reference HMDS, solvent $CDCl_3$. Phosphine in the form of a mixture with hydrogen was generated according to [20]. All the experiments were performed in an inert atmosphere (Ar).

Tribenzylphosphine oxide I and dibenzylphosphine oxide II (see table, run no. 1). Water (15 ml) was added dropwise with stirring to a mixture of 3.1 g of red phosphorus, 2.53 g of benzyl chloride, 0.5 g of benzyltriethylammonium chloride, and 35 g of KOH in 40 ml of dioxane. The mixture was heated for 3 h at 90–95°C and, after cooling, diluted with water and extracted with chloroform. The chloroform extracts were dried over potassium carbonate, and the solvent was removed. The ^{31}P NMR spectrum of the residue (1.42 g) contained the signals of **I** (40.1 ppm) and **II** (35.5 ppm, $^1J_{PH}$ 468 Hz) in 91 : 9 ratio. The product was washed with benzene (3 × 2 ml), and the residue was reprecipitated from chloroform into ether and vacuum-dried to obtain 1.26 g of phosphine oxide **I**, mp 216–217°C (mp 212–213°C [2]). IR spectrum, ν, cm^{-1}: 1190 (P=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.03 d (6H, CH_2, $^2J_{PH}$ 13.6 Hz), 7.27 m (15H, Ph). Found, %: C 78.87; H 6.57; P 9.63. $C_{21}H_{21}OP$. Calculated, %: C 78.73; H 6.61; P 9.67.

The benzene extracts were combined, the solvent was removed, and the residue was reprecipitated from benzene into hexane and vacuum-dried to obtain 0.14 g of **II**, mp 106–107°C (hexane) (mp 109°C [21]). IR spectrum, ν, cm^{-1}: 2320 (PH), 1190 (P=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.16 d.d (4H, CH_2, $^2J_{PH}$ 15.3 Hz), 6.96 d.t (1H, PH, $^1J_{PH}$ 468 Hz), 7.27 m (10H, Ph). Found, %: C 72.87; H 6.57; P 13.63. $C_{14}H_{15}OP$. Calculated, %: C 73.03; H 6.57; P 13.45.

The aqueous phase was acidified with HCl to pH 5 and extracted with chloroform; the chloroform extracts were dried over magnesium sulfate, and the solvent was distilled off. The white crystalline residue (0.19 g) consisted, according to the ^1H and ^{31}P NMR spectra, of 20% **I** and 80% **II**. Pure compounds **I** (0.04 g) and **II** (0.14 g) were isolated as described above. Yields of phosphine oxides **I** and **II** 1.30 (61%) and 0.28 g (12%), respectively.

Benzylphosphinic acid III (see table, run no. 2). Water (15 ml) was added dropwise with stirring to a mixture of 1.03 g of red phosphorus, 0.83 g of benzyl chloride, 0.17 g of benzyltriethylammonium chloride, and 11.7 g of KOH in 20 ml of dioxane. The mixture was heated for 3 h at 60–65°C. After cooling, the aqueous-dioxane layer was analyzed by ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum (δ_P, ppm) contained the following signals (in parentheses are relative intensities, % of the total) belonging, apparently, to benzylphosphine, phosphine **V**, benzylphosphine oxide, potassium benzylphosphonate and benzylphosphinate, and phosphine oxides **II** and **I**, respectively: –122.06 t ($^1J_{PH}$ 193 Hz, 1.5%), –47.78 d ($^1J_{PH}$ 195 Hz, 8%), 12.70 t ($^1J_{PH}$ 475 Hz, 5%), 31.1 d ($^1J_{PH}$ 521 Hz, 3.5%), 33.90 s (8%), 35.5 d ($^1J_{PH}$ 468 Hz, 18%), and 43.68 s (56%). This mixture was diluted with water, and the unchanged phosphorus was filtered off and dried in air; 0.37 g of phosphorus was recovered (63% conversion). The filtrate was extracted with chloroform, the chloroform extracts were dried over potassium carbonate, and the solvent was distilled off. The residue (0.45 g), according to the ^{31}P NMR spectrum, contained phosphine oxides **I** and **II** in a 78 : 22 ratio. These products were isolated as described above; yields 0.32 (46%) and 0.09 g (12%), respectively. The aqueous layer was acidified with HCl to pH 5 and extracted with chloroform, the extracts were dried over magnesium sulfate, and the solvent was distilled off to obtain 0.12 g (11%) of acid **III**, mp 165–166°C (hot water) (mp 165–166°C [22]). ^{1}H NMR spectrum (D_2O), δ, ppm: 3.59 d (2H, CH_2, $^2J_{PH}$ 18.2 Hz), 7.75 m (5H, Ph), 13.19 s (2H, OH). ^{31}P NMR spectrum ($CDCl_3$): δ_P 33.8 ppm. Found, %: C 48.87; H 5.57; P 17.63. $C_7H_9O_3P$. Calculated, %: C 48.85; H 5.27; P 18.00.

Dibenzylphosphinic acid IV (see table, run no. 4). Water (5 ml) was added dropwise with stirring to a mixture of 1.01 g of white phosphorus in 20 ml of dioxane, 0.82 g of benzyl chloride, 0.17 g of benzyltriethylammonium chloride, and 11.67 g of KOH. The mixture was heated for 3 h at 90–95°C, cooled, diluted with water, and extracted with chloroform. The chloroform extracts were washed with water and dried with potassium carbonate. After distilling off the solvent, 0.49 g of a powder was obtained; it contained phosphine oxides **I** and **II** and acid **III** in a 33 : 55 : 12 ratio, according to the ^{31}P NMR spectrum. We failed to isolate pure compounds **I**–**III**. The aqueous layer was acidified with HCl to pH 5 and extracted with chloroform; the extracts were dried with magnesium sulfate, and the solvent was distilled off. The residue (powder, 0.29 g), according to the ^{31}P NMR spectrum, contained acids **III** and **IV** (7 and 93%, respectively). The powder was extracted with hot dioxane, the solvent was removed, and the residue was recrystallized from methanol. Acid **IV** was obtained; yield 0.27 g (34%), mp 187–189°C (methanol) (mp 189–190°C [22, 23]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.85 d (4H, CH_2, $^2J_{PH}$ 16.9 Hz), 7.18–7.28 m (10H, Ph), 9.02 s (1H, OH). ^{31}P NMR spectrum ($CDCl_3$): δ_P 50.2 ppm. Found, %: C 67.62; H 6.25; P 12.63. $C_{14}H_{15}O_2P$. Calculated, %: C 68.29; H 6.14; P 12.58.

Dibenzylphosphine V. A solution of 12.65 g of benzyl chloride in 5 ml of DMSO was added dropwise at 40°C over a period of 1.5 h with stirring and continuous bubbling of phosphine to a suspension of 10 g of KOH, 50 ml of DMSO, and 6.3 ml of H_2O, purged with argon and saturated with phosphine. The mixture was heated at 40–45°C for an additional 1 h in a flow of phosphine, after which the supply of phosphine was stopped, the mixture was purged with argon and cooled, 80 ml of hexane was added, the hexane layer was separated, the solvent was removed, and the residue was fractionated in a vacuum. Dibenzylphosphine was obtained; yield 3.45 g (32%), bp 128–130°C (1 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.96 d (4H, CH_2P, $^2J_{PH}$ 2.8 Hz), 7.25–7.49 m (10H, C_6H_5). ^{31}P NMR spectrum ($CDCl_3$): δ_P –47.9 ppm ($^1J_{PH}$ 196 Hz). The lower layer was diluted with water and extracted with chloroform, the extracts were washed with water and dried over potassium hydroxide, and the solvent was distilled off. Phosphine oxide **II** was obtained; yield 2.55 g (22%).

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