

SYNLETT Spotlight 243

Synthetic Applications of Triphenylphosphine

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

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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, $\text{Ph}_3\text{P}=\text{O}$. This impurity can be removed by recrystallization of Ph_3P from either hot ethanol or hot isopropanol.¹

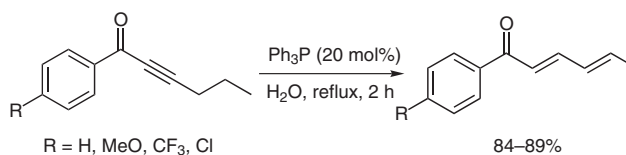
Ph_3P has received increasing attention as versatile and mild reagent in many occasions for various organic transformations under neutral conditions in recent years.²

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

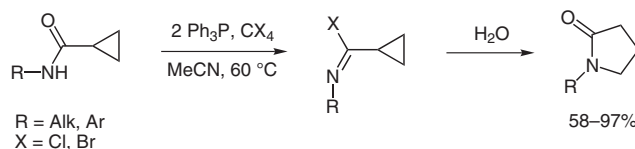
Ph_3P binds well to most transition metals, especially those in the middle and late transition metals of groups 7–10.⁶

Abstracts

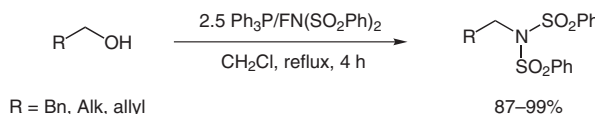
(A) Zhou et al. reported isomerization of alkynyl ketones catalyzed by Ph_3P in water in the absence of organic solvent, which provides a practical method for the synthesis of useful polyenyl carbonyl compounds. (*E,E*)-Diene ketones were obtained in good yields when the reaction was carried out under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



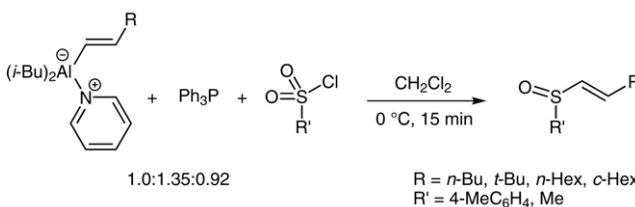
(B) Yang and Shi succeeded in activating cyclopropyl amides (monoactivated cyclopropane) through the corresponding imidoyl halides prepared in situ in the presence of 2 equiv of Ph_3P and 1 equiv of CX_4 , leading to the ring-expanded products (N-substituted pyrrolidin-2-ones) in good yields.⁸



(C) The reaction of various alcohols with 2.5 equiv of Ph_3P and an equimolar quantity of *N*-fluorodibzenesulfonimide led to the corresponding dibzenesulfonimides. 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



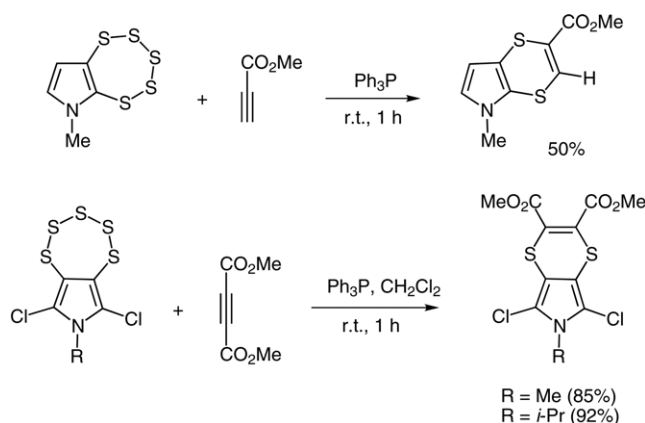
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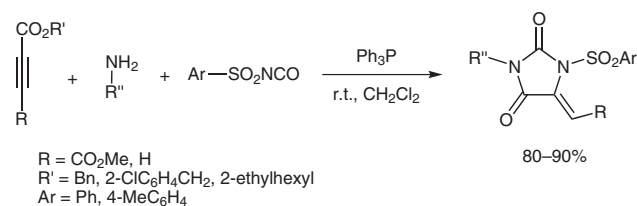
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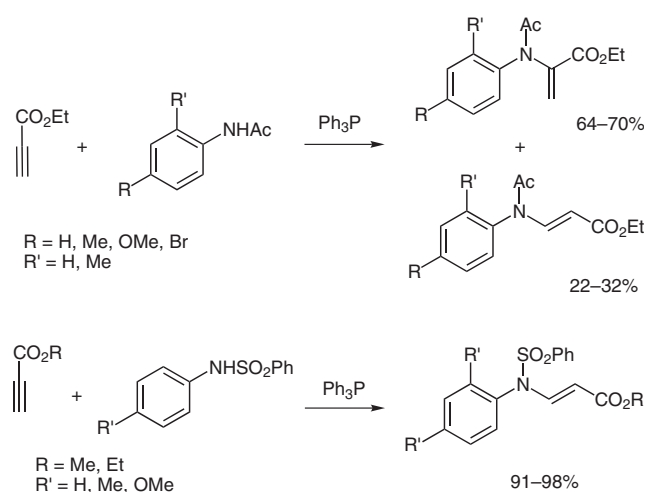
(E) Fused aromatic and heterocyclic 1,2,3,4,5-pentathiepins react with triphenylphosphine and alkynes bearing electron-withdrawing groups to give the corresponding 1,4-dithiins in high yields. Unsymmetrical alkynes add regioselectively to afford products in agreement with the electron distribution in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