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**LETTERS TO THE EDITOR**

# Reaction of Activated Red Phosphorus with Phenylacetylene in the KOH–HMPA System

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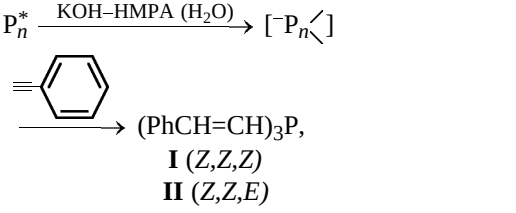
Crude (commercial) red phosphorus reacts with phenylacetylene upon heating (60–65°C) in a system the KOH–HMPA–$H_2O$ to yield 50% of tris[(*Z*)-styryl)phosphine and small amounts of the corresponding tris[(*Z*)-styryl)phosphine oxide [1]. Phosphorylation of phenylacetylene with phosphine generated separately from crude red phosphorus and KOH in water–dioxane medium proceeds under milder conditions (55–57°C), yielding 70% of phosphine **I** [2].

In this work we first showed that the activated red phosphorus obtained by thermal polymerization of white phosphorus in the presence of graphite under ionizing radiation [3] reacts with the phenylacetylene–KOH–HMPA triad in the presence of water at 55–56°C to form the (*Z*,*Z*,*Z*)- and (*Z*,*Z*,*E*)-isomers of tristyrylphosphine (**I**, **II**) in a 3.4 : 1 ratio in a total yield of 31% (per reacted phenylacetylene, conversion 80%). Therewith, the conversion of elemental phosphorus was 97%.




$P_n^*$ is activated phosphorus [3].

The efficiency of nonactivated red phosphorus under similar conditions is much lower: the total yield of isomers **I** and **II** is no higher than 8% per reacted phenylacetylene at its 30% conversion and a 53% conversion of phosphorus. This fact can probably be explained by a lower rate of formation of polyphosphide and phosphide anions under the action of the strong base.

Thus, the activated phosphorus synthesized from white phosphorus under ionizing radiation [3] is a more effective phosphorylating agent than the ordinary red phosphorus obtained by polymerization of white phosphorus at ~400°C.

**Activated red phophorus** containing 4.4 wt% of graphite was synthesized in an yield of 71% by heating (250°C, 6 h) of a mixture of 2 ml of white phosphorus melt and 0.1 g of graphite (special purity grade) under 60°C radiation (dose rate 1.17 Gy/s [3]).

**Reaction of activated phosphorus with phenylacetylene.** A mixture of 1.5 g of activated phosphorus, 5 g of KOH, 5.0 g of phenylacetylene, 2.1 ml of water, and 50 ml of HMPA was heated at 55–56°C for 7 h, then cooled, diluted with water, unreacted phosphorus (0.05 g, 97% conversion) was filtered off, and the filtrate was extracted with ether. The etheral extract was washed with water, dried over potassium carbonate, and the ether and unreacted phenylacetylene (recovery 1.0 g, conversion 80%) were distilled off under reduced pressure. Undistillable residue was dried in a vacuum to obtain 1.35 g of tristyrylphosphine, that, according to the $^1H$ and $^{31}P$ NMR spectra, contained 85% of *Z*,*Z*,*Z* isomer **I** and 15% of *Z*,*Z*,*E* isomer **II** (identical to authentic samples [4]), total yield 30% (per reacted phenylacetylene). The elemental analysis corresponds to calculation.

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