Stereoselective Synthesis of Dihydropyran-4-ones *via* a Formal Hetero Diels−Alder Reaction and Ceric Ammonium Nitrate Dehydrogenation

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The synthesis of pyranoid rings continues to be a topical area of interest owing to the number of biologically important molecules that contain this important moiety.[1,2] Several methods have been developed for dihydropyran-4-one ring construction.[3] However, the hetero Diels−Alder[4] reaction with Danishefsky's diene[5−7] provides one of the most convenient entries into this class of compounds, and has provided the basis for a number of synthetic strategies. Furthermore, the application of asymmetric catalysis to this protocol has made it a very powerful synthetic tool.[8]

In this note, we describe a new approach to the dihydropyran-4-ones **4a**−**f** based on a novel ceric ammonium nitrate-induced dehydrogenation of 4-[(triisopropylsilyl)oxy]dihydropyrans **2a**−**f**,[9] which were prepared by a formal hetero Diels−Alder of the monoactivated (triisopropylsilyl)oxy diene **1**[10,11] with an array of aldehydes (Scheme 1). *The advantage of this strategy is the ability to isolate and directly functionalize the (triisopropylsilyl)oxy enol ethers* ***2***.[12−14] The (triisopropylsilyl)oxy diene **1** is a practical synthetic intermediate, owing to its resistance to acid-catalyzed hydrolysis, compared to the trimethylsilyl derivative, and generally affords the 2,3-disubstituted dihydropyran with improved diastereocontrol.[5,6] This increased stability of triisopropylsilyl derivatives has been attributed to steric hindrance at silicon created by the isopropyl groups which makes them more stable to proto-desilylation.[12−14]

Scheme 1

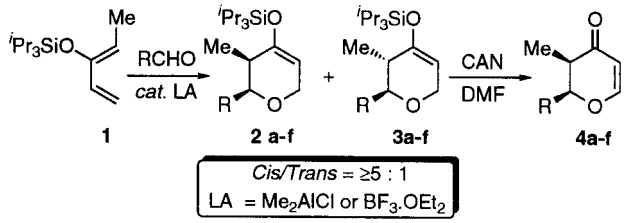

Table 1 summarizes the results for the optimization study using the (triisopropylsilyl)oxy diene **1** and benzaldehyde. The reactions were all carried out by initially precomplexing the aldehyde with the relevant Lewis acid followed by the addition of the diene **1**. Treatment of the aldehyde with stoichiometric zinc chloride followed by the diene **1** furnished the 2,3-disubstituted dihydropyrans **2a**/**3a** in modest yield favoring the *cis*-diastereoisomer (entry 1). The modest yield was attributed to hydrolysis of the diene **1** over the extended reaction time. Treatment of benzaldehyde with stoichiometric boron trifluoride etherate at −78 °C followed by addition of the diene **1** furnished the dihydropyrans **2a**/**3a** in excellent yield in a slightly improved 8.5:1 mixture of stereoisomers (entry 2). The diastereoselectivity was further improved using catalytic boron trifluoride etherate to afford the dihydropyrans **2a**/**3a** in 94% yield with a 28:1 preference for the *cis*-diastereoisomer (entry 3). Two aluminum-based Lewis acids were also examined. Treatment of benzaldehyde and the diene **1** under analogous conditions with a catalytic amount of trimethylaluminum led to recovered starting materials (entry 4). However, the same reaction with catalytic dimethylaluminum chloride at −78 °C furnished the dihydropyrans **2a**/**3a** in 93% yield as a 30:1 mixture of diastereoisomers (entry 5). Interestingly, the stereochemical outcome may be completely reversed by employing a stoichiometric amount of dimethylaluminum chloride at higher temperature (entry 6). The ability to alter the stereochemical outcome in this manner has been attributed to a Mukaiyama aldol (stepwise) rather than a formal hetero Diels−Alder (concerted) mechanistic pathway.[5,6]

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Table 1. Optimization of the Lewis Acid Catalyzed Hetero Diels−Alder of the Triisopropylsilyloxy Diene 1 with Benzaldehyde

entry	lewis acid[a]	(equiv)[b]	temp, °C	time (h)	ratio of **2a**/**3a**[c]	yield (%)[d]
1	$ZnCl_2$	(1.1)	rt	62	5:1	63
2	$BF_3{\cdot}Et_2O$	(1.1)	−78	1.5	8.5:1	93
3	$BF_3{\cdot}Et_2O$	(0.15)	−78	1.5	28:1	94
4	Me_3Al	(0.15)	−78	24	NA	0
5	Me_2AlCl	(0.15)	−78	3	30:1	93
6	Me_2AlCl	(1.1)	−20	1	1:17	80

[a] Reactions carried out on a 1 mmol reaction scale in anhydrous toluene. [b] The Lewis acid was precomplexed with the aldehyde prior to the addition of the TIPS diene **1**. [c] Ratios determined by capillary GLC analysis of the mixture. [d] Isolated yields.

Table 2 summarizes the results of the application of this protocol to various aldehydes. The reactions were all carried out with catalytic boron trifluoride etherate and dimethylaluminum chloride, to allow a direct comparison of the Lewis acids in terms of their efficiency and influence on the diastereoselectivity.[5,6] The alkyl and α,β-unsaturated aldehydes proved to be particularly sensitive under these reaction conditions. In order to circumvent this problem an alternative protocol was developed. The alkyl and α,β-unsaturated aldehydes were premixed (with the diene **1**) at the desired temperature, and a catalytic amount of Lewis acid was added to furnish the dihydropyrans **2**/**3c**−**f** in 75−95% yield with good to excellent diastereoselectivity (entries 3−6). This protocol presumably reduces competitive self-condensation of the aldehydes. The reduced diastereoselectivity for the 2-furaldehyde and 2-[(*tert*-butyldimethylsilyl)oxy]acetaldehyde is presumably due to competitive *exo*-addition under chelation control conditions, which is the direct result of the β-alkoxy substituent present in both aldehydes (entries 2 and 4).[5,6]

The triisopropylsilyl enol ether provides an ambiphilic synthon that may be transformed into a wide array of complementary functionality.[12−14] In this particular study the triisopropylsilyl enol ethers were converted directly to the dihydropyran-4-ones *via* a novel ceric ammonium nitrate-induced dehydrogenation to allow a direct comparison with related synthetic strategies.[9] Treatment of the *cis*-4-[(triisopropylsilyl)oxy]dihydropyrans **2a**−**f** with ceric ammonium nitrate at 0 °C furnished the *cis*-2,3-disubstituted dihydropyran-4-ones **4a**−**f** in excellent yield (entries 1−6). Furthermore, the 3-methyl substituent did not equilibrate to the thermodynamically more stable *trans*-2,3-disubstituted dihydropyran-4-ones under the reaction conditions.

In conclusion, we have applied the novel ceric ammonium nitrate dehydrogenation of triisopropylsilyl enol ethers to a hetero Diels−Alder/dehydrogenation sequence for the conversion of (triisopropylsilyl)oxy dienes, *via* triisopropylsilyl enol ethers, to the corresponding *cis*-2,3-disubstituted dihydropyran-4-ones with improved diastereocontrol. The advantage of this approach is the ability to isolate and further functionalize the triisopropylsilyl enol ethers **2**, making this method for dihydropyran ring construction particularly attractive for target directed synthesis.[12−14]

Experimental Section

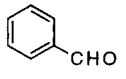
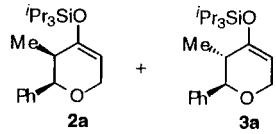
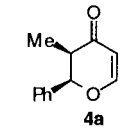
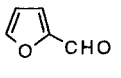
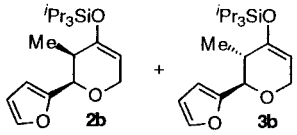
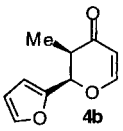
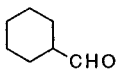
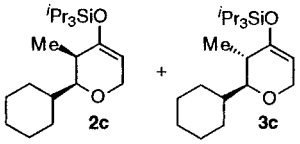
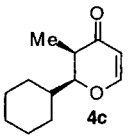
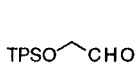
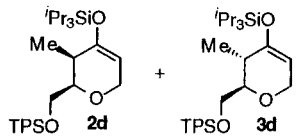
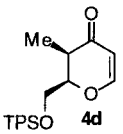
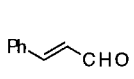
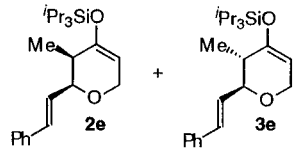
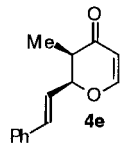
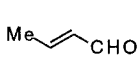
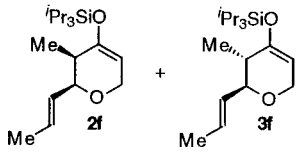
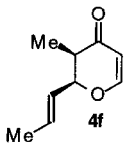
General. The chemical shifts of the ^{1}H-NMR and ^{13}C-NMR spectra were all recorded relative to chloroform or benzene. Multiplicities were determined with the aid of an APT sequence, separating methylene and quaternary carbons = e (even), from methyl and methine = o (odd). GC analysis was carried out using an HP 5890 GC Series 2 using an Rtx-5 high performance capillary column (flow rate: 1 mL/min). The GC temperature program was 150 °C for 1 min, 150−200 °C at 10 °C/min, and then 200−250 °C at 3 °C/min. All compounds were purified as specified and gave spectroscopic data consistent with being ≥95% of the assigned structure. Analytical TLC was carried out on precoated 0.2 mm thick Merck 60 F_{254} silica plates. Flash chromatography was carried out using Merck Silica Gel 60 (230−400 mesh).

(*Z*)-3-[(Triisopropylsilyl)oxy]-1,3-pentadiene (1). Freshly-distilled ethyl vinyl ketone (1.632 g, 20.0 mmol) was dissolved in anhydrous THF (150 mL) and cooled with stirring to *ca.* −78 °C under an atmosphere of dry nitrogen. Triisopropylsilyl trifluoromethanesulfonate (6.6 mL, 24.0 mmol) was then added *via* syringe, followed by the dropwise addition of potassium bis-(trimethylsilyl)amide (5.04 g, 24.0 mmol) in THF (50 mL) over a period of *ca.* 45 min. The resulting cloudy white slurry was stirred at −78 °C for 30 min and then was allowed to warm to room temperature and stirred for an additional 1 h. The reaction mixture was then poured into saturated aqueous sodium bicarbonate and extracted with diethyl ether. The organic layers were combined, washed with saturated NaCl solution, dried over anhydrous Na_2SO_4, and filtered, and the solvent was removed *in vacuo* to afford a colorless crude oil. Purification by flash chromatography on silica gel (eluting with *n*-pentane), followed by Kugelröhr distillation under reduced pressure (oven temperature 100−110 °C at 2.0 mmHg) afforded the diene **1** (4.038 g, 84%) as a colorless oil. The *Z*:*E* ratio was determined by ^{1}H-NMR to be ≥19:1: IR ($CDCl_3$) 2946 (s), 2893 (s), 2868 (s), 1645 (m), 1596 (m) cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6) δ 6.13 (dd, J = 17.1, 10.8 Hz, 1H), 5.43 (dd, J = 17.1, J = 0.6 Hz, 1H), 4.90 (dd, J = 10.5, 0.6 Hz, 1H), 4.69 (q, J = 7.0 Hz, 1H), 1.63 (d, J = 7.0 Hz, 3H), 1.25−1.12 (m, 3H), 1.14 (d, J = 4.9 Hz, 18H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 150.54 (e), 136.16 (o), 111.40 (e), 108.19 (o), 18.03 (o), 13.83 (o), 11.46 (o); HRMS (EI) calcd for $C_{14}H_{28}OSi$ 240.1909, found 240.1904.

General Experimental Procedures for the Hetero Diels−Alder Reactions. (*2R*,3R)-3-Methyl-2-phenyl-4-[(triisopropylsilyl)oxy]-2,3-dihydropyran (2a).** Method A: Precomplexation Protocol. Benzaldehyde (0.107 g, 1.01 mmol) was dissolved in anhydrous toluene (5 mL, freshly distilled from CaH_2) and cooled with stirring to −78 °C under an atmosphere of argon. Dimethylaluminum chloride (150 μL, 0.15 mmol, 1.0 M in hexanes) was added and the colorless solution stirred for 15 min. The (triisopropylsilyl)oxy diene **1** (0.266 g, 1.11 mmol) was then added, resulting in a pale yellow solution. The reaction mixture was then stirred for an additional *ca.* 3 h (TLC control). The reaction was then quenched by the addition of saturated $NaHCO_3$ solution (1 mL) and allowed to warm to ambient temperature. The reaction mixture was poured into saturated $NaHCO_3$ solution and extracted with diethyl ether. The combined organic phases were then washed with saturated NaCl solution and dried over anhydrous Na_2SO_4, and the solvent was removed *in vacuo* to afford a colorless oil. Purification by flash chromatography on silica gel (eluting with 1−4% ethyl acetate in hexane gradient) furnished the dihydropyrans **2a**/**3a** (0.324 g, 93%) in an 30:1 ratio of diastereoisomers as a colorless oil. The stereoisomers were easily separable at this stage to afford the *cis*- and *trans*-diastereoisomers **2a** and **3a** respectively: IR ($CDCl_3$) 3032 (w), 2946 (s), 2894 (m), 2868 (s), 1713 (m), 1683 (m) cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.36−7.19 (m, 5H), 4.79−4.77 (m, 1H), 4.73 (d, J = 3.1 Hz, 1H), 4.39−4.25 (m, 2H), 2.30−2.21 (m, 1H), 1.36−1.02 (m, 3H), 1.10 (d, J = 5.8 Hz, 18H), 0.80 (d, J = 6.9 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 153.34 (e), 140.72 (e), 128.03 (o), 126.74 (o), 125.58 (o), 99.07 (o), 78.64 (o), 65.25 (e), 40.00 (o), 18.06 (o), 12.68 (o), 12.39 (o); HRMS calcd for $C_{21}H_{34}O_2Si$ 346.2328, found 346.2306.

(*2R*,3R)-3-Methyl]-2-[(*E*)-2-phenylethenyl]-4-[(triisopropylsilyl)oxy]-2,3-dihydropyran (2e).** Method B: Internal Quench Protocol. *trans*-Cinnamaldehyde (0.134 g, 1.01 mmol) and the (triisopropylsilyl)oxy diene **1** (0.266 g, 1.11 mmol) were dissolved in anhydrous toluene (5 mL, freshly distilled from CaH_2) and cooled with stirring to −40 °C under an atmosphere of argon. Dimethylaluminum chloride (150 μL, 0.15 mmol) was added to the colorless solution and the resulting pale yellow solution stirred for an additional *ca.* 3.5 h (TLC control). The reaction was quenched, worked-up, and purified as above to

Table 2. Synthesis of 4-[(Triisopropylsilyl)oxy]dihydropyrans 2a–f and Their Conversion to 2,3-Disubstituted Dihydropyran-4-ones 4a–f

entry	aldehyde[a]	tips enol ethers	method[b]	temp	Lewis acid	ratio[c]	yield (%)[d]	dihydropyran-4-ones[e]	yield (%)[d]
1		 **2a** + **3a**	A	–78 °C	$BF_3{\cdot}OEt_2$	≥19 : 1	94	 **4a**	92
			A	"	Me_2AlCl	≥19 : 1	93		
2		 **2b** + **3b**	A	–40 °C	$BF_3{\cdot}OEt_2$	5 : 1	95[f]	 **4b**	72
			A	"	Me_2AlCl	2 : 1	95		
3		 **2c** + **3c**	B	–78 °C	$BF_3{\cdot}OEt_2$	≥19 : 1	85	 **4c**	86
			B	"	Me_2AlCl	≥19 : 1	95		
4		 **2d** + **3d**	B	–40 °C	$BF_3{\cdot}OEt_2$	7 : 1	85[g]	 **4d**	91
			B	"	Me_2AlCl	4 : 1	83		
5		 **2e** + **3e**	B	–40 °C	$BF_3{\cdot}OEt_2$	≥19 : 1	83	 **4e**	91
			B	"	Me_2AlCl	≥19 : 1	93		
6		 **2f** + **3f**	B	–40 °C	$BF_3{\cdot}OEt_2$	≥19 : 1	75	 **4f**	87
			B	"	Me_2AlCl	≥19 : 1	88		

[a] All the reactions were carried out on a 1.0 mmol reaction scale. [b] Method A: Aldehyde pre-complexed with the Lewis acid prior to the addition of the diene **1**; Method B: Lewis acid added to a precooled mixture of the diene **1** and the aldehyde. [c] Ratios of diastereoisomers determined by 400 MHz ^{1}H-NMR integration. [d] Isolated yields. [e] Ceric ammonium nitrate (4.0 eq), anhydrous DMF, 0 °C, 2 hours. [f] The mixture of diastereoisomers **2b/3b** (5 : 1) were separable by column chromatography. [g] The inseparable mixture of diastereoisomers **2d/3d** (7 : 1) was dehydrogenated to give the 2,3-disubstituted dihydropyran-4-one **4d** as a 7 : 1 ratio, favoring the *cis*-diastereoisomer.

afford the dihydropyran **2e** (0.358 g, 93%) as a colorless oil: IR ($CDCl_3$) 2946 (s), 2893 (m), 2868 (s), 1670 (m) cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.41–7.18 (m, 5H), 6.63 (A of AB, J_{AB} = 16.1 Hz, 1H), 6.21 (ABX, J_{AB} = 16.1, J_{BX} = 5.6 Hz, 1H), 4.73 (t, J = 2.7 Hz, 1H), 4.30–4.24 (m, 3H), 2.15–2.11 (m, 1H), 1.22–0.98 (m, 24H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 153.02 (e), 137.12 (e), 130.43 (o), 128.52 (o), 128.28 (o), 127.44 (o), 126.42 (o), 99.09 (o), 77.68 (o), 64.87 (e), 39.20 (o), 18.04 (o), 12.67 (o); HRMS (EI) for $C_{23}H_{36}O_2Si$, calcd 372.2485, found 372.2485.

General Procedure for the Dehydrogenation of Triisopropylsilyl Enol Ethers to Dihydropyran-4-ones. (*2R*, 3R)-3-Methyl-2-((*E*)-2-phenylethenyl)-2,3-dihydro-4*H*-pyran-4-one[8e] (4e).** The triisopropylsilyl enol ether **2e** (0.379 g, 1.02 mmol) was dissolved in anhydrous dimethylformamide (10 mL) and cooled with stirring to 0 °C under a nitrogen atmosphere. Ceric ammonium nitrate (2.183 g, 3.98 mmol) was then added portionwise over *ca.* 30 min. The resulting bright orange solution was then stirred for an additional 3 h (TLC control). The reaction mixture was then poured into water and extracted with diethyl ether. The combined organic phases were washed with saturated $NaHCO_3$ solution, saturated NaCl solution, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to afford a pale yellow oil. Purification by flash chromatography on silica gel (eluting with 10% and then 30% ethyl acetate in hexane) furnished the *cis*-2,3-disubstituted dihydropyran-4-one **4e** (0.199 g, 91%) as a colorless oil.

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Supporting Information Available: Full characterization for compounds **2b**,**c**, **2**/**3d**, **2f**, **3a**/**b**, and **4a–f**, in addition to the ^{1}H-NMR spectra for compounds **1**, **2a–f**, **3a**/**b**, and **4a–f** (19 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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