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Efficient Conversion of Tetrahydropyranyl (THP) Ethers to Their Corresponding Thiocyanates With in-situ–Generated Ph₃P(SCN)₂

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Immediate and efficient one-pot conversion of tetrahydropyranyl (THP) ethers to their corresponding thiocyanates by in-situ–generated $Ph_3P(SCN)_2$ is described. Primary and secondary alkyls and also benzylic THP ethers are converted to their corresponding thiocyanates in excellent yields at room temperature by this method.

Keywords Ph₃P(SCN)₂; tetrahydropyranyl ethers; thiocyanates

INTRODUCTION

Tetrazoles are important aromatic heterocyclic compounds and their use in medicinal chemistry is well established.¹ Thiocyanates are considered important and valuable sulfur-containing compounds for the synthesis of heterocycles such as tetrazoles and traditionally have been used as pesticides.²

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 organometallic reagents, reduction with hydrides, oxidation, oxidative alkylation, and so on. Transformation of protected functional groups to other functionalities is of practical value in organic synthesis.^{3.4} Literature research reveals that few reports are available for direct conversion of THP ethers to other functional

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Address correspondence to Nasser Iranpoor, Shiraz University, Chemistry Department, College of Sciences, Shiraz 71454, Iran. E-mail: iranpoor@chem.susc.ac.ir groups. The examples are conversion to bromides,⁵ sulfides,⁶ acetates⁷ into their esters.⁸ Recently, we have reported the conversion of a variety of silyl ethers⁹ and alcohols¹⁰ to their corresponding thiocyanates by in-situ–generated $Ph_3P(SCN)_2$.

RESULTS AND DISCUSSION

In this article we wish to report the efficient conversion of THP ethers into their corresponding thiocyanates at room temperature (Scheme 1).

> ROTHP $\xrightarrow{Ph_3P(SCN)_2,CH_3CN}_{rt, immediately}$ RSCN R = prim., sec. alkyl and benzyl

SCHEME 1

The reaction has been performed in dry CH_3CN with in-situgenerated $PPh_3(SCN)_2$ obtained from the reaction of $PPh_3 \cdot Br_2$ and NH_4SCN . ³¹P-NMR confirms the in-situ generation of $PPh_3(SCN)_2$ that is in agreement with the data reported in the literature.¹¹ By the presented method, benzyl and 4-substituted benzyltetrahydropyranyl ethers with electron-withdrawing groups were transformed to their corresponding thiocyanates in excellent yields (92–95%) without the formation of any isothiocyanate as a byproduct. A previous report indicates that the preparation of benzylthiocyanate from benzyl alcohol that is free from its isothiocyanate isomer is a difficult task due to the formation of a substantial amount of benzylisothiocyanate.¹²

4-Methoxybenzyltetrahydropyranyl ether was converted to its corresponding thiocyanate in 88% that was accompanied with the formation of isothiocyanate in only a 12% yield (Entry 4, Table I). Primary and secondary saturated tetrahydropyranyl ethers (Entries 5–8, Table I) were also transformed to their corresponding thiocyanates in excellent yields (87–94%).

This method is not suitable for the preparation of thiocyanates from highly hindered THP ethers. For example, the THP ether of diphenylmethanol was converted to its corresponding thiocyanate^{15c} in a 12%yield and isothiocyanate^{15d} in a 73% yield.

In conclusion, in this article we have presented a new useful method for the one-pot preparation of thiocyanates from THP ethers in high yield under mild reaction conditions.

Entry	R-OTHP	% Total yield ^a	$\% \operatorname{RSCN}^{b,c}$	$\% \mathrm{RNCS}^b$
1	C ₆ H ₅ CH ₂ OTHP	94	$100^{11,13,15a}$	0
2	4-NO ₂ C ₆ H ₄ CH ₂ OTHP	95	$100^{11,13}$	0
3	4-ClC ₆ H ₄ CH ₂ OTHP	92	$100^{11,13}$	0
4	4-MeOC ₆ H ₄ CH ₂ OTHP	95	$88^{11,13}$	12
5	C ₆ H ₅ CH ₂ CH ₂ OTHP	94	100^{11}	0
6	CH ₃ (CH ₂) ₆ CH ₂ OTHP	93	97^{11}	3
7	CH ₃ (CH ₂) ₅ CH(CH ₃)OTHP	90	95^{14}	5
8	PhCH(CH ₂ CH ₃)OTHP	87	$96^{15\mathrm{b}}$	4

TABLE I Conversion of THP Ethers to Thiocyanates

^{*a*}The products were identified by comparison of their physical data with those reported for known samples.

^bThe percentage of the products in the reaction mixture was determined by ¹H-NMR and ¹³C-NMR.

^cReference to the product.

EXPERIMENTAL

Products were characterized by comparison of their physical data with those of a known sample. IR spectra were recorded on a Perkin Elmer 781 and Pye Unicam 8725 spectrometers. NMR spectra were recorded on a Bruker DPX 250. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates or GLC on a Shimadzu GC-14A instrument.

GENERAL PROCEDURE FOR THE SYNTHESIS OF 1° AND 2° THIOCYANATES FROM THP ETHERS

A three-necked flask equipped with a dropping funnel, stirrer, drying CaCl₂ tube, and N₂ gas inlet was charged with Ph₃P (2.2 mmol) and dry CH₃CN (5 mL), then Br₂ (2.2 mmol) was added dropwise to the solution at room temperature under N₂ atmosphere. When the addition was completed, a solution of NH₄SCN (4.4 mmol) in CH₃CN (5 mL) was added dropwise. Upon addition of THP ether (2 mmol) to the resulting mixture, an spontaneous reaction occurred. To the resulting mixture, silica gel was added and the solvent was evaporated on a rotary evaporator. The resulting solid was applied on a silica gel column and washed by petroleum ether 60–80°C/EtOAc (9/1) to give the desired thiocyanate (Table I).

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- [15] Spectral data for (a) Benzyl thiocyanate: IR (KBr disc); ν (Cm⁻¹): 3086, 3070, 3009, 2992, 2918, 2148, 1494, 1464, 1427, 1246, 1204, 1076, 769, 698, 645. ¹H-NMR (CDCl₃, 250 MHz), δ (ppm): 4.2 (2H, s), 7.4 (5H, s); ¹³C-NMR (CDCl₃, 63 MHz), $\delta(\rm ppm):$ 134.47, 129.05, 128.93, 128.80, 111.96, 38.20; MS (70 eV) m/z (% relation relation relation of the transmission of transmission of the transmission of transmission o tive intensity): 149(M⁺, 3), 92(8), 91(100), 89(3), 65(12), 63(3), 51(3), 39(6). (b) (1-thiocyanato-propyl)-benzene: IR (CCl₄); v(Cm⁻¹): 3050, 3040, 2980, 2940, 2890, 2165, 1500, 1460, 1240, 1100, 1040, 750, 690. ¹H-NMR(CDCl₃, 250 MHz), δ (ppm): 0.96(3H,t), 2.1(2H,m), 4.6(1H,t), 7.2-7.4(5H,m). ¹³C-NMR(CDCl₃, 63 MHz), δ(ppm): 137.1, 127.8, 127.7, 124.7, 111.9, 54.2, 31.3, 11.1. (c) 1-Thiocyanato-1,1-diphenyl methane: IR(CCl₄); v(Cm⁻¹): 3080, 3040, 2950, 2160, 1500, 1460, 1200, 1120, 1040, 1010, 750, 710. ¹H-NMR(CDCl₃, 250 MHz), δ(ppm): 5.3(1H,s), 7.2–7.5(10H,m). ¹³C-NMR(CDCl₃, 63 MHz), δ(ppm): 131.5, 130.5, 130.4, 130.1, 112.2, 58.1. (d) 1-Isothiocyanato-1,1-diphenyl methane: IR(CCl₄); v(Cm⁻¹): 3060, 3050, 2950, 2060, 1490, 1450, 1180, 1030, 750, 700. ¹H-NMR(CDCl₃, 250 MHz), δ(ppm): 5.8(1H,s), 7.1-7.3(10H,m). ¹³C-NMR(CDCl₃, 63 MHz), δ(ppm): 142.9, 130.8, 129.8, 129.6, 128.2, 65.3.