SYNLETT Spotlight 243

Synthetic Applications of Triphenylphosphine

Compiled by Leandro Ferreira Pedrosa

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Leandro Ferreira Pedrosa was born in Rio de Janeiro, Brazil in 1980. He received his Industrial Pharmacy degree from Universidade Federal Fluminense in 2005 and his M.Sc. in Organic Chemistry from Universidade Federal Fluminense in 2007. He is currently working toward his Ph.D. under the supervision of Prof. Marcos C. de Souza. His research interests focus on the synthesis of organophosphorus and phosphoramidates.

Instituto de Química, Universidade Federal Fluminense, UFF, CEP: 24020-150 Niterói, Rio de Janeiro, Brazil
E-mail: leandropedrosa@globo.com

Introduction

Triphenylphosphine (Ph_3P) is a very versatile reagent extensively used by organic chemists. Ph_3P exists as relatively air-stable, colorless crystals at room temperature. It dissolves in non-polar organic solvents such as benzene and diethyl ether. Ph_3P undergoes slow oxidation by air to give triphenylphosphine oxide, Ph_3PO . This impurity can be removed by recrystallization of Ph_3P from either hot ethanol or hot isopropanol.¹

Ph_3P has received increasing attention as versatile and mild reagent in many occasions for various organic transformations under neutral conditions in recent years.²

The properties that guide its usage are its nucleophilicity and its reducing character.³ The nucleophilicity of Ph_3P is indicated by its reactivity toward electrophilic alkenes such as Michael acceptors⁴ and alkyl halides.⁵

Ph_3P binds well to most transition metals, especially those in the middle and late transition metals of groups 7–10.⁶

Abstracts

(A) Zhou et al. reported isomerization of alkynyl ketones catalyzed by Ph_3P in water in the absence of organic solvent, which provides a practical method for the synthesis of useful polyenyl carbonyl compounds. (*E,E*)-Diene ketones were obtained in good yields when the reaction was carried out under reflux in aqueous media.⁷

(B) Yang and Shi succeeded in activating cyclopropyl amides (monoactivated cyclopropane) through the corresponding imidoyl halides prepared in situ in the presence of 2 equiv of Ph_3P and 1 equiv of CX_4 , leading to the ring-expanded products (N-substituted pyrrolidin-2-ones) in good yields.⁸

(C) The reaction of various alcohols with 2.5 equiv of Ph_3P and an equimolar quantity of *N*-fluorodibenzenesulfonimide led to the corresponding dibenzenesulfonimides. The reaction is high-yielding with primary alcohol substrates.⁹

(D) The reaction between alane-pyridine complexes, Ph_3P , and sulfonyl chlorides affords the aryl alk-1-enyl sulfoxides in good to excellent yields (70–94%) in short reaction times using mild conditions. The optimal ratio between reagents (alane-pyridine/ Ph_3P /sulfonyl chloride = 1.00:1.35:0.92) was obtained performing a chemiometric analysis.³

(E) Fused aromatic and heterocyclic 1,2,3,4,5-pentathiepins react with triphenylphosphine and alkynes bearing electron-withdrawing groups to give the corresponding 1,4-dithiins in high yields. Unsymmetrical alkynes add regioselectively to afford products in agreement with the electron distribution in a proposed reaction intermediate.¹⁰

(F) Alizadeh and Sheikhi showed an effective route to functionalized hydantoin derivatives, involving the reaction of a urea derivative resulting from the addition of a primary amine to an arylsulfonyl isocyanate, and an alkyl propiolate or dialkyl acetylenedicarboxylate in the presence of triphenylphosphine. The reactive 1:1 intermediate obtained from the addition of triphenylphosphine to the alkyl propiolate or dialkyl acetylenedicarboxylate was trapped by NH-acids such as the urea derivative to produce functionalized hydantoin derivatives.¹¹

(G) The addition of acetanilides to ethyl propiolate proceeds under neutral conditions in the presence of triphenylphosphine to give the corresponding β -substituted alkyl acrylates together with variable amounts of the β -substituted isomer with *E*-geometry. Addition of arylsulfonylanilides to alkyl propiolates under similar conditions, produced only the alkyl (*E*)-3-arylsulfonylanilino-2-propenoates.⁸

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