



NbCl₅ as Catalyst in Diels-Alder Reaction of Furan Ring

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INTRODUCTION

Diels-Alder reaction of furan as diene provides an important intermediate — 7-oxanorbonene (**1**) — which is the precursor in the synthesis of many natural products such as terpene (**2**) and prostaglandin (**3**) analogues (Figure 1).¹

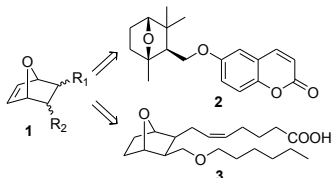


Figure 1. Natural products deriving from 7-oxanorbonene.

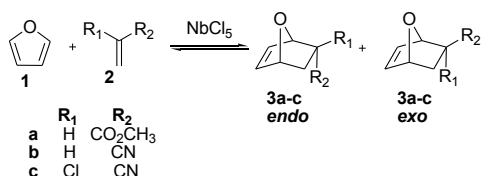
It is reported that uncatalyzed Diels-Alder reactions of furan take several weeks to give low yields due to diene's low reactivity. The use of Lewis acid catalysts or high pressures are described as efficient methods to improve reaction yields.²

Niobium compounds have been used as catalyst in various organic reactions and provided excellent yields with good selectivity in some cases.³

In this study, we describe our investigations on the use of niobium pentachloride (NbCl₅) as catalyst in Diels-Alder reactions between furan and some reactive dienophiles.

RESULTS AND DISCUSSION

The reactions were carried out under nitrogen atmosphere in different temperatures, with 10 mol% of catalyst. The diene was furan in excess and the dienophiles were methyl acrylate (**2a**), acrylonitrile (**2b**) and 2-chloro-acrylonitrile (**2c**) (Scheme 1). We determined 2 hours of reaction time. The results are showed in Table 1.



Scheme 1. Diels-Alder reaction between furan and reactive dienophiles.

The adduct was purified by multiple extractions with ethyl acetate and characterized by

spectroscopic methods. The *endo:exo* ratio was determined through ¹H NMR integration values.

Table 1. Results of Diels-Alder reaction in the presence of NbCl₅.

Dienophile	Temperature	Yield (%) (<i>endo:exo</i>)
2a	rt	47 (61:39)
	0 °C	81 (58:42)
	-20 °C	83 (62:38)
2b	rt	14 (58:42)
	0 °C	3 (57:43)
	-20 °C	6 (56:44)
2c	rt	12 (23:77)
	0 °C	19 (24:76)
	-20 °C	20 (34:66)

Good yields of the adduct **3a** were obtained, especially in lower temperatures. The low yields observed in reactions with **2b** and **2c** can be explained possibly by dienophile polymerization competing with cycloaddition and the reversible character of reaction.

A little excess of *endo* adduct were formed in reactions with **2a** and **2b**. On the other hand, reactions with **2c** showed high selectivity for *exo* adduct.

CONCLUSION

We obtained good yields using NbCl₅ in reactions with methyl acrylate as dienophile, mainly at low temperatures. Reactions with acrylonitrile and 2-chloro-acrylonitrile had low conversion rates.

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