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NEW REACTION INVOLVING OXIDATIVE C-PHOSPHORYLATION OF PYRIDINE BY PHOSPHINE

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Extremely valuable tripyridylphosphines can be synthesized only by C-phosphorylation of metallated pyridines by chlorophospines [1-4]. We have established for the first time that tripyridylphosphine is formed in close-to-quantitative yield in the oxidative C-phosphorylation of pyridine by phosphine. A pyridine solution of CuX_2 (X = Cl, OAc) at 20-50°C rapidly absorbs phosphine even from a dilute gaseous PH₃—Ar mixture (< 1% PH₃) via the reaction

$$3C_{5}H_{5}N + PH_{3} + 6CuX_{2} \longrightarrow (2-C_{5}H_{4}N)_{3}P + 6CuX + 6HX$$
 (1)

The tri(2-pyridyl)phosphine is formed without side products under these conditions. The addition of water gives rise to a side reaction involving oxidative hydroxylation. Reaction (1) is accelerated by copper(I) ions. The rate constant of the reaction in excess pyridine at $25 \,^{\circ}$ C is $1.2 \cdot 10^2 \,\text{mole}^2/\text{liter}^2$ ·sec. The spent solution, which contains Cu(I) ions, is regenerated instantaneously by oxygen and is used repeatedly for reabsorption of PH₃. According to the results of potentiometric studies and data from the UV spectra, pyridine complexes of Cu(I) and Cu(II) dominate in CuX₂—CuX—Py solutions. It was demonstrated by the CNDO method that the incorporation of Py in the coordination sphere and an increase in the positive charge of the phosphine complex of copper(II) lead to deprotonation of phosphine with the formation of a phosphide ion as a consequence of the marked increase in the energies of the bonds between the central atom and the phosphorus atom of PH₃, as well as between the hydrogen atoms of PH₃ and the ligands. In the coordinated pyridine the N and m-C atoms bear negative charges, while the o- and p-C atoms bear positive charges. The coordinated X ligands and the central atom form strong bonds with the ligands and the Cu(II) ion. The bonds between the ligands are primarily ionic, while the bonds between the central atom atom so not create bonds with the ligands are covalent.

Reaction (1) includes the key steps

$$Cu_2X_3(PH_3)(C_5H_5N) \implies Cu_2X_2(PH_2)(C_5H_5N) + HX$$
 (2)

 $Cu_2X_2(PH_2)(C_5H_5N) \longrightarrow Cu_2X_2(H)(C_5H_4NPH_2)$ (3)

$$Cu_2 X_2(H) (C_5 H_4 NPH_2) \longrightarrow Cu + HX + C_5 H_4 NPH_2 + CuX$$
(4)

$$Cu + CuX_2 \implies 2CuX$$
 (5)

Copper(II) phosphide is formed via an electrophilic substitution mechanism with the nucleophilic assistance of (2). The tripyridylphosphine is formed as a result of nucleophilic addition of the phosphide ion to the o-C atom [(2) and (3)] with the subsequent elimination of copper(II) hydride, which decomposes to Cu and HX (4). Monovalent copper accumulates

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because of disproportionation reaction (5). Monopyridylphosphine and dipyridylphosphine were not detected during the experiment, since they participate in similar transformations more rapidly than PH_3 .

Dimeric Cu(II)—Cu(I) complexes of mixed valence bring about reaction (1). The fact is that Cu(I) ions, in contrast to Cu(II) ions, form complexes with PH₃. The optimum conditions for coordination of the PH₃ and C₅H₅N reactants and their interaction in the coordination sphere are created in a complex with mixed valence.

The PH₃ was obtained by the acidic hydrolysis of Zn_3P_2 . The CuX₂ was rendered anhydrous at 100-200°C. The PH₃—Ar and PH₃—O₂ gas mixtures were dried with granulated NaOH. The pyridine was purified by fractional distillation over sodium. The synthesis was carried out in a stirred thermostatted flow reactor. The (2-C₅H₄N)₃P accumulated with repetition of the number of cycles of PH₃ and O₂ absorption in the Py—CuX₂ solution (0.5 mole/liter). The ³¹P NMR spectrum of the solution after precipitation of the Cu(I) ions by means of potassium iodide contained only one intense signal at 3.6-3.8 ppm, which is characteristic for tripyridylphosphine. The IR spectrum of the precipitate after removal of the pyridine contains absorption bands at 430, 500, and 620 cm⁻¹ (P—C) and at 1640 cm⁻¹ (C=C).

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SYNTHESIS OF 3,6-DIALKYL-4,5-DIHYDRO-4,5-DICHLORO-2,1-BENZISOXAZOLES FROM 0-NITROPHENYLCYCLOPROPANES

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Acid-catalyzed reactions of o-nitrophenylcyclopropanes that make it possible to transform them directly to onitroalkenylbenzenes [1] and o-nitrosopropiophenones [2, 3] or to substituted 2,1-benzisoxazoles [4] are known. These reactions are realized through intermediates of a common type — N-oxo-2,1-benzisoxazolinium ions, which are formed as a result of intramolecular interaction of the o-nitro group with the carbonium ion that develops upon opening of the protonated cyclopropane ring of the starting nitro compound.

We have found that, in contrast to the previously studied transformations, the 2,1-benzisoxazolinium ion formed when (4-tert-butyl-2-nitrophenyl)cyclopropane (I) is dissolved in concentrated sulfuric acid is converted by the action of hydrochloric acid not to the corresponding halo-substituted 2,1-benzisoxazole (taking into account the data in [4]) but rather to 6-tert-butyl-4,5-dihydro-4,5-dichloro-3-ethyl-2,1-benzisoxazole (II).



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