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Short Communication

Efficient asymmetric TADDOLs-organocatalyzed cycloaddition for the synthesis of allyltin derivatives

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ABSTRACT

We report here the results obtained in the study of organocatalytic asymmetric Diels–Alder reactions to optimize the synthesis of stereo defined allyltin derivatives using (*Z*)-2-(1-cyclohexenyl)-1-ethenyl(trineophyl)stannane (**1**) as diene and substituted dienophiles in the presence of (4R,5R)-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanol (TADDOL, **I**) and analogs (4R,5R)-α,α,α′,α′-tetra(1-naphtyl)-1,3-dioxolane-4,5-dimethanol (**II**) and (4R,5R)-α,α,α′,α′-tetra(9-phenantryl)1,3-dioxolane-4,5-dimethanol (**III**) as chiral catalysts to enhance stereoselectivity through hydrogen bond activation of the dienophile. Catalyst **II** provided excellent results and ultrasonic radiation at low temperature showed the shorter reaction times.

1. Introduction

Asymmetric organocatalysis is one of the three pillars of asymmetric synthesis. Transition metal complexes and enzymes were the most employed catalysts until the exponential growth of the field of organocatalysis in the last decade [1–3]. This subject now plays a valuable role in the synthesis of complex organic compounds and allows more selective, economically and environmentally friendlier transformations [4]. In these reactions, a small amount of an enantiomerically pure organocatalyst is used to produce large quantities of an optically active compound from a precursor that may be chiral or achiral [5]. On the other side, the field of organic synthesis has been greatly benefited since the development of the Diels–Alder reaction, recognized by the award of the Nobel Prize in Chemistry in 1950. With the potential of forming carbon – carbon, carbon – heteroatom and heteroatom – heteroatom bonds, the reaction is a versatile synthetic tool for constructing simple and complex molecules. Undoubtedly, it is one of the most efficient methods for the construction of six member rings built from a conjugated diene and a dienophile [6–9]. During the last 20 years, considerable research work has been made directed toward the development of enantioselective catalytic Diels–Alder reaction [10]. The enormous development of this reaction involves the use of chiral auxiliaries and chiral catalysts to induce enantioselectivity. The advances in both catalyst and substrate have been achieved regarding [4 + 2] cycloadditions. The latter area is based on the activation of the dienophile by hydrogen bonding with a chiral organocatalyst. This interaction blocks one face for the cycloaddition so the reaction occurs stereoselectively through the other face.

2. Experimental

2.1. General

All the reactions were performed under nitrogen or argon as indicated. The solvents used were dried and distilled in accordance with standard procedures. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded in $CDCl_3$ on a Bruker ARX 300 Multinuclear instrument (300.1 MHz for ^{1}H, 75.5 MHz for ^{13}C and 111.9 MHz for ^{119}Sn) at 23 °C and calibrated by using signals from solvents referenced to $SiMe_4$ (^{1}H, ^{13}C NMR) and with respect to Me_4Sn in the case of ^{119}Sn NMR spectra. Chemical shifts (δ) are reported in ppm and coupling constants (J) are in Hz. Compounds described in this work (**7**–**11**) were characterized by comparing their ^{1}H, ^{13}C and ^{119}Sn NMR spectra to the previously reported data [11]. The progress of the reaction and the purity of compounds were monitored by TLC analytical silica gel plates (Merck 60 F254). Visualization was accomplished by UV light and phosphomolybdic acid solution in ethanol by heating. Optical rotation measurements were performed

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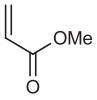
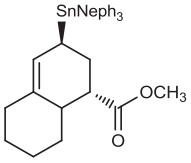
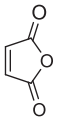
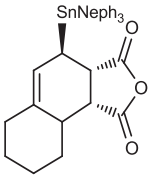
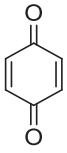
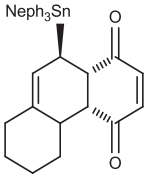
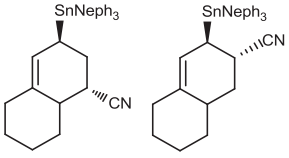
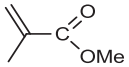
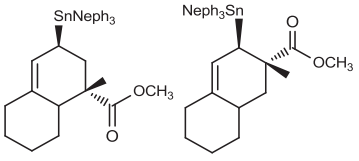
on a digital polarimeter IBZ Messtechnik, Polar L-μP. Gas chromatography (GC) was performed on a Shimadzu GC-14B instrument equipped with a FID detector and an ASTEC capillary column, CHIRALDEX Model, Type B-PM (30 m–0.32 mm i.d., permethyl-β-cyclodextrin as stationary phase). GC conditions are detailed in Supplementary Data. A Cole Parmer 4710 series ultrasonic homogenizer operating at 20 kHz (600 W) provided the high intensity ultrasound. External sonication was carried out using an ultrasonic probe (from Cole-Parmer 4710 series ultrasonic homogenizer of 20 kHz and 375 W) equipped with a 10 mm diameter titanium horn, which was immersed either in a water bath. Reactions were performed under argon in septum lid vials. Column chromatography was performed over neutral aluminum oxide or silica gel 60 70–230 mesh ASTM. All the solvents and reagents were of analytical grade. (*Z*)-2-(1-cyclohexenyl)-1-ethenyl(trineophyl)stannane (**1**) was prepared as described previously [10]. TADDOL derivatives **I**–**III** were prepared as described in the literature [12–14]. All the reactions with reasonable yields (>40%) according to Table 1 were injected as a dilute sample (1 μL) in order to determine the e.e. by GC-chiral chromatography, except in the case of entry 5, method C, catalyst II which was the only reaction with only one regioisomer despite the low yield (25%).

Table 1
Effect of TADDOL and TADDOL analogs (**I**–**III**) in Diels–Alder reactions (methods **A**–**D**) between diene **1** and some different activated dienophiles (**2**–**6**).

Entry	Dienophile	Method[a] (time, h)[b]	Catalyst	Yield (%)[c] (a:b)[f]	Product[e]
1	 **2**	A (70)	I	45	 **7**
		A (24)	II	80	
		A (70)	III	78	
		B (7)	I	15	
		B (2)	II	38	
		B (8)	III	35	
		C (72)	I	[d]	
		C (62)	II	25	
		C (72)	III	[d]	
		D (48)	$CHCl_3$	5	
2	 **3**	A (48)	I	40	 **8**
		A (24)	II	80	
		A (48)	III	75	
		B (7)	I	90	
		B (7)	II	95	
		B (7)	III	93	
		C (48)	I	92	
		C (12)	II	>99	
		C (48)	III	87	
		D (48)	$CHCl_3$	30	
3	 **4**	A (7)	I	85	 **9**
		A (5)	II	>99	
		A (7)	III	>99	
		B (10)	I	>99	
		B (2)	II	>99	
		B (10)	III	>99	
		C (28)	I	>99	
		C (12)	II	>99	
		C (28)	III	>99	
		D (7)	$CHCl_3$	30	
4	 **5**	A (70)	I	38 (80:20)	 **10** **10′** **(a : b)**
		A (72)	II	42 (>99:<1)	
		A (70)	III	[d]	
		B (10)	I	[d]	
		B (2)	II	49 (>99:<1)	
		B (10)	III	[d]	
		C (24)	I	[d]	
		C (24)	II	[d]	
		C (24)	III	[d]	
		D (48)	$CHCl_3$	[d]	
5	 **6**	A (70)	I	70 (50:50)	 **11** **11′** **(a : b)**
		A (72)	II	75 (75:25)	
		A (70)	III	30 (67:33)	
		B (10)	I	[d]	
		B (2)	II	20 (70:30)	
		B (10)	III	15 (69:31)	
		C (28)	I	[d]	
		C (24)	II	25 (>99:<1)	
		C (24)	III	[d]	
		D (48)	$CHCl_3$	[d]	

[a] Method **A**: organocatalyst, $CHCl_3$, 15 °C; Method **B**: organocatalyst, dry toluene, −30 °C, ultrasound (50–60 Hz); Method **C**: organocatalyst, dry toluene, −30 °C; Method **D**: $CHCl_3$, 15 °C, without organocatalyst.
[b] The optimal reaction time was established by taking samples and monitoring the product formation through TLC, ^{119}Sn and ^{1}H NMR until the reaction showed no changes.
[c] After chromatographic purification of the reaction mixture.
[d] Starting material.
[e] Structure characterization in reference [11].
[f] From ^{119}Sn NMR spectra of the reaction crude product.