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Efficient One-pot Thiocyanation of Primary, Secondary and Tertiary Alcohols by *in situ* Generation of $Ph_3P(SCN)_2$. A Modified Procedure†

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The preparation of $Ph_3P(SCN)_2$ is modified by using a combination of Ph_3P, NH_4SCN and Br_2 at room temperature for the efficient conversion of primary, secondary and tertiary alcohols to their corresponding thiocyanates in excellent yields.

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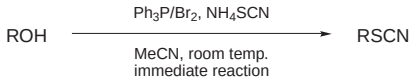
Alkyl thiocyanates are generally prepared *via* nucleophilic displacement of leaving groups attached to C by thiocyanate ion.[1] The use of different phase transfer agents for enhancement of the reaction has also been reported.[1–5] Nucleophilic displacement of the trimethylsilyl group with KSCN–$CuBr_2$ has also been studied in allylic silanes.[6] The reported methods are applied mostly for the synthesis of primary[1,3–6] and in some cases for the synthesis of secondary[2] thiocyanates. The synthesis of *tert*-alkyl thiocyanates, in moderate yields, has been achieved by the use of solid supported potassium thiocyanate.[7] Conversion of alcohols to alkyl thiocyanates has been also achieved by using Ph_3P-diethylazodicarboxylate, Ph_3P or phenylene alkylphosphites and $(SCN)_2$.[8–10] Although the two latter procedures[9,10] are convenient methods for the conversion of alcohols to alkyl thiocyanates, they suffer from disadvantages such as the need for separation of thiocyanogen in the procedure,[9,10] low reaction temperatures (*ca*, −30, −40 and −80 °C, respectively)[9,10] and long reaction times (4 h at −30 °C and then leaving the reaction mixture overnight at room temperature)[9] and formation of isothiocyanates as the sole product from tertiary alcohols.[9,10]



Scheme 1 R = primary, secondary or tertiary group

We now report a modified procedure for one-pot conversion of primary, secondary and also tertiary alcohols to their corresponding alkyl thiocyanates in high to excellent yields at room temperature (Scheme 1). Using this method primary alcohols are converted to their corresponding alkyl thiocyanates without the formation of any isothiocyanates. In the case of secondary and tertiary alcohols, thiocyanates were also formed as the major products together with small amounts of the corresponding isothiocyanates (4–12%). The results of this study are given in Table 1.

Formation of alkyl thiocyanates from primary, secondary and also tertiary alcohols as the major product is a major advantage for this method. The reason for formation of alkyl isothiocyanates as the minor product and in very low yield from the reaction of secondary and tertiary alcohols by this procedure could be due to the slow rate of conversion between $Ph_3P(SCN)_2$ and Ph_3P^+NCS/SCN^- both of which may be present in the reaction mixture.[10] ^{31}P NMR studies of the conversion $Ph_3P(SCN)_2 \rightleftharpoons Ph_3P^+NCS + SCN^-$ shows that it is much easier when lead thiocyanate is used rather than potassium thiocyanate and furthermore is also temperature dependent.[10] Other advantages of the present method are the short reaction time and high yields of the products. This has been shown by comparing some of the results obtained by our method with those reported in the literature (Table 2).

In conclusion, in this modified procedure we can use ammonium thiocyanate instead of the less available lead thiocyanate, and the need to prepare and isolate the poisonous thiocyanogen for further reaction is not required. The one-pot *in situ* generation of $Ph_3P(SCN)_2$ at room temperature provides an efficient and very simple method for

Table 1 Conversion of alcohols to thiocyanates

Alcohol	Yield(%)[a–c]	RSCN(%)[d]	RNCS(%)[d]	IR ν(SCN)[e]/cm^{-1} (CCl_4)	δ_C(SCN) ($CDCl_3$)
Octan-1-ol	95	100[11]	0	2165	110.6
Octan-2-ol	90	96[10]	4	2160	111.2
Cyclohexanol	91	100[9]	0	2165	111.1
Cyclohexyl–CH_2CH_2OH	96	100 (**I**)	0	2165	110.7
$PhCH_2OH$	97	100[9,10]	0	2152	110.6
$PhCH_2CH_2OH$	95	100[9]	0	2165	110.5
$PhCH_2CH_2CH_2OH$	95	100 (**II**)	0	2160	111.1
4-$ClC_6H_4CH_2OH$	94	100[9]	0	2160	111.0
4-$CH_3OC_6H_4CH_2OH$	96	100[9,10]	0	2158	111.2
$PhCH(OH)C_2H_5$	89	92 (**III**)	8	2160	111.9
Ph_2CHOH	88	90 (**IV**)	10	2160	112.2
$Ph_2C(Me)OH$	85	88 (**V**)	12	2150	112.2
Cinnamyl alcohol	93	100[6,9]	0	2160	110.4

[a]Isolated yields. [b]The products were identified by comparison of their physical data with those reported for known samples. [c]Immediate reaction at room temperature. [d]Yield of conversion by GC. Spectral data for products, **I**–**V** are given in the Experimental section. [e]The IR wavenumber and ^{13}C NMR chemical shift of the –SCN group are comparable with literature values.[12–15]

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Table 2 Comparison of the results obtained by the present method with those from literature procedures[9]

Alcohol	Present method[a] yield(%)	Literature[b] yield(%)
$PhCH_2OH$	97	80
Cinnamyl alcohol	93	63
$PhCH_2CH_2OH$	95	48
Octan-1-ol	95	60

[a] Immediate reaction at room temperature. [b] Stirring at −30 °C for 4 h and at room temperature overnight.

immediate conversion of primary, secondary and tertiary alcohols to their corresponding thiocyanates in high to excellent yields.

Experimental

All the products are known compounds and were characterized by comparison of their physical data with literature values. IR spectra were recorded on a Perkin Elmer IR-157 G and a Perkin Elmer 781 spectrometer. NMR spectra were recorded on a Bruker Avance DPX-250. Mass spectra were recorded on a Shimadzu GCMS-QP 1000 EX instrument.

General Procedure for the Synthesis of Primary, Secondary and Tertiary Thiocyanates from Alcohols.—A three-necked flask equipped with a dropping funnel, stirrer, drying $CaCl_2$ tube and nitrogen gas inlet was charged with Ph_3P (2.2 mmol) and dry MeCN (5 ml). Then Br_2 (2.2 mmol) was added dropwise to the solution at room temperature under an N_2 atmosphere. When the addition was complete, a solution of NH_4SCN (4.4 mmol) in MeCN (5 ml) was added dropwise. To the resulting mixture the alcohol (2.1 nmmol) was then added dropwise. GC and TLC of the reaction mixture showed immediate completion of the reaction after addition of the alcohol. The reaction mixture was filtered and the filtrate washed with MeCN. Evaporation of the solvent followed by column chromatography on silica gel using light petroleum (bp 40–60 °C)–ethyl acetate (9 : 1) as eluent yielded the corresponding thiocyanates. Spectral data for compounds **I**–**V** are given below.

Compound **I**. IR (CCl_4) ν/cm^{-1} 2950, 2840, 2165, 1450, 1280, 1250, 1100, 1050; δ_H($CDCl_3$) 2.9 (2H, t), 1.58–1.66 (7H, m), 0.8–1.2 (6H, m); δ_C($CDCl_3$) 110.7, 37.7, 36.6, 33.1, 32.2, 26.7, 26.4.

Compound **II**. IR (CCl_4) ν/cm^{-1} 3080, 3060, 3040, 2940, 2880, 2160, 1500, 1460, 1280, 1260, 1080, 1040, 750, 720; δ_H($CDCl_3$) 2.0 (2H, q), 2.7 (2H, t), 2.9 (2H, t), 7.1–7.5 (5H, m); δ_C($CDCl_3$) 140.3, 129.1, 128.9, 128.8, 111.1, 34.2, 32.4, 30.1.

Compound **III**. IR (CCl_4) ν/cm^{-1} 3050, 3040, 2980, 2940, 2890, 2165, 1500, 1460, 1240, 1100, 1040, 750, 690; δ_H($CDCl_3$) 0.96 (3H, t), 2.1 (2H, q), 4.6 (1 H, t), 7.2–7.4 (5H, m); δ_C($CDCl_3$): 137.1, 127.8, 127.7, 124.7, 111.9, 54.2, 31.3, 11.1.

Compound **IV**.— IR (CCl_4) ν/cm^{-1} 3080, 3040, 2950, 2160, 1500, 1460, 1200, 1120, 1040, 1010, 750, 710; δ_H($CDCl_3$) 5.3 (1H, s), 7.2–7.5 (10H, m); δ_C($CDCl_3$) 142.9, 130.8, 127.8, 127.7, 112.2, 58.1.

Compound **V**. IR (CCl_4) ν/cm^{-1} 3080, 3060, 3020, 2960, 2920, 2150, 1500, 1450, 1240, 1040, 750, 700; δ_H($CDCl_3$) 2.1 (3H, s), 7.2–7.4 (10H, m); δ_C($CDCl_3$) 142.9, 130.3, 130.1, 129.5, 112.2, 70.6, 32.9.

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