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Note

Facile one step synthesis of acyl azides and N^{α} –Fmoc/Boc/Z protected amino acid azides employing benzotriazole-1-yl-oxy-tris-(dimethylamino)-phosphonium hexafluorophosphate (BOP)

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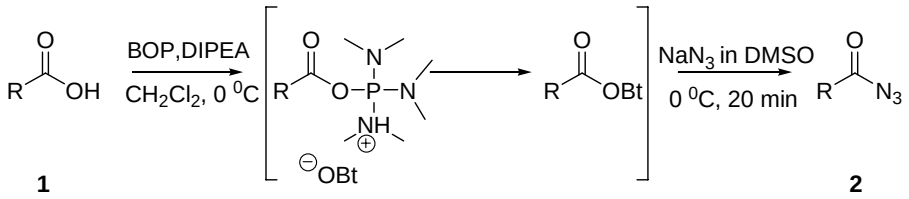
A simple route for the preparation of acyl azides from the corresponding carboxylic acids employing the peptide-coupling agent BOP is described. The procedure is simple, clean and high yielding. The chemistry is also extended to the preparation of several urethane protected amino acid azides (eight examples) as well.

Keywords: One pot reaction, acyl azide, BOP, azidolysis

Acyl azides and *N*-protected amino acid azides have widespread utility in organic synthesis[1] as well as in peptide chemistry[2]. They are extensively used in the synthesis of amides, nitriles, in cycloaddition reactions and also in heterocyclic chemistry[3,4]. Curtius has demonstrated the use of highly reactive acyl azides as acylating agents for the synthesis of peptides[5,6]. The well known Curtius rearrangement of acyl azides under thermal condition leads to another important synthetic intermediate, isocyanate, which has diverse applications such as in the synthesis of amines, partially modified retro-inverso peptides[7], ureas, carbamates and other related derivatives[1,8]. This group has recently demonstrated the application of Curtius rearrangement of N^{α}-protected amino acid azides in assembling new types of peptidomimetics such as ureidopeptides[9], urea tethered glycosylated amino acids[10], N-formamides[11] and amino acid derived isonitriles[12].

Several protocols have been reported for the synthesis of acyl azides in the literature. They are generally prepared by the reaction of sodium azide (NaN_3) with acid derivatives such as acid chlorides, mixed anhydrides which in turn are prepared using acid activators like $SOCl_2$/DMF[13], cyanuric chloride/*N*-methylmorpholine[14], triphosgene/triethylamine[15], ethyl chloroformate/ *N*-methylmorpholine[16,17]. In amino acid chemistry, the acid chloride method is not compatible with Boc as well as Z urethanes. For example, *N*-Boc amino acid chlorides degrade to oxazolidin-2,5-diones (Leuchs' anhydride)[16]. Subhas Bose *et al*., synthesized acyl azides by treating aldehyde with Dess-Martin periodinane and NaN_3 (ref 18). Katritzky's group reported the synthesis of acyl azides by a reaction of NaN_3 with acyl benzotriazoles, in a two-step protocol, which requires 16 hr for completion[19]. Direct conversion of carboxylic acids to acyl azides is accomplished using diphenylphosphoryl azide (DPPA) which is expensive[20,21]. Although some of these methods are beneficial for the preparation of acyl azides, there are drawbacks such as long reaction time, toxic reagents, byproduct formation and tedious reaction conditions. In view of the vast utility of acyl azides, development of an expedient, mild method for the proficient preparation of acyl azides from corresponding acids is warranted (**Scheme I**).

On the other hand Boc as well as Z protected α-amino acid azides have also been obtained from their acyl hydrazides[22-24]. This route requires the use of NO^{+} equivalents and is not compatible with Fmoc urethane. The first report on the preparation of stable Fmoc-amino acid azides was reported from this group[25]. Fmoc-amino acid azides were prepared by converting Fmoc-amino acids to the respective acid chloride or mixed anhydride and then reacted with NaN_3. Recently, interest has turned towards the synthesis of acyl azides employing peptide-coupling agents. The efficacy of these coupling reagents for carboxyl group activation followed by coupling is fully exploited in peptide chemistry. Some of the important advantages of using coupling agents is their commercial availability, solubility in wide range of solvents, easy removal of other products by simple phase extraction, low epimerization and high yield[26,27]. In this regard, this group recently reported the synthesis of acyl azides employing 1-ethyl-3-(3-dimethylaminopropyl)carbodidimide (EDC) and 2-(1*H*-Benzotriazol-1-yl)-1,1,3,3.-tetramethyluronium hexafluorophosphate (HBTU)[28]. Benzotriazole-1-yl-oxy-tris-(dimethylamino)-phosphonium hexafluoro



Scheme I — Synthesis of organic acid azides

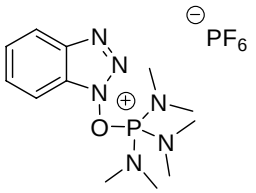
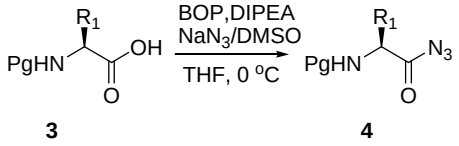


Figure 1 — Benzotriazole-1-yl-oxy-tris-(dimethylamino)-phosphonium hexafluorophosphate



Pg = Fmoc, Boc or Z group

Scheme II — Synthesis of urethane protected amino acid azides

phosphate (BOP), discovered by Castro in the 1970's, is well known as a convenient and efficient coupling agent in peptide synthesis due to its mild, chemo-selective, low epimerization and high yielding nature[29,30]. It has been successfully used in the synthesis of RGD-containing linear or cyclic peptides[31]. A facile synthesis of hydroxamates is described using BOP for the activation of carboxylic acid in the presence of a base and subsequent reaction with hydroxylamine hydrochloride[30]. BOP is a versatile and efficient reagent for the one pot formation of aliphatic isothiocyanates and thioureas on solid phase from the corresponding solid phase anchored amines using carbon disulfide[32]. And, it has been used in the efficient synthesis of phosphono-depsipeptides derived from norleucine[33]. In view of long-term interest on peptidomimetic chemistry in one hand and the understanding on the utility of coupling agents in peptide chemistry, it was reasoned that BOP can be employed in the direct conversion of carboxylic acid to its azide in a single step (**Figure 1**).

Results and Discussion

Initially, the preparation of benzoyl azide **2c** was studied by treating benzoic acid with BOP followed by NaN_3 in DMSO in the presence of diisopropylethyl amine (DIPEA) at 0°C. The reaction mechanism of BOP mediated peptide bond formation is fully known. Briefly, the deprotonated acid first reacts with BOP to generate an activated acyl phosphonium species and HOBt being a co-product of the reaction. HOBt readily reacts with activated acid to produce a reactive OBt ester, which then undergoes azidolysis with NaN_3 leading to acyl azide (**Scheme II**). The reaction went to completion in 15 to 20 min (TLC analysis). After a simple aqueous work up, the benzoyl azide was isolated in 85% yield. The IR analysis showed a strong peak at 2138 cm^{-1} corresponding to the carbonyl stretching frequency of acyl azide moiety. A controlled reaction was carried out in the absence of NaN_3, *i.e.,* a mixture of benzoic acid, BOP, DIPEA in THF was stirred at 0°C. IR analysis of the reaction mixture showed a peak at around 1735 cm^{-1} which confirms the formation of OBt ester. When the reaction was further continued by adding NaN_3, it took 10 min for complete disappearance of OBt ester peak in IR spectrum along with a new peak at around 2150 cm^{-1}. With this encouraging result, this protocol was extended for the synthesis of a series of acyl azides including aliphatic, amino- or hydroxyl substituted, unsaturated, heteroaromatic acids and also those with several other sensitive functionalities. Interestingly, in this study both the yield and purity were found to be good (**Table I**).

It was then decided to utilize this protocol for the preparation of N^{α} –Fmoc/Boc/Z protected amino acid azides. Accordingly, in a typical reaction, N^{α}-Fmoc-Phe-OH in THF was treated with BOP/DIPEA/NaN_3 as explained earlier. In this case also, the reaction was complete in 20 min. A simple work up led to the

Table I — List of organic acid azides

Compd	R	Yield (%)	m.p. (°C)	ES-MS $[M+Na]^+$ *m/z* (Found/Calcd)
2a	*p*-$CH_3C_6H_4$	82	32-34 (32-33) (ref 18)	184.11/184.05
2b	$C_6H_5CH_2$	81	86-88 (88) (ref 28)	184.0476/184.0487[a]
2c	C_6H_5	83	33 (32-34) (ref 19)	170.05/170.03
2d	PhCH=CH	77	84 (83) (ref 28)	174.0632/174.0667[a]
2e	2-furanyl	84	63 (64) (ref 28)	160.01/160.01
2f	2-pyridyl	85	Gum	171.0/171.0
2g	*p*-$NO_2C_6H_5$	81	69 (68) (ref 28)	215.01/215.02

[a] HR-MS analysis

isolation of N^{α}-Fmoc-Phe-N_3 **4d** in 81% yield. Initial confirmation was made by comparing its IR analysis. Further, high-resolution mass spectral analysis was measured using acetonitrile as solvent, which also confirmed the structure of acid azide. As is the case with peptide coupling, the addition of HOBt increased the efficiency of this reaction also. The yield was found to elevate to 85% compared to the one in the absence of HOBt, where the yield was 72%. Then this protocol was extended to synthesize several other N-Fmoc protected acyl azides. Employing this protocol Boc/Z protected acyl azides namely Boc-Aib-N_3 and Z-Ala-N_3, Z-Phe-N_3, Z-Asp(oxa)-N_3 were also obtained in good yield (**Table II**). The optical rotation recorded for L–Fmoc-Phe-N_3 prepared by the present protocol, ($[\alpha]^{25}_D$ (*c*1, $CHCl_3$): +3.1) was in agreement with the reported value ($[\alpha]^{25}_D$ (*c*1, $CHCl_3$): +3.0)[30].

Experimental Section

Melting points were determined on a Buchi model 150 melting point apparatus in open capillaries and are uncorrected. IR spectra were recorded on a Nicolet model impact 400 D FT-IR spectrometer (KBr pellets, 3 cm^{-1} resolution). ^1H NMR spectra were recorded on a Bruker AMX 300 MHz spectrometer. High resolution mass spectra (HR-MS) were recorded on Q-Tof Micromass mass spectrometer.

General procedure

To a solution of an organic acid/*N*-protected amino acid (1 mmole) in 10 mL of THF, was added DIPEA (2 mmole), BOP (1.1 mmole) (HOBt (1.1 mmole) in case of *N*-protected amino acid) at 0°C. The reaction mixture was stirred for 20 min. To this was added NaN_3 in DMSO and stirring was continued for an additional 15 min. The solvent was evaporated *in vacuo*, the residue was diluted with CH_2Cl_2 and the organic layer was washed with 10% $NaHCO_3$ solution, brine and dried over anhydrous Na_2SO_4. The solvent was evaporated *in vacuo* (without heating) to obtain the corresponding acyl azide.

***p*-Toluoyl azide 2a**: m.p. 32-34°C; R_f 0.4 (*n*-hexane/EtOAC 8:2); IR (KBr): 2136 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 2.73 (s, 3H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.98 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 200 MHz): δ 23.2, 128.5, 128.9, 129.7, 129.8, 132.5, 145.2, 180.1; ES-MS: *m/z* Calcd for $C_8H_7N_3O$, $[M+Na]^+$: 184.05. Found: 184.11.

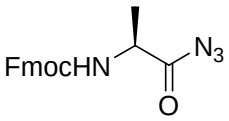
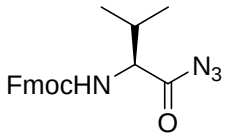
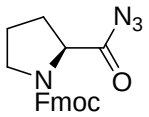
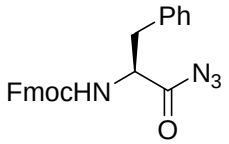
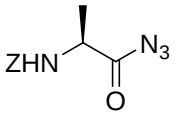
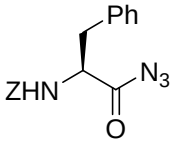
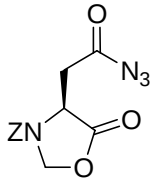
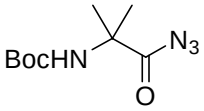
Phenyl acetyl azide 2b: m.p. 87-88°C; R_f 0.4 (*n*-hexane/EtOAC 8:2); IR (KBr): 2137 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 3.91 (s, 2H), 7.22 (m, 1H), 7.29 (d, *J* = 6.9 Hz, 2H), 7.35 (m, 2H); ^{13}C NMR ($CDCl_3$, 200 MHz): δ 38.1, 127.8, 129.4, 129.9, 141.3, 181.5; HR-MS: *m/z* Calcd for $C_8H_7N_3O$, $[M+Na]^+$: 184.0487. Found: 184.0476.

Benzoyl azide 2c: m.p. 33°C; R_f 0.4 (*n*-hexane/EtOAC 8:2); IR (KBr): 2138 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.43-7.48 (m, 2H), 7.61-7.67 (m, 1H), 8.05 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 200 MHz): δ 128.7, 129.5, 130.5, 134.4, 172.5; HR-MS: *m/z* Calcd for $C_7H_5N_3O$, $[M+Na]^+$: 170. 03. Found: 170.05.

Cinnamoyl azide 2d: m.p. 84°C; R_f 0.4 (*n*-hexane/EtOAC 8:2); IR (KBr): 2137 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 6.61 (d, *J* = 8.7 Hz, 1H), 7.15 (d, *J* = 9.2 Hz, 2H), 7.25-7.55 (m, 3H), 7.58 (d, *J* = 8.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 200 MHz): δ 125.1, 126.2, 126.5, 127.6, 133.4, 140.5, 181.8; HR-MS: *m/z* Calcd for $C_9H_7N_3O$, $[M+Na]^+$: 174. 0667. Found: 174.0632.

Furan-2-carboxylic acid azide 2e: m.p. 63°C; R_f 0.4 (*n*-hexane/EtOAC 8:2); IR (KBr): 2132 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 6.87 (m, 1H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.23 (d, J = 6.9 Hz, 1H); ^{13}C NMR

Table II — List of urethane protected amino acid azides

	Compd	Yield (%)	m.p. (°C)	HRMS $[M+Na]^+$ *m/z* (Found/Calcd)
4a		82	162 (163) (ref 28)	359.1123/359.1120
4b		84	168 (169) (ref 28)	387.1425/387.1433
4c		78	73 (74) (ref 28)	385.1273/385.1277
4d		81	174 (175) (ref 28)	435.1438/435.1433
4e		79	123	271.0815/271.0807
4f		86	145 (146) (ref 19)	347.15/347.11[a]
4g		78	gum	327.0713/327.0705
4h		72	gum	251.1128/251.1120

[a] ES-MS analysis

($CDCl_3$, 200 MHz): δ 112.1, 120.5, 144.3, 146.9, 178.9; ES-MS: *m/z* Calcd for $C_5H_3N_3O_2$, $[M+Na]^+$: 160.01. Found: 160.01.

Pyridine-2-carboxylic acid azide 2f: gum; R_f 0.3 (*n*-hexane/EtOAC 8:2); IR (KBr): 2128 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.37 (m, 1H), 7.75 (m, 1H), 7.92 (d, *J* = 7.11 Hz, 1H), 8.53 (d, *J* = 6.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 200 MHz): δ 125.6, 128.4, 137.6, 148.3, 150.2, 172.3; ES-MS: *m/z* Calcd for $C_6H_4N_4O$, $[M+Na]^+$: 171.0. Found: 171.0.

***p*-Nitro benzoyl azide 2g**: m.p. 69°C; R_f 0.4 (*n*-hexane/EtOAC 8:2); IR (KBr): 2138 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.56 (d, *J* = 7.3 Hz, 2H), 7.68 (d, *J* = 7.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 200 MHz): δ 120.5, 128.3, 144.3, 156.7, 179.8; ES-MS: *m/z* Calcd for $C_7H_4N_4O_3$, $[M+Na]^+$: 215.02. Found: 215.01.

Fmoc-Ala-N_3 4a: m.p. 162°C; R_f 0.4 (*n*-hexane/EtOAC 8:2); IR (KBr): 2148 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 1.46 (s, 3H), 4.23-4.27 (br, 1H), 4.29-4.52 (br, 3H), 5.42 (br, 1H), 7.27-7.79 (m, 8H);

^{13}C NMR ($CDCl_3$, 200 MHz): δ 18.5, 47.5, 51.9, 67.6, 120.5, 125.4, 127.6, 128.3, 141.1, 144.4, 150.6, 180.9; HR-MS: *m/z* Calcd for $C_{18}H_{16}N_4O_3$, $[M+Na]^+$: 359.1120. Found: 359.1123.

Fmoc-Val-N_3 4b: m.p. 168°C; R_f 0.4 (*n*-hexane/EtOAC 8:2); IR (KBr): 2138 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.91-0.93 (br, 6H), 2.12 (m, 1H), 4.16-4.32 (m, 2H), 4.38 (d, *J* = 7.2 Hz, 1H), 4.41 (d, *J* = 6.5 Hz, 1H), 5.12 (m, 1H), 7.22-7.75 (m, 8H); ^{13}C NMR ($CDCl_3$, 200 MHz): δ 17.7, 31.5, 47.8, 61.3, 67.6, 125.4, 125.6, 127.6, 128.3, 141.8, 144.2, 156.8, 180.2; HR-MS: *m/z* Calcd for $C_{20}H_{20}N_4O_3$, $[M+Na]^+$: 387.1433. Found: 387.1425.

F-Pro-N_3 4c: m.p. 73°C; R_f 0.4 (*n*-hexane/EtOAC 8:2); IR (KBr): 2142 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.45-1.95 (m, 4H), 3.12 (m, 2H), 4.28 (m, 2H), 4.42 (d, *J* = 5.9 Hz, 2H), 7.25-7.65 (m, 8H); ^{13}C NMR ($CDCl_3$, 200 MHz): δ 24.5, 26.1, 41.3, 43.6, 52.7, 66.2, 126.6, 127.8, 128.1, 129.3, 141.1, 144.6, 156.2, 178.9; HR-MS: *m/z* Calcd for $C_{20}H_{18}N_4O_3$, $[M+Na]^+$: 385.1277. Found: 385.1273.

F-Phe-N_3 4d: m.p. 174°C; R_f 0.5 (*n*-hexane/EtOAC 8:2); IR (KBr): 2146 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.75 (br, 2H), 4.18-4.31 (m, 2H), 4.49-4.53 (br, 1H), 5.29 (br, 1H), 7.29-7.77 (m, 13H); ^{13}C NMR ($CDCl_3$, 200 MHz): δ 26.1, 47.5, 53.9, 68.4, 125.4, 125.8, 126.8, 127.6, 128.3, 129.2, 129.6, 136.7, 141.8, 144.1, 157.9, 179.2; HR-MS: *m/z* Calcd for $C_{24}H_{20}N_4O_3$, $[M+Na]^+$: 435.1433. Found: 435.1438.

Z-Ala-N_3 4e: m.p. 123°C; R_f 0.4 (*n*-hexane/EtOAC 8:2); IR (KBr): 2142 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.38 (s, 3H), 5.01 (m, 1H), 5.12 (s, 2H), 7.23-7.45 (m, 5H); ^{13}C NMR ($CDCl_3$, 200 MHz): δ 18.7, 51.9, 67.5, 127.1, 127.3, 127.5, 128.3, 128.9, 141.2, 156.1, 180.2; HR-MS: *m/z* Calcd for $C_{24}H_{20}N_4O_3$, $[M+Na]^+$: 271.0807. Found: 271.0815.

Z-Phe-N_3 4f: m.p. 145°C; R_f 0.3 (*n*-hexane/EtOAC 8:2); IR (KBr): 2135 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.09-3.18 (m, 2H), 4.68 (m, 1H), 5.11 (s, 2H), 7.25-7.68 (m, 10H); ^{13}C NMR ($CDCl_3$, 200 MHz): δ 38.2, 57.2, 67.6, 128.1, 128.6, 128.8, 129.1, 129.4, 129.8, 135.9, 136.8, 156.5, 179.9; ES-MS: *m/z* Calcd for $C_{17}H_{16}N_4O_3$, $[M+Na]^+$: 347.11. Found: 347.15.

Z-Asp(oxa)-N_3 4g: gum; R_f 0.4 (*n*-hexane/EtOAC 8:2); IR (KBr): 2146 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.18 (s, 1H), 5.35-5.45 (m, 1H), 5.59-5.63 (m, 2H), 7.23-7.45 (m, 5H); ^{13}C NMR ($CDCl_3$, 200 MHz): δ 22.3, 55.8, 66.7, 79.2, 128.6, 128.9, 129.3, 136.9, 154.3, 172.6, 179.1; HR-MS: *m/z* Calcd for $C_{13}H_{12}N_4O_5$, $[M+Na]^+$: 327.0705 Found: 327.0713.

Boc-Aib-N_3 4h: gum; R_f 0.4 (*n*-hexane/EtOAC 8:2); IR (KBr): 2138 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.39 (s, 9H), 1.47 (s, 6H), 5.02 (br, 1H); ^{13}C NMR ($CDCl_3$, 200 MHz): δ 24.5, 28.9, 52.3, 79.3, 155.6, 180.1; HR-MS: *m/z* Calcd for $C_9H_{16}N_4O_3$, $[M+Na]^+$: 251.1120 Found: 251.1128.

Conclusion

In summary, herein is described the synthesis of acyl azides/N^{α}–Fmoc/Boc/Z-amino acid azides in the most simple and convenient protocol. The method can be used as a useful alternative to the existing protocols, thereby avoiding toxic acid activators, costly reagents and multistep procedures. It is free from racemisation. Handling and work up procedure is simple and products are obtained in excellent yield with high purity.

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