

A novel and efficient synthesis of alkyl thiocyanates from alkyl halides in water using phase transfer catalysts

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Abstract

1,4-Bis(triphenylphosphonium)-2-butene dichloride (BTPBDC) and 1,4-bis(triphenyl phosphonium)-2-butene dithiocyanate (BTPBDT) were prepared and used as phase-transfer catalysts. Alkyl halides were converted efficiently to the corresponding alkyl thiocyanates under mild reaction conditions in water. No evidence for the formation of isothiocyanates as by-product of the reaction was observed.

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The toxic and volatile nature of many organic solvents, particularly chlorinated hydrocarbons that are widely used in organic synthesis have posed a serious threat to the environment. Consequently methods that successfully minimize their use are the focus of much attention. One of the recently developed methods is to use water as solvent for organic reactions [1]. Unfortunately its use is limited by the low solubility of organic compounds. One of the most important strategies to overcome this limitation of water, in order to expand the scope of water-based organic synthesis, has been the utilization of phase transfer catalysts [2].

Phase-transfer catalysts (PTCs) facilitate reactions between water-soluble reagents and organic soluble substrates. The most important PTCs, which have been used widely in organic reactions, are quaternary phosphonium salts [3].

Organic sulfur compounds are important and useful building blocks in organic synthesis [4]. Thiocyanation is generally carried out *via* nucleophilic substitution using thiocyanate anions. The low nucleophilicity of the SCN⁻ anion requires rather harsh reaction conditions. Thiocyanates are not very stable when heated or under acidic conditions. Chromatography on silica gel or prolonged heating over 50 °C can cause intramolecular rearrangement [5]. Thus, few methods are reported for the preparation of alkyl thiocyanates, [6] but some of these methods are not applicable as versatile reagents in the preparation of alkyl thiocyanates and suffer from disadvantages such as the formation of isothiocyanates as by-product, long reaction times, using of organic solvents, using of expensive catalysts or low

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yields. Therefore, it seems that there is still a need for development of novel methods that proceed under mild and eco-friendly conditions.

In continuation of our studies on the use of phosphonium salts in organic synthesis [7]. We describe our successful results that led to an extremely convenient method for preparation of alkyl thiocyanates from alkyl halides using phase transfer catalysts in aqueous media and high isolated yields.

1. Experimental

1,4-Bis(triphenylphosphonium)-2-butene dichloride and 1,4-bis(triphenyl phosphonium)-2-butene dithiocyanate were prepared and other chemicals were purchased from Merck Chemical Company Darmstadt, Germany. The purity determination of the products and reaction monitoring was accomplished by TLC on polygram SILG/UV 254 plates. IR spectra were recorded on Bomem MB-Series 1998 FT-IR spectrometer. ^1H NMR and ^{13}C NMR spectra were taken on a 400 MHz Bruker spectrometer. Melting points were measured on a Mettler FP5 apparatus.

1.1. Preparation of 1,4-bis(triphenylphosphonium)-2-butene dichloride (BTPBDC)

To a solution of 1,4-dichlorobutene (5 mmol) in CHCl_3 (10 mL) in a 50 mL round-bottomed flask equipped with a magnetic stirrer and a reflux condenser was added triphenylphosphine (10 mmol). The reaction mixture was refluxed on a water bath for 2.5 h. The solution was cooled to room temperature and then, while vigorously stirred, diethylether was added dropwise until an oily product separated. The ether was removed by decantation and acetone (40 mL) was added. Stirring the acetone solution for 40 min afforded a white precipitate which was filtered, washed with acetone (20 mL) and dried. Yield (80%), mp: 278–279 °C. IR (KBr): ν 3053, 2755, 1613, 1575, 1478, 1437, 1258, 754, 693, 556 (cm^{-1}). ^1H NMR (CDCl_3): δ 5.7 (dd, 4H), 6.3 (m, 2H), 7.7–8.0 (m, 30H). ^{13}C NMR (CDCl_3): δ 20.7, 120.8, 132.15, 134.2, 137.01, 140.17.

1.2. Conversion of alkyl halides to alkyl thiocyanate using KSCN and BTPBDC

The alkyl halide (1 mmol), potassium thiocyanate (1.5 mmol), BTPBDC (0.3 mmol) and water (15 mL) were stirred at room temperature for the time specified in Table 1. The progress of each reaction was monitored by TLC. The reaction mixture was extracted with diethylether (3 \times 10 mL). The combined organic layer washed with cold water (3 \times 10 mL), dried over sodium sulfate and filtered. The filtrate was subjected to a vacuum gave the desired product. It did not require any column chromatography thus avoiding the possibility of rearrangement.

Table 1
Reaction of different alkyl halides with KSCN using BTPBDC as catalyst.

Entry	Substrate	Product	Time (min)	Yield ^a (%)
1	2,4-ClC ₆ H ₃ CH ₂ Cl	2,4-ClC ₆ H ₃ CH ₂ SCN	60(I), 50(II)	88, 89
2	C ₆ H ₅ CH ₂ Br	C ₆ H ₅ CH ₂ SCN	55(I), 40(II)	85, 85
3	C ₆ H ₅ CH ₂ CH ₂ Br	C ₆ H ₅ CH ₂ CH ₂ SCN	45(I), 40(II)	85, 80
4	3-ClC ₆ H ₄ CH ₂ Cl	3-ClC ₆ H ₄ CH ₂ SCN	55(I), 40(II)	80, 83
5	4-NO ₂ C ₆ H ₄ CH ₂ Cl	4-NO ₂ C ₆ H ₄ CH ₂ SCN	60(I), 60(II)	90 ^d , 92 ^d
6	4-BrC ₆ H ₄ COCH ₂ Br	4-BrC ₆ H ₄ COCH ₂ SCN	45(I), 30(II)	83, 85
7	4-CH ₃ OC ₆ H ₄ COCH ₂ Br	4-CH ₃ OC ₆ H ₄ COCH ₂ SCN	55(I), 50(II)	80 ^d , 80 ^d
8	4-BrC ₆ H ₄ CH ₂ Br	4-BrC ₆ H ₄ CH ₂ SCN	45(I), 35(II)	85, 85
9	C ₈ H ₁₇ I	C ₈ H ₁₇ SCN	45(I), 45(II)	90, 92
10	4-CH ₃ OC ₆ H ₄ CH ₂ Cl	4-CH ₃ OC ₆ H ₄ CH ₂ SCN	55(I), 50(II)	87, 85
11	Bromo cyclohexane	–	4h(I), 4h(II)	–

^bI \equiv BTPBDC; II \equiv BTPBDT.

^cIsolated yields.

^a Products were identified by comparison of their physical and spectral data with those of authentic samples [9].

^d GC analysis.

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