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Synthesis and Diels Alder Reactions of (+)-(S)-1-t-Butylsulfonyl-1-p-Tolylsulfinylethene, a New Masked Chiral Ketene Equivalent

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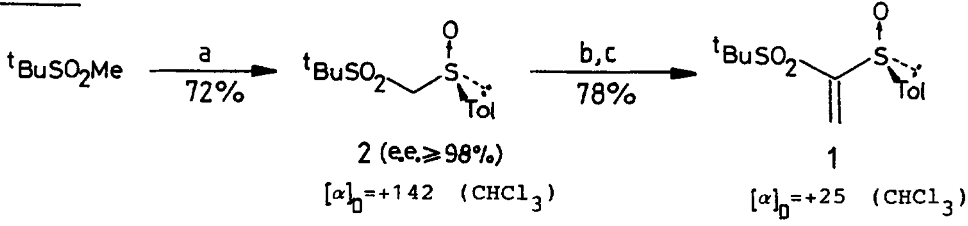
Abstract *Enantiomerically pure (+)-(S)s-1-t-butylsulfonyl-1-p-tolylsulfinylethene (1) was easily prepared in three steps from t-butyl methyl sulfone. The catalyzed Diels-Alder reactions of 1 with cyclopentadiene were highly stereoselective The major adduct was transformed into (+)-(1R,4R)-dehydronorcamphor and (+)-(1R,4S)-2-t-butylsulfonyl-2,5-norbornadiene.*

Enantiomerically pure α,β-unsaturated sulfoxides have currently received a considerable attention as dienophiles in asymmetric Diels-Alder reactions[1]. To the best of our knowledge, only three of them, (+)-(R)-p-tolyl vinyl sulfoxide[2], (+)-(S,S)-1,1-bis(p-tolylsulfinyl)ethene[3] and (+)-(R)-ethynyl p-tolylsulfoxide[4], have been used as masked chiral ketene equivalents However their utility is very limited due to their moderate reactivity and facial stereoselectivity. In this communication we report the synthesis and some Diels-Alder reactions of a new chiral ketene equivalent: (+)-(S)-1-t-butylsulfonyl-1-p-tolylsulfinylethene (1).

Scheme 1



2 (e.e.≥98%)
$[\alpha]_D = +142$ ($CHCl_3$)

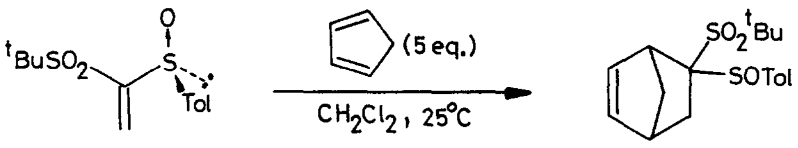
1
$[\alpha]_D = +25$ ($CHCl_3$)

a: ⁿBuLi, THF, -78°C, 30 min; then (S)s-p-tol-SO(OMent) (0.5 eq.), r.t., 5h.
b· Me_2NH (2 eq), CH_2O (2 eq), MeOH, 0°C, 3h. c. IMe, $CaCO_3$, CH_3CN, r.t., 3h.

Unsaturated sulfoxide 1 was easily prepared following the sequence of reactions shown in scheme 1. Deprotonation of t-butyl methyl sulfone with n-BuLi and sulfinylation with (-)-(S)s-menthyl p-toluenesulfinate[5] gave (+)-(S)-t-butylsulfonyl p-tolylsulfinyl methane (2), which was easily purified by silica gel chromatography[6] (72% yield). The optical yield of compound (S)-2 (ee≥98%) has been determined by ^{1}H-NMR using Yb(hfc)$_3$ as chiral shift reagent, while the (S)-configuration has been proposed taking into account that the Andersen reaction takes place with complete inversion at the sulfur center[7]. Treatment of (S)-2 with dimethylamine and formaldehyde in methanol gave a 1:1 mixture of the diastereomeric β-dimethylamino Mannich products, which were directly submitted to cuaternization and elimination of the amine moiety (IMe/CaCO$_3$) yielding crude (S)-1-t-butylsulfonyl-1-p-tolylsulfinylethene (1)[8] (78% yield).

The results corresponding to the Diels-Alder reaction of 1 with cyclopentadiene are summarized in scheme 2.

Scheme 2



1

3a+3b+3c+3d

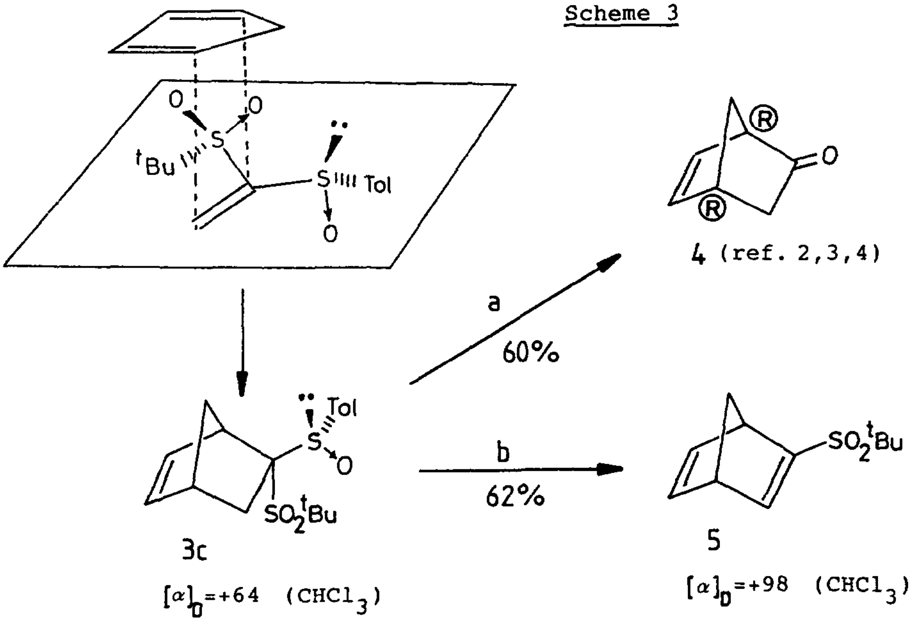
Entry	Lewis acid	Time(h)	Yield 3(%)[a]	3a:3b:3c:3d[b]	Yield 3c(%)[c]
1	---	66	36[d]	9:23:35.23	--
2	ZnBr$_2$ (0.8eq.)	6	68	12:--:88 --	58
3	Eu(fod)$_3$ (1.0eq)	42	70	8:-- 92.--	62
4	SiO$_2$[e]	48	72	10·--:84 6	63

a: Yield of pure adducts 3 after chromatography. b Isomer ratio determined by ^{1}H-NMR. c: Yield of pure adduct 3c after chromatography. d: 60% of (S)-1 was recovered. e: Carried out without solvent[9] (weight ratio SiO$_2$/1=10:1).

In the absence of catalysts the reaction of 1 with cyclopentadiene is very slow (36% of conversion after 66 h at room temperature) and poorly stereoselective (entry 1), while in the presence of strong Lewis acids (BF$_3$ Et$_2$O, Et$_2$ClAl or EtCl$_2$Al) there is no cycloaddition due to the faster decomposition of dienophile 1. Fortunately, in the presence of moderate catalysts such as ZnBr$_2$ (entry 2), Eu(fod)$_3$ (entry 3) and SiO$_2$[9] (entry 4) the Diels-Alder reaction took place mildly, giving good yields of adducts 3. Moreover these catalyzed cycloadditions occur with high stereoselectivity (one diastereomer clearly predominates). The major adduct 3c was easily separated from the mixture by flash chromatography[10] (58-63% yield).

Scheme 3 shows two alternatives for the elimination of the sulfinyl chiral auxiliary. Hydrolysis of 3c with $TiCl_3$ (15% in water) in acetic acid gave the known (+)-(1R,4R)-dehydronorcamphor[2,3,4] (4), showing the utility of (S)-1 as a latent chiral ketene equivalent. On the other hand, the pyrolytic elimination was easily effected by heating 3c at 70°C in toluene containing 2.0 equiv. of trimethylphosphite. (+)-(1R,4S)-2-t-butylsulfonyl-2,5-norbornadiene (5) was obtained in 62% yield after silica gel chromatography[11]. Its enantiomeric purity (ee>80%), has been determined by ^1H-NMR using $Yb(hfc)_3$ as quiral shift reagent.

Scheme 3



a: $TiCl_3$ (15% in water), AcOH, r.t., 5d; b $P(OMe)_3$ (2eq.), toluene, 70ºC, 4d.

Obtaining (1R,4R)-dehydronocamphor by hydrolysis of 3c unambigously shows the 1R,4R configuration of this major adduct. Since Diels-Alder reactions of cyclopentadiene with 1,1-disubstituted olefins usually result in a predominance of the adduct with the bulkier substituent in *endo* configuration[12] (in order to avoid the steric destabilization with the CH_2 fragment on diene), we propose for 3c the configuration 1R,2R,4R shown in scheme 3. This stereochemistry would come from the *endo* approach of diene, with respect to the t-butylsulfonyl group, to the less hindered face of the S-*cis* conformation of dienophile 1[13].

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6.-(±)-2 was prepared in the same way by using (±) methyl p-toluenesulfinate instead of (-)-(S)-menthyl p-toluenesulfinate (76% yield, m p.=88-89°C) Data for (+)-(S)-2. m.p.=116-117°, $[\alpha]_D$=143 (CHCl$_3$, c=1). ^{1}H NMR (CDCl$_3$) δ 7.70 and 7 36 (AA'BB' system, 4H, arom), 4.45 and 4.19 (AB system, 2H, CH$_2$, J=13.6 Hz), 2.44 (s, 3H, CH$_3$) and 1.47 (s, 9H, ^{t}Bu).

7.- The same method has been previously applied to the synthesis of (+)-(S)-phenylsulfonyl p-tolylsulfinyl methane (Annunziata R.; Cinquini M; Cozzi F , *Synthesis*, 1979, 535).

8.- Crude dienophile (+)-(S)-1 was obtained as an oil with a chemical purity >95% ($[\alpha]_D$=+25, CHCl$_3$, c=1). On the contrary (±)-1 (obtained from (±)-2) is a solid (m.p. 116-118°C) ^{1}H-NMR (CDCl$_3$) δ: 7.64 and 7 30 (AA'BB' system, 4H, arom), 7.20 (d, 1H, J=2.0 Hz, C=CH), 6.83 (d, 1H, J=2.0 Hz, C=CH), 2.40 (s, 3H, CH$_3$) and 1.44 (s, 9H, ^{t}Bu).

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10 - Data for (+)-3c: m.p. 109-110°C, R$_f$=0.35 (hexane/ethyl acetate 3:1), $[\alpha]_D$= +64 (CHCl$_3$, c=1). E.e.>80% determined by ^{1}H-NMR with 0.6 eq. of Yb(hfc)$_3$. ^{1}H-NMR (CDCl$_3$) δ· 7.64 and 7.34 (AA'BB' system, 4H, arom), 6.44 (dd, 1H, J=5 7 and 3.1 Hz, C=C$_6$H), 6.06(dd, 1H, J=5.7 and 2.7 Hz, C=C$_5$H), 3.65(m, 1H, C$_1$H), 2.65 (m, 1H, C$_4$H), 2.43 (s, 3H, CH$_3$), 2.03 (dd, 1H, J=14.3 and 3.2 Hz, C$_3$H), 1.68 (s, 9H, ^{t}Bu), 1.66 (d, 1H, J=5.1 Hz, C$_7$H), 1.54 (dd, 1H, J=12.3 and 3.6 Hz, C$_3$H) and 1.42 (d, 1H, J=5.1 Hz, C$_7$H).

11.- ^{1}H-NMR of 5 (CDCl$_3$) δ. 7.70 (d, 1H, J=3.5 Hz, C=C$_3$H), 6.98 (dd, 1H, J=5.1 and 2.9 Hz, C=C$_6$H), 6.83 (dd, 1H, J=5.1 and 3.2 Hz, C=C$_5$H), 3.93 (m, 1H, C$_4$H), 3.83 (m, 1H, C$_1$H), 3.58 (dt, 1H, J=6.66 and 1.5 Hz, C$_7$H), 2.26 (m, 1H, C$_7$H) and 1.31 (s, 9H, ^{t}Bu).

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13.- The greater stability of the *S-cis* conformation with respect to the *S-trans* in related 1,1-disubstituted vinylsulfoxides has been reported (Koizumi T., Aray Y., Takayama H , *Tetrahedron Lett.*, 1987, *28*, 3689).