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Reactions of Elemental Phosphorus and Phosphine with Electrophiles in Superbasic Systems: XIX.[1] Formation of the C–P Bond with Participation of Elemental Phosphorus under Microwave Assistance

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Abstract—Microwave irradiation facilitates phosphorylation of aryl methyl chlorides and styrene with red phosphorus in the presence of strong bases and increases the yield of the main products, tertiary phosphine oxides.

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Synthesis of organophosphorus compounds based on elemental phosphorus is actively developing. It attracts the attention of researchers by its evident simplicity and technological feasibility [1–6]. Substantial contribution to elaboration of the method of direct phosphorylation of organic substrates was made by new approach to activation of elemental phosphorus based on the use of heterogeneous superbasic catalytic media and reagents [7–12] as well as by electrochemical transformation of elemental phosphorus under the action of organic and organometallic compounds [6, 13, 14]. It opened nontraditional approaches to formation of the P–C, P–O, P–N bonds and allowed to realize direct reactions of elemental phosphorus with readily available organic compounds such as alkenes, acetylenes, alkene oxides, organyl halides, aldehydes, etc. Further activation of the electrophile phosphorylation processes with elemental phosphorus by ultrasound [9, 15, 16] and radiation assistance [1, 4, 17] was also reported. At the same time, the data on microwave activation of these reactions are limited to a short communication on the reaction of red phosphorus with vinyl pyridines in the system KOH–DMSO (an increase of the reaction rate was observed [18]).

In the present paper we report on new data of successful application of microwave irradiation for activation of phosphorylation of electrophiles, in particular, of aryl methyl chlorides and styrene, with red phosphorus in the presence of strong bases. As the source of microwave irradiation we used a domestic microwave oven (90, 360 and 600 Wt).

The experiments showed that 10 min action of microwave irradiation of 90 Wt power on the system red phosphorus–benzyl chloride–KOH–dioxane–H_2O–phase transfer catalyst (benzyl triethylammonium chloride) allows one to prepare tribenzyl phosphine oxide (**I**) in high yield (78%) along with small amounts of the products of incomplete benzylation: secondary phosphine oxide (**II**), benzylphosphonous (**III**), benzylphosphonic (**IV**) and dibenzylphosphinic (**V**) acids in total yield of ~15%; the conversion of phosphorus and benzyl chloride were 65 and 85%, respectively (see the table, no. 1). Phosphinic acids **III**–**V** were isolated after acidification of the reaction mixture.

Heating of the above reagents to 90–95°C for 3 h without microwave assistance was reported to lead to full conversion of red phosphorus and benzyl chloride with the formation of tribenzyl and dibenzyl phosphine oxides in 61 and 12%, respectively [19] (see the table, no. 2).

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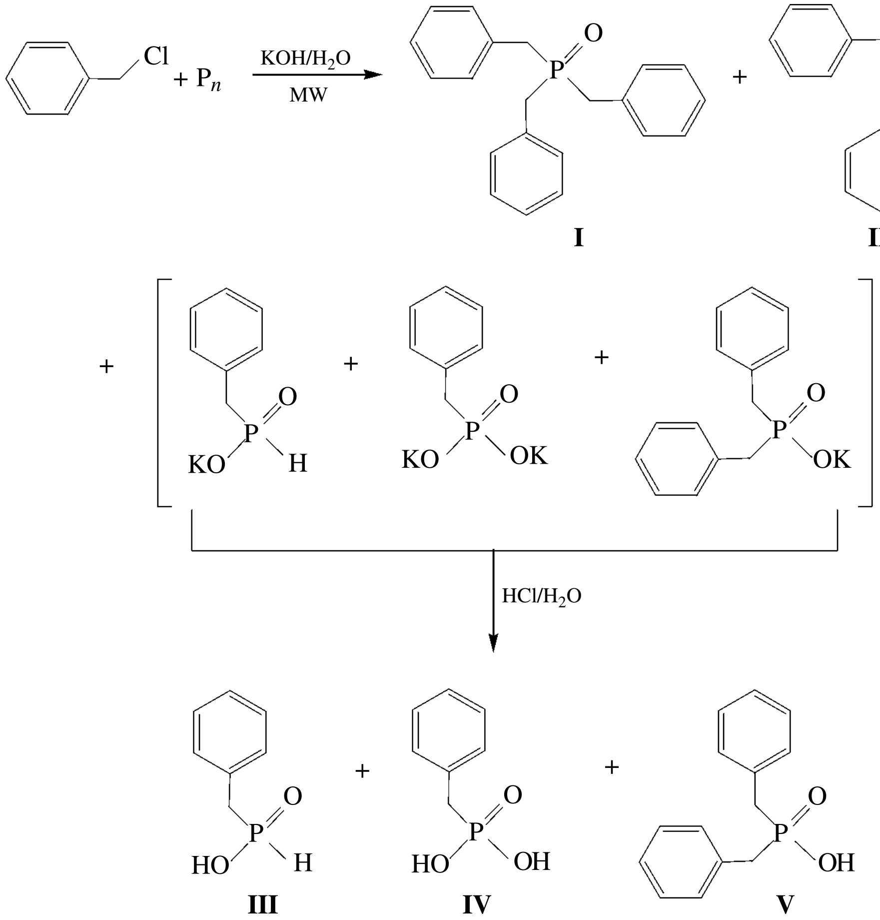
[1] For communication XVIII, see [1].

Upon the increase of the microwave oven power to 360 and 600 Wt with simultaneous decrease of duration of reaction (1) to 2.5–5 min the yield of the tertiary phosphine oxide **I** is slightly reduced but the total yield of compounds **II**–**V** is increased (see the table, nos. 3–5). This is due to more effective destruction of the phosphorus crystal lattice under the action of microwave irradiation, that increases the phosphorus-centered nucleophiles concentration in the reaction medium and, therefore, the yield of the products of their incomplete benzylation.



(1)

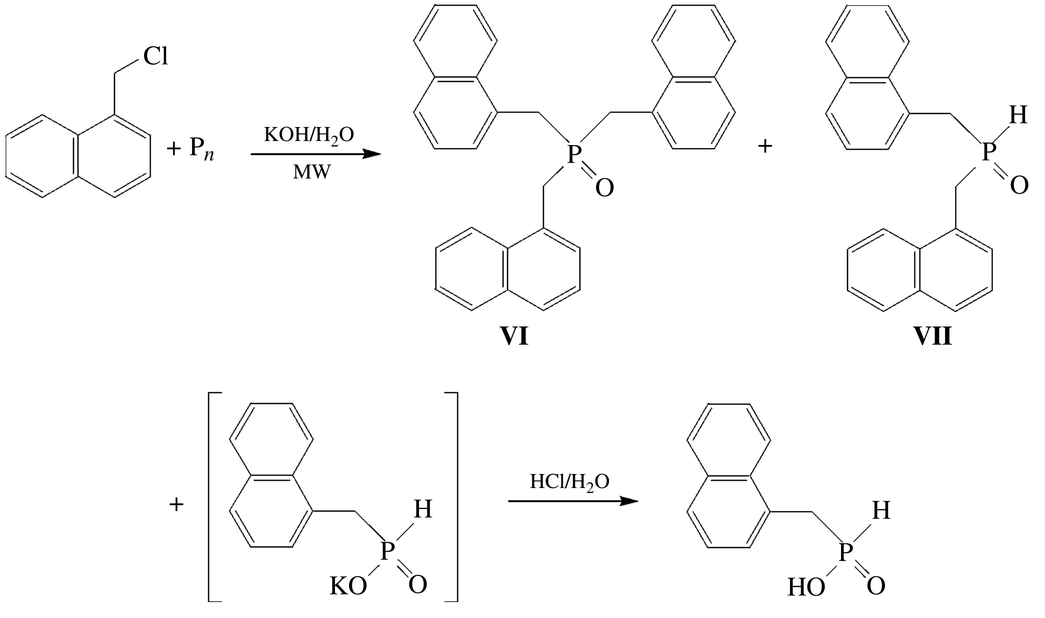
1-Chloromethylnaphthalene is known to react with red phosphorus in the system KOH–dioxane–H_2O–benzyl triethylammonium chloride upon heating (90–95°C, 3 h) [1] to afford tris(1-naphthylmethyl)phosphine oxide (**VI**), bis(1-naphthylmethyl)phosphine oxide (**VII**), (1-naphthylmethyl)phosphonous (**VIII**), and bis(1-naphthylmethyl)phosphinic acids in 69, 18, 6 and 7% yield, respectively (see the table, no. 6). Microwave irradiation (90 Wt) of these reagents allows one to reduce the reaction time to 10min, that is, by more than one order of magnitude, and to obtain compounds **VI**–**VIII** in 68, 8, and 17% yield, respectively (see the table, no. 7).

Phosphorylation of styrene with red phosphorus effectively proceeds in the system KOH–DMSO under microwave irradiation (600 Wt, 4 min) and results mainly in tris(2-phenylethyl)phosphine oxide (**IX**) in 83% yield, the conversion of styrene and red phosphorus being 88 and 100%, respectively (see the table, no. 9). Small amounts of bis(2-phenylethyl)phosphine oxide (**X**), 2-phenylethyl phosphinous (**XI**) and bis(2-phenylethyl) phosphinic (**XII**) acids are also formed under these conditions (see the table, no. 9). The use of microwave irradiation of lower power (360 Wt), in spite of some increase of the reaction time (6 min), results in a decrease of the yield of tertiary phosphine oxide **IX** to 69% (see the table, no. 10). At the same time, without microwave assistance, upon heating of the above reaction mixture to 90–95°C for 3 h the effectiveness of phosphorylation

Phopshorylation of arylmethyl chlorides and styrene with red phosphorus under the conditions of phase transfer catalysis and microwave irradiation[a]

Run no.	Electrophile	W, Wt	Irradiation duration, min	Yield,[b] %					Conversion, %	
				$R_3P{=}O$	$R_2P(O)H$[c]	RP(O)H(OH)	$RP(O)(OH)_2$	$R_2P(O)OH$	electro-phile	phos-phorus
1	$PhCH_2Cl$	90	10	78	8	2	traces	8	85	65
2	$PhCH_2Cl$	d	d	61	12	e	e	e	100	100
3	$PhCH_2Cl$	360	3	72	5	5	6	9	77	64
4	$PhCH_2Cl$	360	5	62	5	13	traces	5	92	76
5	$PhCH_2Cl$	600	2.5	62	17	5	traces	2	94	67
6	$1\text{-}C_{10}H_7CH_2Cl$	d	d	69	18	6	e	7	100	100
7	$1\text{-}C_{10}H_7CH_2Cl$	90	10	68	8	17	e	e	89	64
8	$1\text{-}C_{10}H_7CH_2Cl$	600	2.5	66	16	12	e	e	74	61
9	$PhCH{=}CH_2$	600	4	83	6	traces	e	2	88	100
10	$PhCH{=}CH_2$	360	6	69	2	traces	e	2	90	100
11	$PhCH{=}CH_2$	d	d	34	3	3	e	2	91	100

[a] All experiments were carried out in an argon atmosphere. In nos. 1–5 100 mmol of red phosphorus, 20 mmol of benzyl chloride, 625 mmol of KOH, 15 ml of water, 2.2 mmol of TEBAC and 40 ml of dioxane was used; in nos. 6–8 32.6 mmol of red phosphorus, 6.5 mmol of 1-chloromethylnaphthalene, 208 mmol of KOH, 5 ml of water, 0.75 mmol of TEBAC and 20 ml of dioxane was used; in nos. 9–11 100 mmol of red phosphorus, 104 mmol of styrene, 178 mmol of KOH, 1.5 ml of water, 0.1 g of hydroquinone and 40 ml of DMSO was used. [b] Yield of products is given with respect to the reacted electrophile. [c] Yield of the secondary phosphine oxide in nos. 1, 3, 4, 7, 9–11 was calculated taking into account the data of ^{31}P NMR spectra. [d] nos. 2, 6, and 11 were performed upon heating of the reagents to 90–95°C during 3 h without microwave irradiation. [e] Not formed.

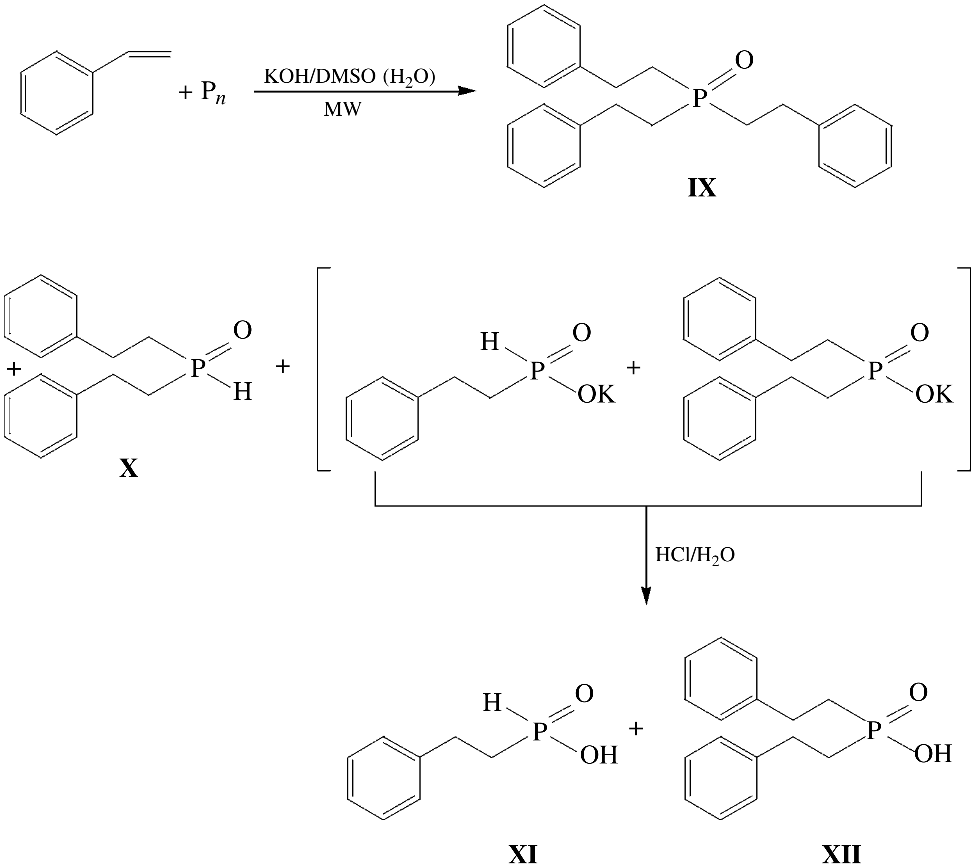


VI **VII** **VIII**

(2)

of styrene substantially decreases: the yield of compounds **IX**–**XII** is 34, 3, 3, and 2%, respectively (see the table, no. 11).

Therefore, on the example of direct reactions of benzyl chloride, 1-chloromethylnaphthalene and styrene with red phosphorus a novel method of combined activation of activation of electrophile phosphorylation that includes simultaneous action of superbases and microwave irradiation is elaborated. As a result, the corresponding tertiary phosphine



(3)

oxides are prepared in high yield. These organophosphorus compounds are the compounds of choice for, e.g., the design of nanomaterials [20, 21]. In addition, tribenzylphosphine oxide was successfully used in the Horner–Wittig reaction of synthesis of substituted alkenes of various structure [11, 22–25]. It was also shown to be an effective antipyrene for polyvinyl chloride plastisols [26, 27]. Catalytic systems based on nickel complexes with tris(2-phenylethyl)phosphine oxide exert high activity and selectivity in the reactions of dimerization and oligo-merization of olefins (in particular, ethylene and styrene) [12, 28]. Tris(1-naphthylmethyl)phosphine oxide was proposed as a luminophore for preparation of special liquid and solid scintillators [1], which can be used for solving of such a fundamental problem as detection of neutrino [29].

EXPERIMENTAL

IR spectra were recorded on a Specord IR-75 instrument. ^{1}H, ^{13}C, and ^{31}P NMR spectra were registered on a Bruker DPX 400 spectrometer (400, 100, and 161.98 MHz, respectively), internal standard HMDS, solvent $CDCl_3$. Microwave irradiation was performed in a modified domestic microwave oven LG Electronics Ins. MS-192 A equipped with condenser. GC analysis was performed on a PAKhV-07 chromatograph, column 1200 × 10 mm, 15% of Carbowax-6000 on Chromaton N-AW-DMGS (0.25–0.36mm), gas-carrier is helium. All experiments were run in an argon atmosphere. Parameters of NMR spectra for compounds **I**–**XII** are identical to the earlier obtained spectral characteristics [1, 19, 30–33]. The yield of compounds **I**–**XII** was calculated with respect to the reacted electrophile.

Tribenzylphosphine oxide (I) (no. 1). Mixture of 3.10 g of red phosphorus, 2.53 g of benzyl chloride, 0.5g of benzyl triethylammonium chloride, 35 g of KOH, 15ml of water and 40 ml of dioxane was irradiated in the microwave oven (90 Wt) for 10 min. The reaction mixture was cooled, diluted with water, the unreacted phosphorus was filtered off, washed with water to neutral reaction and dried in air to recover 1.1 g of phosphorus (conversion 65%). The filtrate was extracted with chloroform, combined chloroform extract washed with water, dried over K_2CO_3, the solvent and unreacted benzyl chloride were removed to recover 0.38 g of benzyl chloride (conversion 85%). The amount of benzyl chloride was determined by GC with octane as a standard. The residue was dried under vacuum to afford 1.6 g of white powder. Its ^{31}P NMR spectrum contains the signals at 40.1 ppm (phosphine oxide **I**) and 35.5 ppm, $^1J_{PH}$ 468 Hz (phosphine oxide **II**) [19] in the ratio of 9 : 1. The reaction product was washed with benzene (3 × 2 ml), dried in vacuum, obtained 1.42 g (78%) of phosphine oxide **I**, mp 214–215°C (mp 216–217°C [19]). Found, %: C 78.64; H 6.70; P9.56. $C_{21}H_{21}OP$. Calculated, %: C 78.73; H 6.61; P9.67.

The aqueous layer was acidified with HCl to pH 4–5, extracted with chloroform, chloroform extract dried over $CaCl_2$ and removed the solvent to obtain 0.27 g of the product containing, according to ^{31}P NMR, phosphine oxide **II** and acids **III**–**V** in the ratio of 8 : 24 : 7 : 61.

Tris(1-naphthylmethyl)phosphine oxide (VI) (run 7). Mixture of 1.01 g of red phosphorus, 1.15 g of 1-chloromethylnaphthalene, 0.17 g of benzyl triethylammonium chloride , 11.67 g of KOH, 5 ml of water and 20 ml of dioxane was irradiated in the microwave oven (90 Wt) for 10 min. The reaction mixture was cooled, diluted with water, the unreacted phosphorus was filtered off, washed with water to neutral reaction and dried in the air to recover 0.36 g of phosphorus (conversion 64%). The filtrate was extracted with chloroform, combined chloroform extract washed with water, dried over K_2CO_3, the solvent removed, the residue evacuated to obtain 0.88 g of beige powder. Its ^{31}P NMR spectrum contains the signals at 42.51 ppm (phosphine oxide **VI**) and 35.36 ppm, $^1J_{PH}$ 475 Hz (phosphine oxide **VII**) [1] in the ratio of 91 : 9. The reaction product was washed with light petroleum ether (2 × 1 ml) and reprecipitated from chloroform into hexane to afford 0.62 g (69%) of phosphine oxide **VI**, mp 258–259°C (mp 260°C [1]). Found, %: C 84.30; H 5.88; P 6.42. $C_{33}H_{27}OP$. Calculated, %: C 84.23; H 5.78; P 6.58. From the ethereal extract 0.13 g of 1-chloro-methylnaphthalene was recovered (conversion 89%).

The aqueous layer was acidified with HCl to pH 5, extracted with chloroform, chloroform extracts dried over $CaCl_2$, chloroform removed to obtain 0.2 g (17%) of acid **VIII** [1].

Tris(2-phenylethyl)phosphine oxide (IX) (run 9). Mixture of 3.1 g of red phosphorus, 10.87 g of styrene, 0.1 g of hydroquinone, 10 g of KOH, 1.5 ml of water and 40 ml of DMSO was irradiated in the microwave oven (600 Wt) for 4 min. The reaction mixture was cooled, diluted with water, extracted with benzene, the benzene extract washed with water, dried over K_2CO_3, the solvent and unreacted styrene distilled off to recover 1.27 g of styrene (conversion 88%). The amount of styrene was determined by GC with octane as a standard. The residue was dried under vacuum to afford 10 g of white powder. Its31P NMR spectrum contains the signals at 45.19 ppm (phosphine oxide **IX**) [30] and 30.56 ppm, $^1J_{PH}$ 455 Hz (phosphine oxide **X**) [31] in the ratio of 93 : 7. This mixture was dissolved in 40 ml of ethanol, added 0.23 ml of H_2O_2 (35.5%, ρ 1.135) and stirred for 1h at 50°C. The solvent was removed, the residue dissolved in 70 ml of benzene, added 0.5 g of KOH and stirred at room temperature for 0.5 h. The suspension obtained was filtered through $NaHCO_3$, benzene distilled off, the residue dried in vacuum to obtain 9.3 g of phosphine oxide **IX**, mp 159°C (mp 157°C [30]). Found, %: C 78.4; H 7.69; P 8.20. $C_{24}H_{27}OP$. Calculated, %: C 79.56; H 7.46; P 8.56.

The aqueous layer was acidified with HCl to pH 5, extracted with chloroform, chloroform extract dried over $CaCl_2$ and removed the solvent to obtain 0.45 g of the product containing, according to ^{31}P NMR, phosphine oxide **X** and acids **XI** and **XII** [32, 33] in the ratio of 12 : 38 : 50.

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