The Chemistry of \(N,N\)-Bis(siloxy)enamines, Part 9.1 A General Method for the Preparation of \(\alpha\)-Hydroxy Oximes from Aliphatic Nitro Compounds

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Abstract: A new convenient procedure for the preparation of a variety of \(\alpha\)-hydroxy oximes from available aliphatic nitro compounds via intermediate \(N,N\)-bis(siloxy)enamines is presented. The mechanism of the key step, the rearrangement of \(N,N\)-bis(siloxy)enamines, is discussed.

Key words: aliphatic nitro compounds, \(N,N\)-bis(siloxy)enamines, \(\alpha\)-hydroxy oximes, rearrangement, silylation

\(N,N\)-Bis(siloxy)enamines (BENA) 1, the products of double silylation of aliphatic nitro compounds (ANC), interact with nucleophiles to give various oximes 2,2 which have modified2,4 or functionalized1,5–10 \(\alpha\)-carbon atom (Scheme 1).

During the synthesis of BENA1,2 and upon their interaction with nucleophiles,3 \(\alpha\)-hydroxy oximes 3 or their bis-silyloxy derivatives 4 are formed as side products. However, under optimal conditions these undesirable processes can be minimized. On the other hand, oximes 3 are convenient precursors to \(\beta\)-amino alcohols,13 amino acids,14 \(\alpha\)-hydroxy carbonyl compounds,15 as well as different heterocyclic systems.16 Therefore, it is advantageous to develop a synthesis of the oximes 3 from available aliphatic nitro compounds via silylation. To reach this objective it is necessary to find conditions that maximize the side process shown in Scheme 1 that detracts major reaction pathway.17 Consequently, the main goal of this investigation is the transformation of readily available BENA1,3 into target oximes 3,18

Two possibilities of generation of derivatives 4 from BENA 1 were discussed in our earlier investigations (Scheme 2). The interaction of BENA 1 with electrophiles \(E \rightarrow X\) [pathway (a)] can give rise to cationic intermediates A (for details, see ref.5), which after interaction with \([X \rightarrow E \rightarrow OSi]^+\) as carrier of trialkysiloxy group, give target bis-silyl derivatives 4. Probably, in tight ion pair this transformation is the most effective, because dissociated \([X \rightarrow E \rightarrow OSi]^+\) is the source of Me3SiO– anion. The latter can inter-

Scheme 1

Scheme 2
act with BENA 1 by pathway (b). Another complication is connected with interaction of electrophiles \( \text{E} - \text{X} \) with the \( \beta \)-carbon atom instead of the oxygen atom of BENA 1.

On the contrary, the interaction of BENA 1 with nucleophiles \( \text{Nu} \) [pathway (b), Scheme 2] gives rise to conjugated nitrosoalkenes via anionic intermediate B. The nitrosoalkenes can generate the target derivatives 4 after interaction with \( \text{Me}_3\text{SiO}^- \) anion (for details, see ref.7). The pathway (b) is complicated by the fact that key intermediates, \( \alpha \)-nitrosoalkenes, are susceptible to polymerization and rearrangement reactions, as well as by their affinity to other nucleophiles in the reaction medium.

A priori, pathway (a) seems more preferable for the generation of derivatives 4. Here the electrophiles bearing the poorly nucleophilic fragment \( \text{X}^- \) are the most effective. This can increase the selectivity of interaction of cation A with \( \text{Me}_3\text{SiO}^- \) anion. The extensive study of transformation of 1 to 4 was carried out using the nitroso acetal 1a as a model substrate (Scheme 3 and Table 1).

### Scheme 3

As indicated in Table 1 (entries 1–4), \( \text{Zn(OTf)}_2 \) is the most effective electrophile. The use of chlorine-containing Lewis acids (for example, see entry 8) leads to the for-

### Table 1 The Optimization of the Rearrangement of BENA 1a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction Conditions</th>
<th>Yield* (%)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Catalyst</td>
<td>Mol%</td>
</tr>
<tr>
<td>1</td>
<td>( \text{Zn(OTf)}_2 )</td>
<td>0.01</td>
</tr>
<tr>
<td>2</td>
<td>( \text{Zn(OTf)}_2 )</td>
<td>0.05</td>
</tr>
<tr>
<td>3</td>
<td>( \text{Zn(OTf)}_2 )</td>
<td>0.05</td>
</tr>
<tr>
<td>4</td>
<td>( \text{Zn(OTf)}_2 )</td>
<td>0.05</td>
</tr>
<tr>
<td>5</td>
<td>( \text{AgOTf} )</td>
<td>0.01</td>
</tr>
<tr>
<td>6</td>
<td>( \text{AgOTf} )</td>
<td>0.05</td>
</tr>
<tr>
<td>7</td>
<td>( \text{Ti(O-Pr)}_4 )</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>( \text{TiCl}_4 )</td>
<td>0.2</td>
</tr>
<tr>
<td>9</td>
<td>( \text{LiClO}_4 )</td>
<td>0.05</td>
</tr>
<tr>
<td>10</td>
<td>( \text{LiClO}_4 )</td>
<td>0.05</td>
</tr>
<tr>
<td>11</td>
<td>( \text{Et}_3\text{Al} )</td>
<td>0.05</td>
</tr>
<tr>
<td>12</td>
<td>( \text{AcOH} )</td>
<td>0.15</td>
</tr>
<tr>
<td>13</td>
<td>( \text{TsOH} )</td>
<td>0.3</td>
</tr>
<tr>
<td>14</td>
<td>( \text{TIOH} )</td>
<td>0.1</td>
</tr>
<tr>
<td>15</td>
<td>( \text{Me}_3\text{SiOTf/ Et}_3\text{N} )</td>
<td>0.1</td>
</tr>
<tr>
<td>16</td>
<td>( \text{Me}_3\text{SiOTf/ Et}_3\text{N} )</td>
<td>0.1</td>
</tr>
<tr>
<td>17</td>
<td>( \text{Me}_3\text{SiOTf} (5%) )</td>
<td>0.05</td>
</tr>
<tr>
<td>18</td>
<td>( \text{Me}_3\text{SiOTf/ Py}_d )</td>
<td>0.3</td>
</tr>
<tr>
<td>19</td>
<td>( \text{Me}_3\text{SiOTf/ Py}_d )</td>
<td>0.3</td>
</tr>
<tr>
<td>20</td>
<td>( \text{NaOH} )</td>
<td>0.1</td>
</tr>
<tr>
<td>21</td>
<td>( \text{NaOSiMe}_3 )</td>
<td>0.1</td>
</tr>
<tr>
<td>22</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

*a Determined by \(^1\text{H} \) NMR spectroscopy with toluene as internal standard.

*b Only 1a (ca. 100%) by \(^1\text{H} \) NMR spectroscopy.

*c The ratio Me\(_3\text{SiOTf/ Et}_3\text{N} \) is 5:1.

*d The ratio Me\(_3\text{SiOTf/ Py}_d \) is 5:1.
formation of the corresponding chloro derivative, Me(ClCH₂)C=NOSiMe₃, as the product.²⁰

The use of OH-acids as electrophiles (E = H⁺, entries 12–14) deserves further comment. It is likely that the active protons can result in the resinification of reaction mixtures. The example with acetic acid (entry 12) is especially interesting. In this case the yield of target 4a is close to quantitative after 50% conversion of the initial nitroso acetal 1a. However, upon completion of the reaction, the yield of 4a is diminished and resinification of reaction mixture takes place. In full accordance with literature data,¹⁷ employment of Me₃SiOTf/Et₃N as catalyst does not give a good yield of 4a, and makes its purification more difficult (entries 15, 16).

As can be seen from Table 1 (entries 20–22), the heating of BENA 1a and the use of some nucleophiles Nu instead of electrophiles E–X [pathway (b), Scheme 2] are less efficient in promoting the desired transformation. The most effective procedure for the conversion of 1a to 4a (Table 1, entry 3) was used for the preparation of other α-hydroxy oximes 3b–i from BENA 1b–i respectively (Scheme 4, Table 2).

Trimethylsilyl derivatives 4a–i were isolated in yields of 75–95% after aqueous work-up of reaction mixtures followed by fractional distillation (see details in the experimental section).

Desilylation of 4a–i was accomplished by treatment with excess methanol at room temperature for 24 hours. Usually the evaporation of solvents provides analytically pure oximes 3 in almost quantitative yields. But in some cases additional purification by recrystallization or column chromatography was required that was accompanied by drop in yields of oximes 3 (cf. Table 2, entries 7–9).²¹

To elucidate the mechanism of the reaction, the rearrangement of BENA 1a' possessing different silyloxy groups was carried out under the conditions given in Table 2 (Scheme 5).

It was shown with the use of two-dimensional ¹H–²⁹Si NMR spectroscopy that only the Me₃SiO group migrates to the β-carbon atom to give the product 4a'. The fact that no products with two Me₃SiO or two t-BuMe₂SiO groups were observed, as well as the structure of 4a', suggests that the rearrangement occurs through pathway (a) (Scheme 2) rather than via formation of α-nitrosoalkene.

In conclusion, a new two-step strategy for the synthesis of α-hydroxy oximes 3 from aliphatic nitro compounds has been presented (Scheme 6).

<table>
<thead>
<tr>
<th>Entry</th>
<th>1,3,4</th>
<th>R¹</th>
<th>R²</th>
<th>Time (h)</th>
<th>4</th>
<th>Yield (%)</th>
<th>3</th>
<th>Yield (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>a</td>
<td>Me</td>
<td>H</td>
<td>6</td>
<td>15:1</td>
<td>88</td>
<td>7:1</td>
<td>83</td>
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<tr>
<td>2</td>
<td>b</td>
<td>H</td>
<td>H</td>
<td>20</td>
<td>9:8</td>
<td>91</td>
<td>3:2</td>
<td>87</td>
</tr>
<tr>
<td>3</td>
<td>c</td>
<td>H</td>
<td>Me</td>
<td>16</td>
<td>5:1</td>
<td>90</td>
<td>6:1</td>
<td>89</td>
</tr>
<tr>
<td>4</td>
<td>d</td>
<td>-(CH₂)₄-</td>
<td></td>
<td>2</td>
<td>only E</td>
<td>86</td>
<td>only E</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>e</td>
<td>Ph</td>
<td>H</td>
<td>20</td>
<td>3:1</td>
<td>95</td>
<td>7:1</td>
<td>93</td>
</tr>
<tr>
<td>6</td>
<td>f</td>
<td>PhCH₂</td>
<td>H</td>
<td>24</td>
<td>6:1</td>
<td>83</td>
<td>5:1</td>
<td>81</td>
</tr>
<tr>
<td>7</td>
<td>g</td>
<td>CO₂Et</td>
<td>H</td>
<td>160⁺</td>
<td>only E</td>
<td>75</td>
<td>8:1</td>
<td>63</td>
</tr>
<tr>
<td>8</td>
<td>h</td>
<td>CO₂Me</td>
<td>Me</td>
<td>18</td>
<td>2:5</td>
<td>83</td>
<td>5:4</td>
<td>78</td>
</tr>
<tr>
<td>9</td>
<td>i</td>
<td>CH₃CH₂CO₂Me</td>
<td>H</td>
<td>16</td>
<td>8:7</td>
<td>80</td>
<td>3:8</td>
<td>71</td>
</tr>
</tbody>
</table>

* Reaction conditions: 0.2 mol/L solution of BENA 1 in CH₂Cl₂ and 5 mol% of Zn(OTf)₂ at 20 °C.
* Desilylation is carried out by treating 4a–i with MeOH at r.t. for 24 h.
* Based on starting BENA 1.
* Reaction conditions: 0.33 mol/L solution of BENA 1g in CH₂Cl₂ and 10 mol% of Zn(OTf)₂ at 20 °C.
Scheme 6

All reactions were performed in oven-dried (150 °C) glassware. All reactions with trimethylsilyl derivatives were performed under dry argon. The following reaction solvents and reagents were distilled from the indicated drying agents: CH₂Cl₂ (CaH₂), THF (LiAlH₄), Me₂O (Na), MeCN (P₂O₅), hexane (Na), MeOH (Mg).

NMR spectra were recorded on Bruker AM-300 instrument (¹H: 300.13 MHz, ¹³C: 75.47 MHz, ²⁹Si: 59.63 MHz) referenced to residual solvent peak or internal standard (SiMe₄); chemical shifts are reported in ppm (δ). The INEPT pulse sequence was used for ²⁹Si signal observation. The configuration of oximino group in 3 and 4 was determined by optical rotations in our earlier discussions.⁹

Melting points (mp) were determined on a Kofler melting point apparatus (uncorrected).

Analytical TLC was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with UV. All solvents for chromatography and extractions were technical grade and distilled from the indicated drying agents: hexane and EtOAc (P₂O₅), THF (LiAlH₄), Et₂O (Na), MeCN (P₂O₅), hexane (Na), MeOH (Mg).

All reactions were performed in oven-dried (150 °C) glassware. All reactions with trimethylsilyl derivatives were performed under dry argon. The following reaction solvents and reagents were distilled from the indicated drying agents: CH₂Cl₂ (CaH₂), THF (LiAlH₄), Me₂O (Na), MeCN (P₂O₅), hexane (Na), MeOH (Mg).

The following chemicals were purchased from the indicated sources: Zn(OTf)₂ (Acros), Me₃SiOTf (Acros), AgOTf (Aldrich), Ti(O(Or)-Pr)₄ (Acros), TICl₄ (Aldrich), LiClO₄ (Acros), Et₂Al (Aldrich), NaO₃SiMe₂ (Aldrich). The following chemicals were purchased from the indicated sources: Zn(OTf)₂ (Acros), Me₃SiOTf (Acros), AgOTf (Aldrich), Ti(O(Or)-Pr)₄ (Acros), TICl₄ (Aldrich), LiClO₄ (Acros), Et₂Al (Aldrich), NaO₃SiMe₂ (Aldrich).

The following compounds were prepared by literature methods: BENA 1a–d, 1i, 1j, 1f, 1e and 1g.¹²

Derivatives 4a–i; General Procedure

A solution of BENA 1a–d (10 mmol) in CH₂Cl₂ (10 mL) was added to a stirred mixture of Zn(OTf)₂ (182 mg, 0.5 mmol) in CH₂Cl₂ (40 mL). The reaction mixture was kept at 20 °C with occasional shaking for the time given in Table 2, diluted with petroleum ether (bp 60–70 °C, 100 mL) and poured into sat. solution of NaHCO₃ in H₂O (30 mL). The organic phase was washed with H₂O (2 × 10 mL), brine (2 × 10 mL) and dried (Na₂SO₄). Concentration in vacuum afforded of 4a–i as clean colorless oils. Analytically pure 2 was obtained by vacuum distillation (Table 2).

1-Trimethylsilyloxypropan-2-one O-(Trimethylsilyl)oxime (4a)

Bp 65–66 °C/6 mm Hg (Lit.¹³).

E-Isomer

†H NMR (CDCl₃): δ = 0.14 [s, 9 H, CO(Si(CH₃)₃)], 0.21 [s, 9 H, Si(CH)₂], 4.23 (d, J = 5.2 Hz, 2 H, CH₂), 7.51 (t, J = 5.2 Hz, 1 H, CH).

¹³C NMR (CDCl₃): δ = –0.8 [Si(CH₂)], –0.3 [CO(Si(CH₃)₃)], 60.3 (CH₂), 153.7 (CH).

²⁹Si NMR (CDCl₃): δ = 20.99 (OSi), 25.93 (NOSi).

Z-Isomer

†H NMR (CDCl₃): δ = 0.14 [s, 9 H, CO(Si(CH₃)₃)], 0.21 [s, 9 H, Si(CH₂)], 4.47 (d, J = 3.7 Hz, 2 H, CH₂), 6.99 (t, J = 3.7 Hz, 1 H, CH).

¹³C NMR (CDCl₃): δ = –0.8 [Si(CH₂)], –0.6 [CO(Si(CH₃)₃)], 57.6 (CH₂), 157.5 (CH).

²⁹Si NMR (CDCl₃): δ = 20.68 (OSi), 26.03 (NOSi).

2-Trimethylsilyloxypropionaldehyde O-(Trimethylsilyl)oxime (4d)

Bp 90–93 °C/24 mm Hg (Lit.¹⁴).

E-Isomer

†H NMR (CDCl₃): δ = 0.11 [s, 9 H, CO(Si(CH₃)₃)], 0.19 [s, 9 H, Si(CH₂)], 1.27 (d, J = 5.9 Hz, 3 H, CH₃), 4.41 (m, J = 5.9 Hz, 1 H, CH₂), 7.36 (d, J = 5.9 Hz, 1 H, HC=NC).

¹³C NMR (CDCl₃): δ = –0.8 [Si(CH₂)], 0.1 [CO(Si(CH₃)₃)], 22.3 (CH₂), 66.3 (CH₃), 157.6 (CN).

²⁹Si NMR (CDCl₃): δ = 18.74 (OSi), 25.79 (NOSi).

Z-Isomer

†H NMR (CDCl₃): δ = 0.11 [s, 9 H, CO(Si(CH₃)₃)], 0.19 [s, 9 H, Si(CH₂)], 1.25 (d, J = 5.2 Hz, 3 H, CH₃), 5.01 (m, J = 5.2 Hz, 1 H, CH₂), 6.85 (d, J = 5.2 Hz, 1 H, HC=NC).

¹³C NMR (CDCl₃): δ = –0.8 [Si(CH₂)], –0.1 [CO(Si(CH₃)₃)], 20.9 (CH₃), 62.1 (CH₂), 159.9 (CN).

²⁹Si NMR (CDCl₃): δ = 18.57 (OSi), 25.49 (NOSi).

2-Trimethylsilyloxy cyclohexanone O-(Trimethylsilyl)oxime (4d)

Bp 52 °C/0.2 mmHg (Lit.¹⁵).

†H NMR (CDCl₃): δ = 0.13 [s, 9 H, CO(Si(CH₃)₃)], 0.29 [s, 9 H, Si(CH₂)], 1.37 (m, 2 H, CH₃), 1.52 (m, 2 H, CH₂), 1.80 (m, 1 H, CH₂), 1.91 (m, 2 H, CH₂), 2.07 (dd, J = 14.0, 12.5, 5.2 Hz, 1 H, CH₂(CN)), 3.07 (dd, J = 14.0, 12.5, 5.2 Hz, 1 H, CH₂(CN)), 4.28 (t, J = 3.0 Hz, 1 H, HC=NC).

¹³C NMR (CDCl₃): δ = –0.7 [Si(CH₂)], 0.0 [CO(Si(CH₃)₃)], 20.0, 21.3, 25.6 (CH₃), 35.5 (CH₂(CN)), 69.9 (CH), 164.3 (CN).

²⁹Si NMR (CDCl₃): δ = 17.29 (OSi), 23.72 (NOSi).

1-Phenyl-2-trimethylsilyloxyethanone O-(Trimethylsilyl)oxime (4e)

Bp 90–95 °C/0.2 mm Hg (Lit.¹⁶).

†H NMR (CDCl₃): δ = 0.12 [s, 9 H, CO(Si(CH₃)₃)], 0.33 [s, 9 H, Si(CH₂)], 4.90 (s, 2 H, CH₂), 7.4–7.6 (2 m, 5 H, C₆H₅).

¹³C NMR (CDCl₃): δ = –0.7 [Si(CH₂)], –0.4 [CO(Si(CH₃)₃)], 55.2 (CH₂), 126.9, 129.0, 129.8 (CH, C₆H₅), 133.1 (C₆H₅), 161.2 (CN).

²⁹Si NMR (CDCl₃): δ = 20.55 (OSi), 26.22 (NOSi).

Z-Isomer
1H NMR (CDCl3): δ = 0.12 [s, 9 H, COSi(CH3)3], 0.33 [s, 9 H, Si(CH3)3], 4.77 (s, 2 H, CH2), 7.4–7.6 (m, 5 H, C6H5).
13C NMR (CDCl3): δ = –0.7 [Si(CH3)3], –0.4 [COSi(CH3)3], 62.0 (CH2), 126.9, 129.0, 129.8 (CH, C6H5), 133.1 (Cipso, C6H5), 158.8 (CN).
29Si NMR (CDCl3): δ = 20.90 (COSi), 26.34 (NOSi).

1-Phenyl-3-trimethylsilyloxypropan-2-one O-(Trimethylsilyl)oxime (4f)
Bp 70–71 °C/0.2 mm Hg (Lit.17).

Methyl Ester (4i)
3-Trimethylsilyloxy-2-(trimethylsilyl)oxyiminopentanoic Acid
Silyl derivatives 4 into Oximes 3; General Procedure

Desilylation of Derivatives 4 into Oximes 3; General Procedure

1-Trimethylsilyloxypropan-2-one O-(tert-Butylsilyl)dimethyloxime (4a')
Compound 4a' was prepared from 1a' adopting the same general procedure given above; 92% yield.

Oil (Lit.17).

Desilylation of Derivatives 4 into Oximes 3; General Procedure

1-Hydroxypropan-2-one Oxime (3a)
Mp 73–75 °C (Lit.23 mp 78 °C).

Hydroxyacetalddehyde Oxime (3b)
Mp 49–52 °C (Lit.24 mp 48–50 °C).

2-Hydroxypropionaldehyde Oxime (3c)
Oil (Lit.13).
E-Oxime
$^1$H NMR (CDCl$_3$): $\delta = 1.38$ (d, $J = 5.1$ Hz, 3 H, CH$_3$), 2.3 (br, 1 H, OH), 4.47 (m, $J = 5.1$ Hz, 1 H, CH), 6.3 (br, 1 H, NOH), 7.44 (d, $J = 5.1$ Hz, 1 H, HC=N).

$^{13}$C NMR (CDCl$_3$): $\delta = 21.0$ (CH$_3$), 65.5 (CH), 153.7 (CN).

Z-Oxime
$^1$H NMR (CDCl$_3$): $\delta = 1.40$ (d, $J = 5.1$ Hz, 3 H, CH$_3$), 2.3 (br, 1 H, OH), 4.95 (m, $J = 5.1$ Hz, 1 H, CH), 6.3 (br, 1 H, NOH), 6.80 (d, $J = 5.1$ Hz, 1 H, HC=N).

$^{13}$C NMR (CDCl$_3$): $\delta = 19.8$ (CH$_3$), 61.9 (CH), 155.2 (CN).

2-Hydroxy-1-phenylethanone Oxime (3f)
Anal. Calcd for C$_5$H$_9$NO$_4$: C, 40.73; H, 6.21; N, 9.19. Found: C, 40.73; H, 7.83; N, 15.40.

2-Hydroxycyclohexanone Oxime (3d)
Anal. Calcd for C$_6$H$_{11}$NO$_4$: C, 40.76; H, 6.05; N, 9.41. Found: C, 40.76; H, 6.05; N, 9.41.

3-Hydroxy-2-hydroxyiminopropionic Acid Ethyl Ester (3g)
$^1$H NMR (CDCl$_3$): $\delta = 7.3$ Hz, 3 H, CH$_3$), 3.8 (br, 1 H, OH), 4.27 (s, 2 H, CH$_2$), 10.0 (br, 1 H, NOH).

$^{13}$C NMR (CDCl$_3$): $\delta = 25.9$ (CH$_3$), 30.6 (CH$_2$O), 51.9 (CH$_2$), 158.9 (CN), 173.9 (C=O).

Acknowledgment
This work was performed at the Scientific Educational Center for young chemists and supported by Russian Foundation for Basic Research (grants # 03-03-32881 and # 03-03-04001), Deutsche Forschungsgemeinschaft (grant MA 673/19), the Federal Target Program 'Integration' (project B0062) and Program of supporting of scientific schools (project # NSH 1442.2003.3).

References


(17) This problem was solved in the earlier paper, which dealt with the double silylation of ANC with Me₃SiOTf/Et₃N, but the yields of target derivatives were modest as a rule, see: Feger, H.; Simchen, G. Liebigs Ann. Chem. 1986, 428.

(18) Our attempts to realize the transformation ANC → 4 as a one-step process (without isolation of BENA) failed because of the conditions needed for steps ANC → 1 and 1 → 4 differ considerably.


(21) Attempts to selectively desilylate oximino group in derivatives 4a–i by use of small quantities of MeOH were unsuccessful because the desilylation of both functional groups proceeded with comparable rates.


