Substitution Reactions at Nitrilimine Skeletons

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Received 14 October 1991

Treatment of N-boranyl nitrilimines by metalolithium and subsequent addition of chlorophosphane or chlorosilane gives rise to the corresponding N-phosphanyl- or N-silylnitrilimines in good yields. Using the ability of boranyldiazolithium salts to isomerize into the corresponding boranylisodiazolithium salts, both boranyl substituents of a C- and N-boranyl nitrilimine can be substituted leading to new stable nitrilimines in good yields. These are the first examples of substitution reactions at nitrilimine skeletons.

Potentially, nitrilimines are powerful building blocks in heterocyclic chemistry, due to their ability to undergo 1,3-dipolar cycloadditions with a variety of dipolarophiles. 1 However, for a long time, they were only considered as transient intermediates, which hampered their use on a preparative scale. 2 Recently, we have shown that using the right set of substituents, nitrilimines can be isolated and stored at room temperature, 3,4,6 and that it is even possible to do reactions at the periphery of the nitrilimine skeleton. 5,10 Up to now, 3 routes were available for preparation of stable nitrilimines: the reaction of electrophiles with diazo lithium salts [route (a)]; 3-6 the addition of halogenated compounds to tin diazo derivatives [route (b)]; 7 the dehydrohalogenation of halogenohydrazones [route (c)]. 8

\[
\begin{align*}
R-\text{CN}_2 &+ \text{Li}^+ + \text{ECl} \rightarrow (a) \\
R-C &+ \text{SnMe}_3 \rightarrow N_2 \rightarrow R-C &+ \text{ECl} \rightarrow (b) \\
R-C &+ \text{N} \rightarrow N &+ \text{E} + \text{Base} \rightarrow (c)
\end{align*}
\]

Herein we report a new synthetic route starting from nitrilimines; these are the first examples of substitution reactions at the carbon and nitrogen ends of the CNN moiety.

Boranyl-substituted nitrilimines 3,6 were chosen as starting materials because of their thermal stability (they can be purified by distillation), and the high reactivity of boron-carbon and boron-nitrogen bonds. Addition of a stoichiometric amount of metalolithium to a THF solution of C-thiophosphoryl-N-boranyl nitrilimine 1,6 followed by addition of one equivalent of chlorobis(diisopropylamino)phosphane 11 or chlorotrisopropylsilane led to the corresponding N-phosphanyl- or N-silylnitrilimine 2 3 or 3 4, in 68 and 85% yield, respectively.

\[
\begin{align*}
1 & \text{MeLi/THF, r.t., 30 min} \\
2 & R_2 \text{P} - C &+ \text{N} \rightarrow N &+ \text{BR}_2 \text{Cl} \rightarrow (r.t., 1h) \\
3 & R_2 \text{P} &- C = N &+ N - O - E \text{Cl} \rightarrow & \text{Si} \rightarrow (r.t., 1h)
\end{align*}
\]

From a mechanistic point of view, it is quite clear that the first step of the reaction is the electrophilic attack of the boron atom, leading to a borate 4, which after elimination of bis(diisopropylamino)methylborane, gives rise to the lithium salt of bis(diisopropylamino)thiophosphoryl-diazomethane 5, which is known to react with bulky electrophiles to give nitrilimines. 3,4 Although, the first postulated borate 4 cannot be observed by spectroscopy, even at low temperature, the lithium salt 5 was characterized in solution by 31P NMR and IR spectroscopy.

\[
\begin{align*}
1 & \text{MeLi/THF, r.t., 30 min} \\
2 & R_2 \text{P} - C &+ \text{N} \rightarrow N &+ \text{BR}_2 \text{Cl} \rightarrow (r.t., 1h) \\
3 & R_2 \text{P} &- C = N &+ N - O - E \text{Cl} \rightarrow & \text{Si} \rightarrow (r.t., 1h)
\end{align*}
\]

Since boron-carbon bonds are also known to be quite reactive, the next question was to know whether substitution of C- and N-boranyl nitrilimines would occur at carbon or nitrogen. Addition of a stoichiometric amount of metalolithium to a THF solution of C- and N-bis(diisopropylamino)boranyl nitrilimine 6,5,6 followed by addition of chlorobis(diisopropylamino)phosphane led to nitrilimine 7,5,6 in 70% yield.
Nitrilimine 7 formally results from a substitution reaction at the carbon end of nitrilimine 6. In fact, an alternative mechanism could be that the first step of the reaction is the cleavage of the boron–nitrogen bond of 6, leading to lithium salt 8a, which is known to isomerize in THF into 8b. Addition of the electrophile to 8b would give rise to the observed product 7.

In order to prove this mechanism and in the hope of obtaining substitution of the 2 boranyl groups, C- and N-[bis(diisopropylamino)boranyl]nitrilimine 6, was first treated with methylolithium, then with chlorobis(dicyclohexylamino)borane. This led to C-[bis(dicyclohexylamino)boranyl]-N-[bis(diisopropylamino)boranyl]nitrilimine (9) in 72% yield. The reaction sequence was repeated on 9 and the fully [bis(dicyclohexylamino)boranyl] substituted nitrilimine 10 was obtained as air stable white crystals, in 85% yield.

The structure of nitrilimine 10 was clearly established by an X-ray crystal study, its molecular structure is illustrated in the Figure, and the pertinent metric parameters are in Tables 1 and 2. There is a strong interaction between B1 and the nitrilimine skeleton since the B1C1N1N2 fragment is almost linear (B1C1N1 = 165.1° and C1N1N2 = 169.4°) and the B1C1 bond length rather short (1.559 Å). The partial boron–carbon double-bond character of B1C1 induces a decrease of the Lewis acidity of B1 which probably explains the regioselective attack of methylolithium at the boron atom bonded to the nitrogen end of the C- and N-boranyl nitrilimines.

![Figure. ORTEP Plot of nitrilimine 10.](image)

From these results, it appears that boranyl substituted nitrilimines are powerful precursors for the synthesis of new stable nitrilimines. This method could be of special interest when the diazomethane derivatives are not stable, preventing the preparation of the corresponding lithium salts.

All experiments were performed in an atmosphere of dry argon. Conventional glassware was used. MeLi was purchased from Aldrich Chemical Co. THF was dried over Na and distilled before use. Pentane was dried over P2O5 and distilled before use. H, 13C, 11B and 31P NMR spectra were recorded on Bruker AC80, AC200 or WM250 spectrometers. H and 13C chemical shifts are reported in ppm relative to TMS as external standard. 31P and 11B downfield shifts are expressed with a positive sign, in ppm, relative to external 85% H3PO4 and BF3·OEt2, respectively. IR spectra were recorded on a Perkin–Elmer 597. Melting points are uncorrected.

**Synthesis of Chlorobis(dicyclohexylamino)borane:**
To a stirred pentane solution (250 mL) of BCl3 (17 g, 150 mmol) and Et3N (45 mL, 165 mmol), at −78°C, was added dropwise dicyclohexylamine (30 mL, 150 mmol). The solution was allowed to warm up to r.t. and was stirred overnight (18 h). Filtration of dicyclohexylammonium hydrochloride and evaporation of the solvent, afforded a white powder. Chlorobis(dicyclohexylamino)borane was crystallized from cold pentane (−20°C); yield: 30 g (50 %), mp 120°C.

C24H44N2·BCl calc. C 70.84 H 10.90 N 6.89 (406.874) found 70.75 11.00 6.81

11B NMR (CDCl3): δ = 30.6 (br).

13C NMR (CDCl3): δ = 26.38, 27.38, 34.50 (s, CH3), 57.82 (s, CHN).

**Reaction of Nitrilimines with Methylolithium; General Procedure:**
To a THF solution (10 mL) of nitrilimine (1 mmol), at r.t., was added dropwise MeLi in Et2O (1.6 M, 1.2 mmol). The solution is stirred for 30 min. The reactions were monitored by 31P NMR and/or IR spectroscopy. The lithium salts were characterized in solution:

<table>
<thead>
<tr>
<th>Lithium Salt</th>
<th>IR (THF) (cm⁻¹)</th>
<th>31P NMR (THF) (δ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-Pr3N)2P(S)CNN−, Li+ (5)</td>
<td>2003 (br s)</td>
<td>+62</td>
</tr>
<tr>
<td>(-Pr3N)2BNNC−, Li+ (8b)</td>
<td>2048 (sharp)</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table 1. Selected Bond Lengths (Å) for Nitrilimine 10**

| C1–N1    | 1.171 (3) |
| C1–B1    | 1.559 (4) |
| N1–N2    | 1.268 (3) |
| N2–B2    | 1.452 (3) |

| C1–N3    | 1.421 (3) |
| B1–N4    | 1.422 (3) |
| B2–N5    | 1.425 (3) |
| B2–N6    | 1.467 (3) |

**Table 2. Selected Bond Angles (degree) for Nitrilimine 10**

| N1–C1–B1 | 165.1 (2) |
| N1–N2–B2 | 122.4 (2) |
| C1–B1–N3 | 115.1 (2) |
| C1–B1–N4 | 118.2 (2) |
To a solution of the lithium salt was added dropwise, at r.t., the stoichiometric amount of electrophile (1 mmol) in THF (5 mL). After the mixture had been stirred for 1 h at r.t., the solvent was removed under vacuum, the residue treated with pentane (20 mL), and filtered. Then, the filtrate was evaporated under reduced pressure, and the residue was purified by distillation on recrystallization. The physical data of known compounds (i.e., 2, 3, 7) were compared with those of original samples prepared by known procedures.

C₂₅H₂₃N₂N₄B₂ (9): obtained as white crystals from an MeCN/Et₂O solution; yield 72%; mp 115°C dec.

C₃₁H₅₁N₈B₂ (9) calc. C 71.37 H 11.66 N 13.50 (622.6) found 71.30 11.76 13.42

IR (THF): ν = 2155 cm⁻¹ (C-N=N-).

1¹¹B NMR (CDCl₃): δ = 27 (br).

1⁴C NMR (CDCl₃): δ = 23.29 (s, CH₃), 25.55, 26.92, 34.85 (s, CH₃), 45.79 (s, CH₂CHN), 57.14 (s, CH₂CHN), 68.01 (br s, -C-N-C-).

C₂₅H₂₃N₂N₄B₂ (9) calc. C 75.17 H 11.33 N 10.74 (782.9) found 75.35 11.44 10.66

IR (THF): ν = 2152 cm⁻¹ (C-N=N-).

1¹¹B NMR (CDCl₃): δ = 25 (br).

1⁴C NMR (CDCl₃): δ = 25.72, 26.23, 26.67, 27.01, 33.94, 34.89 (s, CH₃), 55.74, 57.19 (s, CHN), 66.50 (br s, -C-N-C-).

X-ray Crystallographic Study of 10

C₃₁H₅₁N₈B₂M o M = 782.9, monoclinic, space group P2₁/n, a = 20.281(6), b = 13.232(4), c = 20.414(6) Å, β = 116.07(2)°, V = 4920.9 Å³, Z = 4, D₀ = 1.057 gcm⁻³, μ = 4.270 cm⁻¹. Crystallographic measurements were made at −100°C, using a Philips PW 1100/16 automatic diffractometer, operating in the θ/2θ flying step-scan. The intensity data were collected within the range 3 ≤ θ ≤ 52° using graphite monochromator Cu-Kα radiation (λ = 1.5418 Å). Intensities of 5500 unique reflections were measured. The structure was solved using SIR3. In the refinement, 4008 reflections with I > 3σ(I) were used. Convergence was obtained at R(F) = 0.044 and Rw(F) = 0.066.


