The Chemistry of *N*,*N*-Bis(siloxy)enamines. Part 8.[1] A General Method for the Preparation of α-Azido Oximes from Aliphatic Nitro Compounds

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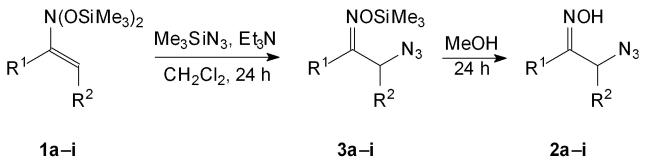
Abstract: A new strategy for the synthesis of α-azido oximes from aliphatic nitro compounds via interaction of *N*,*N*-bis(silyloxy)enamines with trimethylsilylazide was realized to give the target products with good yields.

Key words: aliphatic nitro compounds, azidotrimethylsilane, *N*,*N*-bis(siloxy)enamines, α-azido oximes

The reactivity of aliphatic nitro compounds (ANC) can be significantly increased by the silylation of the nitro group.[2] Among a variety of intermediates involved in this process *N*,*N*-bis(siloxy)enamines (BENA; **1**) have emerged as the most interesting compounds, especially since the recent advent of convenient procedures for their preparation.[3,4]

The unique ability of BENA, to interact at the β-position with some electrophiles[5,6] as well as with various nucleophiles,[7–13] can be used for the functionalization of the β-carbon atom of readily available initial ANC. Earlier, we developed this novel strategy for the synthesis of various α-functionalized[1,7–10,13] or modified[11,12] oximes from the simplest ANC.

Here we present the application of this approach for the synthesis of poorly investigated α-azido oximes **2**.



1a–i **3a–i** **2a–i**

Scheme 1

To date no general procedure for the production of compounds **2** is available and only a few examples of their preparation have been reported, with α-hydroxyoximes[14] or α-acyloxyoximes[15] serving as precursors. On the other hand, azido oximes **2** could be considered as very suitable initial compounds for the synthesis of dinitriles,[16] 1,2-diamines,[17] and amino oximes.[18]

In this context elaboration of a convenient procedure for the preparation of azido oximes **2** from available BENA **1** seems to be the most interesting approach (Scheme 1).

Optimal reaction conditions are presented in Table 1. Nitroso acetals **1** reacted within 24 hours at ambient temperature with an excess of Me_3SiN_3 in dichloromethane in the presence of catalytic amount of triethylamine to give trimethylsilyl derivatives **3**. The latter underwent desilylation in an excess of methanol furnishing target azido oximes **2** in good yields (see Table 1).[19]

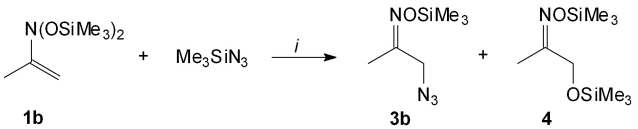
The procedure presented in Scheme 1 has a wide scope; terminal and internal BENA, as well as BENA bearing functional groups, can be involved in this reaction.

The formation of α-nitroso olefins as key intermediates and the contribution of chain-type processes in the interaction of BENA with various nucleophiles were discussed in our earlier paper.[10] Presumably, a similar interpretation can be applied for the coupling of **1** with Me_3SiN_3.

In the present case the α-silyloxy oximes **4** were observed as by-products (Scheme 2), which is similar to coupling reactions of BENA with other nucleophiles.[10] Compounds **4** result from the well known rearrangement of BENA (see for example[3,4]).

In order to minimize the amount of **4** and achieve maximum yields of target oximes **2** the coupling conditions of model BENA **1b** (reagents ratio, solvent, use of Et_3N) were extensively varied (see Table 2).

As indicated in Table 2, some impurities present in Me_3SiN_3, (HMPA or HN_3, entries 8–10) connected with the specific method used for its preparation, gave rise to an increase in the yield of by-product **4**.



1b **3b** **4**

Scheme 2

The same effect was observed in the absence of Et_3N or by decreasing the ratio Me_3SiN_3:**1**. Interestingly, an induction period for the coupling reaction was found under these conditions.

Therefore, the optimal procedure for the preparation of oximes **4** requires a large excess of Me_3SiN_3 (see Table 1).

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Table 1 Optimal Conditions for **1** and Me_3SiN_3 Interaction and Yields of Target Products

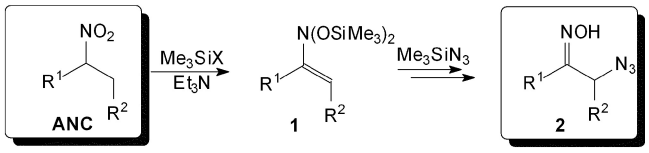
Entry	1–3	R^1	R^2	Ratio of Me_3SiN:**1**	Yield of **3** (%)			Yield[b] of **2** (%)	
					Crude Product[a]	Pure Product	*E*/*Z*	Pure Product	*E*/*Z*
1	**a**	H	H	2	89	84	13:10	79	3:4
2	**b**	Me	H	5	95	87	Only *E*	87	6:1
3	**c**	H	Me	5	90	82	16:1	80	3:1
4	**d**	$(CH_2)_2CO_2Me$	H	3	94	–	3:1	85	2:1
5	**e**	CH_2OSiMe_3[c]	H	2	98	–	3:5	92	5:4
6	**f**	Ph	H	2	ca.100	93	2:1	95	5:1
7	**g**	Bn	H	2	ca. 100	91	4:1	91	3:2
8	**h**	CO_2Et	H	2	91	–	14:1	87	13:1
9	**i**	CO_2Me	Me	2	96	–	12:1	93	10:1

[a] Determined by NMR spectroscopy with internal standard (toluene or nitromethane).
[b] Based on starting BENA **1**.
[c] $R^1 = CH_2OH$ for product **2e**.

This allows one to simplify substantially the purification of derivatives **2** and **3**. Although an application of equimolar amount of Me_3SiN_3 results only in a slight decrease of yield of target oximes **2**, the presence of large quantities of by-product **4** necessitates more complicated techniques for the purification of target compounds (for instance, column chromatography instead of filtration through silica gel).

The structure of oximes **2** and derivatives **3** was confirmed by ^1H and ^{13}C NMR spectroscopic data, as well as by elemental analysis of oximes **2**. For a few oximes **2** the azido group was identified by ^{14}N NMR and IR spectroscopy. To determine the configuration of the oximino group the same rules we formulated previously were applied.[10]

In conclusion, a novel two-step strategy for the synthesis of α-azido oximes from available ANC was developed (Scheme 3).[20]



Scheme 3

Further efforts will be directed towards the use of oximes **2** as starting materials for the synthesis of various polyfunctional compounds and intermediates.

All reactions were performed in oven-dried (150 °C) glassware under an inert atmosphere of dry Ar. The following reaction solvents and reagents were distilled from the indicated drying agents: Et_3N (CaH_2), CH_2Cl_2 (CaH_2), hexane (Na), HMPA (CaH_2), MeOH (Mg).

NMR spectra were recorded on Bruker AM-300 instrument (^1H: 300.13 MHz, ^{13}C: 75.47 MHz, ^{29}Si: 59.63 MHz) referenced to a residual solvent peak or internal standard (TMS). Chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). The INEPT pulse sequence was used for ^{29}Si signal observation. Elemental analyses were performed by the Analytical Center of the Moscow Chemical Lyceum. MP's were determined on a Koffler melting point apparatus (uncorrected). Analytical thin-layer chromatography was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with UV light or with ninhydrine in ethanol.

All solvents for chromatography and extractions were technical grade and distilled from the indicated drying agents: petroleum ether (60–70 °C) and EtOAc (K_2CO_3). Column chromatography was performed using Merck Kieselgel 60 230–400-mesh silica gel. The following chemicals were purchased from the indicated sources: chlorotrimethylsilane (Aldrich), bromotrimethylsilane (Fluka), 2-nitro-1-propanol (Acros), sodium azide (Acros). The following compounds were prepared by literature methods: (2-nitro-propyl)-benzene,[21] BENA **1a–d**,[3] **1f**,[22] and **1i,j**.[4]

Azidotrimethylsilane

Chlorotrimethylsilane (23.0 mL, 180 mmol) was added dropwise to a stirred solution of NaN_3 (12.4 g, 190 mmol) in HMPA (25 mL). The reaction mixture was stirred at 20 °C for 2 h after which time the azidotrimethylsilane (21.0 mL) was distilled from the mixture.

Yield: 87%; bp 52 °C/144 mmHg.[23]

2-[*N*,*N*-Bis(trimethylsilyloxy)]amino-3-trimethylsilyloxyprop-1-ene (1e)

A solution of bromotrimethylsilane (2.64 mL, 20 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of 2-nitro-1-propanol (0.53 g, 5 mmol) and Et_3N (4.17 mL, 30 mmol) in CH_2Cl_2 (5 mL) at 20 °C. The reaction mixture was maintained at this temperature with occasional stirring for 72 h. The mixture was then diluted with petroleum ether (50 mL) and poured into water (20 mL). The organic phase was washed with aq $NaHSO_4$ [2 g in H_2O (20 mL)], H_2O (2 × 10 mL), and brine (2 × 10 mL). Activated carbon was added,

Table 2 The Optimization of Interaction BENA **1b** with Me_3SiN_3

Entry	Ratio Me_3SiN_3:**1**	Procedure[a]	Yield[b] (%) **3b**	**4**
1	1	20 °C, without solvent, 48 h	73	18
2	2	20 °C, without solvent, 48 h	79	10
3	5	20 °C, without solvent, 48 h	88	3
4	1	20–40 °C,[c] CH_2Cl_2, Et_3N (5%), 6 h	86	12
5	2	20–40 °C,[c] CH_2Cl_2, Et_3N (5%), 6 h	87	9
6	3	20–40 °C,[c] CH_2Cl_2, Et_3N (5%), 6 h	90	5
7	5	20–40 °C,[c] CH_2Cl_2, Et_3N (5%), 6 h	95	–
8	5	20–40 °C,[c] CH_2Cl_2, H_2O (10%), 24 h	43	41
9	5	20–40 °C,[c] CH_2Cl_2, Et_3N (5%), H_2O (10%), 24 h	67	28
10	5	20–40 °C,[c] CH_2Cl_2, Et_3N (5%), HMPA (5%), 24 h	71	20
11	0	NaN_3, Et_2O, 1 h	ca. 10	–
12	0	NaN_3, DMF, 1 h	ca. 10	ca. 10
13	5	20 °C,[d] without solvent, 48 h	61	12
14	5	20–40 °C,[c] CH_2Cl_2, Et_3N (5%), 6 h	88	–

[a] For entries 1–12: 1 mmol of **1b**; for entries 13 and 14: 100 mmol of **1b**.
[b] By ^1H NMR spectroscopy with toluene as the internal standard.
[c] A short increase of temperature during BENA addition is possible.
[d] An inductive period after BENA addition, followed by a spontaneous increase of temperature.

the organic phase was dried (Na_2SO_4), and concentrated in vacuum to afford **1e** as a clean colorless oil.

Yield: 1.28 g (80%).

^1H NMR ($CDCl_3$): δ = 0.15 (s, 9 H, $COSiMe_3$), 0.20 (s, 18 H, $SiMe_3$) 4.43 (s, 2 H, CH_2O), 4.94 (s, 1 H, CH_2), 5.08 (s, 1 H, CH_2).

^{13}C NMR ($CDCl_3$): δ = –0.6 ($COSiMe_3$), 0.0 ($SiMe_3$), 58.3 (CH_2O), 102.0 (CH_2), 158.7 (CN).

^{29}Si NMR ($CDCl_3$): δ = 20.10 (COSi), 24.60 (NOSi).

Anal. Calcd for $C_{12}H_{31}NO_3Si_3$: C, 44.81; H, 9.71; N, 4.35. Found: C, 44.98; H, 9.77; N, 4.54.

2-[*N*,*N*-Bis(trimethylsilyloxy)]amino-3-phenylprop-1-ene (1g)
Bromotrimethylsilane (0.91 mL, 6.9 mmol) was added dropwise to a solution of (2-nitropropyl)benzene (0.50 g, 3 mmol) and Et_3N (1.05 mL, 7.5 mmol) in CH_2Cl_2 (10 mL) at 0 °C. After stirring for 1 h at 0 °C the temperature was allowed to rise to 20 °C. The reaction mixture was maintained at this temperature with occasional stirring for 72 h. The mixture was then diluted with petroleum ether (30 mL) and poured into water (10 mL). The organic phase was washed with aq $NaHSO_4$ [0.5 g in H_2O (10 mL)], water (2 × 10 mL), and brine (2 × 10 mL). Activated carbon was added, the organic phase was dried (Na_2SO_4), and concentrated in vacuum to afford **1g** as a clean colorless oil.

Yield: 0.81 (87%).

^1H NMR ($CDCl_3$): δ = 0.24 (s, 18 H, $SiMe_3$), 3.68 (s, 2 H, CH_2Ph), 4.38 (s, 1 H, CH_2), 5.11 (s, 1 H, CH_2), 7.2–7.4 (m, 5 H, Ph).

^{13}C NMR ($CDCl_3$): δ = 0.8 ($SiMe_3$), 33.8 (CH_2Ph), 105.4 (CH_2), 126.0, 128.2, 129.6 (Ph), 139.3 (*ipso*-Ph), 159.6 (CN).

^{29}Si NMR ($CDCl_3$): δ = 24.05.

Anal. Calcd for $C_{15}H_{27}NO_2Si_2$: C, 58.20; H, 8.79; N, 4.52. Found: C, 58.61; H, 8.91; N, 4.40.

Derivatives 3a–i; General Procedure (Table 1)
A solution of BENA **1a–i** (10 mmol) in CH_2Cl_2 (10 mL) was added to a stirred solution of Me_3SiN_3 and Et_3N (0.7 mL, 0.5 mmol) at 20 °C. (The addition of BENA is an exothermic reaction; on a larger scale BENA was added at such a rate so as to maintain a gentle reflux.) The reaction mixture was maintained at 20 °C for 24 h with occasional shaking. The CH_2Cl_2 was evaporated in vacuum, toluene (1.07 mL, 10 mmol) or nitromethane (0.54 mL, 10 mmol) was added to the residue and the yield of **3** was determined by NMR. Pure samples of **3a–c** and **3f**,**g** were obtained by vacuum distillation or column chromatography.

Azido-acetaldehyde *O*-(Trimethylsilyl)oxime (3a)
Bp 89–92 °C/36 mmHg.

***E*-Oxime**
^1H NMR ($CDCl_3$): δ = 0.23 (s, 9 H, $SiMe_3$), 3.88 (d, *J* = 5.9 Hz, 2 H, CH_2), 7.57 (t, *J* = 5.9 Hz, 1 H, CH).

^{13}C NMR ($CDCl_3$): δ = –0.9 ($SiMe_3$), 49.0 (CH_2), 148.8 (CH).

^{29}Si NMR ($CDCl_3$): δ = 27.31.

***Z*-Oxime**
^1H NMR ($CDCl_3$): δ = 0.23 (s, 9 H, $SiMe_3$), 4.19 (d, *J* = 4.4 Hz, 2 H, CH_2), 6.97 (t, *J* = 4.4 Hz, 1 H, CH).

^{13}C NMR ($CDCl_3$): δ = –0.9 ($SiMe_3$), 45.8 (CH_2), 150.2 (CH).

^{29}Si NMR ($CDCl_3$): δ = 27.53.

1-Azido-propan-2-one *O*-(Trimethylsilyl)oxime (3b)
Bp 68–70 °C/9 mmHg.

***E*-Oxime**
^1H NMR ($CDCl_3$): δ = 0.23 (s, 9 H, $SiMe_3$), 1.95 (s, 3 H, Me), 3.83 (s, 2 H, CH_2).

^{13}C NMR ($CDCl_3$): δ = –0.9 ($SiMe_3$), 12.7 (Me), 54.4 (CH_2), 156.5 (C=N).

^{29}Si NMR ($CDCl_3$): δ = 25.64.

2-Azido-propionaldehyde *O*-(Trimethylsilyl)oxime (3c)
Bp 87–89 °C/27 mmHg.

***E*-Oxime**
^1H NMR ($CDCl_3$): δ = 0.21 (s, 9 H, $SiMe_3$), 1.34 (d, *J* = 6.6 Hz, 3 H, Me), 4.14 (m, *J* = 6.6 Hz, 1 H, CH), 7.40 (d, *J* = 6.6 Hz, 1 H, HC=N).

^{13}C NMR ($CDCl_3$): δ = –1.0 ($SiMe_3$), 17.7 (Me), 55.9 (CH), 153.2 (C=N).

^{29}Si NMR ($CDCl_3$): δ = 27.05.

***Z*-Oxime**

^{1}H NMR ($CDCl_3$): δ = 0.21 (s, 9 H, $SiMe_3$), 1.27 (d, *J* = 6.6 Hz, 3 H, Me), 4.89 (m, *J* = 6.6 Hz, 1 H, CH), 6.80 (d, *J* = 6.6 Hz, 1 H, HC=N).

^{13}C NMR ($CDCl_3$): δ = –0.9 ($SiMe_3$), 17.2 (Me), 51.3 (CH), 154.1 (C=N).

^{29}Si NMR ($CDCl_3$): δ = 27.26.

5-Azido-4-(trimethylsilyl)oxyiminopentanoic Acid Methyl Ester (3d)

Compound **3d** was detected in the reaction mixture by NMR spectroscopy.

***E*-Oxime**

^{1}H NMR ($CDCl_3$): δ = 0.28 (s, 9 H, $SiMe_3$), 2.6 (m, 4 H, CH_2CH_2), 3.72 (s, 3 H, Me), 3.93 (s, 2 H, CH_2).

^{13}C NMR ($CDCl_3$): δ = –1.0 ($SiMe_3$), 22.6 (CH_2CN), 29.8 (CH_2CO), 51.4 (Me), 53.6 (CH_2), 158.6 (C=N), 172.6 (C=O).

***Z*-Oxime**

^{1}H NMR ($CDCl_3$): δ = 0.28 (s, 9 H, $SiMe_3$), 2.6 (m, 4 H, CH_2CH_2), 3.72 (s, 3 H, Me), 4.17 (s, 2 H, CH_2).

^{13}C NMR ($CDCl_3$): δ = –1.0 ($SiMe_3$), 27.5 (CH_2CN), 30.0 (CH_2CO), 47.0 (CH_2), 51.3 (Me), 157.5 (C=N), 172.6 (C=O).

1-Azido-3-hydroxypropan-2-one *O*-(Trimethylsilyl)oxime (3e)

Compound **3e** was detected in the reaction mixture by NMR spectroscopy.

***E*-Oxime**

^{1}H NMR ($CDCl_3$): δ = 0.12 (s, 9 H, $COSiMe_3$), 0.26 (s, 9 H, $SiMe_3$), 4.13 (s, 2 H, CH_2N), 4.36 (s, 2 H, CH_2).

^{13}C NMR ($CDCl_3$): δ = –0.7 and –0.6 ($SiMe_3$), 44.1 (CH_2N), 62.1 (CH_2), 160.5 (C=N).

***Z*-Oxime**

^{1}H NMR ($CDCl_3$): δ = 0.12 (s, 9 H, $COSiMe_3$), 0.26 (s, 9 H, $SiMe_3$), 3.95 (s, 2 H, CH_2N), 4.53 (s, 2 H, CH_2).

^{13}C NMR ($CDCl_3$): δ = –0.7 and –0.5 ($SiMe_3$), 49.7 (CH_2N), 57.3 (CH_2), 158.2 (C=N).

2-Azido-1-phenylethanone *O*-(Trimethylsilyl)oxime (3f)

Oil; R_f 0.80 (silica gel, hexane–EtOAc, 1:1).

***E*-Oxime**

^{1}H NMR ($CDCl_3$): δ = 0.24 (s, 9 H, $SiMe_3$), 4.31 (s, 2 H, CH_2), 7.2 and 7.5 (2 m, 5 H, Ph).

^{13}C NMR ($CDCl_3$): δ = –0.7 ($SiMe_3$), 53.08 (CH_2), 126.1, 128.4 and 129.5 (Ph), 133.2 (*ipso*-Ph), 155.8 (CN).

***Z*-Oxime**

^{1}H NMR ($CDCl_3$): δ = 0.24 (s, 9 H, $SiMe_3$), 4.58 (s, 2 H, CH_2), 7.2 and 7.5 (2 m, 5 H, Ph).

^{13}C NMR ($CDCl_3$): δ = –0.7 ($SiMe_3$), 43.8 (CH_2), 126.8, 128.4 and 129.5 (Ph), 134.6 (*ipso*-Ph), 157.2 (CN).

1-Azido-3-phenylpropan-2-one *O*-(Trimethylsilyl)oxime (3g)

Oil; R_f 0.75 (silica gel, hexane–EtOAc, 1:1).

***E*-Oxime**

^{1}H NMR ($CDCl_3$): δ = 0.13 (s, 9 H, $SiMe_3$), 3.57 and 3.64 (2 s, 4 H, CH_2Ph and CH_2), 7.0–7.2 (m, 5 H, Ph).

^{13}C NMR ($CDCl_3$): δ = –0.9 ($SiMe_3$), 32.3 (CH_2Ph), 52.0 (CH_2), 126.5, 128.5, 128.8 and 135.6 (Ph), 157.8 (C=N).

***Z*-Oxime**

^{1}H NMR ($CDCl_3$): δ = 0.23 (s, 9 H, $SiMe_3$), 3.44 (s, 2 H, CH_2Ph), 4.83 (s, 2 H, CH_2), 7.0–7.2 (m, 5 H, Ph).

^{13}C NMR ($CDCl_3$): δ = –0.9 (Me_3Si), 38.6 (CH_2Ph), 45.5 (CH_2), 126.7, 128.6, 128.8 and 135.6 (Ph), 158.1 (C=N).

3-Azido-2-(trimethylsilyl)oxyiminopropionic Acid Ethyl Ester (3h)

Compound **3h** was detected in the reaction mixture by NMR spectroscopy.

***E*-Oxime**

^{1}H NMR ($CDCl_3$): δ = 0.39 (s, 9 H, $SiMe_3$), 1.39 (t, *J* = 7.3 Hz, 3 H, Me), 4.26 (s, 2 H, CH_2), 4.38 (q, *J* = 7.3 Hz, 2 H, CH_2O).

^{13}C NMR ($CDCl_3$): δ = –0.9 ($SiMe_3$), 14.1 (Me), 42.5 (CH_2), 62.0 (CH_2O), 151.9 (C=N), 162.9 (C=O).

***Z*-Oxime**

^{1}H NMR ($CDCl_3$): δ = 0.39 (s, 9 H, $SiMe_3$), 1.39 (t, *J* = 7.3 Hz, 3 H, Me), 4.08 (s, 2 H, CH_2), 4.38 (q, *J* = 7.3 Hz, 2 H, CH_2O).

^{13}C NMR ($CDCl_3$): δ = –0.9 ($SiMe_3$), 14.1 (Me), 46.1 (CH_2), 61.7 (CH_2O), 151.9 (C=N), 162.9 (C=O).

3-Azido-2-(trimethylsilyl)oxyiminobutyric Acid Methyl Ester (3i)

Compound **3i** was detected in the reaction mixture by NMR spectroscopy.

***E*-Oxime**

^{1}H NMR ($CDCl_3$): δ = 0.17 (s, 9 H, $SiMe_3$), 1.42 (d, *J* = 7.3 Hz, 3 H, Me), 3.68 (s, 3 H, OMe), 4.86 (q, *J* = 7.3 Hz, 1 H, CH).

^{13}C NMR ($CDCl_3$): δ = –1.1 ($SiMe_3$), 15.5 (Me), 50.4 (OMe), 52.0 (CH), 155.0 (C=N), 162.7 (C=O).

***Z*-Oxime**

^{1}H NMR ($CDCl_3$): δ = 0.39 (s, 9 H, $SiMe_3$), 1.30 (d, *J* = 7.3 Hz, 3 H, Me), 3.68 (s, 3 H, OMe), 4.22 (q, *J* = 7.3 Hz, 1 H, CH).

^{13}C NMR ($CDCl_3$): δ = –1.3 ($SiMe_3$), 16.8 (Me), 50.4 (OMe), 56.5 (CH), 154.6 (C=N), 162.7 (C=O).

Desilylation of Pure 3a–c,f,g; General Procedure

Pure compound **3a**–**c**,**f**,**g** (1 mmol) was added to a stirred solution of MeOH (5 mL). The reaction mixture was maintained at 20 °C with occasional shaking for 24 h. The solvent was evaporated in vacuum to give analytically pure products **2**.

Desilylation of Crude Products 3a-i; General Procedure

Crude derivative **3a**–**i** (1 mmol) was added dropwise to a stirred solution of MeOH (5 mL). The reaction mixture was maintained at 20 °C with occasional shaking for 24 h. The solvents were evaporated in vacuum and the residue was subjected to column chromatography on silica gel (for yields of **2** see Table 1).

Azido-acetaldehyde Oxime[14] (2a)

Oil; R_f 0.49 (silica gel, hexane–EtOAc, 1:1).

***E*-Oxime**

^{1}H NMR ($CDCl_3$): δ = 3.88 (d, *J* = 5.9 Hz, 2 H, CH_2), 7.45 (t, *J* = 5.9 Hz, 1 H, CH), 9.33 (br, 1 H, OH).

^{13}C NMR ($CDCl_3$): δ = 48.9 (CH_2), 146.1 (CH).

***Z*-Oxime**
^{1}H NMR ($CDCl_3$): δ = 4.16 (d, *J* = 4.4 Hz, 2 H, CH_2), 6.81 (t, *J* = 4.4 Hz, 1 H, CH), 9.33 (br, 1 H, OH).

^{13}C NMR ($CDCl_3$): δ = 45.4 (CH_2), 147.3 (CH).

Anal. Calcd for $C_2H_4N_4O$: C, 24.00; H, 4.03; N, 55.98. Found: C, 24.26; H, 3.95; N, 55.96.

1-Azidopropan-2-one Oxime (2b)
Oil; R_f 0.54 (silica gel, hexane–EtOAc, 1:1).

IR (KBr): 3384, 2921, 2105 (N_3), 1634 (C=NO), 1438, 1371, 1258, 1170, 1051, 933, 882 cm^{-1}.

^{14}N NMR ($CDCl_3$): δ = –313 ($\Delta\nu_{1/2}$ ca.500 Hz, N_2–*N*), –167 ($\Delta\nu_{1/2}$ ca.250 Hz, *N*–N_2), –134.1 ($\Delta\nu_{1/2}$ ca.100 Hz, N–*N*–N), –30 ($\Delta\nu_{1/2}$ ca.1000 Hz, NOH).

Anal. Calcd for $C_3H_6N_4O$: C, 31.58; H, 5.30; N, 49.10. Found: C, 31.63; H, 5.37; N, 49.33.

***E*-Oxime**
^{1}H NMR ($CDCl_3$): δ = 1.94 (s, 3 H, Me), 3.85 (s, 2 H, CH_2), 9.66 (br, 1 H, OH).

^{13}C NMR ($CDCl_3$): δ = 12.2 (Me), 54.2 (CH_2), 153.8 (C=N).

***Z*-Oxime**
^{1}H NMR ($CDCl_3$): δ = 2.03 (s, 3 H, Me), 4.15 (s, 2 H, CH_2), 9.66 (br, 1 H, OH).

^{13}C NMR ($CDCl_3$): δ = 17.7 (Me), 47.5 (CH_2), 154.4 (C=N).

2-Azidopropionaldehyde Oxime (2c)
Oil; R_f 0.52 (silica gel, hexane–EtOAc, 1:1).

IR (KBr): 3420, 2985, 2936, 2113 (N_3), 1632 (C=NO), 1454, 1379, 1247, 1047, 955 cm^{-1}.

^{14}N NMR ($CDCl_3$): δ = –300 ($\Delta\nu_{1/2}$ ca.500 Hz, N_2–*N*), –164 ($\Delta\nu_{1/2}$ ca.250 Hz, *N*–N_2), –135.7 ($\Delta\nu_{1/2}$ ca.100 Hz, N–*N*–N), –20 ($\Delta\nu_{1/2}$ ca.1000 Hz, NOH).

Anal. Calcd for $C_3H_6N_4O$: C, 31.58; H, 5.30; N, 49.10. Found: C, 31.79; H, 5.30; N, 49.22.

***E*-Oxime**
^{1}H NMR ($CDCl_3$): δ = 1.40 (d, *J* = 6.6, 3 H, Me), 4.18 (m, *J* = 6.6 Hz, 1 H, CH), 7.37 (d, *J* = 6.6 Hz, 1 H, HC=N), 8.4 (br, 1 H, OH).

^{13}C NMR ($CDCl_3$): δ = 17.7 (Me), 55.8 (CH), 150.0 (C=N).

***Z*-Oxime**
^{1}H NMR ($CDCl_3$): δ = 1.34 (d, *J* = 6.6, 3 H, Me), 4.88 (m, *J* = 6.6 Hz, 1 H, CH), 6.71 (d, *J* = 6.6 Hz, 1 H, HC=N), 8.4 (br, 1 H, OH).

^{13}C NMR ($CDCl_3$): δ = 17.0 (Me), 51.2 (CH_2), 150.8 (C=N).

5-Azido-4-hydroxyiminopentanoic Acid Methyl Ester (2d)
Oil; R_f 0.55 (silica gel, hexane–EtOAc, 1:1).

***E*-Oxime**
^{1}H NMR ($CDCl_3$): δ = 2.64 (s, 4 H, CH_2CH_2), 3.65 (s, 3 H, Me), 3.92 (s, 2 H, CH_2), 8.9 (br, 1 H, OH).

^{13}C NMR ($CDCl_3$): δ = 22.2 (CH_2CN), 29.5 (CH_2CO), 51.9 (Me), 53.4 (CH_2), 155.1 (C=N), 173.2 (C=O).

***Z*-Oxime**
^{1}H NMR ($CDCl_3$): δ = 2.58 and 2.62 (2 m, 4 H, CH_2CH_2), 3.65 (s, 3 H, Me), 4.17 (s, 2 H, CH_2), 8.9 (br, 1 H, OH).

^{13}C NMR ($CDCl_3$): δ = 27.2 (CH_2CN), 30.4 (CH_2CO), 46.8 (CH_2), 51.9 (Me), 154.6 (C=N), 173.2 (C=O).

Anal. Calcd for $C_6H_{10}N_4O_3$: C, 38.71; H, 5.41; N, 30.09. Found: C, 38.92; H, 5.58; N, 30.24.

1-Azido-3-hydroxypropan-2-one Oxime (2e)
Oil; R_f 0.33 (silica gel, hexane–EtOAc, 1:1).

***E*-Oxime**
^{1}H NMR ($CDCl_3$): δ = 3.2 (br, 1 H, OH), 4.28 and 4.31 (2 s, 4 H, CH_2N and CH_2), 9.0 (br, 1 H, NOH).

^{13}C NMR ($CDCl_3$): δ = 45.3 (CH_2N), 61.5 (CH_2), 155.0 (C=N).

***Z*-Oxime**
^{1}H NMR ($CDCl_3$): δ = 3.2 (br, 1 H, OH), 4.05 (s, 2 H, CH_2N), 4.56 (s, 2 H, CH_2), 9.0 (br, 1 H, NOH).

^{13}C NMR ($CDCl_3$): δ = 50.5 (CH_2N), 57.2 (CH_2), 156.7 (C=N).

Anal. Calcd for $C_3H_6N_4O_2$: C, 27.69; H, 4.65; N, 43.06. Found: C, 27.89; H, 4.68; N, 43.13.

2-Azido-1-phenylethanone Oxime (2f)
Oil, R_f 0.71 (silica gel, hexane–EtOAc, 1:1).

***E*-Oxime**
^{1}H NMR ($CDCl_3$): δ = 4.21 (s, 2 H, CH_2), 7.4 and 7.6 (2 m, 5 H, Ph), 9.8 (br, 1 H, OH).

^{13}C NMR ($CDCl_3$): δ = 53.8 (CH_2), 126.4, 128.8 and 129.9 (Ph), 133.6 (*ipso*-Ph), 153.9 (C=N).

***Z*-Oxime**
^{1}H NMR ($CDCl_3$): δ = 4.48 (s, 2 H, CH_2), 7.2 and 7.6 (2 m, 5 H, Ph), 9.8 (br, 1 H, OH).

^{13}C NMR ($CDCl_3$): δ = 43.7 (CH_2), 126.4, 128.1 and 128.5 (Ph), 134.1 (*ipso*-Ph), 155.1 (C=N).

Anal. Calcd for $C_8H_8N_4O$: C, 54.54; H, 4.58; N, 31.80. Found: C, 54.21; H, 4.65; N, 31.57.

1-Azido-3-phenylpropan-2-one Oxime (2g)
Oil; R_f 0.64 (silica gel, hexane–EtOAc, 1:1).

***E*-Oxime**
^{1}H NMR ($CDCl_3$): δ = 3.84 and 3.89 (2 s, 4 H, CH_2, CH_2N), 7.2–7.4 (m, 5 H, Ph), 9.7 (br, 1 H, OH).

^{13}C NMR ($CDCl_3$): δ = 32.2 (CH_2), 52.2 (CH_2N), 127.0, 128.8 and 129.2 (Ph), 135.3 (*ipso*-Ph), 155.3 (C=N).

***Z*-Oxime**
^{1}H NMR ($CDCl_3$): δ = 3.71 (s, 2 H, CH_2), 4.17 (s, 2 H, CH_2N), 7.2–7.4 (m, 5 H, Ph), 9.7 (br, 1 H, OH).

^{13}C NMR ($CDCl_3$): δ = 38.4 (CH_2), 45.8 (CH_2N), 127.1, 128.8 and 129.1 (Ph), 135.5 (*ipso*-Ph), 156.1 (C=N).

Anal. Calcd for $C_9H_{10}N_4O$: C, 56.83; H, 5.30; N, 29.46. Found: C, 56.72; H, 5.35; N, 29.18.

3-Azido-2-hydroxyiminopropionic Acid Ethyl Ester (2h)
Mp 70–71 °C; R_f 0.50 (silica gel, hexane–EtOAc, 1:1).

***E*-Oxime**
^{1}H NMR ($CDCl_3$): δ = 1.37 (t, *J* = 7.3 Hz, 3 H, Me), 4.25 (s, 2 H, CH_2), 4.33 (q, *J* = 7.3 Hz, 2 H, CH_2O), 9.8 (br, 1 H, OH).

^{13}C NMR ($CDCl_3$): δ = 14.0 (Me), 41.9 (CH_2), 62.6 (CH_2O), 147.0 (C=N), 162.5 (C=O).

Z-Oxime
^{1}H NMR ($CDCl_3$): δ = 1.37 (t, *J* = 7.3 Hz, 3 H, Me), 4.12 (s, 2 H, CH_2), 4.33 (q, *J* = 7.3 Hz, 2 H, CH_2O), 9.8 (br, 1 H, OH).

^{13}C NMR ($CDCl_3$): δ = 14.0 (Me), 50.6 (CH_2), 62.6 (CH_2O), 147.0 (C=N), 162.5 (C=O).

Anal. Calcd for $C_5H_8N_4O_3$: C, 34.89; H, 4.68; N, 32.55. Found: C, 34.69; H, 4.64; N, 32.20.

3-Azido-2-hydroxyiminobutyric Acid Methyl Ester (2i)
Oil; R_f 0.48 (silica gel, hexane–EtOAc, 1:1).

E-Oxime
^{1}H NMR ($CDCl_3$): δ = 1.55 (d, *J* = 7.3 Hz, 3 H, Me), 3.85 (s, 3 H, OMe), 4.92 (q, *J* = 7.3 Hz, 1 H, CH), 10.1 (br, 1 H, OH).

^{13}C NMR ($CDCl_3$): δ = 15.6 (Me), 50.2 (OMe), 52.8 (CH), 150.3 (C=N), 162.4 (C=O).

Z-Oxime
^{1}H NMR ($CDCl_3$): δ = 1.47 (d, *J* = 7.3 Hz, 3 H, Me), 3.85 (s, 3 H, OMe), 4.35 (q, *J* = 7.3 Hz, 1 H, CH), 10.1 (br, 1 H, OH).

^{13}C NMR ($CDCl_3$): δ = 16.8 (Me), 50.2 (OMe), 56.6 (CH), 150.3 (C=N), 162.4 (C=O).

Anal. Calcd for $C_5H_8N_4O_3$: C, 34.89; H, 4.68; N, 32.55. Found: C, 34.53; H, 4.55; N, 32.27.

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