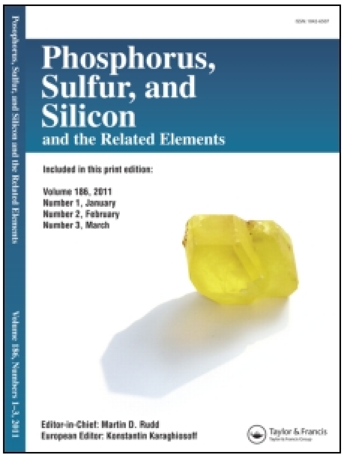

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# Triphenylphosphine/2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ)/[*n*-$Bu_4$N]OCN as a Useful System for the Efficient Conversion of Tetrahydropyranyl (THP) Ethers to the Corresponding Alkyl Isocyanates

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*Triphenylphosphine/2,3-dichloro-5,6-dicyanobenzoquinone/tetrabutylammonium cyanate was used as an efficient system for the conversion of tetrahydropyranyl ethers to the corresponding alkyl isocyanates.*

**Keywords** Alkyl isocyanate; 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ); tetrahydropyranyl ether (ROTHP); triphenylphosphine (TPP)

## INTRODUCTION

Isocyanates are useful compounds capable of participating in a variety of reactions including nucleophilic addition reactions with alcohols and amines to produce carbamates and ureas, cycloaddition reactions to generate heterocycles, and polymerization reactions to produce commodities such as polyurethanes.[1] The high yields and the lack of byproducts associated with isocyanate chemistry have led to their widespread application in the pharmaceutical, agrochemical, and polymer industries.

Typically, aliphatic and aromatic isocyanates are generated from amines in the reaction with phosgene[2] or phosgene equivalents, such as diphosgene (trichloromethyl chloroformate)[3] or triphosgene [bis(trichloromethyl) carbonate],[4] or via thermal dissociation of

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carbamic acid derivatives using chloroformates,[5] diphenylcarbonate,[6] or *N*,*N*′-carbonyldiimidazole.[7] Aryl isocyanates can also be generated from non-amine precursors via the rearrangements of acyl azides (Curtius rearrangement)[8] and hydroxamic acids (Lossen rearrangement).[9]

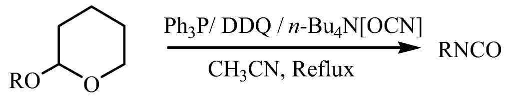
Tetrahydropyranylation is one of the most practical and popular ways of protecting hydroxy groups of alcohols and phenols, especially in the synthesis of multifunctional organic molecules. THP ethers show remarkable stability towards some reagents such as organometallic reagents and hydrides, as well as reducing and oxidizing agents. Chemical transformation of protected functional groups to other functional groups is an important step in organic synthesis.[10] Literature search reveals that only a few reports are available for the direct conversion of THP ethers to other functional groups. The known examples include conversion of THP ethers to bromides,[11,12] iodides,[13] sulfides,[14] acetates,[15] and esters.[16]

In this study, a novel and simple method for the efficient conversion of tetrahydropyranyl ethers to alkyl isocyanates is reported.

## RESUTS AND DISCUSSION

Recently, we have reported the application of $Ph_3P/DDQ/R_4NX$ (X = Cl, Br, I, CN, $N_3$, $NO_2$, OCN) and 2,4,6-trichloro[1,3,5]triazine (TT)/$R_4NX$ (X = CN, $NO_2$) systems for the conversion of alcohols, thiols, selenols, trimethylsilyl ethers, $N_3$, OCN, and tetrahydropyranyl ethers to the corresponding alkyl halides, cyanides, azides, nitrites, and isocyanates.[17] Due to the wide applicability of tetrahydropyranyl ethers in multistep syntheses and in continuation of the study on the conversion of tetrahydropyranyl ethers to alkyl cyanides[17d] and azides,[17e] the transformation of THP ethers to alkyl isocyanates using the $Ph_3P/DDQ/[n\text{-}Bu_4N]OCN$ system under neutral and mild reaction condition was investigated (Scheme 1).

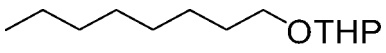
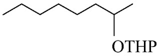
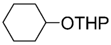
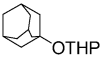
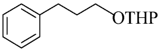
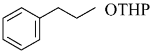
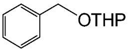
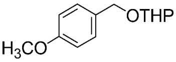
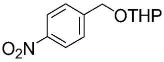
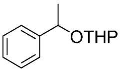
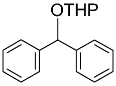
In order to optimize the reaction conditions, at first the effects of different ratios of $ROTHP/PPh_3/DDQ/[n\text{-}Bu_4N]OCN$, solvent, and temperature for the conversion of $PhCH_2OTHP$ to $PhCH_2NCO$ were



R = primary, secondary, and tertiary alkyl

**SCHEME 1**

**TABLE I Conversion of Tetrahydropyranyl Ethers to Alkyl Isocyanates in Dry Acetonitrile Under Reflux Conditions**

| ROTHP | Time (h) | Conversion (%)[a] | Isolated yield (%) |
|---|---|---|---|
|  | 8 | 100 | 95 |
|  | 11 | 100 | 90 |
|  | 11.5 | 100 | 94 |
|  | 30 | 100 | 89 |
|  | 9 | 100 | 97 |
|  | 8.5 | 100 | 96 |
|  | 7 | 100 | 98 |
|  | 5 | 100 | 98 |
|  | 9 | 100 | 93 |
|  | 11 | 100 | 90 |
|  | 34 | 100 | 97 |

[a]GC yield using internal standard.

examined. Employing the ratio of 1:2:2:2 in refluxing $CH_3CN$ gave the best result and produced benzyl isocyanate after 7 h in 98% yield. These optimized conditions were applied for the conversion of structurally different tetrahydropyranyl ethers to the corresponding alkyl isocyanates. The results are shown in Table I.

As shown in Table I, this method is very suitable for the conversion of primary, secondary, and tertiary tetrahydropyranyl ethers to alkyl isocyanates in excellent yields.

A $^{13}C$ NMR signal at 127 ppm is assigned to the quaternary carbon atom of the N=C=O group. A strong and sharp absorption band at 2280–2230 $cm^{-1}$ and a weak absorption band at 1450–1380 $cm^{-1}$ are typical for the isocyanate moiety.

In conclusion, the present investigation has demonstrated that the use of $Ph_3P$/DDQ/[$n$-$Bu_4N$]OCN offers a simple, novel, and convenient method for the conversion of a wide variety of tetrahydropyranyl ethers to the corresponding alkyl isocyanates.

## EXPERIMENTAL

Chemicals were obtained from Merck and Fluka. FT-IR spectra were recorded on a Perkin Elmer RXI spectrophotometer. NMR spectra were recorded with a Bruker Avance DPX 250 MHz instrument. The products were purified by column chromatography, and the purity of the products was determined by GC on a Shimadzu model GC 10-A instrument using *n*-octane as internal standard or by thin layer chromatography on silica gel polygram on SIL G/UV 254 plates.

### Typical Procedure for Conversion of Tetrahydropyranyl Ethers to Alkyl Isocyanate

To a flask containing a mixture of DDQ (2 mmol, 0.454 g) and $Ph_3P$ (2 mmol, 0.524 g) in dry $CH_3CN$ (5 mL), while stirring $Bu_4N[OCN]$ (2 mmol, 0.568 g) was added. Tetrahydropyranyl ether (1 mmol) was then added to this mixture. The reaction mixture was refluxed. GC analysis showed the completion of the reaction. The solvent was evaporated under reduced pressure. Column chromatography of the crude product on silica-gel using *n*-hexane as eluent gave alkyl isocyanates. The product was identified by comparison of its physical constants and spectral data with those of an authentic sample.

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