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## Carbocation Catalysis: Oxa-Diels-Alder Reactions of Unactivated Aldehydes and Simple Dienes

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The versatility of the trityl cation ( $TrBF_4$ ) as a highly efficient Lewis acid organocatalyst is demonstrated in the oxa-Diels– Alder reaction of various unactivated aromatic and aliphatic aldehydes and simple unactivated dienes, such as isoprene and 2,3-dimethylbutadiene. The transformation proceeds smoothly to give 3,6-dihydropyrane adducts in high to mod-

#### Introduction

Functionalized pyran rings are found in a large number of naturally occurring compounds and these heterocycles have attracted much interest among both chemists and biologists because they are challenging synthetic targets and have diverse biological activity.<sup>[1]</sup> Over the years, a variety of synthetic strategies for the preparation of functionalized pyrans has been developed and among these, the oxa-Diels– Alder reaction has evolved as the most straightforward strategy.<sup>[2,3]</sup>

However, in contrast to the corresponding Diels-Alder reaction of electron deficient alkenes, the oxa-Diels-Alder reaction of aldehydes is much more challenging due to the substantially higher LUMO level of the  $\pi_{C-O}$  bond compared with an electron-deficient  $\pi_{C-C}$  bond. This strongly limits the general applicability of the oxa-Diels-Alder reaction in synthetic applications to the use of either highly activated dienes, such as Danishefsky's,<sup>[3b,4]</sup> Brassard's<sup>[3b,5]</sup> or Rawal's diene<sup>[6]</sup> or highly activated aldehydes containing electron-withdrawing groups, e.g., glyoxylates.<sup>[7]</sup> Thus, there is a challenging demand for the development of oxa-Diels-Alder reactions of unactivated dienes with unactivated aldehydes. The few scattered strategies reported so far require elevated temperatures and/or strong Brønsted acids,[8] Lewis acid<sup>[9,10]</sup> or transition metal catalysis<sup>[11]</sup> and are in general restrained by low yields, harsh reaction conditions, high catalyst loadings and poor substrate scope.

erate yields with catalyst loadings down to 1.0 mol-% under mild reaction conditions. In contrast to most previously reported strategies, this protocol does not require substrate functional group activation, neither by electron-deficient aldehydes (2-oxo aldehydes) or electron-rich dienes (methoxy or amino-butadiene).

However, Matsubara et al. recently reported two strategies that exceed the previous work in this area. They showed that 5.0 mol-% iron(III)porphyrin {[Fe(TPP)]-BF<sub>4</sub>}<sup>[12a]</sup> (TPP = *meso*-tetraphenylporphyrinato) or iron(IV)corrole<sup>[12b]</sup> complexes efficiently catalyzed the oxa-Diels–Alder reaction of unactivated dienes with unactivated aldehydes under mild reaction conditions in high yields with a relatively broad substrate scope (Scheme 1, c).



Scheme 1. a)  $TrBF_4$ -catalyzed Diels-Alder, b)  $TrBF_4$ -catalyzed aza-Diels-Alder, c) oxa-Diels-Alder catalyzed by  $[Fe(TPP)]BF_4$  and trityl ion.

In our group we have recently applied carbocations as novel Lewis acid organocatalysts for various transformations, often with remarkably low catalyst loading and high yields.<sup>[13,14]</sup> In the course of our work we found that the

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trityl ion [e.g. triphenylcarbenium tetrafluoroborate (TrBF<sub>4</sub>)] is highly efficient for the activation of  $\alpha$ , $\beta$ -aldehydes and tosyl imines in the Diels–Alder reaction<sup>[14a,14b]</sup> and the aza-Diels–Alder reaction,<sup>[14b]</sup> respectively (Scheme 1, a and b).

Here we show the expansion of our research in this area by applying trityl tetrafluoroborate (TrBF<sub>4</sub>) as a catalyst for the oxa-Diels–Alder reaction of unactivated dienes with unactivated aldehydes under mild reaction conditions (Scheme 1, c). The reaction shows high efficiency with low catalyst loadings and constitutes a cheap, commercially available and metal free complement to Matsubara's previously reported iron complexes.<sup>[12]</sup>

#### **Results and Discussion**

The positively charged carbon atom of the trityl ion is isoelectronic to boron and owes its Lewis acidity to its lowlying empty  $p_{\rm C}$ -orbital capable of accepting electrons and thereby activating an interactive species. We therefore anticipated that the free electron pair on benzaldehyde would interact with the empty  $p_{\rm C}$ -orbital of the trityl ion to give oxonium ion intermediate **A** (Scheme 2). This would lower the LUMO of the carbon–oxygen bond facilitating the cycloaddition with unactivated dienes giving adduct **B**. Release of the 3,6-dihydropyran will regenerate the trityl ion catalyst.



Scheme 2. Trityl ion catalyzed oxa-Diels-Alder reaction.

Gratifyingly, in our initial experiments we found that in the presence of only 1.0 mol-% of trityl tetrafluoroborate (TrBF<sub>4</sub>), benzaldehyde (**1a**) and 2,3-dimethylbutadiene (**2a**) smoothly converted into the corresponding 3,6-dihydropyran adduct **3a** in 83% yield within 24 h at room temperature (Table 1, entry 2). Increasing of the catalyst loading to 5.0 mol-% had no effect on the yield; however, it substantially decreased the reaction time from 24 h to full conversion within one hour (Table 1, entry 1).

On the other hand, when the catalyst loading was reduced to 0.5 mol-% the conversion dropped dramatically and the reaction proceeded to 22% yield over 48 h before stopping, most likely due to catalyst deactivation (Table 1, entry 3).

The trityl ion constitutes a rather unique center of Lewis acidity that can be easily tuned by alteration of the elec-



Table 1. Optimization of reaction conditions for the hetro-Diels-Alder reaction.<sup>[a]</sup>

	+ +	Cat.	C C	X
	1a 2a		-	3a
Entry	Cat. [mol-%]	Solvent	<i>t</i> [h]	Yield <sup>[b]</sup> [%]
1	$TrBF_{4}(5.0)$	$CH_2Cl_2$	1	85
2	$TrBF_{4}$ (1.0)	$CH_2Cl_2$	24	83
3	$TrBF_4$ (0.5)	$CH_2Cl_2$	48	22
4	(p-MeOPh)(Ph)2Cl	$BF_4 CH_2Cl_2$	24	40
5	BF <sub>3</sub> OEt <sub>2</sub> (5.0)	$CH_2Cl_2$	24	54
6	$TiCl_4$ (5.0)	$CH_2Cl_2$	24	30
7	$HBF_{4}(5.0)$	$CH_2Cl_2$	24	29
8	AlCl <sub>3</sub> (5.0)	$CH_2Cl_2$	24	0
9	$TrBF_{4}$ (1.0)	DCE	24	61
10	$TrBF_{4}$ (1.0)	PhMe	24	32
11	$TrBF_{4}$ (1.0)	Et <sub>2</sub> O	24	5
12	$TrBF_{4}$ (1.0)	$CH_3NO_2$	24	0
13	$TrBF_{4}$ (1.0)	CH <sub>3</sub> CN	24	0

[a] The catalyst was added to a solution (0.3 M) of benzaldehyde and 2,3-dimethylbutadiene. [b] Determined by <sup>1</sup>H NMR spectroscopy using 1-methylnaphthalene as internal standard; DCE = dichloroethene.

tronic properties of the pendant aromatic rings.<sup>[14a,14b]</sup> As expected, the rate of reaction decreased as electron density of the aromatic ring increased (e.g., decreasing Lewis acidity of the carbocation), going from hydrogen to methoxy (Table 1, entry 4).

To evaluate the catalytic ability of the trityl ion, 5.0 mol-% of a series of Lewis and Brønsted acids were screened as catalyst for the oxa-Diels–Alder reaction.  $BF_3 \cdot OEt_2$ ,  $HBF_4 \cdot OEt_2$ , and  $TiCl_4^{[9b]}$  were found to be potent catalysts, although substantially less efficient than the trityl ion (Table 1, entries 5–7 vs. entry 1). Furthermore,  $AlCl_3$  was completely inactive as a catalyst for this reaction (Table 1, entry 8).

Performing the reaction in other solvents had a negative effect on the yield and less polar solvents DCE and toluene gave 61 and 32% yield of the product after 24 h, respectively (Table 1, entries 9 and 10). More polar solvents (Et<sub>2</sub>O, CH<sub>3</sub>NO<sub>2</sub> and CH<sub>3</sub>CN) almost completely suppressed the reactivity, most likely due to blocking of the Lewis acidic site of the carbocation, and only starting material was recovered (Table 1, entries 11–13).

After establishing the optimal reaction conditions for the oxa-Diels–Alder reaction we started to investigate the reaction of various benzaldehydes 1a-p with 2,3-dimethylbutadiene (2a; Table 2). Thus, under the standard reaction conditions (1.0 mol-% TrBF<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, room temp.) 2-naphthaldehyde 1b gave the corresponding 3,6-dihydropyran 3b in 93% yield (90% isolated yield, Table 2). Halogenated benzaldehydes were also found to be very good substrates for this transformation and gave the corresponding cycloaddition adducts 3c-h in high to excellent yields (Table 2). *p*-Nitro- and *o*-nitrobenzaldehyde 1i and 1j gave the cycloaddition products 3i and 3j in 95 and 99% yield, respec-

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tively. In contrast to the inhibiting effect of using acetonitrile as the solvent (cf. Table 1, entry 13), cyanobenzaldehyde derivatives (1k and 1l) were well tolerated to give the corresponding products 3k and 3l in good yields with only a slight decrease compared with the corresponding halogen and nitro substituents.

Table 2. Trityl catalysed hetro-Diels–Alder of aromatic aldehydes.  $^{[a,b]}$ 



[a] TrBF<sub>4</sub> (1.0 mol-%) was added to a solution (0.3 M) of aldehyde (1.5 equiv.) and diene (1.0 equiv.). [b] Yield was determined by <sup>1</sup>H NMR using 1-methylnaphthalene as internal standard. Yields in brackets are isolated yields. [c] 2.0 mol-% TrBF<sub>4</sub> was used. [d] 3.0 mol-% TrBF<sub>4</sub> was used. [e] 48 h reaction time. [f] After 72 h reaction time only decomposition of diene was observed.

In contrast to what could be expected, increasing the electron density on the aromatic ring of the aldehyde [Me-, MeO- (3m-p)] had only minor effect, both on yield and rate of the reaction. Thus, electron-donating moieties such as methyl (1m and 1n) or methoxy groups (1o and 1p) on the benzaldehyde gave high but in general somewhat lower yields than the electron-withdrawing groups and pyrans 3m-p could be isolated in 73–82% yield. Following this, we turned our attention towards different dienes. Isoprene (2b) turned out to be less reactive towards benzaldehyde (1a) than 2,3-dimethylbutadiene (2a), under the optimized reac-

tion conditions (1.0 mol-% TrBF<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, room temp.) and resulted in low yield and poor conversion. However, by increasing the catalyst loading to 2.0 mol-% full conversion of starting material was observed within 24 h and **3q** was isolated as a single regioisomer in 71% yield (Table 2). For the reaction of 2-naphthaldehyde **1b** and *p*-chlorobenzaldehyde with isoprene **2b** the catalyst loading had to be increased to 3.0 mol-% to obtain full conversion and under these reaction conditions the corresponding pyrans **3r** and **3s** were isolated as single regioisomers in excellent yields (Table 2).

The more sterically demanding 2,3-dibenzylbutadiene (2c) gave the corresponding adduct 3t in high yield in the presence of 2.0 mol-% TrBF<sub>4</sub>. Unfortunately, 1,3-cyclohexadiene (1u), cyclopentadiene (1v), 1,4-dipheylbutadiene (1w) and 2,4-hexadiene (1x) did not undergo oxa-Diels–Alder reactions, even after extensive optimization in terms of catalyst loading, reaction temperature or screening of different aromatic aldehydes (Table 2).

Although aromatic aldehydes provided satisfactory results in the oxa-Diels–Alder reactions, the use of alkyl aldehydes turned out to be more challenging. Thus, dihydrocinnamic aldehyde (**4a**) underwent an oxa-Diels–Alder reaction with 2,3-dimethylbutadiene (**2a**) under the optimized reaction conditions (1.0 mol-% TrBF<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, room temp.) to give pyran **5a** in only 44 % yield after 5 days. After further optimization of the reaction conditions the yield of **5a** was improved to 61 % by using 2.0 mol-% TrBF<sub>4</sub> and 24 h reaction time (Table 3). For the corresponding reaction with the less reactive diene, isoprene (**2b**), the catalyst loading had to be further increased to 3.0 mol-% to give dihydropyran **5e** in 69% yield. The more sterically demanding cyclohexanecarbaldehyde (**4b**) reacted very smoothly with 2,3-dimethylbutadiene (**2a**) in the presence of 2.0 mol-%

Table 3. Trityl-catalyzed oxa-Diels–Alder reactions of aliphatic aldehydes.  $^{[a,b]}$ 



[a] TrBF<sub>4</sub> (2.0 mol-%) was added to a solution (0.3 M) of aldehyde (1.5 equiv.) and diene (1.0 equiv.). [b] Yield was determined by <sup>1</sup>H NMR using 1-methylnaphthalene as internal standard. Yields in brackets are isolated yields. [c] 3.0 mol-% TrBF<sub>4</sub> and 48 h reaction time was used.

TrBF<sub>4</sub>, to give pyran **5b** in moderate yield over 24 h (Table 3). We were also intrigued to find that the acid sensitive acetaldehyde (**4c**) smoothly underwent an oxa-Diels-Alder reaction in the presence of 2.0 mol-% TrBF<sub>4</sub> to give 2,4,5-trimethyl-3,6-dihydro-pyran (**5c**) in 63% yield (Table 3). Interestingly, cyclopropanecarbaldehyde (**4d**) underwent the cycloaddition both with 2,3-dimethylbutadiene (**2a**) and isoprene (**2b**) to give **5d** and **5f**, respectively, in moderate yields without affecting the  $\alpha$ -cyclopropyl group.

#### Conclusions

In conclusion we have developed a trityl cation  $(TrBF_4)$ catalyzed oxa-Diels-Alder reaction of unactivated dienes and unactivated aldehydes that provides easy access to different 3,6-dihydropyran derivatives in good to excellent yields under mild reaction conditions and remarkably low catalyst loadings. In contrast to most previously reported strategies, this protocol does not require functional group activation of the substrates, neither by electron-deficient aldehydes (2-oxo aldehydes) or electron-rich dienes (methoxy or amino-butadiene) and this overcomes a severe limitation often associated with the oxa-Diels-Alder reaction. Further to the obvious benefits; cheap, commercially available and metal free catalyst, the low catalyst loadings, mild reaction conditions and high yields, this protocol stands out as a highly efficient complement to the few previously reported strategies.[8-12]

Despite the fact that the carbocation is a highly interesting and well-studied Lewis acid, it has received very limited attention as a catalyst for organic transformations and the selective reactivity demonstrated here shows the future potential of the carbocation as an environmentally friendly compliment to traditional metal and metalloid based Lewis acid catalysts. We are continuing to explore the scope and limitation of carbocation catalysis and these results will be reported in due course.

## **Experimental Section**

**General:** All reactions were performed in pre-dried solvents under nitrogen atmosphere (for further details see the Supporting Information).

**Preparation of 4,5-Dimethyl-2-phenyl-3,6-dihydro-2H-pyran (3a):** Benzaldehyde (**1a**; 192 mg, 1.8 mmol) and 2,3-dimethylbutadiene (**2a**; 100 mg, 1.2 mmol) were added to a solution of TrBF<sub>4</sub> (4 mg, 0.012 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL). After full conversion of the starting material (determined by <sup>1</sup>H NMR), the reaction mixture was quenched with a saturated NaHCO<sub>3</sub> aqueous solution. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (× 3), the combined organic phases were dried with MgSO<sub>4</sub> and the solvent was distilled off at ambient temperature. The residue was purified by flash chromatography (pentane/ethyl acetate; 95:5) to give the title compound (181 mg, 80% isolated yield). Spectral data were in accordance with those previously reported.<sup>[12a]</sup>

**Supporting Information** (see footnote on the first page of this article): Experimental procedures for the synthesis of all compounds. Characterization and spectroscopic data for all new compounds.

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