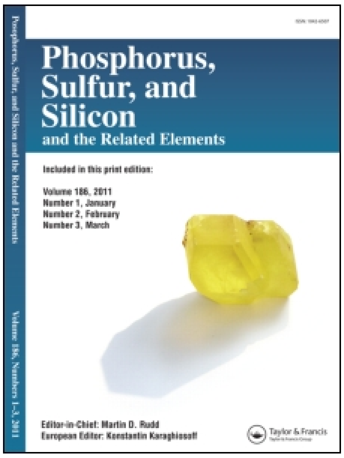


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

EFFICIENT CONVERSION OF TETRAHYDROPYRANYL (THP) ETHERS TO THEIR CORRESPONDING CYANIDES WITH TRIPHENYLPHOSPHINE/2,3-DICHLORO- 5,6-DICYANOBENZOQUINONE/n-Bu_4 NCN

Batool Akhlaghinia[a]
[a] Department of Chemistry, Damghan University of Basic Sciences, Damghan, Iran

To cite this Article Akhlaghinia, Batool(2004) 'EFFICIENT CONVERSION OF TETRAHYDROPYRANYL (THP) ETHERS TO THEIR CORRESPONDING CYANIDES WITH TRIPHENYLPHOSPHINE/2,3-DICHLORO- 5,6-DICYANOBENZOQUINONE/n-Bu_4 NCN', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 9, 1783 — 1786
To link to this Article: DOI: 10.1080/10426500490466463
URL: http://dx.doi.org/10.1080/10426500490466463

Phosphorus, Sulfur, and Silicon, 179:1783–1786, 2004
Copyright © Taylor & Francis Inc.
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490466463

EFFICIENT CONVERSION OF TETRAHYDROPYRANYL (THP) ETHERS TO THEIR CORRESPONDING CYANIDES WITH TRIPHENYLPHOSPHINE/2,3-DICHLORO-5,6-DICYANOBENZOQUINONE/n-Bu_4 NCN

Batool Akhlaghinia
Department of Chemistry, Damghan University of Basic Sciences, Damghan, Iran

(Received December 9, 2003; accepted January 8, 2004)

Tetrahydropyranyl ethers were converted to their corresponding alkyl cyanides efficiently by using the triphenylphosphine / 2,3-dichloro-5,6-dicyanobenoquinone / n-Bu_4 NCN system in refluxing acetonitrile with good-to-excellent yields.

Keywords: 2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ); alkyl cyanide; cyanation; tetrahydrophenyl ether (ROTHP); triphenylphosphine (TPP)

INTRODUCTION

The nitrile functional group is widely used as a useful intermediate in organic transformations.[1,2] A variety of synthetic methods for the introduction of a cyano group to organic compounds has been documented.[3] A general procedure for the preparation of nitriles involves the nucleophilic substitution of a leaving group with a metal cyanide.[4] Organic halogen compounds, aryl sulfonates, alcohols, esters, ethers, nitro or amino compounds, and diazonium salts could be used as substrates suitable for this type of reaction. In most cases the substitution reaction follows an S_N2 mechanism.

Tetrahydropyranylation (THP) 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

The author acknowledges the partial support of this study by the Damghan University Research Council.

Address correspondence to Batool Akhlaghinia, Department of Chemistry, Damghan University of Basic Sciences, Damghan, Iran. E-mail: b-akhlaghinia@dubs.ac.ir

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.[5] Aliterature search reveals that only few reports are available for direct conversion of THP ethers to other functional groups. The examples are conversion of THP ethers to bromides,[6,7] iodides,[8] sulfides,[9] acetates,[10] and esters.[11]

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

RESULTS AND DISCUSSION

Recently, Iranpoor et al.[12] have reported the application of Ph_3P/DDQ/R_4NX ($X = Cl$, Br, I, CN) for conversion of alcohols, thiols, and selenols into their corresponding alkyl halide and cyanides. Due to the wide applicability of tetrahydropyranyl ethers in multistep synthesis, we decided to study the use of a similar system for the transformation of this functional group to the nitrile group.

In this research, the conversion of tetrahydropyranyl ethers to the corresponding alkyl cyanides by using Ph_3P/DDQ/n-Bu_4NCN system was investigated. This method is very efficient and performs under neutral and very mild reaction conditions (Scheme 1).

$$\mathrm{ROTHP} \xrightarrow[\mathrm{CH_3CN,\ reflux}]{\mathrm{Ph_3P/DDQ/n\text{-}Bu_4NCN}} \mathrm{RCN}$$

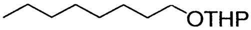
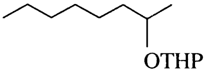
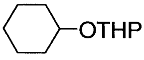
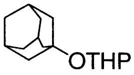
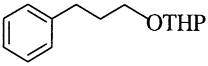
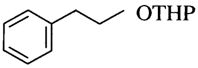
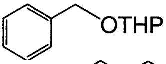
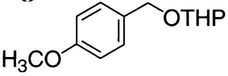
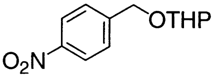
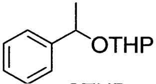
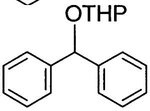
R = primary, secondary and tertiary alkyl

SCHEME 1

In order to optimize the reaction conditions, at first the effect of different ratios of ROTHP/PPh_3/DDQ/n-Bu_4NCN, solvent, and temperature for conversion of $PhCH_2OTHP$ to $PhCH_2CN$ were examined. Employing the ratio of 1/2/2/2 in CH_3CN at reflux gave the best result and produced benzyl cyanide after 4 h in 96% yield. We then applied these optimized conditions for conversion of structurally different tetrahydropyranyl ethers into their corresponding alkyl cyanides. 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 cyanides in excellent yields.

TABLE I Conversion of Tetrahydropyranyl Ethers into Alkyl Cyanides in Dry Acetonitrile Under Reflux Condition

Entry	ROTHP	Time (h)	Conversion (%)[a]	Isolated yield (%)
1		4	100	95
2		5	100	97
3		7	100	90
4		24	100	90
5		4	100	94
6		4	100	93
7		4	100	96
8		3	100	95
9		4.5	100	95
10		6	100	94
11		6.5	100	90

[a]GC yield using internal standard.

In conclusion, the present investigation has demonstrated that the use of Ph_3P/DDQ/n-Bu_4NCN offers a simple, novel, and convenient method for the conversion of a wide varieties of tetrahydropyranyl ethers to their corresponding alkyl cyanides.

EXPERIMENTAL

Chemicals were obtained from Merck and Fluka chemical companies. Fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer RXI spectrometer. All tetrahydropyranyl ethers were synthesized as described in the literature.[13] 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 Bruker Advance DPX 250 MHz instrument.

Typical Procedure for Conversion of Benzyl Tetrahydropyranyl Ether to Benzyl Cyanide

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_4NCN (2 mmol, 0.537 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 4 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 96% yield. The product was identified by comparison of its physical constants and spectral data with those of an authentic sample.

REFERENCES

[1] a) T. G. Lease and K. J. Shea, . *J. Am. Chem. Soc.*, **115,** 2248 (1993); b) S. L. Gwaltney, S. T. Sakata, and K. J. Shea, *J. Org. Chem.*, **61,** 7438 (1996); c) F. F. Fleming, A. Huang, V. A. Sharief, and Y. Pu, *J. Org. Chem.*, **62,** 3036 (1997).

[2] S. Patai and Z. Rappoport (Eds.), *The Chemistry of the Triple-bond Functional Groups* (Wiley Interscience, New York, 1983).

[3] Z. Rappoport (Ed.), *The Chemistry of Cyano Group* (Interscience Wiley, New York, 1970).

[4] N. Kornblum, R. A. Smily, R. K. Blackwood, and D. C. Iffiand, *J. Am. Chem. Soc.*, **77,** 6269 (1955).

[5] a) P. J. Kocienski, *Protecting Groups* (Thiem, 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).

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

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

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

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

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

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

[12] a) N. Iranpoor, H. Firouzabadi, Gh. Aghapour, and A. R. Vaezzadeh, *Tetrahedron*, **58,** 8689 (2002); b) N. Iranpoor, H. Firouzabadi, B. Akhlaghinia, and N. Nowrouzi, *J. Org. Chem.* (in press).

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