IRANIAN JOURNAL OF CATALYSIS

Triphenylphosphine in conjunction with TCCA/ or NCBT/ or DDQ/ or DEAD provide practical and convenient systems for the synthesis of a wide range of organic compounds

Compiled by Maryam Sadat Ghasemzadeh

Maryam Sadat Ghasemzadeh was born in Ghaen/ Southern Khorasan, Iran. She received her B.Sc. in Pure Chemistry from Imam Khomeini International University and M.Sc. in Organic Chemistry from Birjand University under the supervision of Professor Sara Sobhani. She is currently studying her Ph.D. in Ferdowsi University of Mashhad under the supervision of Professor Batool Akhlaghinia. Her current research focuses on new heterogeneous nanocatalysts to develop new methods of organic synthesis.

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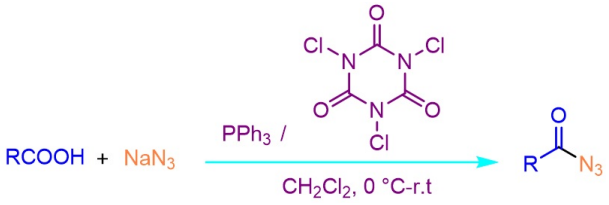
This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Introduction

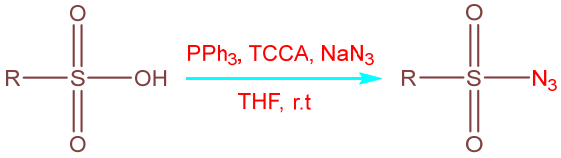
N-Halo compounds are versatile reagents that have been employed as potentially reactive intermediates and are widely used in organic synthesis. Nevertheless, depending on the conditions, a number of highly reactive intermediates can be formed: halogen radicals, halogen cations, halogen anions, *N*-radicals, *N*-cations, *N*-anions, *etc*. Consequently, *N*-halo reagents have the potential to promote important reactions such as halogenations, oxidation, protection and deprotection as well as formation of C-X, C-O and C=O bonds. Additionally, the numerous *N*-halo reagents play an especially important role as Lewis acid catalysts in the chemistry of heterocyclic compounds [1].

Abstracts

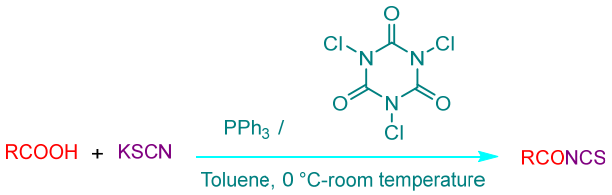
(A) Acyl azides as important intermediates in organic chemistry especially in pharmaceuticals, dyes, and agrochemicals, prepared in the presence of trichloroisocyanuric acid–triphenylphosphine (TCCA/TPP) through the reaction of carboxylic acids and sodium azide at 0 °C-room temperature in dichloromethane [2].



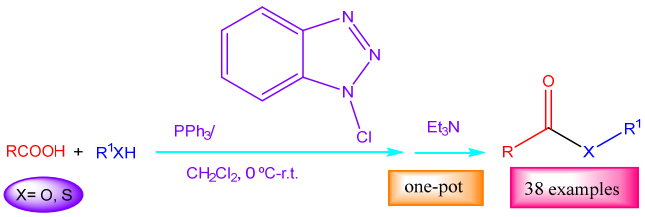
(B) In 2013, a new method for the synthesis of a variety of alkanesulfonyl, arenesulfonyl, and heteroarenesulfonyl azides were described using the triphenylphosphine/trichloroisocyanuric acid/sodium azide (PPh_3/TCCA/NaN_3) system at room temperature. A wide range of arenesulfonyl and alkanesulfonyl azides was achieved in excellent yields under mild conditions [3].



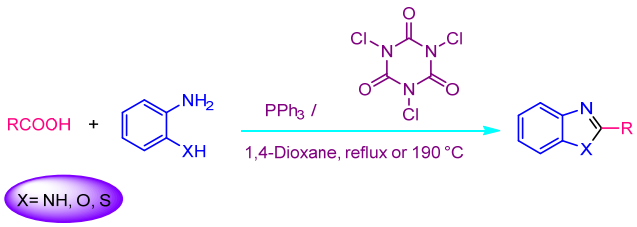
(C) Acyl isothiocyanates have found a wide application in the synthesis of several acyclic and heterocyclic compounds. However, the methods of preparation of isothiocyanates are limited. In 2014, Akhlaghinia and co-workers, reported one-step synthesis of alkanoyl and aroyl isothiocyanates from carboxylic acids using a trichloroisocyanuric acid/triphenylphosphine system at room temperature. Short reaction time, excellent yield of products and mild reaction conditions make this procedure a useful method for preparation of acyl isothiocyanates [4].



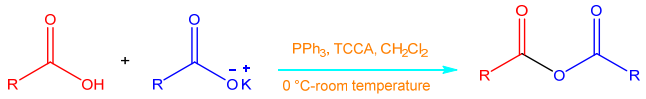
(D) Akhlaghinia *et al.* in 2014 reported an efficient method for esterification and thioesterification of a wide range of carboxylic acids (aromatic and aliphatic) with alcohols /or phenols and thiols using *N*-chlorobenzotriazole (NCBT, as an *N*-halo reagent) PPh_3 system in CH_2Cl_2 at room temperature. The reagents (PPh_3 and NCBT) offers easy handling and simple work-up. Nevertheless, this method provided satisfactory yields of a variety of esters and thioesters in contrast to the previously reported systems [5].



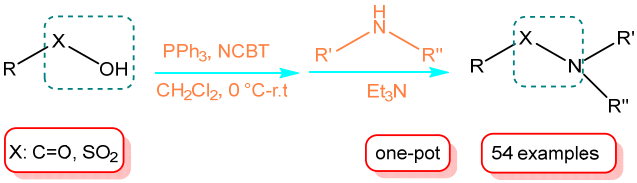
(E) In 2015, Akhlaghinia and co-workers reported simple, practical and highly efficient method for the synthesis of benzimidazoles, benzoxazoles, and benzothiazoles *via* the condensation of *o*-phenylenediamine, *o*-aminophenol, and *o*-aminothiophenol with various carboxylic acids using trichloroisocyanuric acid/triphenylphosphine-mediated (TCCA/TPP). However, carboxylic acids as the starting materials has eliminated the need for toxic oxidants that are necessary for the reaction to proceed when either alcohols or aldehydes are used [6].



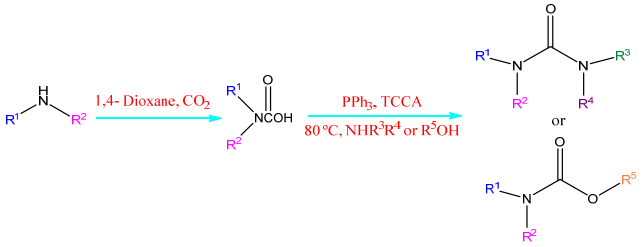
(F) Akhlaghinia *et al.* in 2015, reported direct synthesis of symmetrical carboxylic anhydrides using PPh_3/TCCA/RCO_2H/RCOOK. Carboxylic acids are converted to anhydrides by triphenylphosphine/ trichloroisocyanuric acid under mild reaction conditions at room temperature. Direct conversion of acids to anhydrides in a short reaction time at room temperature, mild reaction conditions, simple experimental procedure and easy work-up of the products are the main advantages of the present method [7].



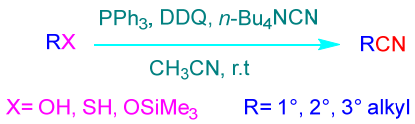
(G) A one-pot amidation of carboxylic acids, α-amino acids and sulfonic acids using triphenylphosphine (PPh_3)/N-chlorobenzotriazole (NCBT) were reported by Akhlaghinia *et al* in 2015. The reported protocol represents inexpensive and rapid route for the preparation of desired structures with excellent yields [8].



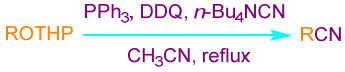
(H) The synthesis of symmetrical, unsymmetrical di, tri-, and tetra-substituted ureas and carbamates from amines and alcohols were reported by triphenylphosphine (PPh_3)/trichloroisocyanuric acid system. Experimental investigation demonstrates that the present methodology is experimentally simple, mild and represents a valuable alternative to the existing methods [9].



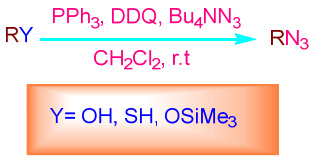
(I) Iranpoor *et al.* in 2004 reported conversion of alcohols, thiols, and trimethysilyl ethers to alkyl cyanides using triphenylphosphine/2,3-dichloro-5,6-dicyanobenzoquinone/*n*-Bu_4NCN system. Safety, ease in handling of the reagents and excellent yield of products make this method unique for direct conversion of alcohols, thiols, and trimethylsilyl ethers into cyanides [10].



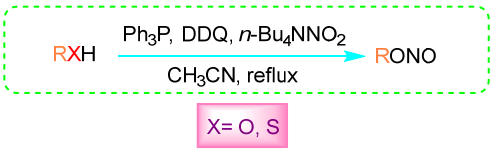
(J) One of the most practical and popular ways of protecting hydroxyl groups of alcohols and phenols, especially in the synthesis of multifunctional organic molecules is tetrahydropyranylation (THP). In 2004, Akhlaghinia offered a simple, novel, and useful method for the conversion of a wide varieties of tetrahydropyranyl ethers to their corresponding alkyl cyanides using Ph_3P/DDQ/*n*-Bu_4NCN system [11].



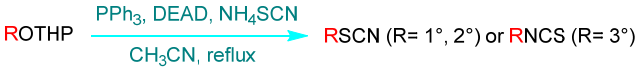
(K) In 2004, Iranpoor and co-workers reported converting alcohols, thiols, and silyl ethers into alkyl azides in good to excellent yields by PPh_3/DDQ/*n*-Bu_4NN_3 in CH_2Cl_2 at room temperature. Furthermore, replacement of DEAD with DDQ and HN_3 with *n*-Bu_4NN_3 in combination with Ph_3P provides a safe and available reagent for the conversion of alcohols, thiols, and trimethylsilylethers into the corresponding azides [12].



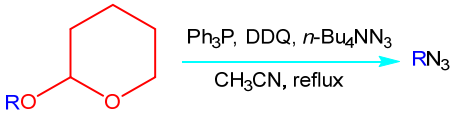
(L) In another assay, alkyl nitrites were prepared in good to excellent yields using alcohols and thiols with triphenylphosphine/2,3- dichloro-5,6-dicyanobenzoquinone/Bu_4NNO_2 in CH_3CN. The paper represented that this method is highly selective for the conversion of primary alcohols to alkyl nitrites in the presence of secondary and tertiary alcohols and thiols [13].



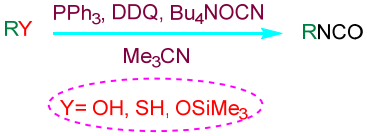
(M) In another investigation, the conversion of 1° and 2° tetrahydropyranyl (THP) ethers to their corresponding thiocyanates and 3° ones to isothiocyanates using a triphenylphosphine/diethyl azodicarboxylate (DEAD)/NH_4SCN system were described. The strong point favoring this method is the high selectivity for conversion of 1° and 2° tetrahydropyranyl ethers to their corresponding thiocyanates and 3° ones to isothiocyanates and selectivity between themselves [14].



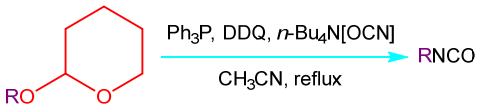
(N) In 2005, Akhlaghinia reported a novel and simple method for efficient conversion of tetrahydropyranyl ethers to alkyl azides using triphenylphosphine/2,3-dichloro-5,6-dicyanobenzoquinone/tetrabutylammonium azide system [15].



(O) Isocyanates have been found valuable compounds participating in a diversity of reactions including cycloaddition reactions to generate heterocycles, nucleophilic addition reactions with alcohols and amines to produce carbamates and ureas and polymerization reactions to produce commodities such as polyurethanes. In this investigation, alkyl isocyanates were produced from alcohols, thiols and trimethylsilyl ethers by triphenylphosphine/2,3-dichloro-5,6-dicyanobenzoquinone/Bu_4NOCN [16].



(P) Akhlaghinia *et al.* in 2009 offered a method for the conversion of a wide variety of tetrahydropyranyl ethers to the corresponding alkyl isocyanates by Ph_3P/DDQ/*n*-Bu_4N[OCN] as a simple, novel and convenient technique [17].



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