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Highly diastereoselective Diels-Alder reactions with (R)-ethoxy p-tolyl vinyl sulfonium tetrafluoroborate

B. Ronan and H. B. Kagan*

Laboratoire de Synthèse Asymétrique
URA CNRS 255
Université Paris-Sud, 91405-Orsay, France.

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Abstract:
p-Tolyl vinyl sulfoxide has been efficiently activated for Diels-Alder reactions by transformation into a sulfonium salt **3a** or by addition of TMSOTf. Very high diastereomeric excesses have been achieved (>98%) at -20°C in many cases. Best results have been obtained with cyclopentadiene, furan and 2,3-dimethyl-1,3-butadiene. In this way enantiomerically pure oxanorbornenone **19a** has been prepared. The reaction mechanism is briefly discussed.

Introduction

Chiral α,β-unsaturated sulfoxides are interesting dienophiles in the Diels-Alder reaction[1-5]. Some representative examples are indicated in Figure 1. Chiral sulfinyl-dienes have also been used in Diels-Alder reactions[6]. A limitation of the use of chiral α,β-unsaturated sulfoxides is the lack of reactivity, unless there is an additional electron-withdrawing group in the α or β-position. Catalysis by Lewis acids is not easy to manage because of a tendency for racemization at sulfur[7]. We wish to report here our results concerning the use of simple chiral alkoxy sulfonium salts (easily derived from the corresponding sulfoxides) as dienophile components in the Diels-Alder reaction.

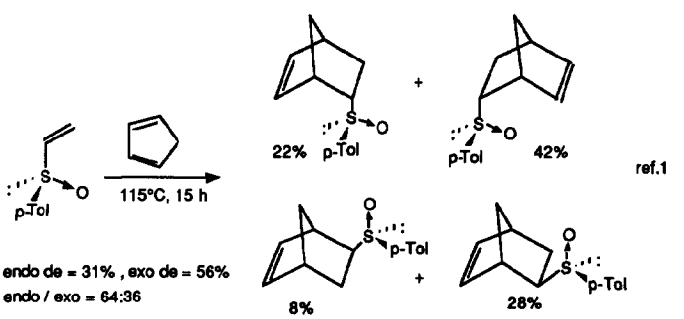
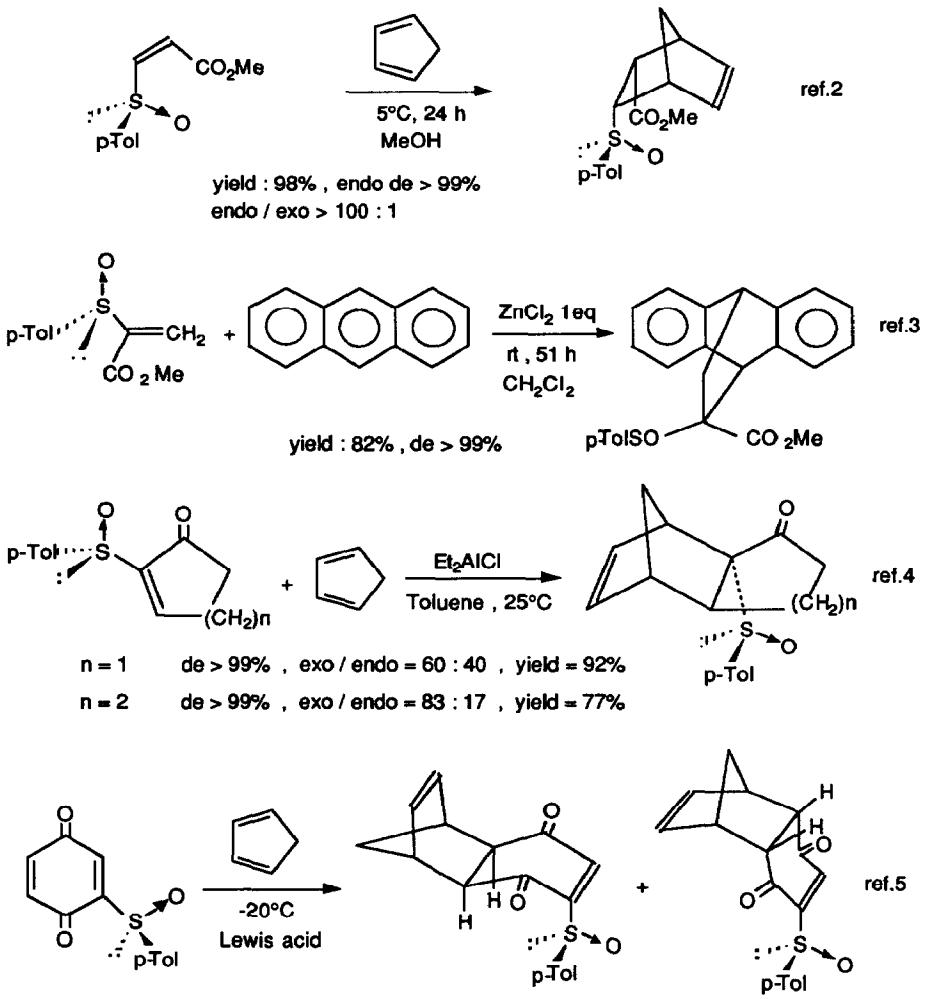


Figure 1

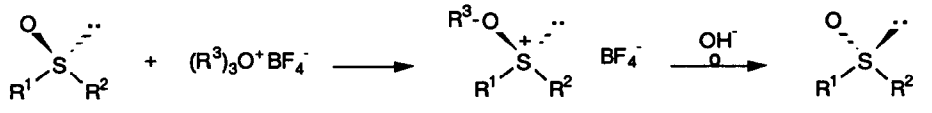


a) CH_3CN, $Eu(fod)_3$, de = 82%, yield = 62% b) $CHCl_3$, BF_3OEt_2, de = 80%, yield = 89%

Chiral sulfoxides in asymmetric Diels-Alder reactions (refs. 1-5)

Figure 1

It is well known that sulfoxides **1** are stereoselectively transformed (retention at sulfur) into alkoxy sulfonium salts **3** by treatment with trialkyloxonium salts **2** (Scheme 1). The sulfur atom in **3** is prone to nucleophilic substitution with inversion of configuration[8] (eg sodium hydroxide gives sulfoxide **4**, enantiomer of **1**). The sulfonium moiety is also well known to act as a leaving group, for example β-hydroxysulfoxides on treatment with Meerwein's reagent followed by deprotonation of the β-hydroxyl are smoothly transformed into epoxides[9,10]. We have discovered that vinyl sulfoxides are activated for the Diels-Alder reaction by O-alkylation with trialkyloxonium salts, allowing cycloadditions to be performed under mild conditions with high stereoselectivities. Another mode of activation of vinyl sulfoxides which has been investigated is the addition of stoichiometric or catalytic amounts of TMSOTf.



1 **2** **3** **4**

a) R^1 = p-Tol, R^2 = $CH=CH_2$ d) R^1 = p-Tol, R^2 = (E)-CH=CHEt
b) R^1 = t-Bu, R^2 = $CH=CH_2$ e) R^1 = p-Tol, R^2 = (Z)-CH=CHMe
c) R^1 = p-Tol, R^2 = (E)-CH=CHPh

Scheme 1

Preparation of chiral α,β-unsaturated sulfoxides and their ethoxysulfonium salts

(S)-p-Tolyl vinyl sulfoxide **1a** was prepared in 75% yield by the Andersen method through the action of vinylmagnesium chloride on (+)-menthyl (R)-p-toluenesulfinate according to the procedure of ref.11. (E)-(R)-β-Styryl-p-tolyl sulfoxide **1c** was synthetized in good yield according to ref.12a by aldol condensation of (R)-methyl p-tolyl sulfoxide on benzaldehyde followed by O-methylation and β-elimination in basic conditions. The same procedure was applied for the synthesis of (E)-(R)-butenyl p-tolyl sulfoxide **1d**. (Z)-(S)-Propenyl p-tolyl sulfoxide **1e** was obtained in 50% yield from (+) menthyl (R)-p-toluenesulfinate and the Grignard reagent by a known procedure[12b]. We prepared (R)-t-butyl vinyl sulfoxide **1b** by the new method recently reported by one of us (Grignard reagents on a chiral cyclic sulfite)[13]. Unfortunately the easy polymerization of **1b** in presence of magnesium salts made both scale up of the preparation and its use in Diels-Alder reaction inconvenient. O-alkylation of sulfoxides **1** was easily

realized in methylene chloride at room temperature by addition of one equivalent of Meerwein reagent (OEt_3^+ BF_4^-).

Diels-Alder reaction of ethoxy p-tolyl vinyl sulfonium salts

Ethoxy p-tolyl vinyl sulfonium tetrafluoroborate **3a** was found to react with cyclopentadiene at room temperature over 1.5 h to give cycloadducts (endo/exo= 92:8) in 50% isolated yield after treatment by sodium hydroxide which leaves sulfoxides **5-8** (with inversion at sulfur) (Figure 2). Diastereomeric excess is quite high (86% de) for exo or endo isomers. By decreasing temperature (-20°C or -78°C) one *achieves almost perfect diastereoselectivity*: there is only formation of endo cycloadduct (exo isomer is not detectable by ^1H nmr or tlc); moreover the diastereomeric excess (**5** versus **6**) is higher than 99% (Table 1). This result has to be compared to Diels-Alder reaction with p-tolyl vinyl sulfoxide **1a** which has been described as giving a mixture of endo-exo isomers (endo/exo = 64:36), each one being obtained with about (31% de) for exo and (56% de) for endo[1].

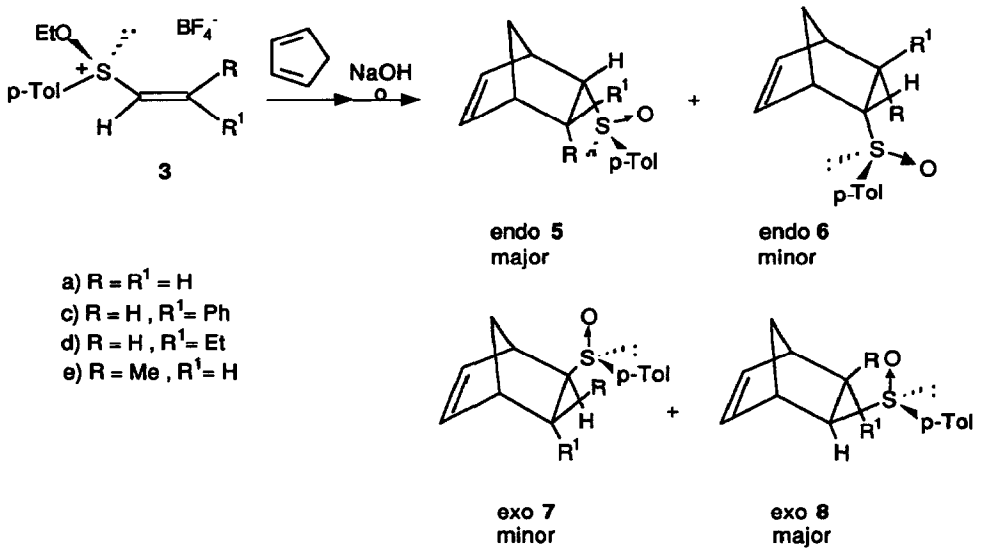


Figure 2

Ethoxy p-tolyl vinyl sulfonium salts with a substituent in the β-position on the double bond also have been investigated in cycloadditions with cyclopentadiene (Figure 2). The reactivity drops dramatically with respect

to ethoxy p-tolyl vinyl sulfonium salt **3a** itself. At room temperature (E)-sulfonium salts **3c** and **3d** are unreactive, while (Z)-sulfonium salt **3e** gives the endo **5e** cycloadduct with 84% de in 25% yield (Table 1).

Table 1 : Diels-Alder reaction between ethoxy sulfonium salts **3** and cyclopentadiene

Salt	Temp. (°C)	Time (h)	Total yield[a] (%)	Endo de[b] (%)	Exo de[b] (%)	Endo/Exo[b]
3a	25	1.5	50	86	86	92 : 8
3a	0	15	46	96	97	91 : 9
3a	-20	48	32	> 99	-	> 99 : 1
3a	-78	36	62	> 99	-	> 99: 1
3c	-78	36	0	-	-	-
3c	25	24	0	-	-	-
3d	25	15	0	-	-	-
3e	25	20	25[c]	84[c]	-	> 99 : 1[c]

a) Isolated yield after transformation of crude sulfonium cycloadducts by 0.2 N NaOH into sulfoxides **5-8** (inversion at S) and flash chromatography on silica.

b) Measured by ^{1}H NMR as described in ref. 1.

c) Measured by ^{1}H NMR.

Since ethoxy p-tolyl vinyl sulfonium salt **3a** appeared very promising for asymmetric synthesis we checked its reactivity towards various dienes (Figure 3). Results are reported in Table 2. Cyclohexadiene oligomerizes instead of giving cycloaddition. Anthracene is unreactive. 2,3-Dimethylbutadiene gives 40% of adduct **9**. The reaction is highly stereoselective (de> 98%), although the relative stereochemistry of the product has not been established. Furan readily reacts at room temperature or at 0°C (90% after 60 h). Regardless of the temperature (entries 5-7, Table 2), the endo/exo ratio is approximatively equal to 1. Each endo or exo adduct can be obtained in very high diastereomeric excess (>98% de at -20°C).

Replacement of methylene chloride by chloroform, acetonitrile or toluene (entries 8-10) does not change the yield and the various diastereoselectivities.

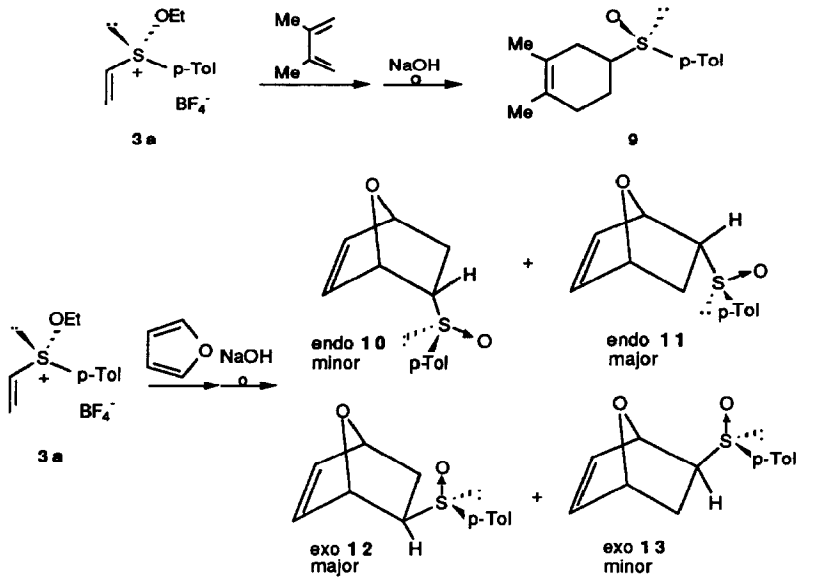


Figure 3

Table 2 : Diels-Alder reaction between ethoxy sulfonium salt **3a** and various dienes.

Diene	Temp. (°C)	Time (h)	Total yield[a] (%)	Endo de[b] (%)	Exo de[b] (%)	Endo/Exo[b]
2,3-diMe-butadiene	25	15	40	> 99[c]		-
Anthracene	25	12	0	-		-
Cyclohexadiene	25	6	6[d]	-	-	-
Furan	25	4.5	70	80	78	48 : 52
Furan	0	60	90	93	89	55 : 45
Furan	-20	60	35	> 98	> 98	59 : 41
Furan [e]	-10	60	86	91	85	56 : 44
Furan [f]	-10	60	66	92	87	56 : 44
Furan [g]	-10	60	69	89	84	55 : 45

a) See Table 1 note a. b) Measured by ^1H NMR.
c) The relative stereochemistry of the major diastereomer is unknown.
d) Main product : trimerisation of cyclohexadiene , same results at 20°C and -5°C. e) In chloroform. f) In acetonitrile. g) In toluene.

Diels-Alder reaction of p-tolyl vinyl sulfoxide **1a** promoted by TMSOTf

It is well known that TMSOTf can promote hetero Diels-Alder reactions, presumably by TMS^+ attack on the carbonyl oxygen[14]. We decided to investigate whether activation of vinyl sulfoxides for Diels-Alder reactions could be realized by TMSOTf instead of O-alkylation by Meerwein's reagent. The model system that we chose was p-tolyl vinyl sulfoxide **1a** and cyclopentadiene (Figure 4). The reaction was performed in the presence of one or less equivalents of TMSOTf and results are shown in Table 3. In the presence of 1 mol eq. of TMSOTf, cycloaddition occurs at 0°C, giving 60% of endo (**14b**, **15b**): exo (**16b**, **17b**) adducts (89:11) after 3 hours, each compound being of very high de. Thus TMSOTf is able to function as a catalyst but the reaction is slower than when Meerwein's reagent is used.

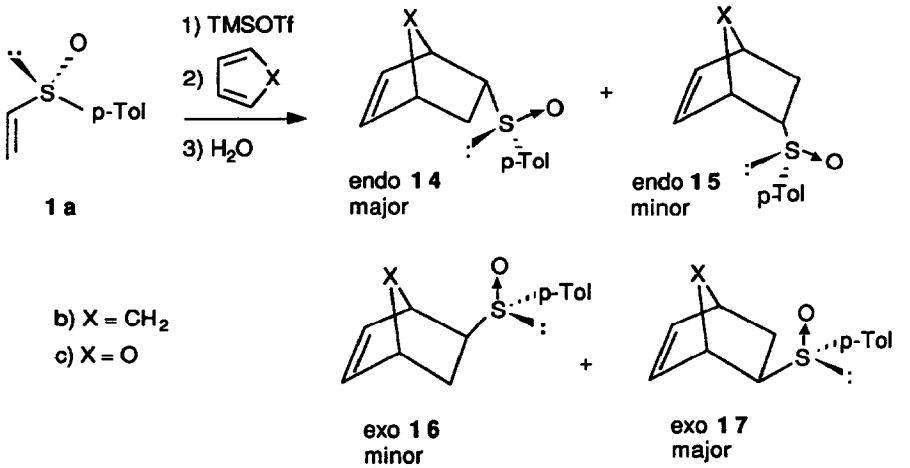


Figure 4

Comparisons of data in Table 3 (entry 4) with those in Table 1 (entry 2) for similar reactions with the sulfonium salt **3a**, show approximately the same reactivities and diastereoselectivities. One should notice here that the two reactions give sulfoxides which are epimeric at sulfur since there is an inversion of configuration on conversion of the sulfonium cycloadducts to the corresponding sulfoxides. The vinyl sufonium salt **3a** reacts more stereoselectively if one considers the endo/exo ratio. Activation by TMSOTf remains an interesting possibility since it could be in principle carried out catalytically, and there is no need of an additionnal reaction for recovering the cycloadducts as sulfoxides. The reaction between p-tolyl vinyl sulfoxide

1a and furan (Figure 4) which was performed at 20°C gives an endo/exo ratio equal to 1. Each endo or exo adduct is obtained in good diastereomeric excess (71-73%) (Table 3, entry 5).

Table 3 : Diels-Alder reaction between (S)-p-tolyl vinylsulfoxide **1a** and cyclopentadiene or furan promoted by TMSOTf

Entry[a]	Mol.eq.of TMSOTf[b]	Time (h)	Total yield[c] (%)	Endo de[d] (%)	Exo de[d] (%)	Endo/Exo[d]
1	0	-	0	-	-	-
2	0.05	15	20	57	-	> 99 : 1
3	0.20	15	60	96	63	92 : 8
4	1.00	3	61	92	> 99	89 : 11
5	1.00	36	72	71	73	55 : 45

a) Entries 1-4 : cyclopentadiene, entry 5 : furan.
b) By respect to vinyl sulfoxide **1a**. Reaction performed at 0°C in CH_2Cl_2 except entry 5 (20°C).
c) Isolated yield after flash chromatography on silica.
d) Measured by ^1H NMR.

Discussion

It was very gratifying to see that O-alkylation of several vinyl sulfoxides greatly increased both their reactivity and stereoselectivity in the Diels-Alder reaction.

The stereochemistry of the reaction could be easily analyzed in the condensation of cyclopentadiene and vinyl sulfonium salt **3a** thanks to nmr data published for the four stereoisomeric sulfoxides **5a-8a**[1]. In the case of (Z)-propenyl sulfonium salt **3e** the similarities of nmr spectra of **5e-8e** allowed non ambiguous structural assignements. Cycloadducts with furan (**10-13**) had their stereochemistry proved by degradation into oxanorbornenone **19a**. This compound has been prepared by Vogel[15], and is a useful chiral synthon in asymmetric synthesis of various modified sugars. Sulfoxide **11** was degraded into oxanorbornenone **19a** by the two-steps procedure shown in Figure 5. Compound (1R,4R) **19a** was isolated with 100% ee ($[\alpha]_D^{25}$=+959 (c=0.1, $CHCl_3$))[15] while the mixture of endo and exo sulfoxides ((**10**+**11**)/(**12**+**13**)=55:45, endo:93%de, exo:89%de) was degraded into oxanorbornenone (1S,4S)**19b** with 11%ee. A simple calculation shows that indeed the absolute configuration at carbon atoms is as shown in Figure 3, the other combinations would lead to much higher specific rotations for the resulting oxanorbornenone mixture.

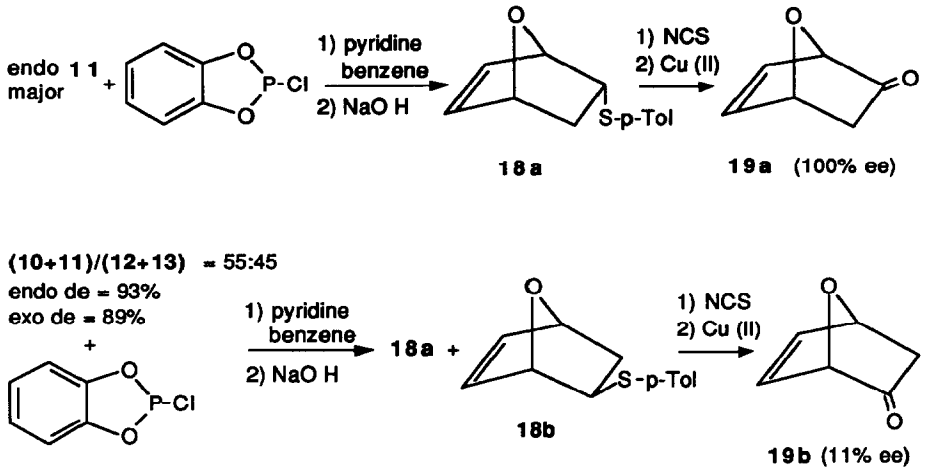
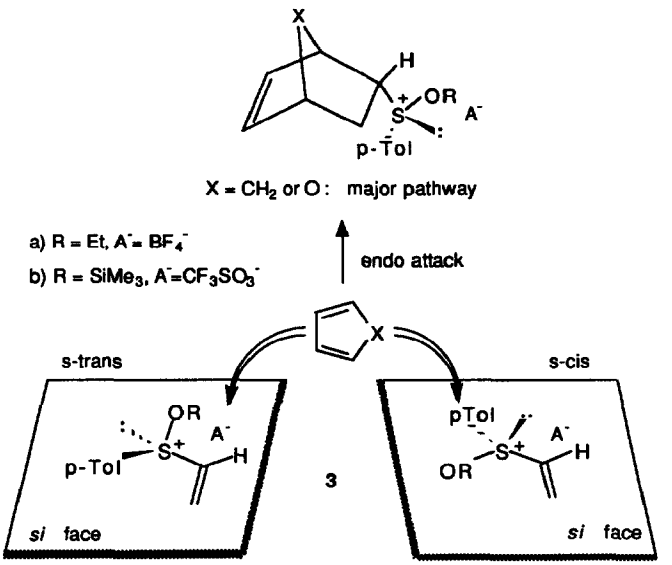


Figure 5

Tentative transition states leading to the major diastereomers are depicted in Scheme 2. When vinyl sulfonium salt **3a** reacts by endo attack we may consider the reacting species with s-cis or s-trans conformations (S-OEt versus C=C) by analogy with characteristic conformations of vinyl sulfoxides[16,17]. In the both cases attack of the vinyl plane arised from the *si* side (Scheme 2). For steric reasons we propose a reaction pathway through the s-cis conformation (attack from electron pair and not by the face hindered by p-tolyl group).

In conclusion, ethoxy p-tolyl vinyl sulfonium salt **3a** is a useful chiral synthon for ring formation by Diels-Alder reaction in smooth conditions in absence of catalyst. Diastereoselectivities are very high in many cases and much improved with respect to the corresponding sulfoxide. We are currently expanding this methodology for ring formation using dienes with donor substituents or functionalized vinyl sulfonium salts.



Scheme 2

Acknowledgments
We acknowledge Rhône-Poulenc Co for a fellowship (to B.R.) and for financial support. We thank Dr X. Radisson for fruitful discussions.

Experimental

Apparatus ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AM 250 MHz and Bruker AM 200 MHz spectrometers in deuteriochloroform using tetramethylsilane as internal standard, chemical shifts are expresed in ppm. IR spectra (KBr) were recorded on Perkin Elmer 883 spectrometer. Mass spectra were recorded on Riber Mag R10-10 instrument. Optical rotations were measured on a Perkin-Elmer 241 polarimeter at 20°C. Melting points were determined on Reichert apparatus and are uncorrected. Microanalyses were performed at the Service microanalyse du CNRS (Gif sur Yvette).

Chemicals Dichloromethane was distilled over calcium hydride and stored under argon. Tetrahydrofuran and diethyloxide were distilled over sodium/benzophenone ketyl before use. (1S)-(+)-Menthyl-(R)-p-toluene

sulfinate ($[\alpha]^{20}_D$+197, c=2 acetone), trimethylsilyl trifluoromethanesulfonate and triethyloxonium tetrafluoroborate (purum: 95%) were purchased from Fluka. All dienes were distilled and stored under argon and over 4 Å molecular sieves at -20°C before use. Cyclopentadiene was prepared from dicyclopentadiene and used immediately.

(S)-(-)-p-Tolyl vinyl sulfoxide **1a**

Prepared from (1S)-(+)-menthyl-(R)-p-toluene sulfinate and 1 mol eq. of C_2H_3Mg Cl in ether according to ref.11. Yield : 75% ; colourless oil ; $[\alpha]_D$ -446 (c=1.65, acetone), (lit. $[\alpha]_D$ -390, acetone) ; ^{1}H NMR δ 7.56-7.30 (4H, dd), 6.59 (1H, dd), 6.20 (1H, d), 5.89 (1H, d), 2.40 (3H, s).

(E)-(R)-(+)-β-Styryl p-tolyl sulfoxide **1c**

Prepared according to ref. 12a. Yield : 77% ; white solid ; mp : 82°C, (lit. 81.5-82°C); $[\alpha]_D$ + 164 (c=1.16, $CHCl_3$), (lit. $[\alpha]_D$ + 164.3, $CHCl_3$) ; ^{1}H NMR δ 7.60-7.30 (10H, m), 6.82 (1H, d, J trans = 17Hz), 2.41 (3H, s).

(E)-(R)-(+)-Butenyl p-tolyl sulfoxide **1d**

Prepared by a similar procedure as for **1c**. Yield : 78% ; colourless oil ; $[\alpha]_D$ + 83 (c=1.46, $CHCl_3$) ; ^{1}H NMR δ 7.58-7.25 (4H, dd), 6.65 (1H, dt), 6.21 (1H, d, J trans = 15Hz), 2.41 (3H, s), 2.26 (2H, m), 1.08 (3H, t); Anal. Calcd. for $C_{11}H_{14}$ SO : C, 68.00 ; H, 7.26 ; O, 8.24 ; S, 16.50. Found C, 67.73 ; H, 7.50 ; O, 8.36 ; S, 16.24.

(Z)-(S)-(+)-Propenyl p-tolyl sulfoxide **1e**

Prepared according to ref.12b. Yield : 44% ; white solid ; mp : 50°C, (lit. 54-55°C) ; $[\alpha]_D$ +289 (c=1.045, acetone), (lit. $[\alpha]_D$ + 306, EtOH) ; ^{1}H NMR δ 7.52-7.23 (4H, dd), 6.22 (2H, m), 2.40 (3H, s), 2.22 (3H, d).

Preparation of chiral α,β-unsaturated ethoxy sulfonium salts

General method. To a solution of 5 mmol of α,β - unsaturated sulfoxide in 5 mL of methylene chloride was added 5 mmol of triethyloxonium tetrafluoroborate. After 1.5 h with stirring under argon, the salt was precipitated with ether. This solution was cooled to -78°C and etheral fraction was eliminated by decanting (washing by ether was repeated three

times). The colourless oil was dried under reduced pressure (unsatisfactory analyses were obtained since the compounds are thermally unstable).

(S)-(-)-Ethoxy p-tolyl vinyl sulfonium tetrafluoroborate **3a**

Yield : 90% ; yellow oil ; $[\alpha]_D$ -59 (c=1, $CHCl_3$) ; ^1H NMR δ 8.00-7.51 (4H, dd), 7.28-7.16 (1H, m), 6.80-6.62 (2H, m), 4.57-4.38 (2H, m), 2.50 (3H, s), 1.46 (3H, t).

(E)-(R)-(+)-Ethoxy-β-styryl p-tolyl sulfonium tetrafluoroborate **3c**

Yield 83% ; yellow oil ; $[\alpha]_D$ + 6 (c=1, $CHCl_3$) ; ^1H NMR δ 8.20 (1H, d, J trans = 15Hz), 8.05-7.30 (10H, m), 4.51-4.28 (2H, m), 2.43 (3H, s), 1.40 (3H, s).

(E)-(R)-Butenyl ethoxy p-tolyl sulfonium tetrafluoroborate **3d**

Yield : 74% ; brown oil ; ^1H NMR δ 8.00-7.40 (5H, m), 6.92 (1H, d, J trans = 16Hz), 4.40 (2H, q), 2.62-2.40 (3H + 2H, m), 1.42 (3H, t), 1.17 (3H, t).

(Z)-(S)-(+)-Ethoxy propenyl p-tolyl sulfonium tetrafluoroborate **3e**

Yield : 84% ; yellow oil ; $[\alpha]_D$ +130 (c=1, $CHCl_3$) ; ^1H NMR δ 8.00 (2H, d), 7.58 (2H, d), 7.23 (1H, m), 7.05 (1H, m), 4.40 (2H, q), 2.51 (3H, s), 2.36 (3H, dd), 1.42 (3H, t).

Diels-Alder reaction between (S)-**3a** and cyclopentadiene

The following standard procedure was followed at -78°C.
3.11 g of (S)-**3a** (11 mmol) dissolved in 15 mL dichloromethane under argon was cooled to -78°C. To this solution was added cyclopentadiene (1.2 mL,17 mmol) at -78°C. After standing at -78°C for 36 h the reaction was quenched by addition of NaOH 0.2N (11 mmol) and stirring 30 min. A dichloromethane extraction, washing by saturated NaCl solution, drying on $MgSO_4$ and concentration *in vacuo* yielded 2.66 g oily **5a**. Isolated yield : 62% ; endo/exo > 100:1 ; de > 99% (measured by ^1H NMR). Purification by flash chromatography on silica (ether/AcOEt = 4:1) gave (1R, 2R, 4R, R_S)-(+)-**5a** 1.6 g as a yellow oil (62% yield); $[\alpha]_D$ + 207.6 (c=1.18, acetone), (lit.[1] $[\alpha]_D$ +180.4, acetone) ; ^1H NMR δ 7.41 (4H, dd), 6.35 (2H, m), 3.48 (1H, br, s), 3.37 (1H, m), 2.9 (1H, br, s), 2.4 (3H, s), 1.7-0.7 (4H, m) ; data are in agreement with lit.[1].

Diels-Alder reaction between (S)-**3a** and 2,3-dimethyl-1,3-butadiene

A similar procedure to above was followed using 1.41 g of (S)-**3a** (5 mmol) and 1.2 mL 2,3-dimethyl-1,3-butadiene (10 mmol) at 25°C for 15 h yield 1.25 g oily **9**. Isolated yield : 40% ; d.e.> 99% (measured by ^1H NMR and ^{13}C NMR). Purification by flash chromatography on silica (ether/AcOEt = 4:1) gave 0.49 g white solid (40% yield) of **9** ; $[\alpha]_D$ + 196 (c=0.385, acetone) ; mp : 94-95°C ; ^1H NMR δ 7.52-7.29 (4H, dd), 2.79 (1H, m), 2.5-2.21 (4H, m), 2.11-1.8 (4H, m), 1.7-1.5 (7H, m) ; ^{13}C NMR d 141.3, 138.7, 129.6, 125.4, 124.8, 123.5, 60.3, 30.9, 28.4, 23.3, 21.4, 19, 18.7 ; MS (NH_3, CI) m/e 109 (19%); 249 (MH^+, 100). Anal. Calcd. for $C_{15}H_{20}SO$: C, 72.53 ; H, 8.12 ; O, 6.44 ; S, 12.91. Found C, 72.35 ; H, 7.99 ; O, 6.19 ; S, 13.03.

Diels-Alder reaction between (S)-**3a** and furan

A similar procedure to above was followed using 1.43 g of (S)-**3a** (5.1 mmol) and 1.1 mL furan (16 mmol) at 0°C for 60 h gave 1.2 g of yellow oil. Flash chromatography on silica (ether/AcOEt = 4:1) gave the mixture of adducts **10-13** as an oil (1.07 g, 90% yield) ; endo de = 93% ; exo de = 89% ; endo/exo = 55:45 (measured by ^1H NMR). Washing by ether with stirring gave **11** pure (de : 100%) as a white solid. The filtrate was concentrated and purified by flash chromatography on silica (ether/AcOEt = 4:1) to give pure **12** (de : 100%) as a yellow oil.

(1R, 2R, 4R, R_S)-**11** : $[\alpha]_D$ + 186 (c=0.975, acetone) ; mp : 105-110°C ; ^1H NMR δ 7.60-7.25 (4H, dd), 6.71-6.53 (2H, m), 5.31 (1H, br, d), 5.04 (1H, br, d), 3.53 (1H, q), 2.4 (3H, s), 1.82 (1H, m), 1.05 (1H, dd) ; IR (KBr) cm^{-1}: 3048, 2945, 1595, 1498, 1445, 1403, 1317, 1214, 1084, 1031, 1004, 985 ; MS (NH_3, CI) m/e 118 (11%), 235 (MH^+, 100), 252 (MNH_4^+, 13) ; Anal. Calcd. for $C_{13}H_{14}SO_2$: C, 66.64 ; H, 6.02 ; O, 13.66 ; S, 13.68. Found C, 66.44 ; H, 5.88 ; O, 13.88 ; S, 12.85.

(1S, 2R, 4S, R_S)-**12** : $[\alpha]_D$ + 58 (c=0.965, acetone) ; ^1H NMR δ 7.57-7.22 (4H, dd), 6.33 (2H, m), 5.48 (1H; br, s), 5.02 (1H, br, d), 2.79 (1H, dd), 2.35 (3H, s), 1.51 (1H, dt), 1.14 (1H, dd) ; Anal. Calcd. for $C_{13}H_{14}SO_2$: C, 66.64, ; H, 6.02 ; O, 13.66 ; S, 13.68. Found C, 66.35 ; H, 5.83 ; O, 13.61 ; S, 12.98 ; IR and MS are identical to above **11**.

(1R, 2R, 4R)-(+)-Oxabicyclo-[2.2.1]-hept-5-ene-2-p-tolyl sulfide **18a**

To a stirred solution of 0.97 g of (+)-**11** (4.15 mmol) and pyridine (0.33 mL) in benzene (7 mL) was slowly added 2-chloro-1,3,2-benzodioxa-

phosphole[18,19] (0.73 g, 4.15 mmol) ; a precipitate formed almost immediately. After one hour 2N sodium hydroxide (5 mL) was added and the benzene layer washed several times with aqueous NaOH and finally with water. The benzene solution was dried ($MgSO_4$), the solvent evaporated and the residue purified by chromatography on silica gel (hexane/ether = 3:1) to give **18a** (0.8g Yield : 89%) as a white solid; mp : 35°C ; $[\alpha]_D$ + 114.3 (c=0.56, acetone) ; ^1H NMR δ 7.32-7.09 (4H, dd), 6.44 (2H, m), 5.02 (2H, m), 3.6 (1H, m), 2.43 (1H, m), 2.33 (3H, s), 1.1 (1H, dd) ; MS (NH_3, CI) m/e 150 (34%), 201 (22), 219 (MH^+, 85), 236 (MNH_4^+, 100) ; Anal. Calcd. for $C_{13}H_{14}SO$: C, 71.52 ; H, 6.46 ; O, 7.33 ; S, 14.69. Found C, 71.31 ; H, 6.55 ; O, 7.56 ; S, 14.87.

(±)-Oxabicyclo-[2.2.1]-hept-5-ene-2-p-tolyl sulfides **18a** and **18b**

A similar procedure as above using 1.04 g (4.5 mmol) of a mixture **10-13** (endo/exo = 55:45 ; endo de = 93% ; exo de = 89%) gave, after flash chromatography on silica (hexane/ether = 3:1) 0.72 g of a mixture of pure **18a** (de : 100%) and pure **18b** (de : 100%) ; **18a/18b** = 52:48 ; yield : 74%. Diastereomer (1S, 2R, 4S)-**18b** : $[\alpha]_D$ + 38 (c=0.675, acetone) ; white solid ; mp : 35-40°C ; ^1H NMR δ 7.35-7.11 (4H, dd), 6.38 (1H, dd), 6.26 (1H, dd), 5.07 (1H, br, dd), 4.8 (1H, br, d), 3.1 (1H, dd), 2.34 (3H, s), 1.81 (1H, dd), 1.65 (1H, dt). MS and Anal. are identical to above **18a**.

(1R, 4R)-(+)-7-Oxabicyclo-[2.2.1]-hept-5-ene-2-one **19a**

A mixture of sulfide (+)-**18a** (0.8 g, 3.7 mmol), N-chlorosuccinimide (0.49 g, 3.7 mmol) and CCl_4 (5 mL) was heated under reflux under nitrogen for one hour[20]. Cooling, filtration and evaporation furnished a residue which was immediately treated with acetone (16 mL), water (0.53 mL), $CuCl_2$ (1.06 g) and CuO (1.06 g) and the mixture heated under reflux for 30 min. It was then cooled, filtered, diluted with water (10 mL) and extracted with ether. Drying ($MgSO_4$) and evaporation of the ether gave a residue (0.64 g) which was purified by flash chromatography on silica (hexane/ether = 6:1 followed by CH_2Cl_2) giving **19a** (0.13g Yield : 33%) as a yellow oil; $[\alpha]_D$ + 876 (c=0.28, $CHCl_3$).Distillation under, reduced pressure (1 mm Hg) gave an analytical sample $[\alpha]_D$ + 959 (c=0.1, $CHCl_3$)[15] ; ee > 99% ; ^1H NMR δ 6.77 (1H, dd), 6.5 (1H, dd), 5.37 (1H, br, dd), 4.58 (1H, br, d), 2.29 (1H, dd), 1.89 (1H, d) ; data are in agreement with lit.[15].

(±)-7-Oxabicyclo-[2.2.1]-hept-5-ene-2-one **19a** and **19b**

In a similar procedure to above, a mixture of sulfide **18a/18b** (0.48 g ; 2.2 mmol ; **18a/18b** = 55:45 : de **18a** = 100% ; de **18b** = 100%) gave 0.1 g of **19a** and **19b**. Yield : 42% ; $[\alpha]_D$-109 (c=0.775, $CHCl_3$), (ee = 11% ; **19a/19b** = 45:55), data are in agreement with lit.[15].

Diels-Alder reaction between cyclopentadiene and (S)-**1a** promoted by TMSOTf

The following standard procedure was followed in the presence of one equivalent of TMSOTf.
0.83 g of (S)-**1a** (5 mmol) dissolved in 10 mL dichloromethane under argon was cooled to 0°C. To this solution was added TMSOTf (0.97 mL 5 mmol) at 0°C. After stirring at 0°C for 1h, 0.55 mL cyclopentadiene (7.5 mL) was introduced. After stirring at 0°C for 3 h, the reaction was quenched by addition of NaOH 0.2N (5 mmol) and stirring 30 min. A dichloromethane extraction, washing with saturated NaCl solution, drying on $MgSO_4$ and concentration *in vacuo* gave a yellow oil. Endo/exo = 89:11 ; endo de = 92% ; exo de > 99% (measured by ^1H NMR). Purification by flash chromatography on silica (ether/AcOEt = 4:1) gave a mixture of **14b-17b** (0.71g Yield : 61%); data are in agreement with lit.[1].

Diels-Alder reaction between furan and (S)-**1a** promoted by TMSOTf

In a similar procedure to above, 0.71 g of (S)-**1a** (4.3 mmol), 0.78 mL TMSOTf (4.3 mL) and 1 mL furan (13 mmol) at 25°C for 36 h gave a mixture of **14b-17b** (0.72g Yield : 71%); endo de = 71% ; exo de = 73% ; endo/exo = 55:45 (measured by ^1H NMR). The major diastereomers were separated by flash chromatography on silica (AcOEt/cyclohexane = 1:1).
(1R, 2R, 4R, S_S)-**14c** : $[\alpha]_D$ -137.5 (c=0.99, acetone) ; white solid ; mp : 135°C ; ^1H NMR δ 7.60-7.32 (4H, dd), 6.58 (1H, dd), 6.35 (1H, dd), 5.09 (1H, br, d), 4.64 (1H, br, d), 3.45 (1H, m), 2.45 (3H, s), 2.2 (1H, m), 1.83 (1H, dd). Anal. Calcd. for $C_{13}H_{14}SO_2$: C, 66.64 ; H, 6.02 ; O, 13.66 ; S, 13.68. Found C, 66.69 ; H, 6.06 ; O, 13.42 ; S, 13.46 ; IR and MS are identical to above **10**.
(1S, 2R, 4S, S_S)-**17c** : $[\alpha]_D$ -204.7 (c=0.95, acetone) ; white solid ; mp : 123-127°C ; ^1H NMR δ 7.65-7.32 (4H, dd), 6.45 (1H, br, d), 6.22 (1H, br, d), 5.16 (1H, br, d), 4.88 (1H, br, s), 2.79 (1H, dd), 2.44 (3H, s), 2.37 (1H, dt), 1.63 (1H, dd) ; Anal. Calcd. for $C_{13}H_{14}SO_2$: C, 66.64 ; H, 6.02 ; O, 13.66 ; S, 13.68. Found C, 66.57 ; H, 6.06 ; O, 13.68 ; S, 13.44 ; IR and MS are identical to **10** above.

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