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Selective [2+1] aziridination of conjugated dienes with a nitridomanganese complex: a new route to alkenylaziridines

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Abstract

Conjugated dienes were successfully aziridinated using a nitridomanganese complex as a nitrogen source. The reaction proceeded selectively and in good yield via [2+1] addition to give alkenylaziridines, with no evidence for the formation of any [4+1] addition products. The first asymmetric version of the reaction was revealed in the aziridination of diene **5** with chiral complex **1**. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: aziridination; conjugated diene; alkenylaziridine; nitridomanganese complex.

Alkenylaziridines are well known as useful building blocks, which can be converted to allylamines via regioselective ring opening reactions[1] and to pyrroline derivatives by means of ring expansion reactions,[2] and have been applied to the synthesis of a variety of natural products.[3] Typically, several steps are required for the synthesis of alkenylaziridines.[4] Although there are many reports of one-step synthesis by the direct addition of nitrenes to 1,3-dienes, problems are often encountered with the photolysis or thermolysis of azides, resulting in the formation of a variety of by-products.[5] The reaction of conjugated dienes with [*N*-(*p*-toluenesulfonyl)imino]phenyliodinane, PhI=NTs, a potent reagent for metal-catalyzed nitrogen atom transfer to olefins,[6,7] has often been observed to give mixtures of alkenylaziridines and pyrroline derivatives.[8] More recently, we reported an alternative and unique nitrogen source, a chiral nitridomanganese complex, for the asymmetric aziridination of styrene derivatives.[9,10] From these points of view, we report herein some aziridination reactions of conjugated dienes with a nitrido complex, wherein alkenylaziridine derivatives (via a [2+1] addition) are selectively produced without the formation of pyrroline derivatives (via a [4+1] addition).

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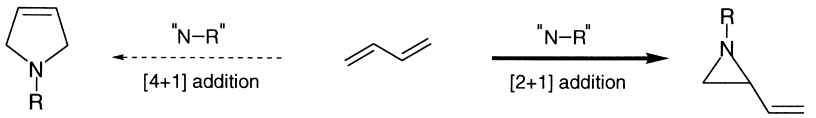
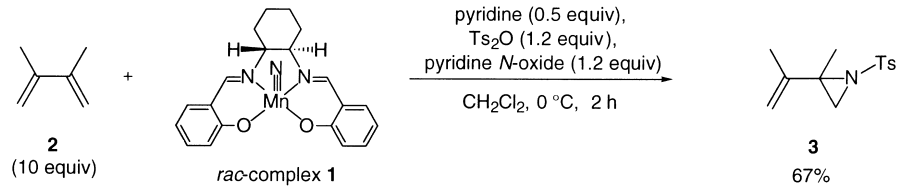


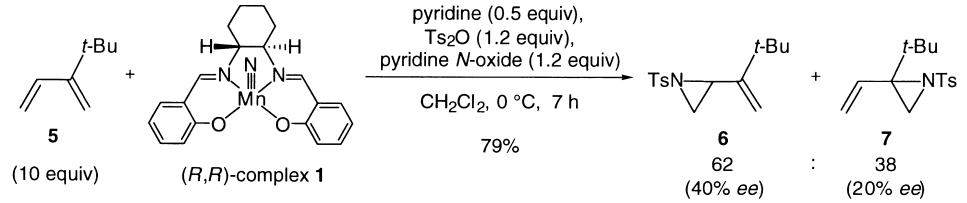
When 2,3-dimethyl-1,3-butadiene (**2**, 10 equiv.) was treated with racemic nitridomanganese complex **1** in methylene chloride at 0°C for 2 h in the presence of Ts_2O (1.2 equiv.), pyridine (0.5 equiv.) and pyridine *N*-oxide (1.2 equiv.), *N*-(*p*-toluenesulfonyl)-2-methyl-2-(2-propenyl)aziridine (**3**) was obtained in 67% yield.[11] No bisaziridinated product was detected. The reaction proceeded selectively via a [2+1] type addition, with no detectable formation of the [4+1] addition product, a pyrroline derivative.



(1)

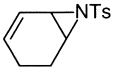
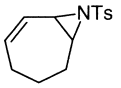
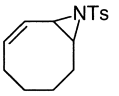
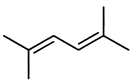
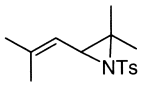
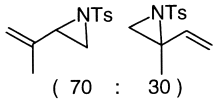
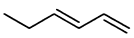
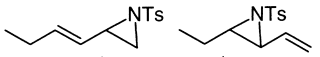
The present aziridination with the nitrido complex **1** was successfully applied to a range of unfunctionalized 1,3-dienes, as shown in Table 1. Cyclic conjugated dienes were smoothly aziridinated under mild conditions with no evidence of [4+1] adducts (entries 1–4). Of the compounds examined, the 1,3-dienes, which are embedded in six- and seven-membered rings, reacted with complex **1** with high efficiency. In the case of an acyclic diene, such as 2,5-dimethyl-2,4-hexadiene, the corresponding aziridine was obtained as the major product, along with its isomeric product, a homodienyl amine **4** (entry 5). When unsymmetrical dienes were employed in the reaction, the less substituted double bonds were preferentially aziridinated (entries 6 and 7). It is noteworthy in this respect that the aziridination of *trans*-1,3-hexadiene took place selectively at the terminal olefin (entry 7). The reason for the preference for aziridination at the less hindered double bond can be explained by the bulkiness of the reactive intermediate[10a,f] derived from nitridomanganese complex **1**. The chemoselectivity opposite to our results was reported in the case of the copper-catalyzed aziridination of 1,3-dienes with PhI=NTs, where the selectivity was explained by the electron density of each double bond in the conjugated dienes.[8]

Since the nitridomanganese complex **1** was found to be a very useful reagent for the aziridination of 1,3-dienes, chiral complex **1** was applied to the reaction. Treatment of 2-*tert*-butyl-1,3-butadiene (**5**) with (*R*,*R*)-complex **1** gave two regioisomeric alkenylaziridines in a ratio of 62:38. Although the enantioselectivity of the major isomer **6** was moderate (40% ee) at the present stage, this is the first example of the successful reagent-controlled direct asymmetric aziridination of a conjugated diene.[12]

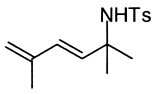


(2)

Table 1
Aziridination of conjugated dienes with nitridomanganese complex **1**[a]

entry	substrate	conditions	product	yield (%)[b]
1		−78 °C→−20 °C, 5 h		53
2		0 °C, 30 min		82
3		0 °C, 40 min		85
4		0 °C, 7 h		55
5		0 °C, 3 h		48[c]
6		0 °C, 3 h	 (70 : 30)	61
7		0 °C, 1.5 h	 (94 : 6)	56

[a] Reaction conditions; complex **1** (1 equiv), pyridine (0.5 equiv), Ts_2O (1.2 equiv), pyridine *N*-oxide (1.2 equiv), diene (10 equiv), CH_2Cl_2. [b] ^{1}H-NMR yields[11] based on complex **1**. [c] Compound **4** was obtained in 24% yield.



4

In summary, we report here, for the first time, on the use of a nitridomanganese complex as a nitrogen transfer reagent for the aziridination of conjugated dienes. The present reaction selectively proceeded with [2+1] type addition to afford alkenylaziridines. Having found a basis for the asymmetric aziridination of 1,3-dienes, a search for more efficient reactions is presently in progress.

Acknowledgements

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11. A typical experimental procedure is as follows. Pyridine (0.25 mmol), 2,3-dimethyl-1,3-butadiene (5.0 mmol) and a solution of *p*-toluenesulfonic anhydride (0.6 mmol) in CH_2Cl_2 (3 ml) were added to a mixture of **1** (0.5 mmol) and pyridine *N*-oxide (0.6 mmol) in CH_2Cl_2 (2 ml) under nitrogen, and the mixture was stirred at 0°C for 2 h. Pentane (15 ml) and Celite (500 mg) were added, and the mixture was stirred for 5 min. The reaction mixture was then passed through a 3-cm pad of silica gel using diethyl ether (15 ml×5) as the eluent. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography on silica gel (EtOAc/hexane). Since chromatography on both silica and alumina reduced the yields of the products to 10–20% due to ring opening reactions, ^{1}H NMR yields are shown in Table 1.
12. Enantiomeric excesses were determined by HPLC analysis using Daicel Chiralpak AD (hexane:2-propanol, 120:1, 1.0 ml/min, 254 nm, 30°C; compound **6**: $t = 18.6$ and 21.4 min; compound **7**: $t = 25.0$ and 27.0 min). Absolute configurations were not determined.