

# 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

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### Introduction

Triphenylphosphine ( $\text{Ph}_3\text{P}$ ) is a very versatile reagent extensively used by organic chemists.  $\text{Ph}_3\text{P}$  exists as relatively air-stable, colorless crystals at room temperature. It dissolves in non-polar organic solvents such as benzene and diethyl ether.  $\text{Ph}_3\text{P}$  undergoes slow oxidation by air to give triphenylphosphine oxide,  $\text{Ph}_3\text{P}=\text{O}$ . This impurity can be removed by recrystallization of  $\text{Ph}_3\text{P}$  from either hot ethanol or hot isopropanol.<sup>1</sup>

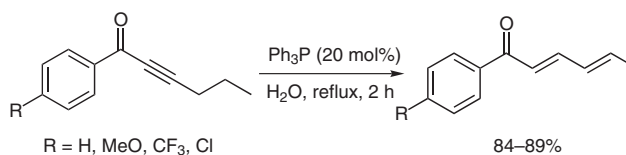
$\text{Ph}_3\text{P}$  has received increasing attention as versatile and mild reagent in many occasions for various organic transformations under neutral conditions in recent years.<sup>2</sup>

The properties that guide its usage are its nucleophilicity and its reducing character.<sup>3</sup> The nucleophilicity of  $\text{Ph}_3\text{P}$  is indicated by its reactivity toward electrophilic alkenes such as Michael acceptors<sup>4</sup> and alkyl halides.<sup>5</sup>

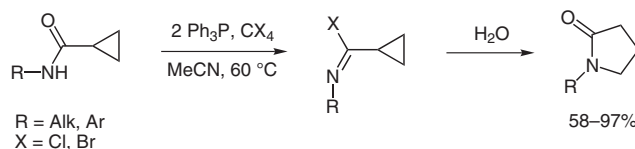
$\text{Ph}_3\text{P}$  binds well to most transition metals, especially those in the middle and late transition metals of groups 7–10.<sup>6</sup>

### Abstracts

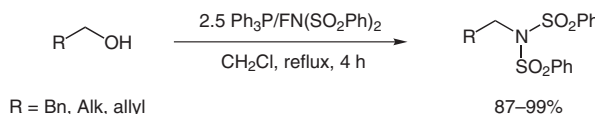
(A) Zhou et al. reported isomerization of alkynyl ketones catalyzed by  $\text{Ph}_3\text{P}$  in water in the absence of organic solvent, which provides a practical method for the synthesis of useful polyenyl carbonyl compounds. (*E,E*)-Diene ketones were obtained in good yields when the reaction was carried out under reflux in aqueous media.<sup>7</sup>



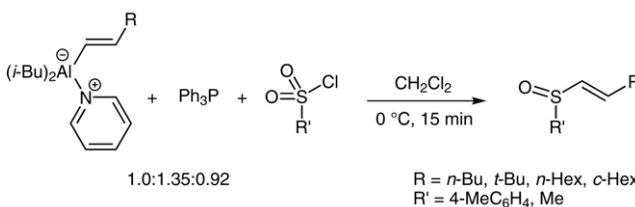
(B) Yang and Shi succeeded in activating cyclopropyl amides (monoactivated cyclopropane) through the corresponding imidoyl halides prepared in situ in the presence of 2 equiv of  $\text{Ph}_3\text{P}$  and 1 equiv of  $\text{CX}_4$ , leading to the ring-expanded products (N-substituted pyrrolidin-2-ones) in good yields.<sup>8</sup>



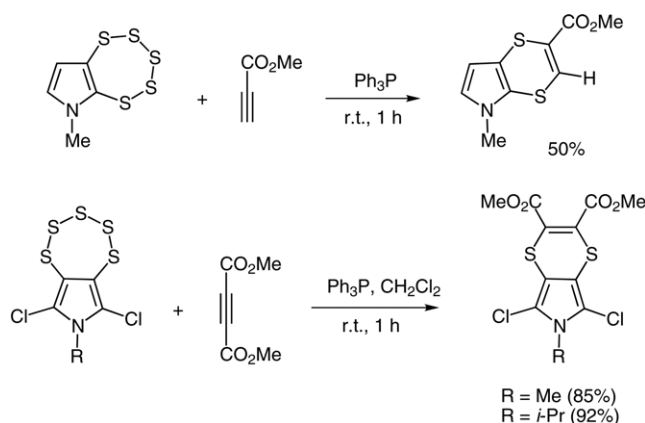
(C) The reaction of various alcohols with 2.5 equiv of  $\text{Ph}_3\text{P}$  and an equimolar quantity of *N*-fluorodibenzene sulfonimide led to the corresponding dibenzene sulfonimides. The reaction is high-yielding with primary alcohol substrates.<sup>9</sup>



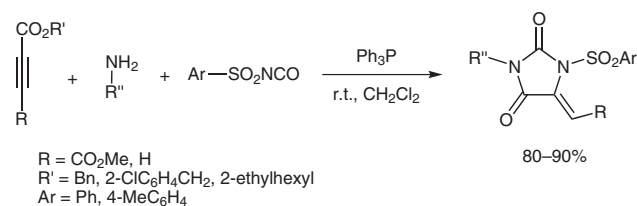
(D) The reaction between alane-pyridine complexes,  $\text{Ph}_3\text{P}$ , and sulfonyl chlorides affords the aryl alk-1-enyl sulfoxides in good to excellent yields (70–94%) in short reaction times using mild conditions. The optimal ratio between reagents (alane-pyridine/ $\text{Ph}_3\text{P}$ /sulfonyl chloride = 1.00:1.35:0.92) was obtained performing a chemiometric analysis.<sup>3</sup>



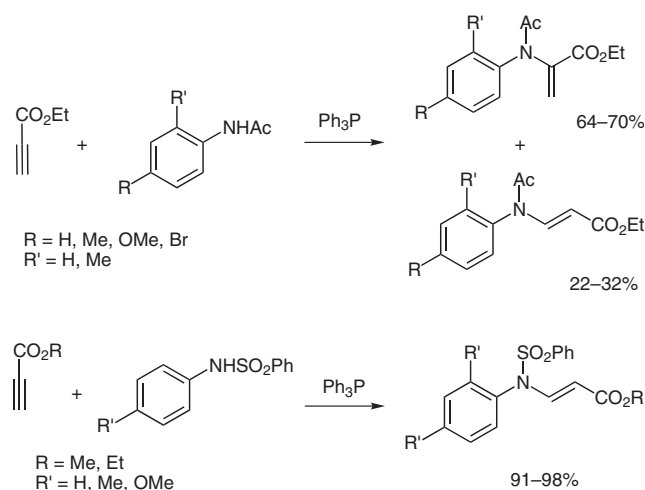
(E) Fused aromatic and heterocyclic 1,2,3,4,5-pentathiepins react with triphenylphosphine and alkynes bearing electron-withdrawing groups to give the corresponding 1,4-dithiins in high yields. Unsymmetrical alkynes add regioselectively to afford products in agreement with the electron distribution in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



(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.<sup>11</sup>



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



## References

- (1) Corbridge, D. E. C. *Phosphorus: An Outline of its Chemistry, Biochemistry, and Technology*, 5th ed.; Elsevier: Amsterdam, **1995**, 68.
- (2) Yadav, J. S.; Reddy, B. V. S.; Krishna, A. D.; Reddy, Ch. S.; Narsaiah, A. V. *J. Mol. Catal. A: Chem.* **2007**, *261*, 93.
- (3) Signore, G.; Calderisi, M.; Malanga, C.; Menicagli, R. *Tetrahedron* **2007**, *63*, 177.
- (4) (a) Bhuniya, D.; Mohan, S.; Narayanan, S. *Synthesis* **2003**, 1018. (b) Luis, A. L.; Krische, M. J. *Synthesis* **2004**, 2579. (c) Bensa, D.; Rodriguez, J. *Synth. Commun.* **2004**, *34*, 1515.
- (5) Sato, A.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2006**, *128*, 4240.
- (6) Yavari, I.; Hazeri, N.; Maghsoodlou, M. T.; Souri, S. *J. Mol. Catal. A: Chem.* **2007**, *264*, 313.
- (7) Zhou, Q. F.; Yang, F.; Guo, Q. X.; Xue, S. *Chin. Chem. Lett.* **2007**, *18*, 1029.
- (8) Yang, Y.; Shi, M. *J. Org. Chem.* **2005**, *70*, 8645.
- (9) Giovanelli, E.; Doris, E.; Rousseau, B. *Tetrahedron Lett.* **2006**, *47*, 8457.
- (10) Amelichev, S. A.; Konstantinova, L. S.; Obruchnikova, N. V.; Rakin, O. A.; Rees, C. W. *Org. Lett.* **2006**, *8*, 4529.
- (11) Alizadeh, A.; Sheikhi, E. *Tetrahedron Lett.* **2007**, *48*, 4887.