



Synthesis and [2+4]cycloadditions of two 1-aza-1,3-butadiene-1-carbonitriles

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ABSTRACT

3-Methyl- and 3-ethyl-1-aza-1,3-butadiene-1-carbonitriles were synthesized by reaction of the corresponding 3-alkylacroleins with bis(trimethylsilyl)-carbodiimide using titanium tetrachloride as catalyst. They were highly reactive and difficult to purify rigorously. Attempted anionic polymerizations gave only oligomers of molecular weight ~500 Da. These 3-alkyl-azadienecarbonitriles cycloadded to the electron-rich olefins *iso*-butyl vinyl ether and *p*-methoxystyrene to give [2+4] cycloadducts with moderate yields. © 2009 Elsevier Ltd. All rights reserved.

1. Introduction

During the investigation of 1-aza-1,3-butadiene compounds containing *N*-electron-withdrawing groups as potential monomers,^{1–3} it was observed 1-phenylsulfonyl-3-methyl-1-aza-1,3-butadiene was found to be only moderately reactive. When the more electron-attracting carbethoxy moiety was placed on the nitrogen, the 3-methyl derivative could again be obtained. This compound was highly reactive, dimerizing and hydrolyzing readily making it difficult to purify rigorously. Anionic initiators gave only oligomers in the range of 2K Da, possibly because of this inability to rigorously purify the monomer.

In the course of these investigations, we noticed a growing interest in the use of 1- and 2-azabutadienes for the synthesis of heterocyclic compounds by cycloaddition reactions.^{4–12} The azadienes carried either electron-donating aryl substituents or electron-attracting carboalkoxy groups. Accordingly, they readily cycloadded to olefins of opposite polarity, varying from tetracyanoethylene to vinyl ethers. Our 3-methyl-1-carbethoxy-1-azabutadiene also cycloadded to the electron-rich olefins which accords with the moderately electron-poor character of the diene. This work extends our studies on an even more electron-attracting group, namely the 1-azabutadienecarbonitriles.

2. Results

The 3-substituted-1-azabutadiene-1-carbonitriles **1** and **2** were synthesized, respectively, by the condensation of methacrolein or ethacrolein with bis(trimethylsilyl)-carbodiimide using titanium tetrachloride with yields of 30–50% (Scheme 1).¹³ The 1-azabutadiene-1-carbonitrile readily hydrolyzed during attempted purification by silica-gel chromatography, and oligomerized to afford a

highly viscous oil during removal of the solvent. It could be distilled under high vacuum. However, synthesis of the unsubstituted monomers from acrolein did not succeed, as with previous monomers, probably owing to Michael addition.

Treatment of monomers **1** and **2** with various anionic initiators gave only oligomers, the highest molecular weight being ~500 Da. The highly electron-accepting cyano group makes these monomers difficult to isolate and to purify extensively, and this may account for the observed low molecular weights.

The Diels–Alder reaction of 3-methyl-1-azabutadiene-1-carbonitrile with electron-rich olefins was slow at room temperature. However, complexation of the *N*-cyano substituent with titanium tetrachloride accentuated the electron-deficient nature and accelerated the [2+4] cycloaddition. The reaction was carried out with *iso*-butyl vinyl ether and *p*-methoxystyrene. There was no observed cycloaddition with the electron-poor benzoquinone. Other Lewis acids such as boron trifluoride etherate and trimethylsilyl triflate catalyst gave very low yields of cycloadduct and spontaneous homopolymerization occurred. Solvent effects were observed, with tetrahydrofuran giving the highest yield of cycloadduct, while solvents such as methylene chloride, toluene, and diethyl ether enhanced competitive spontaneous polymerization.

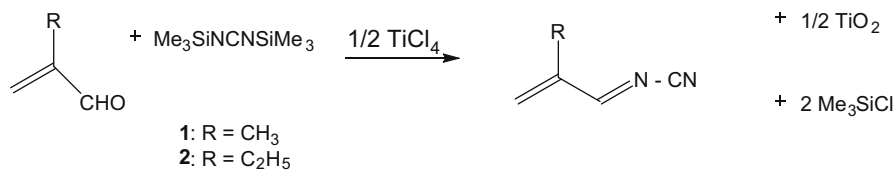
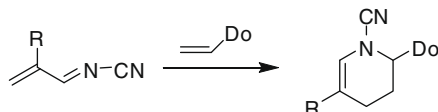
3. Reactions

Both 3-substituted-1-azabutadiene-1-carbonitriles **1** and **2** participated in inverse [2+4] Diels–Alder reactions (Scheme 2).

4. Conclusions

Two 3-alkyl-1-aza-1,3-butadiene-1-carbonitriles were synthesized. They were reactive in oligomerization and cycloadditions, reacting with electron-rich alkenes to give [2+4] cycloadducts in moderate yields.

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**Scheme 1.** Synthesis of 1-azabutadiene-1-carbonitriles **1** and **2**.

- 3:** R = CH₃, Do = *i*-BuO-
4: R = C₂H₅, Do = *i*-BuO-
5: R = CH₃, Do = *p*-CH₃C₆H₄-
6: R = C₂H₅, Do = *p*-CH₃C₆H₄-

Scheme 2. cycloaddition of 1-azabutadiene-1-carbonitriles with electron-rich donor olefins.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tetlet.2009.09.146](https://doi.org/10.1016/j.tetlet.2009.09.146).

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