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Rapid and efficient synthesis of benzyl thiocyanates via microwave assisted heating

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ABSTRACT

A rapid and efficient synthesis of series benzyl thiocyanates via microwave assisted heating is described. The reaction is solvent free and environmental friendly, using Polyethylene glycol 400 (PEG400) as catalyst, and yield can reach up to 90% in several minutes.

KEYWORDS

Benzyl thiocyanates;
Sodium thiocyanate;
Microwave;
PEG400;
Solvent free.

INTRODUCTION

Benzyl thiocyanates are widely used as intermediates in organic synthesis and as crude materials in pesticide, dyestuff, phytocide and others[1,2]. Thiocyanates are also considered to be series important compounds in some anti-cancer natural products formed by deglycosylation of glucosinolates[3], and had attracted a great deal of attention in organosulfur chemistry[4]. Some drugs which contain the group of isothiazole could use thiocyanates as crude materials too. One of traditional methods for synthesis of thiocyanates is reaction of sodium thiocyanate (NaSCN) with aryl chloride or alkyl chloride in solvent of alcohol, but several hours were needed[5]. Another way to preparation is to form intermediate of $(SCN)_2$, however, $Ph_3P(SCN)_2$ is a heavy toxicity reagent which is necessary in this method. These traditional ways are easy to lead to environmental pollution. Research of a new efficient, safe and environment-friendly route for synthesis of benzyl thiocyanates is significant.

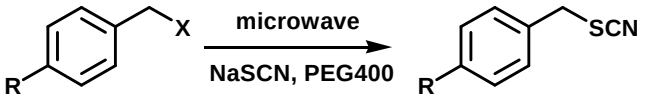
Until now, the application of phase-transfer catalyst (PTC) has drawn a great deal of attention[6]. Attractive features of PEG include their low cost, readily availability and apparent lack of significant toxicological properties. In many cases, they are good alternative substitutes for the traditional PTC, such as the crown ether, which is toxic and expensive, and quaternary ammonium salts or quaternary phosphonium compounds, which are predominantly used in a liquid-liquid two-phase reaction. In contrast with crown ethers, PEG has more powerful ability to solubilise the inorganic salts in a nonpolar organic solvent due to the fact that they have two terminal polar hydroxyl groups[7].

Microwave irradiation has been widely applied in organic chemistry[8,9]. We now report a new method for synthesis of benzyl thiocyanates with benzyl chloride and NaSCN by PEG400 under microwave irradiation. It is a rapid and efficient reaction which is environmental friendly, the yield is satisfying.

EXPERIMENTAL

Reactions proceed in a commercial domestic mi-

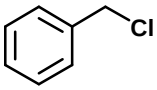
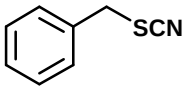
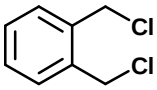
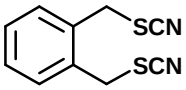
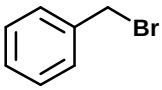
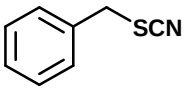
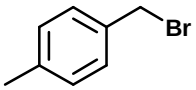
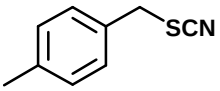
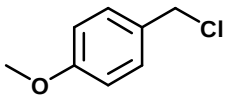
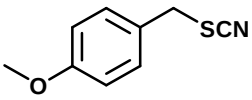
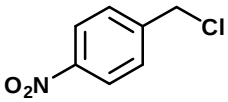
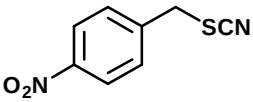
crowave oven (Midea PJ21C-BF). The reaction process was monitored by Thin-Layer Chromatography (TLC) on silica gel GF254 plate using petroleum ether/ethyl acetate (10:1v/v) as the developing solvent. Melting points were determined on a microscopy apparatus (SGW X-4) and uncorrected. The products were characterized by comparison of their melting points and boiling points with the literature values[10].



General procedure

Benzyl chloride (3.16g, 25mmol), NaSCN (4.05 g, 50mmol) and PEG 400 (0.5g, 1.25mmol) were put in a conical flask, mixed thoroughly and subjected to microwave irradiation at 136W for 3 min. After completion of the reaction, 50ml water added into mixture and stirred well, placed stay over night and crystal separated out. Then extracted with CH_2Cl_2 (2×30ml), dried with anhydrous sodium sulfate and evaporated. The products were dried in a vacuum tank, characterized by comparison of their melting points with the literature values.

TABLE 1 : Conversion of benzyl chloride to thiocyanates

Entry	Substrate	Product	Time (min)	Yield (%)	m.p./°C Found/Reported
1			3	92	40-42/41-43
2			4	90	132-134/134
3			3	92	40-42/41-43
4			3	93	20-22/21.5-22.5
5			3	95	Oil/Oil
6			4	90	81-83/83

RESULTS AND DISCUSSION

In TABLE 1, a variety of substituted benzyl chlorides were successfully thiocyanated by utilization of microwave irradiation and polyethylene glycol (PEG). The electron density on the benzyl was shown to have some effect on the yield of thiocyanation reaction. Highly activated compound, 1-chloromethyl-4-methoxybenzene (entry5), could be converted to the corresponding thiocyanates in excellent yields. As the results shown, compounds which are substituted by the electron donating group make reaction proceeded more completely. However, there is not distinct difference in the yield between compounds with electron donating group and electron withdrawing group, although the electron donating group could make the benzyl cation stable during reaction process.

With a medium molecular weight, PEG is a particularly desirable phase-transfer catalyst for non-aqueous heterogeneous reactions. It is important that features of PEG include its low cost, stability, availability and lack of toxicological problems, so the application of PEG as

an eco-friendly PTC for activation of reaction has now become a very popular and useful method. These reactions may not be completed if there is no catalyst. So, PEG400 as a phase transfer to this reaction has been studied, and the effects of PEG400 as well as the effect of time using microwave were shown in TABLE 2. The best amount to use was 5 mol%. It was found that lower dosage of PEG400 could not catalyze the reaction effectively and higher dosage would lead to more loss of products during the washing procedure. The power of microwave irradiation also had great influence on the rate of production.

TABLE 2 : The amount of PEG400

Power (w)	Time (min)	Amount (mol%)	Yield (%)
136	3	1	70
136	3	3	80
136	3	5	93
136	3	7	85
264	3	5	72
440	2	5	63

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