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REACTION OF VINYLPYRIDINES WITH ACTIVE MODIFICATIONS OF ELEMENTAL PHOSPHORUS IN KOH/DMSO

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The phosphorylation of 2-vinyl- and 4-vinylpyridines by white phosphorus and active modifications of red phosphorus (obtained by thermal polymerization of white phosphorus in the presence of graphite or the action of ionizing radiation in benzene) in the KOH/DMSO superbase system at room temperature leads to the formation of tris[2-(2-pyridyl)ethyl]- and tris[2-(4-pyridyl)ethyl]phosphine oxides in 58-72% yield. These oxides are promising ligands for design of metal complex catalysts. These vinylpyridines react less efficiently with ordinary red phosphorus and the yield of the corresponding tris(2-pyridylethyl)phosphine oxides does not exceed 10%.

Keywords: active red phosphorus, white phosphorus, vinylpyridines, superbases, tris(2-pyridylethyl)phosphine oxides, phosphorylation, complexes, $PdCl_2$.

New direct reactions of red phosphorus with electrophiles such as organic halides, dihaloalkanes, oxiranes, arylalkenes, hetarylalkenes, arylalkynes, and hetarylalkynes carried out by the action of superbase catalytic systems such alkali hydroxide in a polar nonhydroxyl solvent or in a system containing an aqueous solution of alkali hydroxide, organic solvent, and phase transfer catalyst or alkali metal, tertiary alcohol, and liquid ammonia hold promise as convenient methods for formation of the C–P bond and open new possibilities for the synthesis of previously unreported or not readily available secondary and tertiary phosphines and phosphine oxides, and their derivatives with unsaturated and heterocyclic substituents [1-3], which are promising ligands for metal complex catalysts, synthones, and intermediates [4, 5].

The direct phosphorylation of vinylpyridines by elemental phosphorus was first achieved for ordinary red phosphorus. Heating red phosphorus with 2-vinyl-, 4-vinyl-, and 2-methyl-5-vinylpyridines in $KOH/DMSO/H_2O$ at 70-95°C gave the corresponding tris(2-pyridylethyl)phosphine oxides in 30-52% yield [6, 7]. Ultrasonic activation of the reagents leads to an increase in the rate of phosphorylation of vinylpyridines [6]. Under comparable conditions, white phosphorus is a more active phosphorylating agent than red phosphorus [7].

To obtain new data on the regularities of the reaction of vinylpyridines with various modifications of elemental phosphorus and to extend their further preparative capabilities we have studied the phosphorylation of 2-vinyl- (**1a**) and 4-vinylpyridines (**1b**) by white and activated red phosphorus obtained by the thermal polymerization of white phosphorus in the presence of graphite (P_n^1) or the action of ionizing radiation in benzene

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(P_n^2) [8]. White phosphorus (P_4) and both active red phosphorus modifications P_n^1 and P_n^2 react readily with vinylpyridines **1a** and **1b** in a suspension of KOH in DMSO with a slight trace of water even at room temperature to give tris[2-(2-pyridyl)ethyl]phosphine oxide (**2a**) and tris[2-(4-pyridyl)ethyl]phosphine oxide (**2b**), respectively.

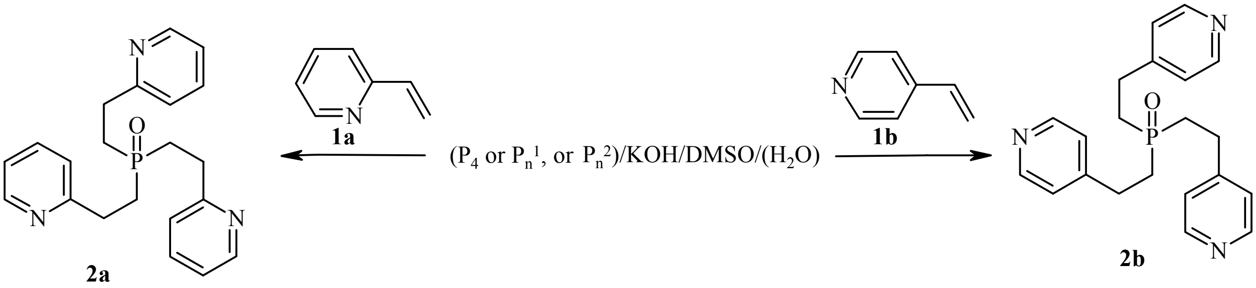
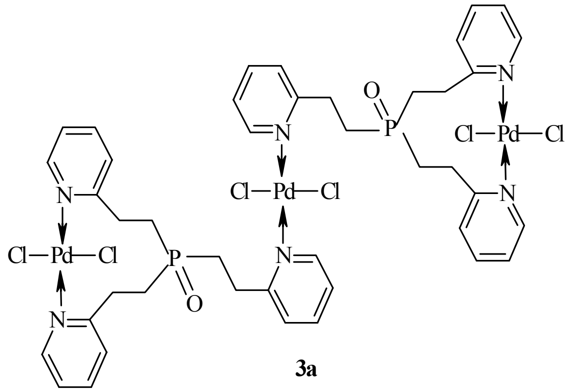


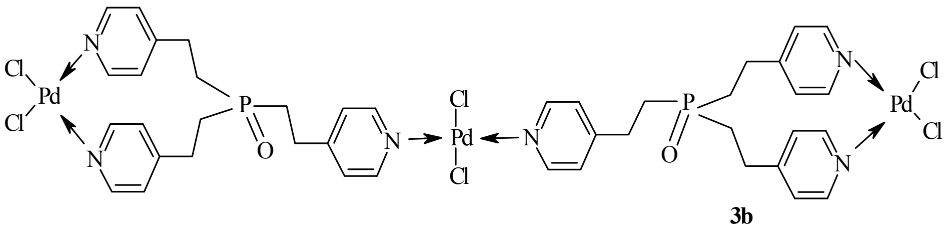
Table 1 shows that the reactivity of white phosphorus and both modifications of activated red phosphorus relative to 4-vinylpyridine is comparable. The yield of phosphine oxide **2b** is 51-58%, while the phosphorus conversion is 90-100%. On the other hand, white phosphorus reacts more efficiently than activated red phosphorus with 2-vinylpyridine to give phosphine oxide **2a** in 72% yield, while the yield using P_n^1 and P_n^2 was 56 and 48%, respectively (experiments 1-3, Table 1). Under comparable conditions, unactivated red phosphorus displays low reactivity with vinylpyridines **1a** and **1b**. The yield of phosphine oxides **2a** and **2b** does not exceed 10% with phosphorus conversion 28-55% (experiments 4 and 8, Table 1).

Thus, fundamental feasibility of using activated red phosphorus in the reaction with vinylpyridines has been demonstrated. Activated red phosphorus, which is nonpyrophoric and has low toxicity, similar to ordinary red phosphorus [8], is much more reactive than ordinary red phosphorus and has similar reactivity to white phosphorus.

The first evidence has been obtained demonstrating the use of pyridinylphosphine oxides **2a** and **2b** in the synthesis of complexes. Thus, phosphine oxides **2a** and **2b** readily react with $PdCl_2$ in aqueous media at room temperature to give trinuclear complexes [$(PdCl_2)_3L_2$] (**3a** and **3b**), where L = **2a** and **2b**.



3a



3b

TABLE 1. Phosphorylation of 2-Vinyl- and 4-Vinylpyridines by Elemental Phosphorus*

Exp. No.	Phosphorus, mmol	Vinylpyridine, mmol	KOH, mmol	H_2O, ml	Yield of phosphine oxide, %*[2]	Phosphorus conversion, %
1	P_4, 42	**1a**, 21.0	71	1.7	**2a**, 72	100
2	P_n^1, 21	**1a**, 10.5	36	0.9	**2a**, 56	83
3	P_n^2, 32	**1a**, 16.0	55	1.3	**2a**, 48	100
4	P_n, 42	**1a**, 21.0	71	1.7	**2a**, 7	28
5	P_4, 32	**1b**, 16.0	59	1.4	**2b**, 56	90
6	P_n^1, 29	**1b**, 15.0	55	1.3	**2b**, 51	93
7	P_n^2, 32	**1b**, 16.0	55	1.3	**2b**, 58	100
8*[3]	P_n, 32	**1b**, 16.0	59	1.4	**2b**, 10	55

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* All the experiments were carried out in an inert argon atmosphere in 30 ml DMSO at room temperature for 5-6 h. In experiments 2 and 6, activated red phosphorus P_n^1 containing 65 mass % phosphorus and 35 mass % graphite was used. In experiments 3 and 7, activated red phosphorus P_n^2 containing 70 mass % phosphorus and unidentified organophosphorus compounds was used.

*[2] The yield was calculated relative to the amount of vinylpyridines **1a** or **1b** taken.

*[3] In this experiment, 15% oligomeric phosphine oxides, identical to those formed in our previous work [6] from red phosphorus and 4-vinylpyridine, were obtained in addition to **2b**.

The IR spectra of complexes **3a** and **3b** showed that the band characteristic for vibration of the pyridine ring is shifted by 19 cm^{-1} relative to the analogous band in starting pyridylphosphine oxides **2a** and **2b** and is found at 1606 and 1617 cm^{-1}, respectively, while the absorption for the P=O band (at 1158-1164 cm^{-1}) is virtually unchanged. These findings indicate that the donor–acceptor bond of the ligand with the metal in complexes **3a** and **3b** involves the pyridine fragment and served for assignment of the structures proposed.

EXPERIMENTAL

The IR spectra were taken for KBr pellets on a Bruker IFS-25 spectrometer and the ^{1}H NMR spectra were registered on a Bruker DPX-400 spectrometer for solutions in $CDCl_3$ with HMDS as the internal standard. The ^{31}P NMR spectra were taken on a Jeol FX-90Q spectrometer for solutions in $CDCl_3$. The ^{1}H and ^{31}P NMR spectra of **2a** and **2b** were identical for samples of these compounds prepared in our previous work [6, 7].

Modification of Activated Red Phosphorus (P_n^1) with 65 mass % phosphorus content was prepared using an ampule technique by heating white phosphorus in a mixture with 13% graphite at 250°C. The conversion after removal of unreacted white phosphorus was 23% [8].

Modification of Activated Red Phosphorus (P_n^2) with 70 mass % phosphorus was obtained at room temperature by the action of ^{60}Co ionizing radiation. The absorbed dose rate was 1.17 Gr/sec on saturated solutions of white phosphorus in benzene. IR and X-ray photoelectron spectroscopy revealed the presence of P–P, P–C, P–O–C bonds in the sample of P_n^2 obtained [8].

The spontaneous combustion temperature of P_n^1 and P_n^2 activated red phosphorus is about 160°C.

Tris[2-(2-pyridyl)ethyl]phosphine Oxide (2a) (exp. 2, Table 1). A solution of KOH (2 g) in water (0.9 ml) was added dropwise with stirring to an argon-blown mixture of activated red phosphorus P_n[1] (1.0 g, 21 mmol relative to the pure element) and 2-vinylpyridine (1.1 g, 10.5 mmol) in DMSO (30 ml). The reaction mixture was stirred for 5 h at ~20°C in an argon atmosphere, diluted with water, filtered to remove unreacted elemental phosphorus and graphite (0.44 g black powder was isolated, the phosphorus conversion was 62%), and extracted with chloroform. The chloroform extracts were dried over potassium carbonate, chloroform and DMSO was distilled off at reduced pressure. The residue was dried in vacuum to give 0.71 g (56%) phosphine oxide **2a**; mp 140-141°C (ethyl acetate). IR spectrum (KBr), cm^{-1}: 3081, 3070, 3035 (ν_{CH} pyridine), 2960, 2944, 2909 (ν_{CH_2}), 1587, 1567, 1474, 1436 ($\nu_{C=C,C=N}$ pyridine), 1225 (δ_{CH}, pyridine), 1154 ($\nu_{P=O}$), 1049, 1019, 946, 793, 772, 752 (δ_{CH} pyridine). Found, %: C 68.90; H 6.83; P 8.00. $C_{21}H_{24}N_3OP$. Calculated, %: C 69.04; H 6.57; P 8.49.

Tris[2-(4-pyridyl)ethyl]phosphine oxide (2b) (exp. 7, Table 1). A solution of KOH (3.1 g) in water (1.3 ml) was added dropwise with stirring to an argon-blown mixture of activated red phosphorus P_n[2] (1.4 g, 32 mmol relative to the pure element) and 4-vinylpyridine (1.7 g, 16 mmol) in DMSO (30 ml). The reaction mixture was then treated as in the above experiment to give 1.14 g (58%) phosphine oxide **2b**; mp 190°C (ethyl acetate). IR spectrum in KBr, cm^{-1}: 3094, 3064, 3017 (ν_{CH} pyridine), 2985, 2940, 2914 (ν_{CH_2}), 1598, 1556, 1494, 1413 ($\nu_{C=C,C=N}$ pyridine), 1432 (ν_{CH_2}), 1219 (δ_{CH} pyridine), 1167 ($\nu_{P=O}$), 1068, 992, 951, 831, 803, 778 (δ_{CH} pyridine). Found, %: C 68.89; H 6.60; N 11.51; P 7.94. $C_{21}H_{24}N_3OP$. Calculated, %: C 69.04; H 6.57; N 11.50; P 8.49.

Bis{μ-tris[2-(2-pyridyl)ethyl]phosphine oxide}tris(dichloropalladium (3a). A suspension of $PdCl_2$ (0.051 g, 0.29 mmol) and KCl (0.043 g, 0.58 mmol) in water (10 ml) was heated at 50-60°C with stirring until complete dissolution of $PdCl_2$. A solution of tris[2-(2-pyridyl)ethyl]phosphine oxide (0.105 g, 0.29 mmol) in water (5 ml) was added at room temperature to the solution obtained. The reaction mixture was stirred for 1 h at ~20°C. The precipitate was filtered off, washed consecutively with water and acetone, and dried in vacuum to give 0.119 g (98%) complex **3a**, as a light yellow powder; mp 178°C (dec.). IR spectrum in KBr, cm^{-1}: 3114, 3070, 3032 (ν_{CH} pyridine), 2936, 2903 (ν_{CH_2}), 1606, 1570, 1483, 1440 ($\nu_{C=C,C=N}$ pyridine), 1230 (δ_{CH} pyridine), 1158 ($\nu_{P=O}$), 1097, 1067, 951, 800 sh, 770 (δ_{CH} pyridine). Found, %: C 40.10; H 4.18; Cl 16.23; N 6.80; Pd 23.12; P 4.11. $C_{42}H_{48}Cl_6N_6O_2Pd_3Pd_2$. Calculated, %: C 39.95; H 3.83; Cl 16.84; N 6.65; Pd 25.28; P 4.91.

Bis{μ-tris[2-(4-pyridyl)ethyl]phosphine oxide}tris(dichloropalladium) (3b). Complex **3b** was obtained analogously from pyridylphosphine oxide **2b** and $PdCl_2$ in 95% yield as a light yellow powder; mp 195°C (dec.). IR spectrum in KBr, cm^{-1}: 3091, 3068, 3043, 3017 (ν_{CH} pyridine), 2923, 2903, 2855 (ν_{CH_2}), 1617, 1559, 1501, 1413 ($\nu_{C=C,C=N}$ pyridine), 1432 (δ_{CH_2}), 1220 (δ_{CH} pyridine), 1164 ($\nu_{P=O}$), 1068, 817, 777 (δ_{CH} pyridine). Found, %: C 38.26; H 4.54; Cl 14.25; N 7.38; Pd 25.11; P 4.84. $C_{42}H_{48}Cl_6N_6O_2Pd_3P_2$. Calculated, %: C 39.95; H 3.83; Cl 16.84; N 6.65; Pd 25.28; P 4.91.

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