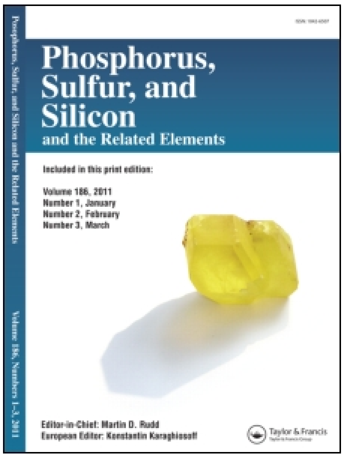

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Triphenylphosphine/2,3-Dichloro-5,6-dicyanobenzoquinone in the Presence of n-Bu_4NN_3 Is a Useful System for Efficient Conversion of Tetrahydropyranyl (THP) Ethers to Their Corresponding Alkyl Azides

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Triphenylphosphine / 2,3-dichloro-5,6-dicyanobenzoquinone / tetrabutylammonium azide was used as an efficient system in conversion of tetrahydropyranyl ethers to corresponding alkyl azides.

Keywords 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ); alkyl azide; azidation; tetrahydro pyranylether (ROTHP); triphenylphosphine (TPP)

INTRODUCTION

Azides[1] are versatile functional groups for many purposes in organic synthesis. Azides have been used extensively in organic synthesis, especially for the introduction of primary amino groups and the construction of heterocyclic structures.[2] In most cases, aliphatic azides are prepared by nucleophilic substitution of the corresponding halides or sulfonates by the azide anion.[3]

Tetrahydropyranylation is one of the most practical and popular ways of protecting hydroxyl groups of alcohols and phenols, especially, in the synthesis of multifunctional organic molecules. THP ethers show remarkable stability toward some reagents such as organometallic reagents, hydrides, and reducing and oxidizing agents. Chemical transformation of protected functional groups to other functional groups is an important step in organic synthesis.[4] Literature reveals that only few reports are available for direct conversion of THP ethers to

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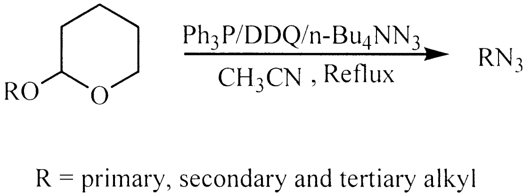
other functional groups. The examples are conversion of THP ethers to bromides,[5,6] iodides,[7] sulfides,[8] acetates,[9] and esters.[10]

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

RESULTS AND DISCUSSION

Recently, Iranpoor et al.[11] have reported the application of Ph_3P/DDQ/R_4NX (X = Cl, Br, I, CN, N_3) for conversion of alcohols, thiols, and selenols into their corresponding alkyl halides, cyanides, and azides. Due to wide applicability of tetrahydropyranyl ethers in multistep synthesis, and in continuation of the study on the conversion of tetrahydropyranyl ethers to alky cyanides,[12] transformation of THP ethers to alkyl azides by using the Ph_3P/DDQ/n-Bu_4NN_3 system under neutral and mild reaction conditionwas investigated (Scheme 1).

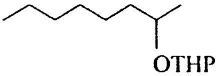
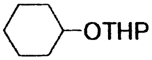
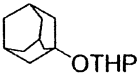
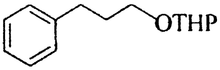
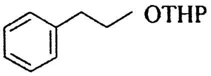
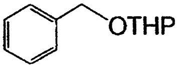
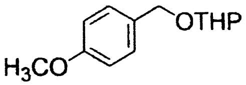
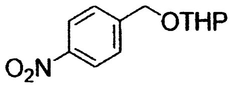
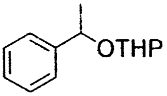
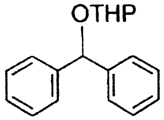


SCHEME 1

In order to optimize the reaction conditions, at first the effects of different ratios of ROTHP/PPh_3/DDQ/n-Bu_4NN_3, solvent, and temperature for conversion of $PhCH_2OTHP$ to $PhCH_2N_3$ were examined. Employing the ratio of 1/1.5/2/2 in CH_3CN at reflux gave the best result and produced benzyl azide after 19 h in 98% yield. To obtain high isolated yields of alkyl azides, different ratios of Ph_3P/DDQ were examined. The additional amount of Ph_3P in the presence of alkyl azides produces iminiphosphoranes,[13] which reduces the isolated yields of reactions. These optimized conditions were applied for conversion of structurally different tetrahydropyranyl ethers into their corresponding alkyl azides. 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 azides in excellent yields.

In conclusion, the present investigation has demonstrated that the use of Ph_3P/DDQ/n-Bu_4NN_3 offers a simple, novel, and convenient method for the conversion of a wide variety of tetrahydropyranyl ethers to their corresponding alkyl azides.

TABLE I Conversion of Tetrahydropyranyl Ethers into Alkyl Azides in Dry Acetonitrile under Reflux Condition

Entry	ROTHP	Time (h)	Conversion %[a]	Isolated yield %
1		22	100	95
2		23	100	90
3		23	100	94
4		24	100	89
5		21	100	97
6		21	100	96
7		19	100	98
8		18.5	100	98
9		20	100	93
10		21.5	100	90
11		21	100	97

[a] GC yield using internal standard.

EXPERIMENTAL

Chemicals were obtained from Merck and Fluka chemical companies. FT-IR spectra were recorded on a Perkin Elmer RXI spectrometer. All tetrahydropyranyl ethers were synthesized as described in the literature.[14] The products were purified by column chromatography and the purity determination of the products was accomplished by GLC 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. NMR spectra were recorded on a Brucker Avance DPX 250 MHz instrument.

Typical Procedure for Conversion of Benzyl Tetrahydropyranyl Ether to Benzyl Azide

To a flask containing a mixture of DDQ (2 mmol, 0.454 g) and Ph_3P (1.5 mmol, 0.393) in dry CH_3CN (5 mL), while stirring Bu_4NN_3 (2 mmol, 0.568 g), was added. Benzyl tetrahydropyranyl ether (1 mmol, 0.192 g) was then added to this mixture. The reaction mixture was refluxed. GC analysis showed that the reaction was completed after 19 h. The solvent was evaporated under reduced pressure. Column chromatography of the crude product on silica-gel using n-hexane as eluent gave benzyl cyanide in 98% yield. The product was identified by comparison of its physical constants and spectral data with those of an authentic sample.

REFERENCES

[1] E. F. V. Scriven and K. Turnbull, *Chem. Rev*. **88,** 351 (1988).

[2] T. Sheradsky, In *The Chemistry of Azido Groups*; S. Patai (Ed.) (Interscience Publishers, New York, 1971).

[3] a) M. E. C. Biffin, J. Miller, and D. B. Paul, In *The Chemistry of Azido Groups*, S. Patai (Ed.) (Interscience, New York, 1971); b) S. G. Alvarez and M. T. Alvarez, *Synthesis*, **4,** 413 (1997).

[4] a) P. J. Kocienski, *Protecting Groups*, Thieme (Verlag New York, 1994); b) T. W. Green and P. G. M. Wuts, *Protective Groups in Organic Synthesis*, 2nd ed. (John Wiley, New York, 1991); c) A. J. Pearson and N. J. Roush, *Handbook of Reagents for Organic Synthesis Activating Agents and Protecting groups*, 1st ed. (John Wiley, New York 1999).

[5] A. Wagner, M. Heitz, and C. Mioskowski, *Tetrahedron Lett.*, **30,** 557 (1989).

[6] A. Tanaka and T. Oritani, *Tetrahedron Lett.*, **38,** 1995 (1997).

[7] H. Firouzabadi, N. Iranpoor, and H. Hazarkhani, *Tetrahedron Lett.*, **43,** 7139 (2002).

[8] T. Sato, J. Otera, and H. Nozaki, *J. Org. Chem.*, **55,** 4770 (1990).

[9] S. Chandrrasekhar, T. Ramachandar, M. V. Reddy, and M. Takhi, *J. Org. Chem.*, **65,** 4729 (2000).

[10] S. Kim and W. J. Lee, *Synth. Commun.*, **16,** 659 (1986).

[11] a) N. Iranpoor, H. Firouzabadi, G. Aghapour, and A. R. Vaezzadeh, *Tetrahedron*, **58,** 8689 (2002); b) N. Iranpoor, H. Firouzabadi, B. Akhlaghinia, and N. Nowrouzi, *J. Org. Chem.*, **69,** 2562 (2004); c) N. Iranpoor, H. Firouzababi, B. Akhlaghinia, and N. Nowrouzi, *Tetrahedron Lett.*, **45,** 3291 (2004).

[12] B. Akhlaghinia, *Phosphors, Sulfur, and Silicon*, **179,** 1783 (2004).

[13] H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2,** 635 (1919).

[14] A. Molnar and T. Beregszaszi, *Tetrahedron Lett.*, **37,** 8597 (1996).