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RESEARCH LETTER

PEG 400 promoted nucleophilic substitution reaction of halides into organic azides under mild conditions

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Polyethylene glycol 400 (PEG 400) has been demonstrated as an efficient and eco-friendly reaction medium for the preparation of organic azides from structurally diverse halides by nucleophilic substitution reaction with NaN_3 under mild conditions. The advantages of this protocol are: operational simplicity, environmental safety, broad substrate scope, excellent functional group tolerance, and short reaction time. The PEG 400 can be recovered and reused.

Keywords: polyethylene glycol 400; nucleophilic substitution reaction; halide; azide

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Introduction

In recent years there has been a growing interest in the development of environmentally benign chemical synthesis both in academia and industrial research (*1,2*). In this context, traditional volatile organic solvents (VOCs) as reaction media are continuously being replaced either by the use of solvent-free techniques (*3,4*), or by using environmentally benign solvents such as water (*5–7*), ionic liquids (ILs) (*8–11*), and polyethylene glycols (PEGs) (*12–14*). Solvent-free processes, to some extent, have succeeded in some reactions, but in performing the majority of organic transformations, solvents play a critical role in mixing the ingredients to allow molecular interactions to be more efficient. Although most traditionally popular, highly volatile solvents in products can be removed by evaporation or distillation, spillage and evaporation inevitably lead to atmospheric pollution and harm workers' health (*15*). Meanwhile, using water as green solvent has been well documented, but the practical utilization is limited due to the hydrophobic nature of organic compounds and the sensitivity of catalysts to moisture (*7*). The ILs, as another alternative reaction media instead of water and organic solvents, require tedious preparation, and their environment safety is still debatable (*8–11*). On the contrary, PEGs have recently attracted great interest and have been explored as a novel, powerful, eco-friendly reaction medium for various organic transformations (*16–27*) due to their relatively inexpensive, thermally stable, readily recyclable, and biodegradable material.

Organic azides, a unique class of flexible intermediates in organic chemistry due to their synthetic usefulness and versatile reactivity, have enjoyed considerable interest (*28–30*). There are many methods available for the preparation of azides (*28–30*), and the most common route to organic azides involves the classic nucleophilic substitution reaction of halides with sodium azide (NaN_3) (*31–43*) or lithium azide (LiN_3) (*44*) as azido sources in various solvents such as DMSO (*31–35*), benzene/DMF (*36–38*), acetone (*39–41*), and so on (*42,43*). However, these methodologies often suffer from either complex procedures, long reaction time, elevated temperature, or substrate limitations. In addition, there are usually purification problems associated with the distillation (*45,46*) of products from the incomplete reactions since some alkyl azides decomposes rapidly with danger of explosion (*47*). Importantly, from an environmental point of view, they do not meet the requirement of green chemistry. Since nucleophilic substitution reactions of halides involve a non-polar organic compound and a polar ionic salt, the heterogenous reactions are often troublesome because the polar and non-polar reagents are often not soluble in a single solvent system. Consequently, to improve the yields and to facilitate the product isolation, the nucleophilic displacement reactions are often carried

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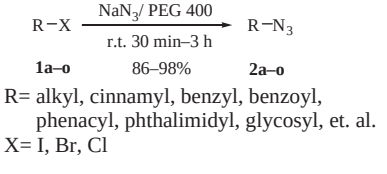
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out under phase-transfer catalysis (PTC) conditions (*48–51*). Recently, ILs have demonstrated the possibility as a catalyst and solvent for the nucleophilic substitutions of halides (*52–54*). As the emerging nonconventional methods being recognized as viable environmentally benign alternatives, microwave irradiation (*55*) and ultrasound irradiation (*56,57*) have also been employed as powerful synthetic tools to accomplish these reactions. Unfortunately, in conventional PTCs the organic solvents used are environmentally undesirable species, and extra PTCs are responsible for billions of dollars in industrial processes. Additionally, microwave irradiation and ultrasound irradiation process are difficult to apply in the industrial processes until now.

Thus, the new availability of azido compounds appears crucial and the development of new eco-friendly procedures for their preparation remains an important goal. Besides numerous advantages associated with this eco-friendly elements mentioned above, it has previously been suggested that PEGs also possess unique physicochemical property: PEGs can be used as complexing solvent of inorganic salts in order to enhance the reactivity of the anion brought into solution with the organic substrate (*58–61*). As part of our continued activities (*62*) to explore PEG as an efficient, versatile, and eco-friendly reaction medium we report here a simple and practical synthesis of organic azides by using sodium azide in PEG 400 (Scheme 1).

Results and discussion

Initially, we have compared the effectivity of PEG (400 MW) with other reaction media reported for the model reaction of nucleophilic substitution of benzyl bromide (1.0 mmol) with sodium azide (Table 1). The model reaction can be carried out in different solvents such as DMSO and IL-H_2O for the specified time (entries 1 and 4, Table 1). The reaction can also be progressed in ethanol but at an elevated temperature and prolonged reaction time (entry 5, Table 1). Although good results are obtained in H_2O under microwave (entry 2, Table 1), conversion of benzyl bromide to the corresponding benzyl azide must be reacted at 120°C, which may exist potential explosion danger of azidation. It is clear from Table 1, most prominently, that PEG 400 was found to be the best reaction medium in terms of short reaction time (50 min) and excellent yield (entry 6, Table 1). In a typical experimental procedure, the optimum reaction condition is that a mixture containing benzyl bromide (1.0 mmol), NaN_3 (1.2 mmol), and PEG 400 (0.1 g) was vigorously stirred without another catalyst for 50 min at room temperature. The desired benzyl azide as a colorless oil was obtained in 98% yield after a standardized workup protocol. In addition, we examined the possibility of recovery and reuse of PEG 400. As shown in Table 1, the recovered PEG 400 was recycled for three runs with no apparent loss in activity under the same reaction condition (entry 6, Table 1).

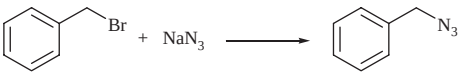


Scheme 1. Synthesis of organic azides from halides.

To explore the scope and generality of the method, various halogenated substrates were tested for the nucleophilic substitution with NaN_3 in PEG 400 at room temperature and results are summarized in Table 2. As the data in Table 2 indicate, nucleophilic substitutions of structurally diverse aliphatic, cinnamyl, primary and secondary benzyl (Bn), benzoyl (Bz), benzyloxycarbonyl (Cbz), α-acetophenone/-ketoester, phthalimide (PHT), and sugar halogenated substrates were carried out with NaN_3 using PEG 400 as a reaction medium at room temperature. For most of the substitution reactions, a higher yield (90% up) and shorter reaction time (less 1 hr) were obtained than those with most conventional procedures (*31–43,48–57*). More importantly, it was found that the reaction of halides with NaN_3 tolerate a variety of functional groups such as nitrile, nitro (*63*), imide, ester, carbonyl, acetoxy, and isopropylidene. Benzyl halides both containing electron-deficient and electron-donating groups like Me, NO_2, and CN underwent the conversion quickly and smoothly (entries 4–6, Table 2). Relatively, benzyl halides with electron-deficient substituents seemed to react faster than those with electron-donating substituents. Another notable feature of the reaction is that secondary halide and cinnamyl halides also reacted with NaN_3 smoothly to afford the corresponding azides in 97% and 98% yields, respectively (entries 7 and 8, Table 2). As for halides including iodides (entries 8 and 15, Table 2), bromides (entries 1–2, 4–7, 9–11, and 14, Table 2) and chlorides (entries 3, 12, and 13, Table 2), they all were efficiently converted to the corresponding various organic azides.

The advantages of using PEG 400 as a reaction medium over the prior reported methods may be further demonstrated by the following representative examples. First, α-azidoacetophenones represent important substructures in a variety of azides. Quite unlike other organic azides, α-azidoketones have

Table 1. Comparison of reaction media effect on the reaction time and yield of benzyl azide from benzyl bromide and sodium azide.



Entry	NaN_3 (eq.)	Catalyst/Solvent	Method/Temperature	Reaction time	Yield[a]
1	1.1	DMSO (*31*)	Stirring, ambient temperature	1 hr	98[b]
2	1.3	H_2O (*55*)	Microwave, 120°C	30 min	95
3	1.3	Clays/PE-H_2O (*49*)	Stirring, 90–100°C	6 hr	84
4	2.0	[bmim][PF_6]-H_2O (*52*)	Stirring, 25°C	5 hr	84
5	1.1	EtOH (*34*)	Stirring, reflux	24 hr	No report
6	1.2	PEG 400	Stirring, room temperature	50 min	98, 95,[c] 91[d]

[a]Pure isolated yield.
[b]GC analyses yield.
[c]The second run.
[d]The third run.

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significant synthetic utility in organic synthesis especially for the synthesis of a variety of biologically important heterocyclic compounds such as oxazoles, pyrazines, 2-acylimidazoles, substituted pyrroles, and many others (*64–70*). In sharp contrast with the result in DMSO (*31,32*), α-azidoacetophenone **2j** obtained after only 30 min at room temperature in PEG 400 in 90% yield (entry 10, Table 2). Notably, the complex mixture can also be observed in our experiment at elevated temperatures (about 50°C) or prolonged reaction time (about after 1.5 hr), possibly because its pyrolysis leads to α-iminoketones (*64,65*) or 2-acylimidazoles if β-carbon atoms are not present (*64*).

Since acyl azides are valuable synthetic intermediates in organic chemistry (*71–73*) and especially in pharmaceuticals (*74*), dyes (*75*), and agrochemicals (*76*), we further explored the reaction and found that acyl chlorine derivatives such as benzoyl chlorine, benzyloxycarbonyl chlorine have been successfully converted into their corresponding acyl azides in good to excellent yields (entries 12 and 13, Table 2), and no Curtius rearrangement type products were observed (*28–30*).

Finally, inspired by the above excellent results and to explore the scope and generality as possible, we proceeded to investigate halogenated sugars as substrates. Glycosyl azides have been widely recognized as important classes of carbohydrate derivatives due to the versatile reactivities of the azido group (*77, 78*). Notably, peracetylated α-glycosyl bromide **1n** in PEG 400 provided the S_N2 product peracetylated β-glycosyl azide **2n** in quantitative yield and its β-D-gluco configuration was confirmed by the ^1H NMR spectrum, in which the signal for the anomeric proton appeared as a doublet at 4.64 ppm ($J_{1,2} =$ 8.8 Hz) (*41, 79*). In addition, 6-iodo-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactose **1o** can also yield 6-azido-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactose **2o** within 30 min.There was no reaction in the absence of PEG 400. Thus, based on the reported literature (*58–61,80*), a plausible mechanism for the nucleophilic substitution of halogenated compounds with NaN_3 employing PEG 400 as the reaction medium is proposed. As PEG 400 can be regarded as open-chain crown ethers and they are able to form complexes with alkaline and alkaline-earth cations (*81,82*), we presume this may be because the sodium azide is dissociated into free ions and a complex forms from the sodium cation with the oxygen atom of PEG 400. The formation of a complex will loosen the interaction between the sodium cation and the azido anion. Then the dissociated azide anion could be brought into solution and acts as the elevated active component to enhance the nucleophilic substitution reaction rate and to increase the reaction yield.

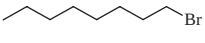
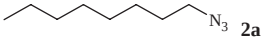
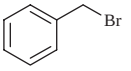
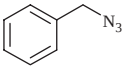
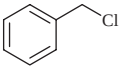
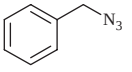
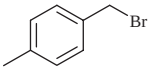
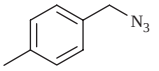
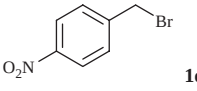
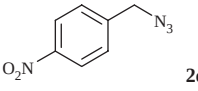
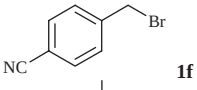
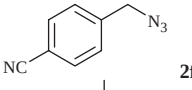
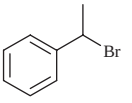
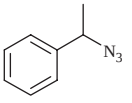
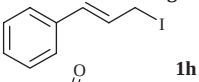
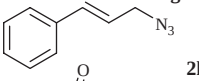
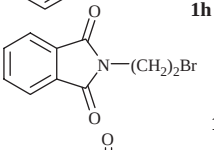
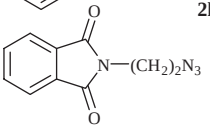
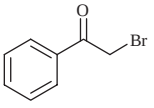
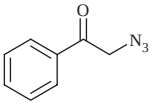
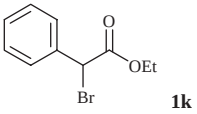
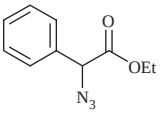
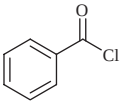
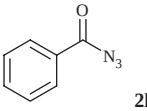
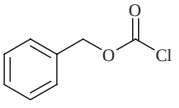
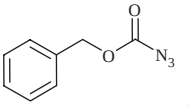
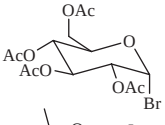
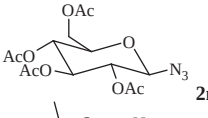
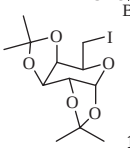
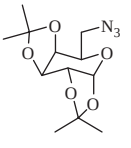
Experimental

Apparatus and analysis

All reagents were purchased from commercial sources and all were further purified by recrystallization or distillation using standard procedures unless otherwise stated. TLC was carried out on silica gel 60 F254 precoated plates (0.20–0.25 mm thickness) and visualized with UV light (254 nm). Melting points were determined with X-6 (Beijing Fukai Co. Ltd.) melting point apparatus and were uncorrected. ^1H NMR and ^{13}C NMR (600 and 150 MHz, respectively) spectra were recorded on a Bruker Avance 600 spectrometer using TMS as an internal standard. Compounds **1h** (*83*), **1n** (*50*), and **1o** (*84*) were prepared by following the reported methods.

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Table 2. PEG 400 promoted nucleophilic substitution reaction of halides into organic azides.[a]

Entry	Alkyl bromide	Product	Time (min)	Yield (%)[b]
1	 **1a**	 **2a**	180	95
2	 **1b**	 **2b**	50	98
3	 **1c**	 **2c**	150	95
4	 **1d**	 **2d**	50	93
5	 **1e**	 **2e**	30	99
6	 **1f**	 **2f**	30	98
7	 **1g**	 **2g**	50	97
8	 **1h**	 **2h**	30	98
9	 **1i**	 **2i**	30	90
10	 **1j**	 **2j**	40	90
11	 **1k**	 **2k**	40	90
12	 **1l**	 **2l**	90	86
13	 **1m**	 **2m**	30	93
14	 **1n**	 **2n**	30	93
15	 **1o**	 **2o**	30	95

[a]Reaction conditions: alkyl azide (1.0 mmol), sodium azide (1.2 mmol), PEG 400 (0.1 g) at r.t.
[b]Yield of pure isolated product.

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Typical procedure for synthesis of organic azides

A mixture of halides (1.0 mmol) and NaN_3 (1.2 mmol) in PEG 400 (0.1 g) was vigorously stirred at room temperature for the appropriate time until TLC indicated total disappearance of the halide. After completion, the reaction mixture was extracted with dry ether, concentrated under reduced pressure afford pure organic azides in good to excellent yield. The crude products were generally of sufficient purity to be used without further purification. [**CAUTION:** Sufficient care has to be exercised while distilling organic azides because of their explosive nature (*47*)]. The PEG 400, after the extraction with dry ether, can be reused for a number of cycles without significant loss of activity. All the products were identified by comparing their physical and spectral data with those of reported compounds.

Product characterization data

4-Nitrobenzyl azide (2e) (32). Pale-yellow oil, ^{1}H NMR ($CDCl_3$): δ 4.51 (s, 2H), 7.50 (d, $J = 8.4$ Hz, 2H), 8.23 (d, $J = 8.6$ Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 53.8, 124.0, 128.6, 142.7, 147.8; IR (neat) ν/cm^{-1}: 2932, 2105, 1607, 1520, 1346, 1296, 1110, 848.

4-Cyanobenzyl azide (2f) (37). Colorless oil, ^{1}H NMR ($CDCl_3$): δ 4.45 (s, 2H), 7.44 (d, $J = 8.0$ Hz, 2H), 7.66 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 54.0, 112.1, 118.4, 128.5, 132.6, 140.8; IR (neat) ν/cm^{-1}: 2927, 2229, 2104, 1609, 1506, 1414, 1346, 1292, 816.

2-Azido-acetophenone (2j) (64–66). Pale-yellow solid, m.p. 17–18°C, ^{1}H NMR ($CDCl_3$): δ 4.55 (s, 2H), 7.49 (overlap, 2H), 7.62 (m, 1H), 7.90 (overlap, 2H); ^{13}C NMR ($CDCl_3$): δ 54.9, 127.9, 128.9, 134.1, 134.4, 193.2; IR (KBr) ν/cm^{-1}: 3067, 2898, 2254, 2194, 2106, 1698, 1598, 1450, 1348, 1283, 1217, 911, 754, 655.

Benzoyl azide (2l) (85, 86). Pale solid, m.p. 25–26°C, ^{1}H NMR ($CDCl_3$): δ 7.46 (overlap, 2H), 7.61 (overlap, 1H), 8.03 (overlap, 1H); ^{13}C NMR ($CDCl_3$): δ 128.6, 129.5, 130.7, 134.3, 172.5; IR (KBr) ν/cm^{-1}: 2173, 2138, 1686, 1597, 1450, 1251, 1188, 988, 698.

Benzyl azidoformate (2m) (87). Colorless oil, ^{1}H NMR ($CDCl_3$): δ 5.19 (s, 2H), 7.34 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 70.1, 128.5, 128.7, 128.9, 134.5, 157.5; IR (KBr) ν/cm^{-1}: 2141, 1730, 1497, 1456, 1377, 1234, 961, 748, 697.

2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosylazide (2n) (35, 41). Colorless solid, m.p. 124–125°C, ^{1}H NMR ($CDCl_3$): δ 2.01 (s, 3H, $COCH_3$), 2.03 (s, 3H, $COCH_3$), 2.08 (s, 3H, $COCH_3$), 2.10 (s, 3H, $COCH_3$), 3.78–3.81 (m, 1H, H-5), 4.17 (dd, $J_{5,6a} = 2.2$, $J_{6a,6b} = 12.5$ Hz, 1H, H-6a), 4.27 (dd, $J_{5,6b} = 4.8$, $J_{6a,6b} = 12.5$ Hz, 1H, H-6b), 4.64 (d, $J_{1,2} = 8.8$ Hz, 1H, H-1), 4.96 (dd, $J_{1,2} = 8.8$, $J_{2,3} = 9.3$ Hz, 1H, H-2), 5.11 (apparent triplet, $J_{3,4} = 9.8$, $J_{4,5} = 9.8$ Hz, 1H, H-4), 5.22 (dd, $J_{2,3} = 9.3$, $J_{3,4} = 9.8$ Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 20.5, 20.6, 61.7, 67.9, 70.7, 72.6, 74.0, 87.9, 169.2, 169.3, 170.1, 170.6; IR (KBr) ν/cm^{-1}: 2969, 2909, 2118, 1756, 1732, 1372, 1239, 1213, 1059, 1039, 908.

6-Azido-6-deoxy-1,2:3,4-di-O-isopropylidene-α-D-galactose (2o) (88, 89). Pale yellow syrup, ^{1}H NMR ($CDCl_3$): δ 1.33 (s, 3H, $COCH_3$), 1.34 (s, 3H, $COCH_3$), 1.45 (s, 3H, $COCH_3$), 1.55 (s, 3H, $COCH_3$), 3.35 (dd, $J_{5,6a} = 5.4$, $J_{6a,6b} = 12.7$ Hz, 1H, H-6a), 3.51 (dd, $J_{5,6b} = 7.8$, $J_{6a,6b} = 12.7$ Hz, 1H, H-6b), 3.91 (ddd, $J_{5,6a} = 5.4$, $J_{5,6b} = 7.8$ Hz, 1H, H-5), 4.19 (dd, $J_{4,5} = 1.8$, $J_{3,4} = 7.8$ Hz, 1H, H-4), 4.33 (dd, $J_{2,3} = 2.4$, $J_{1,2} = 4.9$ Hz, 1H, H-2), 4.63 (dd, $J_{2,3} = 2.4$, $J_{3,4} = 7.8$ Hz, 1H, H-3), 5.54 (d, $J_{1,2} = 5.0$ Hz, 1H, H-1); ^{13}C NMR ($CDCl_3$): δ 24.4, 24.8, 25.9, 25.9, 50.7, 66.9, 70.4, 70.8, 71.2, 96.3, 108.7, 109.6; IR (KBr) ν/cm^{-1}: 2989, 2937, 2103, 1455, 1383, 1256, 1213, 1070, 1008, 893.

Conclusion

In summary, we have developed an environmentally friendly method for the synthesis of variously organic azides. PEG 400, which offers an alternative to the traditional VOCs and some ILs, has been demonstrated to be a versatile, convenient, inexpensive and recyclable reaction medium for the preparation of organic azides by nucleophilic substitution reaction from various readily available halides with NaN_3 at room temperature. Compared to the previous reported methods, this protocol has some notable advantages such as good capability, excellent functional group tolerance, more environmentally benign, shorter reaction time, and higher reaction yield. Further investigations on the application of PEG 400 on other catalytically synthetic reactions will be reported in due course.

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