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Highly Stereoselective Hetero Diels-Alder Reactions of Chiral 3-(*p*-Tolylsulfinyl)-2-furaldehyde with Danishefsky's Diene Promoted by a Lanthanoid Lewis Acid

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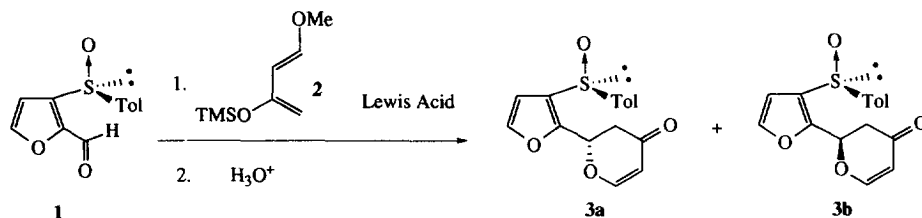
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Abstract: Hetero Diels-Alder reactions of optically active 3-(*p*-tolylsulfinyl)-2-furaldehyde with 1-methoxy-3-(trimethylsilyloxy)-buta-1,3-diene (Danishefsky's diene) in the presence of a Lewis acid has been examined. The reaction in the presence of 1.0 equiv. of Ln(OTf)₃ (Ln = Yb, Nd and Sm) followed by acidic work-up produced in good yields (68-88%) the hetero Diels-Alder adduct with high diastereoisomeric excesses (93-98% d.e.'s), whereas in the presence of an NMR shift reagent, tris(2,2,6,6-tetramethyl-3,5-heptanedionate)europium [Eu(thd)₃] the corresponding diastereoisomer was obtained as the major adduct in excellent yield with 77% d.e. Copyright © 1996 Elsevier Science Ltd

Asymmetric hetero Diels-Alder reactions have provided a useful method for construction of an enantio-enriched six-membered heterocyclic ring.¹ Particularly for the enantioselective synthesis of six-membered O-heterocycles, two hetero Diels-Alder methodologies have been developed: 1) the reactions of aldehyde and silyloxy diene by the use of a chiral Lewis acid promoter,² especially, NMR shift reagents and 2) the use of the oxy-diene bearing a chiral auxiliary attached to the oxy group³ and of the aldehyde bearing a chiral auxiliary.⁴

Having shown that the aldehydic part of the chiral sulfinyl furfural **1**⁵ gave high diastereoselectivity in Lewis acid-mediated allylation reaction, we were intrigued by the dienophilic reactivity and diastereoselectivity of the aldehyde **1** in hetero Diels-Alder reactions with 1-methoxy-3-(trimethylsilyloxy)-buta-1,3-diene (Danishefsky's diene) **2**. To date, most studies⁶ on Lewis acid-promoted Diels-Alder reactions using chiral sulfoxides as a dienophile have dealt with α -sulfinylacrylate derivatives whose sulfinyl oxygen should coordinate tightly with the Lewis acid and the acrylic carbonyl, resulting in a favorable formation of a conformationally rigid six-membered chelate. However, there have been no reports concerning the sulfinyl's directing role with respect to a remote reactive site, *i.e.*, the β -position with respect to the sulfinyl group, in Diels-Alder reactions including hetero Diels-Alder reactions. We describe here a highly diastereoselective hetero Diels-Alder reaction between a β -sulfinyl aldehyde **1** and Danishefsky's diene **2**.

Table 1: Hetero Diels-Alder Reaction of **1** with Danishefsky's Diene **2** in the presence of a Lewis Acid

| Entry | Lewis acid | (Equiv.) | Reaction Conditions | | | Total Yield / % | D.e. / % ^{b)} |
|-------|------------------------------------|----------|---------------------------------|------------|----------|-----------------|------------------------|
| | | | Solvent | Temp. / °C | Time / h | | |
| 1 | ZnCl ₂ | 1.0 | CH ₂ Cl ₂ | 25 | 18 | 67 | 0 |
| 2 | ZnCl ₂ | 1.0 | THF | 25 | 15 | 63 | 0 |
| 3 | ZnI ₂ | 1.0 | THF | 25 | 8 | 62 | 0 |
| 4 | YbCl ₃ | 1.0 | toluene | 25 | 12 | 56 | 54 |
| 5 | CeCl ₃ | 1.0 | CH ₂ Cl ₂ | 25 | 11 | 58 | 81 |
| 6 | Yb(OTf) ₃ | 1.0 | toluene | -20 | 13 | 59 | 85 |
| 7 | Yb(OTf) ₃ | 1.0 | CH ₂ Cl ₂ | -20 | 10 | 29 | 92 |
| 8 | Yb(OTf) ₃ | 1.0 | THF | -20 | 2 | 88 | 93 |
| 9 | Nd(OTf) ₃ | 1.0 | THF | -20 | 2 | 68 | 98 |
| 10 | Sm(OTf) ₃ | 1.0 | THF | -20 | 2 | 73 | 97 |
| 11 | Yb(OTf) ₃ | 0.2 | THF | 25 | 9 | 26 | 85 |
| 12 | Eu(thd) ₃ ^{a)} | 1.0 | CH ₂ Cl ₂ | 25 | 21 | 92 | -77 |
| 13 | Eu(thd) ₃ | 0.5 | CH ₂ Cl ₂ | 25 | 20 | 93 | -75 |
| 14 | Eu(thd) ₃ | 0.1 | CH ₂ Cl ₂ | 25 | 17 | 21 | -55 |
| 15 | Eu(thd) ₃ | 0.5 | THF | 25 | 16 | 3 | -66 |

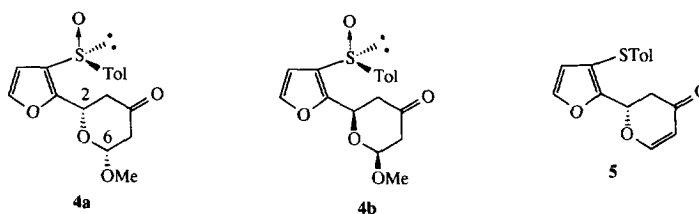
^{a)} Eu(thd)₃ = Tris(2,2,6,6-tetramethyl-3,5-heptanedionate)europium. ^{b)} The negative sign indicates that the adduct **3b** in excess is diastereoisomeric to the adduct **3a**.

All the reactions were carried out by using 1.5 equimolar amounts of **2** to **1** in 0.1-0.4 mmol scale (Table 1). At first we examined the reactions utilizing Lewis acids of the type ZnX₂ as a reaction promoter. Although these reactions proceeded smoothly to give the adduct in good yields after an acidic work-up, essentially equal amounts of two diastereoisomers **3a** and **3b** were produced (entries 1-3). The disappointing level of asymmetric induction led us to examine the other Lewis acids. The reactions under the same conditions performed by some other Lewis acids (YbCl₃ and CeCl₃) gave good diastereoselectivity with up to 81% diastereoisomeric excess (d.e.) (entries 4 and 5).

On the other hand in the presence of 1.0 equiv. of a lanthanide triflate in THF at -20 °C the reaction furnished the adduct **3a** with high diastereoselectivity (up to 98% d. e.) in high yields (entries 8-10), whilst the use of smaller amounts of the lanthanide triflate or the reactions in other solvent (toluene and dichloromethane) gave lower selectivity (up to 85% d.e.) and/or unsatisfactory yields (entries 6, 7 and 11). Furthermore the reaction conducted with higher temperature *i.e.* 25 °C also resulted in lower selectivity.

In contrast, in the presence of 1.0 equiv. of an NMR shift reagent, tris(2,2,6,6-tetramethyl-3,5-heptanedionate)europium [Eu(thd)₃] in CH₂Cl₂, the other diastereoisomeric adduct **3b** was formed as the major product in 92% combined yield with 77% d.e. (entry 12). The yield of the hetero Diels-Alder adduct **3b** decreased with the catalytic amount of the Lewis acid (entry 14). The use of tetrahydrofuran (THF) as the solvent in the reaction did not give the product in substantial yield (entry 15).

Major adduct **3a** derived from the reactions using the lanthanide triflate was easily isolated by simple crystallization from the original mixture of **3a** and **3b**. Major isomer **3b** in Eu(thd)₃-promoted cycloaddition was isolable as an oily material after a trifluoroacetic acid work-up followed by HPLC separation.



The stereochemistry of both the adducts **3a** and **3b** was assigned to be as shown in Table 1 by the following reaction sequence. It was found that a crystalline material **3a** was unsuitable for single-crystal X-ray analysis due to its mobility. Since the primary products in the hetero Diels-Alder reaction were supposed to be **4a** and **4b**, we decided to use these adducts instead of **3** for determination of the relative stereochemistry with respect to the sulfinyl center and the pyranone ring. Fortunately the major adduct, derived from the reaction of (\pm)-**1** with **2** in the presence of 1.0 equiv. of Eu(thd)₃ followed by successive treatment with triethylamine, was isolable and found to be suitable for X-ray analysis, possessing structure **4b** (Fig. 1). The primary product (\pm)-**4b** obtained was converted into (\pm)-**3b** upon exposure to trifluoroacetic acid. Therefore, the major adduct from the lanthanide triflate-promoted hetero Diels-Alder reaction possessed structure **3a**, and the stereochemistry of **3a** was thus assigned as 2*S*. Attempts to isolate the primary adduct **4a** were unsuccessful because the product is unstable to acid which is needed for an isolative work-up after the cycloaddition. The diastereoisomeric relationship between **3a** and **3b** was also confirmed by deoxygenation of the sulfinyl group of **3a** with Zn/TiCl₄⁷ followed by oxidation of the resulting sulfide **5** with 3-chloroperoxybenzoic acid to give rise to a 1:1 mixture of **3a** and the enantiomer of **3b** (= *ent*-**3b**).

In conclusion, it is worth to note that the use of lanthanide triflates as a reaction promoter in hetero Diels-Alder reaction of sulfinyl aldehyde and the diene gave the adduct with a high degree of diastereoselectivity. On the other hand the reaction using Eu(thd)₃ showed a dramatical reversal in diastereoselectivity. Investigation on the mechanistic aspects for the reaction is now in progress.

Experimental

Melting points were taken with a Yanagimoto micro melting-point apparatus and are uncorrected. IR spectra were measured in CHCl₃ solution on a JASCO IRA-1 spectrophotometer. ¹H-NMR spectra were recorded on a JEOL JNM-GX270 (270 MHz) spectrometer with CDCl₃ as the solvent; *J* values are in hertz (Hz). Tetramethylsilane was used as an internal standard. Mass spectra were recorded with a JEOL JMS D-300 spectrometer. Optical rotations were measured on a JASCO DIP-360 digital polarimeter. All organometallic and low temperature reactions were carried out in oven-dried glassware under a slightly positive pressure of argon. All solvents were distilled prior to use. Extracts were dried over anhydrous

MgSO₄ before evaporation of solvents in a rotary evaporator. 3-Chloroperoxybenzoic acid was used after purification by washing with phosphate buffer of pH 7.5 according to the literature method.⁸ Flash chromatography was performed with Merck 230-400 mesh silica gel. Preparative HPLC was carried out on a ceramic pump (Eyela VSP-3050) using a prepacked silica-gel column (Kusano Kagaku, 5 μm). HPLC and chiral HPLC analyses were performed on a Shimadzu LC-6A pump using a silica-gel column (Develosil 60, Nomura Chemicals) and Chiralcel OD (Daicel Chemical Industries Ltd), respectively, with monitoring of the 254 nm. Peak ratios on HPLC were measured with an integrator (Shimadzu Chromatopac C-R6A).

Typical Procedure for the Hetero Diels-Alder Reaction of 1 with 2 Promoted by a Lewis Acid In a flame-dried flask was placed ytterbium triflate (397 mg, 0.64 mmol) and **1**⁵ (150 mg, 0.64 mmol) in dry THF (18 ml) at -20 °C and the mixture was stirred for 30 min at that temperature. Diene **2** (0.19 ml, 0.96 mmol) in dry THF (3 ml) was then added to this solution *via* a syringe, and the mixture was stirred for 2 h. The resulting mixture was treated with 3% HCl (7 ml) and the mixture was stirred for 30 min. The organic phase was separated and the aqueous layer was extracted with EtOAc (15 ml x 3). The combined extracts were washed with saturated brine (20 ml), dried, and concentrated *in vacuo*. The crude product was subjected to flash chromatography on silica with hexane/AcOEt (3:2→1:2) to give a mixture of **3a** and **3b** (170 mg, 88%) in a ratio of 96.5:3.5. The diastereoisomeric excess was determined by HPLC analysis [hexane/EtOAc (1:1); flow rate 1 ml/min; *t*_R **3a** 28 min; *t*_R **3b** 23 min]. The major adduct **3a** for the reaction was purely isolated by recrystallization from the mixture of **3a** and **3b** with hexane-EtOAc in 64% yield. The other adduct **3b** was also isolable by preparative HPLC (hexane-AcOEt, 5:2) of the enriched mixture derived from the reaction in the presence of Eu(thd)₃.

(2*S*,*S*₈)-2-[3-(*p*-Tolylsulfinyl)-2-furyl]-2,3-dihydro-4*H*-pyran-4-one **3a**⁹: mp 98-100 °C (from hexane/EtOAc), [α]_D²⁰ -34.2 (*c* = 1.0, acetone). IR (CHCl₃): 3000, 1680, 1600, 1400, 1270, 1080, 1020, 980 cm⁻¹. ¹H-NMR (CDCl₃) δ: 2.42 (3 H, s, Me), 2.74 (1 H, ddd, *J* = 17.1, 3.9, 1.0, CHH), 3.24 (1 H, dd, *J* = 17.1, 13.4, CHH), 5.57 (1 H, dd, *J* = 6.1, 1.0, CH=), 5.95 (1 H, dd, *J* = 13.4, 3.9, COH), 6.38 (1 H, d, *J* = 2.0, furan), 7.33 (2 H, d, *J* = 8.3, Tol), 7.41 (1 H, d, *J* = 6.1, CH=), 7.44 (1 H, d, *J* = 2.0, furan), 7.53 (2 H, d, *J* = 8.3, Tol). MS: *m/z* 285 (M⁺-OH), 229, 215, 203, 187, 169. *Anal.* Calcd for C₁₆H₁₄O₄S: C, 63.56; H, 4.67. Found: C, 63.40; H, 4.66.

(2*R*,*S*₈)-2-[3-(*p*-Tolylsulfinyl)-2-furyl]-2,3-dihydro-4*H*-pyran-4-one **3b**: an oil, [α]_D²¹ -118.7 (*c* = 1.1, acetone). IR (CHCl₃): 3000, 1680, 1600, 1400, 1270, 1080, 1020, 980 cm⁻¹. ¹H-NMR (CDCl₃) δ: 2.41 (3 H, s, Me), 2.67 (1 H, ddd, *J* = 16.8, 3.9, 1.0, CHH), 3.25 (1 H, dd, *J* = 16.8, 13.5, CHH), 5.55 (1 H, dd, *J* = 6.2, 1.0, CH=), 5.92 (1 H, dd, *J* = 13.5, 3.9, COH), 6.38 (1 H, d, *J* = 1.9, furan), 7.32 (2 H, d, *J* = 8.2, Tol), 7.42 (1 H, d, *J* = 6.2, CH=), 7.43 (1 H, d, *J* = 1.9, furan), 7.54 (2 H, d, *J* = 8.2, Tol). MS: *m/z* 285 (M⁺-OH), 215, 203, 187, 169, 161. HRMS *m/z* M⁺-OH Calcd for C₁₆H₁₃O₃S : 285.0585. Found: 285.0596.

(2*R**,6*S**,*S*₈*)-2-[3-(*p*-Tolylsulfinyl)-2-furyl]-6-methoxy-2,3,5,6-tetrahydro-4*H*-pyran-4-one **4b**: A mixture of (±)-**1**⁵ (100 mg, 0.42 mmol) and Eu(thd)₃ (150 mg, 0.21 mmol) in CH₂Cl₂ (5 ml) was treated with **2** (0.12 ml, 0.64 mmol) at 25 °C for 20 h. The mixture was then treated with triethylamine (3 ml) in MeOH (1.5 ml) and the solvents were evaporated. The residue was purified by flash chromatography on silica with hexane-EtOAc (3:1→1:1) to give the adducts (135 mg, 95%) as a semi-solid, which was recrystallized from hexane-EtOAc, giving an analytical sample of (±)-**4b** for X-ray crystallography.

(±)-**4b**: mp 115 °C (hexane/EtOAc). IR (CHCl₃): 3020, 1730, 1385, 1270, 1145, 1040, 895 cm⁻¹. ¹H-NMR (CDCl₃) δ: 2.41 (3 H, s, Me), 2.59 (1 H, ddd, *J* = 14.9, 8.1, 1.5, CH), 2.64 (1 H, dd, *J* = 14.9, 8.1, CH), 2.79 (1 H, ddd, *J* = 15.3, 3.1, 1.5, CH), 3.08 (1 H, dd, *J* = 15.3, 11.8, CH), 3.54 (3 H, s, OMe), 4.82 (1 H, dd, *J* = 8.1, 2.9, CHOMe), 5.25 (1 H, dd, *J* = 11.8, 3.1, COH), 6.38 (1 H, d, *J* = 2.1, furan), 7.31 (2 H, d, *J* = 8.1, Tol), 7.40 (1 H, d, *J* = 2.1, furan), 7.54 (2 H, d, *J* = 8.1, Tol). MS: *m/z* 317 (M⁺-OH), 285, 233, 217, 187, 83. *Anal.* Calcd for C₁₇H₁₈O₅S: C, 61.06; H, 5.43. Found: C, 60.85; H, 5.41.

Conversion of (\pm)-4b into (\pm)-3b by Acid Treatment The acetal (\pm)-4b (8.1 mg) was treated with trifluoroacetic acid (4 drops) in CHCl_3 (0.5 ml) and CCl_4 (0.5 ml) at room temperature for 19 h. The solvents were evaporated off and the crude mixture was purified by preparative TLC (hexane-EtOAc 1:1) to afford (\pm)-3b (5.7 mg, 78%), whose spectral data were in good agreement with those of ($-$)-3b.

Reduction of 3a with Zn/TiCl₄ To a solution of 3a (60 mg, 0.2 mmol) in dry Et_2O (8 ml) at 0 °C was added activated Zn (52 mg, 0.79 mg atom) followed by TiCl_4 (0.5 M in CH_2Cl_2 , 0.79 ml, 0.4 mmol). After being stirred at 0 °C for 10 min, the mixture was quenched with H_2O (8 ml). The organic phase was separated and the aqueous layer was extracted with Et_2O (8 ml x 3). The combined extracts were washed with saturated brine (15 ml), dried, and concentrated. The residue was purified by flash chromatography on silica with hexane-AcOEt (4:1) to give (+)-5 (34 mg, 60%).

The reduction of 3b under the same conditions afforded ($-$)-5. The enantiomeric excesses of (+)-5 and ($-$)-5 were shown to be 96% and 95%, respectively, by chiral HPLC [hexane/2-propanol (100:1); flow rate 0.7 ml/min; t_R (+)-5 47 min; t_R ($-$)-5 43 min]. The e.e.'s of 3a and 3b were thus estimated as $\geq 96\%$ and $\geq 95\%$, respectively. A racemic sample (\pm)-5 was prepared by deoxygenation of the product derived from the reaction of (\pm)-1 and 2.

(2S)-2-[3-(*p*-Tolylsulfonyl)-2-furyl]-2,3-dihydro-4H-pyran-4-one 5: an oil, $[\alpha]_D^{25} +35.0$ ($c = 1.7$, acetone). IR (CHCl_3): 1675, 1600, 1495, 1275, 1035, 980, 920 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ : 2.31 (3 H, s, Me), 2.55 (1 H, dddd, $J = 17.0, 3.7, 1.2, 0.5$, CHH), 3.28 (1 H, dd, $J = 17.0, 14.2$, CHH), 5.50 (1 H, dd, $J = 6.1, 1.2$, CH=), 5.70 (1 H, dd, $J = 14.2, 3.7$, COH), 6.42 (1 H, d, $J = 2.0$, furan), 7.07 (2 H, d, $J = 8.7$, Tol), 7.11 (2 H, d, $J = 8.7$, Tol), 7.38 (1 H, dd, $J = 6.1, 0.5$, CH=), 7.51 (1 H, d, $J = 2.0$, furan). MS: m/z 286 (M^+), 216, 201, 183, 155, 131. HRMS: m/z M^+ Calcd for $\text{C}_{16}\text{H}_{14}\text{O}_3\text{S}$: 286.0663. Found: 286.0659.

Oxidation of 5 with 3-Chloroperoxybenzoic Acid To a solution of 5 (12 mg, 0.04 mmol) in dry CH_2Cl_2 (0.5 ml) at 0 °C was added purified 3-chloroperoxybenzoic acid (7.7 mg, 0.044 mmol). After being stirred at 0 °C for 20 min, the mixture was diluted with CHCl_3 (10 ml). The organic phase was washed with saturated brine (5 ml), dried, and concentrated. The residue was purified by preparative TLC with hexane-AcOEt (1:1, 2 developments) to give a 1:1 mixture of 3a and *ent*-3b (10.5 mg, 82%). These spectral data were in good agreement with those of 3a and 3b obtained from the Diels-Alder reaction. The product ratio was determined by HPLC.

X-Ray Crystallographic Analysis of (\pm)-4b¹⁰

Crystal data: empirical formula, $\text{C}_{17}\text{H}_{18}\text{O}_5\text{S}$; crystal system, monoclinic; crystal habit, prismatic; crystal dimensions, 0.40 x 0.30 x 0.10 mm; space group, $\text{P}2_1/\text{n}$ (#14); lattice parameters, $a = 10.467(2)$ Å, $b = 9.118(3)$ Å, $c = 17.475(2)$ Å, $\beta = 94.92(1)^\circ$, $V = 1661.6(6)$ Å³; $Z = 4$; $D_{\text{calc}} = 1.377$ g cm^{-3} ; μ (Cu-K α) = 19.34 cm^{-1} ; number of observations, 1588 ($I > 3.00\sigma(I)$); $R = 0.040$; $R_w = 0.066$. Intensity data were collected on a Rigaku AFC7R diffractometer in ω -2 θ scan mode using Cu-K α radiation ($\lambda = 1.54178$ Å).

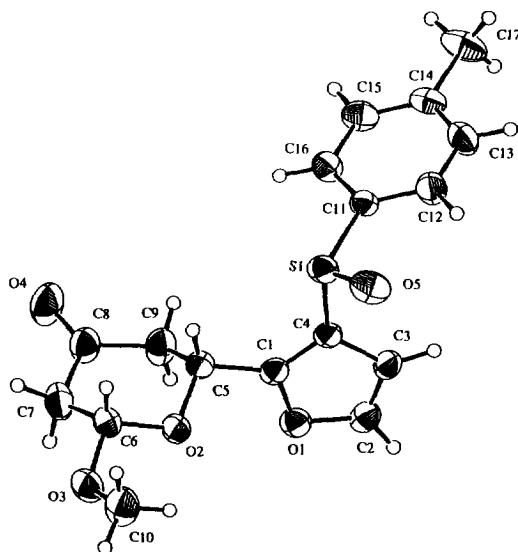


Fig. 1. X-ray structure of (\pm)-4b

Acknowledgments

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- 9 The symbol S_5 given in this text expresses that the absolute configuration of the sulfanyl center as S.
- 10 Full details of the structure determination have been deposited at the Cambridge Crystallographic Data Centre.

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