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Reactions of Elemental Phosphorus and Phosphines with Electrophiles in Superbasic Systems: XIII.[1] Phosphorylation of Phenylacetylene with Active Modifications of Elemental Phosphorus

N. K. Gusarova, B. G. Sukhov, S. F. Malysheva, T. I. Kazantseva, Yu. V. Smetannikov, N. P. Tarasova, and B. A. Trofimov

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, Irkutsk, Russia

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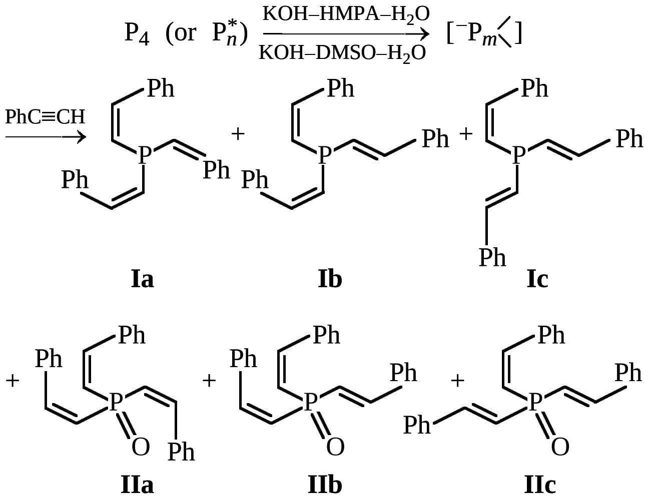
Abstract—Phosphorylation of phenylacetylene with white or activated red phosphorus (prepared from white phosphorus under the action of ionizing radiation) occurs in KOH–DMSO or KOH–HMPA systems with heat evolution and stereoselective formation of *Z* isomers of tristyrylphosphine and -phosphine oxide in yields of 48–49% and 10–15%, respectively. Under the comparable conditions the commercial red phosphorus is considerably less reactive toward phenylacetylene: The total yield of the above-mentioned products is 5%.

Direct phosphorylation of acetylenes with elemental phosphorus in the presence of bases was for the first time carried out and studied with commercial red phosphorus and phenylacetylene [2–4]. The reaction occurs on heating of the reactants in the superbasic KOH–HMPA system at 60–65°C in the presence of small amounts of water to give tris(*Z*-styryl)phosphine (yield up to 50%) and small amounts of tris(*Z*-styryl)phosphine oxide. Ultrasonic [3] and mechanochemical [4] treatment of the reactants accelerate the reaction of phenylacetylene with the system red phosphorus–KOH–HMPA, but the stereoselectivity of the process decreases. It was reported [5] that phenylacetylene can be phosphorylated with white phosphorus in the presence of superstrong bases, but no experimental conditions were published.

With the aim of obtaining new data on the reactivity of various modifications of elemental phosphorus and acetylenes toward each other, we have studied the reaction of phenylacetylene with white (P_4) and activated red phosphorus (P_n^*) which was prepared by thermal polymerization of white phosphorus in the presence of graphite and simultaneous exposure of the reaction mixture to ionizing radiation [6]. In the KOH–polar hydroxyl-free solvent (HMPA, DMSO)–H_2O system the reaction occurs with a high conversion of phenylacetylene (72–92%) and practically quantitative conversion of white or activated red phosphorus to form *Z,Z,Z*, *Z,Z,E*, and *Z,E,E* isomers **Ia**–**Ic** of tristyrylphosphine and also the corresponding isomers **IIa**–**IIc** of tristyrylphosphine oxide. The yield and the ratio of these compounds depend on the nature of the phosphorylating agents and reaction conditions (see table).



Ia **Ib** **Ic**

IIa **IIb** **IIc**

The reaction shows a pronounced stereoselectivity: The main products are *Z,Z,Z* isomers **Ia** and **IIa**. Their yield reaches 49% and 15%, respectively, whereas the total yield of the other isomers **Ib**, **Ic** (**IIb**, **IIc** for phosphine oxides) does not exceed 11% (see table).

We found that in the reaction under study P_4 and P_n^* show comparable efficiency. For example, the

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

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Phosphorylation of phenylacetylene with elemental phosphorus

Run no.	Elemental phosphorus, mmol	Phenylacetylene, mmol	KOH, mmol	Solvent, ml	H_2O, ml	Temperature, °C	Reaction time, h	Yield, %^{b}					Conversion, %	
								Ia	**Ib**	**IIa**	**IIb**	**IIc**	phosphorus	phenylacetylene
1	P_4, 28	29.0	52	HMPA, 25	1.20	55–56	5.0	24	4	2	3	1	100	72
2^{c}	P_n^*, 48	50.0	90	HMPA, 50	2.10	55–56	7.0	26	5	^{d}	^{d}	^{d}	97	80
3	P_n, 48	50.0	90	HMPA, 50	2.10	55–56	7.0	8	^{d}	2	1	^{d}	53	30
4	P_4, 35	52.0	105	HMPA, 50	1.30	80	4.5	26	7	^{d}	^{d}	^{d}	100	^{d}
5^{e}	P_4, 19	19.6	35.7	HMPA, 25	0.82	24–45	5.5	22	2	3	6	>1	100	75
6	P_4, 20	19.6	35.7	DMSO, 25	0.82	24	6.0	33	^{d}	6	5	^{d}	100	92
7	P_4, 22	12.0	40	DMSO, 25	0.95	24	6.0	48	^{d}	10	^{d}	^{d}	100	91
8^{c}	P_n^*, 20	10.0	40	DMSO, 25	0.90	24	3.0	49	^{d}	15	5	3	94	80
9	P_n, 19	10.0	36	DMSO, 25	0.82	24	3.0	4	^{d}	1	<1	^{d}	17	91

[a] All the experiments were carried out under argon. In run nos. 2 and 8, activated red phosphorus containing, respectively, 4.4 and 11.8% graphite [6] was used. In run nos. 1–6 the reactants were added practically simultaneously before the start of the reaction. In run nos. 7–9 phenylacetylene was added dropwise over a period of 1 h to a stirred mixture of elemental phosphorus, KOH, DMSO, and water. [b] Yield based on converted phenylacetylene. [c] In run nos. 2 and 8 graphite was recovered (10 and 40 mg, respectively). [d] Product is not detected. [e] In run no. 5 the temperature of the reaction mixture increased owing to the exothermic effect and was maintained in the range 28–45°C for 1 h. Under these conditions phosphine **Ic** (2%) and 0.1 g of phosphorus-containing polymeric product are also formed.

total yield of the products of phenylacetylene phosphorylation with white and activated red phosphorus in a suspension of KOH in HMPA at 55–56°C is 34% and 31%, respectively (see table, run nos. 1, 2). Commercial red phosphorus under these conditions is considerably less active. The total yield of the products (**Ia**, **IIa**, **IIb**) is as low as 11% at the conversion of phosphorus and phenylacetylene of 53% and 30%, respectively (see table, run no. 3).

Phosphorylation of phenylacetylene with P_4–KOH–HMPA system in the temperature range under study leads to practically the same result when performed at 55–80 (see table, run nos. 1, 4) and 26–45°C (run no. 5). In the latter case the growth of temperature was due to the heat evolution in the reaction mixture. Under the comparable conditions (run no. 6) the superbasic catalytic system KOH–DMSO is somewhat more effective than the suspension of KOH in HMPA: The yield of the major product **Ia** is 33% and 22%, respectively, and the conversion of phenylacetylene is 92% against 75%. Furthermore, we increased reaction efficiency by decreasing the phenylacetylene : white phosphorus molar ratio by a factor of 1.8 and by adding phenylacetylene into the reaction mixture in portions. Under these conditions phosphine **Ia** and phosphine oxide **IIa** are formed in 48% and 10% yields, respectively (see table, run no. 7). Under the similar conditions the total yield of the products of phenylacetylene phosphorylation with activated red phosphorus is still higher (72%), and the yield of phosphine **Ia** and phosphine oxide **IIa** is 49% and 15%, respectively (see table, run no. 8). Commercial red phosphorus under these conditions is ineffective, its conversion is as low as 17%, and the yield of the major product **Ia** is 4% (see table, run no. 9). At the same time, the conversion of phenylacetylene in this experiment is high (91%, run no. 9). Evidently, in the P–KOH–DMSO system phenylacetylene undergoes not only phosphorylation but also some other processes such as, e.g., dimerization [7], but we failed to isolate from the reaction mixture and identify any other compounds except phosphine **I** and phosphine oxide **II**.

High activity of white and activated red phosphorus in the reaction with phenylacetylene is evidently due to the higher rate of formation of polyphosphide and phosphide anions under the action of a superstrong base (KOH–HMPA and KOH–DMSO). Their addition to the triple bond of phenylacetylene is stereoselective, yielding mainly *Z* isomer **Ia** [2, 8]. Formation of considerable amounts of phosphine oxide **IIa**, especially in the case of the KOH–DMSO system, is evidently due to oxidation of the corresponding phosphine **Ia**.

Thus, with phenylacetylene as example we demonstrated the possibility of using activated red phosphorus [6] for preparing organophosphorus compounds. Its reactivity is not lower than that of white phosphorus, and it is much more safe in handling. Similarly to the commercial red phosphorus, it ignites in air only above 250°C and is much less toxic than white phosphorus [9].

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 spectrometer in thin layer in the frequency range 4000–400 cm^{-1} with an accuracy of ±2 cm^{-1}. The ^{1}H NMR spectra were obtained on a Bruker DPX-400 spectrometer (400 MHz), and the ^{31}P NMR spectra, on a Jeol FX-90Q spectrometer ($CDCl_3$).

The isomers of phosphine **Ia**–**Ic** and phosphine oxide **IIa**–**IIc** were identified by IR, ^{1}H, and ^{31}P NMR spectroscopy using authentic samples [4].

Activated red phosphorus containing 4.4% graphite was obtained in a 71% yield by heating (250°C, 6 h) of 2 ml of a melt of white phosphorus and 0.1 g of graphite (ultrapure grade) at simultaneous irradiation with a ^{60}Co source at an absorbed dose rate of 1.17 Gy s^{-1}. Unchanged white phosphorus was washed off with benzene [6]. Shortening of the reaction time to 4 h (all the other conditions remain the same) leads to formation of activated red phosphorus containing 11.8 wt % graphite in a 38% yield.

Reaction of white phosphorus with phenylacetylene in the KOH–DMSO system (see table, run no. 7). To a mixture of 0.7 g of white phosphorus, 2.3 g of KOH, 25 ml of DMSO, and 0.95 ml of water we added dropwise a solution of 1.17 g of phenylacetylene in 5 ml of DMSO over a period of 1 h at 24°C. The reaction mixture was stirred for an additional 5 h at 24°C, diluted with water, and extracted with ether. The ether extracts were washed with water and dried over potassium carbonate. The ether and unchanged phenylacetylene were removed at reduced pressure; 0.1 g of unchanged phenylacetylene was recovered (conversion 91%). The bottom residue was dried in a vacuum, and 0.7 g of the product was obtained. By ^{1}H and ^{31}P spectroscopy it was identified as a mixture of *Z* isomers of **Ia** and **IIa** in a 4.4 : 1 ratio. Their yield was 48 and 10%, respectively.

Reaction of activated red phosphorus with phenylacetylene in the KOH–DMSO system (see table, run no. 8). Under the conditions of run no. 7, 0.66 g of activated red phosphorus, 1.12 g of phenylacetylene, 2.25 g of KOH, 0.9 ml of water, and 25 ml of DMSO in 3 h form phosphine **Ia** and phosphine oxides **IIa**–**IIc** in yields of 49, 15, 5, and 3%, respectively. The conversion of phenylacetylene is 80%.

Reaction of commercial red phosphorus with phenylacetylene in the KOH–DMSO system was performed similarly (run no. 9).

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