

ARYLATION OF RED PHOSPHORUS: A NEW WAY TO TRIPHENYLPHOSPHINE OXIDE AND TRIPHENYLPHOSPHINE

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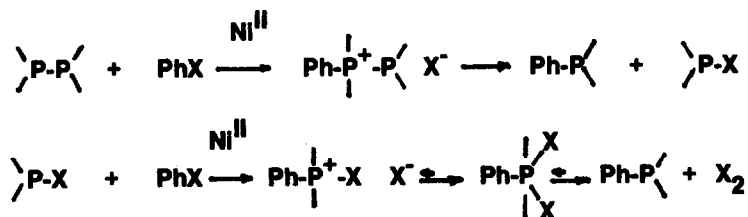
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Summary: Nickel bromide catalyses the arylation of amorphous red phosphorus. This provides a new way to triphenylphosphine oxide and triphenylphosphine

The chemistry of organophosphorus compounds starting from elemental phosphorus is still a recent one¹. Among the three types of the reactions usually met (reactions under oxidative conditions, reactions with nucleophiles, alkylations and arylations) the last ones are of a great synthetic interest, chiefly for the use of the allotropic amorphous form *red* phosphorus (P_r) which is of safe and easy handling. But it is well known that the very low reactivity of the red phosphorus implies the compulsory use of at least a catalytic amount of an activating agent. Thus iodine seems to be an efficient agent, as mentioned in the literature², for the alkylation of P_r . Nevertheless, to our best knowledge, there is no example of an arylation of P_r ³.

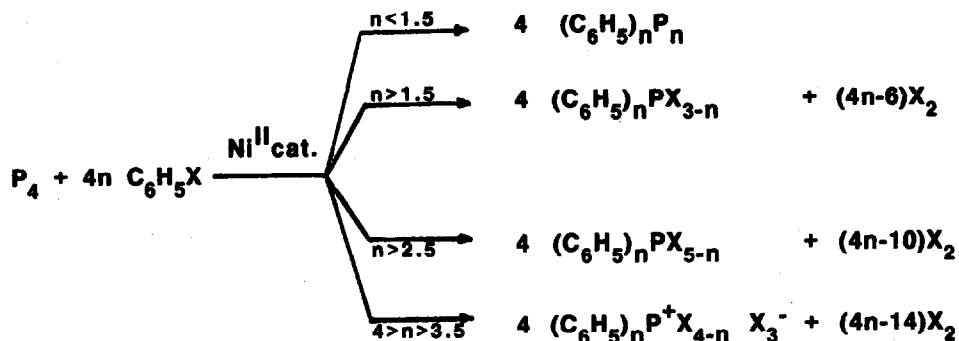
At the present time, such compounds as the potential precursor of triphenylphosphine triphenylphosphine oxide⁴ (TPPO) or triphenylphosphine (TPP) itself take important place in the market, which led us to evaluate their approach from P_r . We wish to report here an activation process of P_r leading to the easy formation of the P-C_{Ar} bonding, by the way of a common nickel bromide catalysis, the catalyst acting as a simultaneous activating agent for both substrate and arylating reactant.

The activation by the Ni^{II} salts, through a cyclic "oxidative addition-reductive elimination" mechanism, has been already used in the arylation of not very reactive tricoordinated phosphorus compounds such as aromatic phosphines⁵. Applied to the tricoordinated P_r , the phenylation scheme (Sch. 1) implies the apparition of a positive charge on one of the phosphorus atoms, that would bring on the cleavage of the P-P bond and therefore the depolymerization of the red phosphorus:



Scheme 1

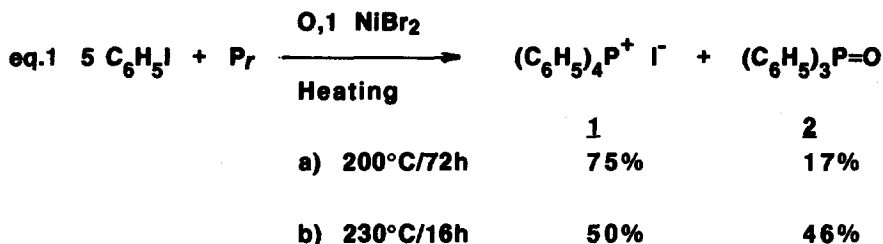
The overall process, which is an oxidative one between red phosphorus and the phenyl halogenide as described in Sch.2, will actually result in successive arylations, occurring on Ph-P and X-P species, with free halogen formation from the time where the phenylation index will be more than 1.5.



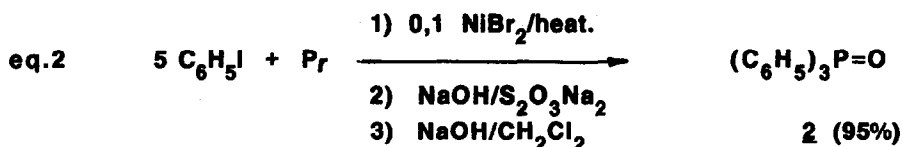
Scheme 2

Bearing in mind our previous work on the catalytic arylation of molecular tricoordinated phosphorus species⁵, we decided to use iodobenzene as an arylating reagent. In presence of NiBr₂, a reaction occurred above 200°C, but it did not work without the catalyst. After heating, the mild reductive hydrolysis of the mixture gave tetraphenylphosphonium iodide **1** and triphenylphosphine oxide **2**⁶. At

230°C, the reaction was completed after only 16h., and was optimum for a C₆H₅I/P_r ratio of 5 (eq.1).

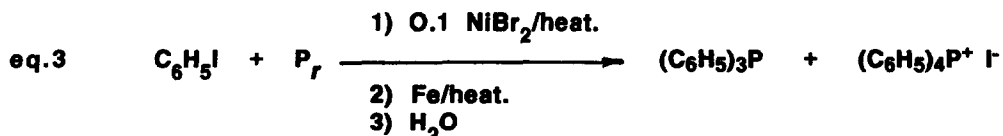


As a PTC basic hydrolysis wholly converted the salt 1 to the oxide 2, the overall yield in triphenylphosphine oxide 2 was more than 95% (eq.2):



Among the tested 3d row's transition metals in their most common oxidation state, the Ni^{II} derivatives were found to be the best catalyst. In addition, too much of nickel bromide hindered perphenylation by stopping the reaction at the triphenylphosphine step (this complexation could become an advantage in the case where this compound is desired); on the other hand, a too small NiBr₂/P ratio (<5%) led to a limited transformation of phosphorus, as a consequence of a limited turn-over of the catalyst.

From the preparative point of view, an interesting point was to isolate directly triphenylphosphine from the reaction mixture. Among the reductive species which could be added at the end of the process, iron seemed a good one: it has been shown to work successfully in the reduction of triphenylphosphine oxide in the presence of a halo-complexing agent^{4b}. Indeed, heating the crude reaction mixture at 210°C with an excess of iron led, after hydrolytic work-up to the expected triphenylphosphine (eq.3):



Thus, the use of iodobenzene as an arylating agent of red phosphorus represents an easy and novel way for the synthesis of triphenylphosphine oxide⁷ and triphenylphosphine. The substitution of this halide by the cheaper bromobenzene is now under consideration.

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