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DIASTEREOSELECTIVITY IN THE [2,3]-SIGMATROPIC REARRANGEMENT OF SUBSTITUTED ALLYLIC N,N-DIALKYLAMIDOSULFOXYLATES. X-RAY MOLECULAR STRUCTURE OF [(1'S^*, (S)S^*]-(2'E)-4-[[3'-(4"-BROMOPHENYL)-1'-METHYL-2'-PROPENYL] SULFINYL]-MORPHOLINE [1].

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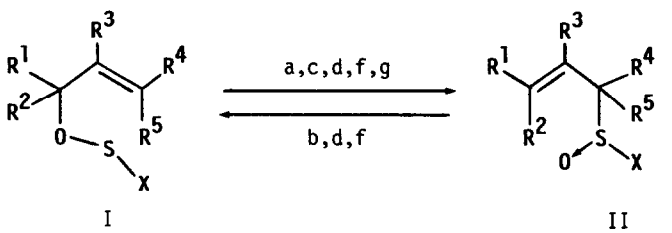
Summary:
By the reaction with three N,N-dialkylamidosulfenyl chlorides **2** bearing representative sizes for the R groups on the nitrogen atom, several substituted secondary E or Z allylic alcohols (**1a-h**) have been converted into the corresponding pairs of diastereoisomeric allylic sulfinamides (**3+3'a-v**), whose ratios have been determined by ^{1}H NMR spectroscopy. Five cases of entirely diastereoselective [2,3]-sigmatropic rearrangement have been observed.
The stereochemistry of one pure diastereoisomer **3'm** has been determined by single crystal X-Ray analysis.
When treated with 4-morpholinesulfenyl chloride, cyclohex-2-en-1-ol is stereoselectively converted to one diastereoisomer of the sulfinamide **5b** which, by unambiguous procedures, led to the same p.tolylsulfoxide **5a** already obtained by treatment of cyclohex-2-en-1-ol with toluene-p-sulfenyl chloride.

Since its discovery two decades ago, the reversible interconversion of allylic sulfenates to sulfoxides [2] has become one of the best known [2,3]-sigmatropic rearrangements. The trichloromethyl [3], methyl [4], and n-propyl [5] allylic sulfoxides have been not widely used in comparison to the numerous aryl allylic sulfoxides which proved their remarkable synthetic utility in the stereospecific syntheses of a variety of functionalised compounds [7].



a) X = CCl_3 (ref. 3)
b) X = CH_3 (ref. 4)
c) X = nC_3H_7 (ref. 5)
d) X = Aryl (ref. 2,6,7)
e) X = OR (ref. 8)
f) X = SR (ref. 9)
g) X = NR_2 (ref. 10)

Scheme 1.

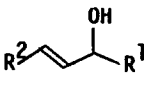
The classic [2,3]-sigmatropic rearrangement of allylic sulfenates (I, X= alkyl or aryl)

has been extended to sulfoxylates (I, X= OR) [8], thiosulfoxylates (I, X =SR) [9] and recently to 4-morpholinosulfenates (I, X= N[$(C_2H_4)_2$] O) [10] which are characterized by the interesting presence of three contiguous heteroatoms. In part IV of this series [10b], we recorded the rearrangements of nine substituted allylic morpholinosulfenates which were generally of low diastereoselectivity except for the esters arising from three alcohols **1f**, **1'f** and **1'h** (**Table 1**, entries 28, 29, 41). These pairs of diastereoisomeric substituted allylic sulfinamides **(3+3')o,u** were found to be stable to equilibration at room temperature whereas some pairs of diastereoisomeric substituted allylic sulfoxides can equilibrate in more or less mild conditions [11]. Seeking a better understanding of the factors influencing the stereochemistry of this [2,3] -sigmatropic rearrangement, we focused our study on the influence of the substituents R^1, R^2 and particularly R upon the ratios of the diastereoisomeric allylic sulfinamides **3** and **3'**.

The task was simplified by the easy access [12,13] to N,N-dimethyl and N,N-bis(1-methylethyl)amidosulfenyl chlorides (**2a,c**). By the reaction with chlorides (**2,a,b** or **c**) carried out in the presence of triethylamine, the representative fifteen secondary (E) or (Z) allylic alcohols (**1a-h**) were converted via the transient N,N-dialkylamidosulfoxylates (Ig) to the corresponding substituted allylic sulfinamides **3** and **3'**. The results are summarised in **Table 1**, the following features being particularly worthy of comment:

- During this work, we have not detected any equilibration between **3** and **3'** *(vide infra)* and their tabulated ratios must therefore be considered as unambiguous.
- When the R groups on nitrogen are small or medium-sized (Me or morpholino), the rearrangements were generally effected in reasonable times (4-6h), except for compounds **(3+3'a,b,e)**; this being probably due to the sulfur atom of the intermediate dialkylamidosulfoxylate approaching a secondary carbon whilst the oxygen leaves a primary or an equivalently substituted carbon. Logically therefore, the N,N-diisopropylamidosulfoxylates required longer times (18-120 h) for complete conversion.
- The yields of sulfinamides were lowered by the presence of bulky groups R^1= iPr, tBu and particularly R= iPr. In each of the seven series starting with (E) and (Z) alcohols (**1,1'a-h**) the use of morpholinesulfenyl chloride gave consistently the best yields of sulfinamides and the reasons for the rather low yields of N,N-dimethylsulfinamides are, at present, unclear.
- The rearrangement of the N,N-dialkylamidosulfoxylates examined was found to be regioselective and moreover led to the exclusive formation of the *trans* olefinic sulfinamides **(3+3')**.
- The diastereoselectivity of the rearrangement of the intermediate (E) allylic N,N-dialkylamidosulfoxylates was generally low except for four N,N-diisopropyl compounds bearing relatively bulky R^1 groups (entries 17,23,30,42). Starting with (Z)-alcohols, the rearrangement took a better level of stereocontrol in nine cases (entries 4,12,16,20,25,29,33,35,41) and became entirely stereoselective in five cases

(entries 18,22,31,37,43).



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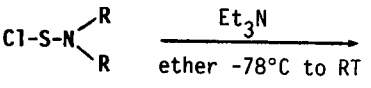
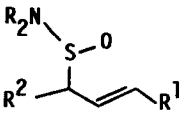


2a R,R= CH_3
2b R,R= $[(C_2H_4)_2]O$
2c R,R= $CH(CH_3)_2$



3+3'

Table 1.

Entry	Alcohol (E)	Alcohol (Z)	R^2	R^1	R	Time (h)	Chemical Yield (%)	ratios of diastereoisomers* 3 : 3'		
1	1a					60	37	(3+3')a	60	: 40
2		1'a	Me	H	Me	5	41			25 : 75
3	1a					72	71	(3+3')b	65	: 35
4		1'a	Me	H		72	90			10 : 90
5	1a					24	4	(3+3')c	65	: 35
6		1'a	Me	H	iPr	120	0			- : -
7	1b					4	52	(3+3')d	60	: 40
8		1'b	Me	Me	Me	4	36			35 : 65
9	1b					48	70	(3+3')e	55	: 45
10		1'b	Me	Me		72	46			30 : 70
11	1b					60	21	(3+3')f	60	: 40
12		1'b	Me	Me	iPr	48	37			10 : 90
13	1c					4	16	(3+3')g	60	: 40
14		1'c	Me	iPr	Me	4	17			30 : 70
15	1c					4	35	(3+3')h	70	: 30
16		1'c	Me	iPr		4	33			5 : 95
17	1c					120	18	(3+3')i	95	: 5
18		1'c	Me	iPr	iPr	48	25			<5 : >95
19	1d					4	33	(3+3')j	65	: 35
20		1'd	Me	tBu	Me	4	28			15 : 85
21	1d					4	64	(3+3')k	65	: 35
22		1'd	Me	tBu		4	54			<5 : >95
23	1d					24	26	(3+3')l	95	: 5
24		1'd	Me	tBu	iPr	120	0			
25		1'e	Me	pBr-C_6H_4		4	83	(3+3')m		5 : 95
26	1f					4	11	(3+3')n	70	: 30
27		1'f	Me	p.Tol	Me	4	60			30 : 70
28	1f					4	73	(3+3')o	77	: 23
29		1'f	Me	p.Tol		4	86			5 : 95
30	1f					18	60	(3+3')p	90	: 10
31		1'f	Me	p.Tol	iPr	72	47			<5 : >95

Table 1. (continued)

32	**1g**		Me	nHept	Me	4	58	(3+3')**q**	65	: 35	
33		**1'g**				4	52			10 :	90
34	**1g**		Me	nHept	O	4	73	(3+3')**r**	55	: 45	
35		**1'g**				4	60			10 :	90
36	**1g**		Me	nHept	iPr	120	35	(3+3')**s**	75	: 25	
37		**1'g**				48	42			<5 :	>95
38	**1h**		iPr	nHept	Me	6	40	(3+3')**t**	50	: 50	
39		**1'h**				4	15			10 :	90
40	**1h**		iPr	nHept	O	4	75	(3+3')**u**	65	: 35	
41		**1'h**				4	75			20 :	80
42	**1h**		iPr	nHept	iPr	72	26	(3+3')**v**	95	: 5	
43		**1'h**				48	11			<5 :	>95

* The ratios of diastereoisomers were determined by ^{1}H NMR.

As well as being pleased by the diastereoselectivity shown in the formation of some of the substituted allylic sulfinamides, we were particularly gratified to find that the pure compounds **3'm**, **3o** and **3'o** are crystalline. The X-ray single crystal diffraction study of **3'm** thus provided an extremely valuable addition to the somewhat sparce information concerning X-ray data of sulfinamides [14].

One part of the molecule is in disorder with occupation of two positions. The two conformations correspond to each other by rotation around Br atom [$<C_7$-Br-C_7'= 6(1)°] and the S-C_1 bond [$<C_2$-C_1-C_2'= 26(2)°; $<C_{14}$-C_1-C_{14}'= 22(2)°]. The perspective view with the atom numbering is given in **Fig. 1**. The fractional coordinates with equivalent isotropic thermal factors are given in **Table 2**.

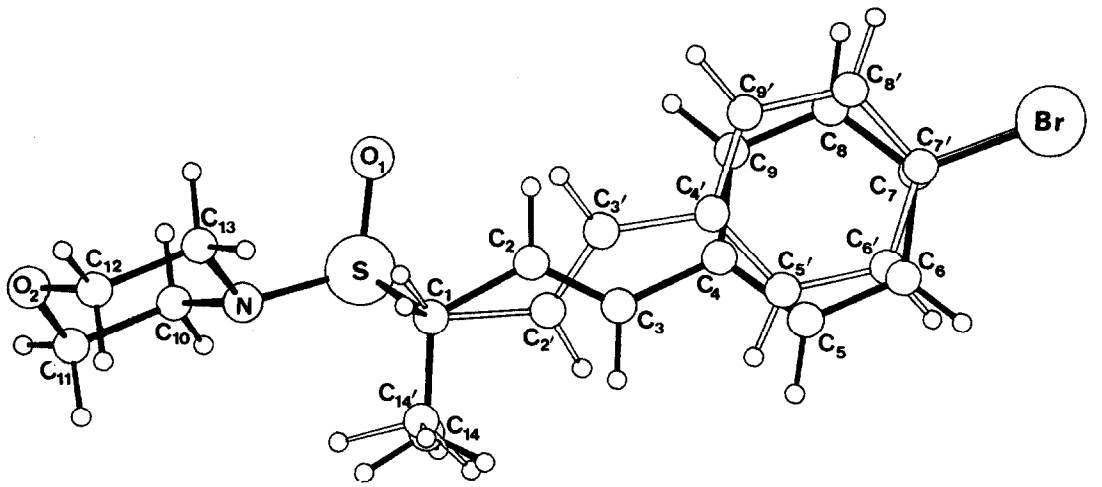


Fig. 1. ORTEP drawing of the molecule **3'm** showing the direction of the free pair on sulfur: filled bonds between atoms with occupation factor 0.6667, empty bonds between atoms with occupation factor 0.3333.

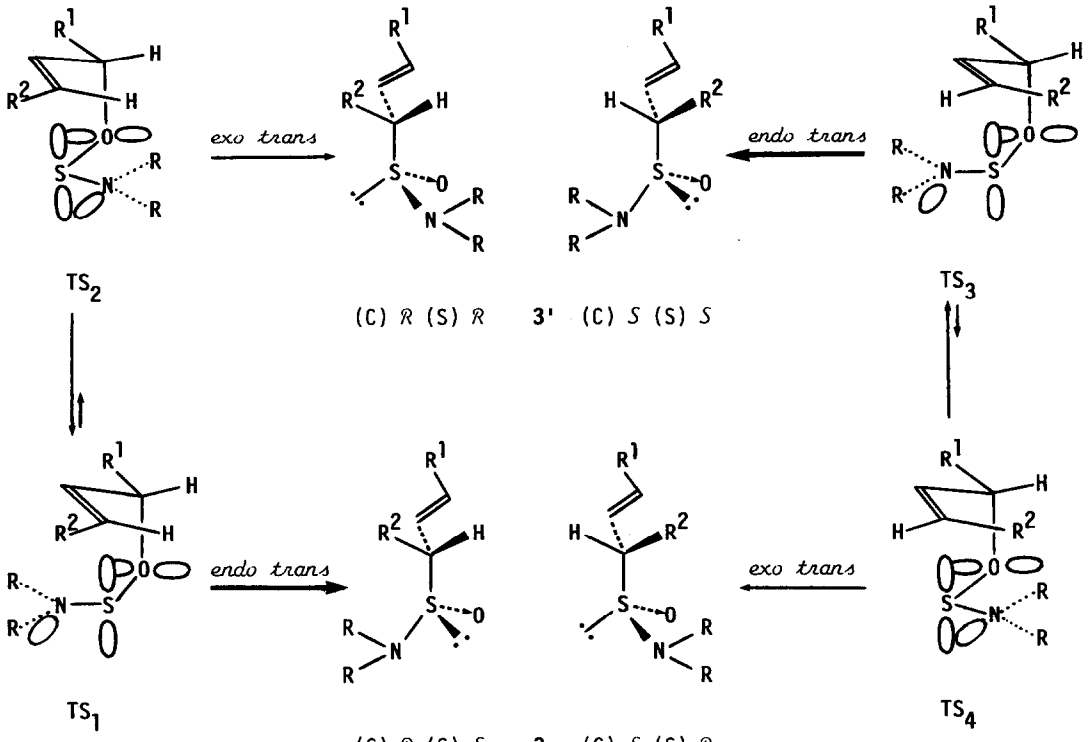
Table 2. Fractional atomic coordinates (x 10^4) for non H-atoms and equivalent isotropic thermal parameters ($Å^2$,x10^3) with esd's in parentheses. The molecular part in disorder concerns the atoms C_2 to C_9 and C_{14} and the corresponding primed atoms, with occupation factors respectively 0.6667 and 0.3333.

$$U_{eq} = 1/3 \sum_i \sum_j U_{ij}\, a_i^*\, a_j^*\, \vec{a}_i.\vec{a}_j$$

	X	Y	Z	U_{eq} ou U_{iso}
Br	9430 (1)	5716 (1)	8103 (1)	76 (1)
S	3587 (2)	1203 (3)	8691 (3)	57 (2)
O_1	3554 (5)	1715 (8)	7503 (6)	75 (8)
O_2	454 (5)	623 (10)	8747 (7)	83 (10)
N	2462 (5)	1077 (8)	9045 (7)	54 (8)
C_{10}	1792 (7)	2202 (12)	8647 (11)	82 (14)
C_{11}	840 (8)	1936 (15)	9116 (12)	95 (17)
C_{12}	1108 (7)	-467 (12)	9172 (11)	80 (14)
C_{13}	2052 (7)	-294 (10)	8695 (10)	68 (12)
C_1	4034 (7)	2653 (10)	9636 (9)	60 (11)
C_2	4880 (12)	3230 (18)	9130 (16)	54 (4)
$C_{2'}$	5125 (28)	2922 (37)	9627 (33)	62 (10)
C_3	5760 (12)	3207 (18)	9646 (14)	59 (4)
$C_{3'}$	5426 (25)	3853 (34)	8915 (29)	61 (8)
C_4	6620 (6)	3788 (13)	9216 (10)	53 (4)
C_5	6593 (6)	4274 (13)	8089 (10)	61 (4)
C_6	7423 (6)	4834 (13)	7728 (10)	59 (5)
C_7	8279 (6)	4907 (13)	8495 (10)	42 (6)
C_8	8306 (6)	4420 (13)	9623 (10)	73 (7)
C_9	7476 (6)	3861 (13)	9983 (10)	53 (4)
$C_{4'}$	6437 (12)	4236 (25)	8816 (20)	49 (7)
$C_{5'}$	6571 (12)	4965 (25)	7817 (20)	56 (8)
$C_{6'}$	7493 (12)	5404 (25)	7652 (20)	49 (8)
$C_{7'}$	8282 (12)	5113 (25)	8486 (20)	60 (26)
$C_{8'}$	8148 (12)	4384 (25)	9485 (20)	48 (10)
$C_{9'}$	7226 (12)	3945 (25)	9650 (20)	69 (10)
C_{14}	4178 (14)	2000 (23)	10860 (18)	73 (6)
$C_{14'}$	4012 (25)	2554 (42)	10858 (33)	59 (10)

The distances and angles found in compound **3'm** are consistent with expected values. We point out the following representative values relative to the olefinic group and the contiguous sulfur atoms: S-N : 1.687 Å (7); S-O_1 : 1.470 Å (8); S-C_1 : 1.823 Å (10); C_2-C_3 : 1.294 Å (24); $C_{2'}$-$C_{3'}$: 1.324 Å (50); $N\widehat{S}O_1$: 110.5° (4); $N\widehat{S}C_1$: 99.0° (4); $C_1\widehat{S}O_1$: 106.7° (4).

Concerning an approximate analysis of the above stereochemical results, one can indeed use the classical interpretation of the reversible [2,3]-sigmatropic rearrangement of allylic arenesulfenates to allylic aryl sulfoxides and *vice-versa*, which includes the concepts of *exo-transoid, exo-cisoid, endo-transoid* and *endo-cisoid* transition states [2,15]. As the substrates in **Table 1** have always given *trans* olefinic sulfinamides, **Scheme 2** shows only four transition states TS_{1-4} [16].



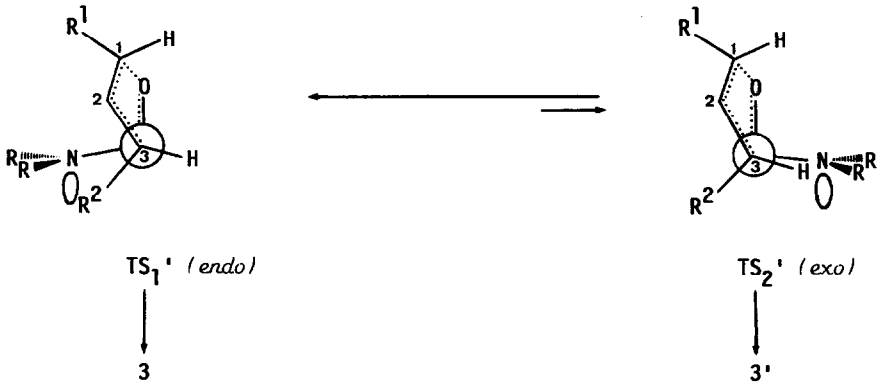
Scheme 2.

Since, to our knowledge, theoretical data on the molecular orbitals of the chain >N-S-O- do not appear in the literature, the following assumptions have been made:

- The angles S-O-C and O-S-N would be close to 110° and 100° respectively, the dihedral angle C-O-S-N is near to 90°, from analogy with the reported calculations of the lower energy conformations for some singly bonded compounds R-S-O-R' and R-S-NR'_2 [17a-e].
- The lone pair of nitrogen and the S-O bond are antiperiplanar for stereoelectronic reasons [18].
- The energy levels and the exact geometry of the lone pairs of sulfur and oxygen are unknown. **Scheme 2** proposes the orthogonal position of these lone pairs i) as a lower energy conformation for a minimal repulsive interaction on the one hand and ii) for putting an overlap of a lone pair of sulfur with the π^* orbital of the double bond.
- The sulfur d orbitals are not taken into account in our proposed transition states [19].

The above reported X-ray structure of compound **3'm** shows clearly that it has arisen from the corresponding morpholinosulfenate through the *endo* transition state TS_3, which should also be favoured for all the other (Z)-allylic dialkylamidosulfoxylates owing to the experimental results of the **Table 1**. The reason for which is probably that the *exo* S-NR_2 group has severe steric interaction with R^2 in the alternative transition state TS_4.

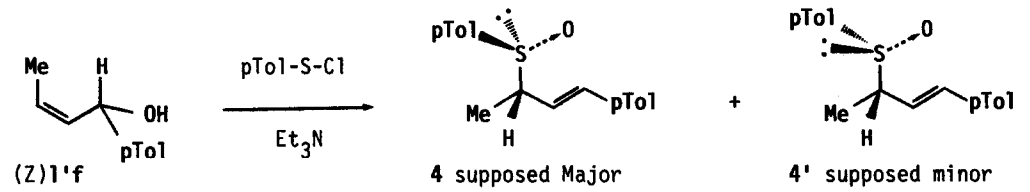
The results of **Table 1** indicate that the formation of the (C) R^* (S) S^* sulfinamides **3** from the (E)-allylic N,N-dialkylamidosulfoxylates is somewhat preferred and thus occurs through an *endo* transition state for reasons which are not obvious from the **Fig.** TS_1 and TS_2. **Scheme 3** represents therefore another views, TS_1' and TS_2' of these transition structures along the axis C_3-S with S behind C_3, and the partially formed C_3····S and O_1····C_1 bonds are almost eclipsed with each other. In the *exo* transition structure, TS_2', from (E)-allylic alcohols, the S-NR_2 and C_3-H bonds are almost eclipsed and this interaction increases with the increasing bulk of the R substituents of the nitrogen. The high diastereoselectivity showed by some N,N-diisopropylamidosulfoxylates (**Table 1**, entries 17,23,30,42) could be explained by the preferred *endo* transition structure TS_1' although the favorable influence of the bulky R^1 groups in these substrates is difficult to rationalize.



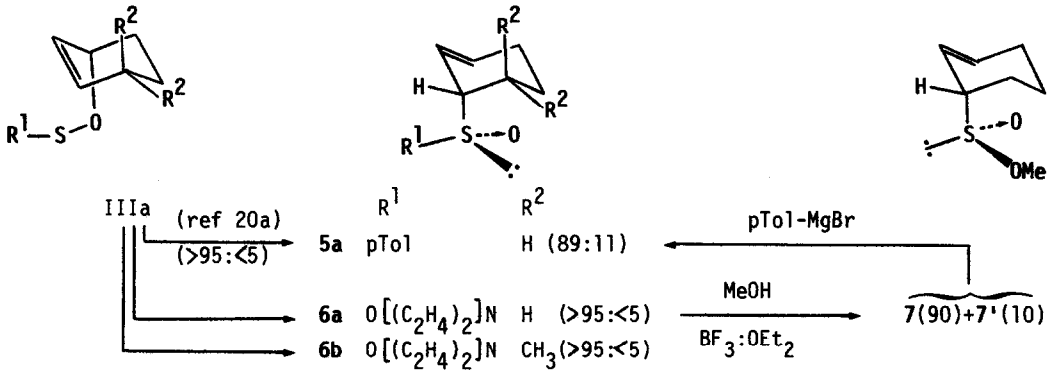
Scheme 3

The above mentioned stability of the diastereoisomeric ratios of some substituted allylic sulfinamides **3**:**3'** to equilibration at room temperature, neat or in non-chlorinated solvents for reasonable times, may be explained by the lack of reversibility during the dialkylamidosulfoxylates Ig ⟶ sulfinamides rearrangements. Furthermore, this view is strengthened by our observations on the stability of the allylic sulfinamides (**3**:**3'r**) when treated with excess of trimethylphosphite or diethylamine in THF for 18h at room temperature: no alcohol **1g** was detected in ^{1}H NMR. These properties of substituted allylic sulfinamides are obviously in contrast to the known reversibility of the sulfenate-sulfoxide rearrangement and offer unique opportunities for the regio- and stereo-controlled manipulation of sulfur functionality.

In order to examine the validity of the favoured *endo* transition state for the conversion of some allylic alcohols to the corresponding sulfoxides, the (Z) alcohol **1'f** was treated with toluene p.sulfenyl chloride in the presence of triethylamine in the usual conditions to provide the corresponding p.Tolyl sulfoxides **4**:**4'**.



The crude product showed in ^{1}H NMR a ca. 55:45 mixture of diastereoisomers; this ratio was probably due to a rapid equilibration [11a] despite the presence of a styrenic group. It thus became difficult to establish a correlation between these sulfoxides **4**:**4'** and the sulfinamides **3**:**3'o**. Therefore, cyclohex-2-en-1-ol was chosen on account of its recorded highly stereoselective transformation [20a] into the sulfoxide **5a** and was treated with 4-morpholinesulfenyl chloride in our usual conditions to afford a single diastereoisomer **6a** of the corresponding sulfinamide. Conversion of this sulfinamide **6a** by a known procedure [21] into the methyl sulfinates **7**:**7'** was not entirely stereoselective (90:10) (^{1}H NMR) and then reaction of **7**:**7'** with p.tolyl magnesium bromide furnished a mixture of sulfoxides (**5**:**5'**)**a** (89:11)(HPLC) in which the major diastereoisomer **5a** showed ^{1}H NMR data very similar to those described in the literature [20a].



The results reported here are of particular interest for a deeper understanding of the factors influencing the diastereoselectivity in the [2,3]-sigmatropic rearrangement of allylic N,N-dialkylamidosulfoxylates into the corresponding sulfinamides. It is apparent that opportunities abound for the development of useful applications of these little-studied classes of sulfur-nitrogen compounds.

EXPERIMENTAL SECTION

The general experimental conditions have been described previously [1b].

The substituted propargyl alcohols were prepared according to Brandsma [22] from freshly distilled commercial aldehydes and lithium derivatives of propyne and 3-methyl-1-butyne [23] *3-pentyn-2-ol, 2-methyl-4-hexyn-3-ol, 2,2-dimethyl-4-hexyn-3-ol, 2-undecyn-4-ol and 2-methyl-3-dodecyn-5-ol* have been described previously [1b].

1-(4-Bromophenyl)-2-butyn-1-ol; mp. 49°C (pentane); IR: 3300 and 2200 cm^{-1}. ^1H NMR: 7.5-7.4 (m,2H); 7.4-7.3 (m,2H); 5.36 (q,J=2Hz,1H); 2.55-2.35 (m,1H); 1.89 (d,J=2Hz,3H). ^{13}C NMR: 140.1 (4°); 131.5 (3°); 128.3 (3°); 122.1 (4°); 83.7 (4°); 78.7 (4°); 64.0 (3°); 3.7 (1°). MS (CI): 244 (M^++18,3); 243 (M^++17,6); 242 (M^++18,4); 241 (M^++17,6); 227 (M^++1,4); 226 (M^++1,35); 225 (M^+,6); 224 (M^+,39); 210 (6); 209 (52); 208 (9); 207 (100).

1-(4-Methylphenyl)-2-butyn-1-ol; $bp_{0.05}$= 94°C; IR: 3380 and 2215 cm^{-1}. ^1H NMR: 7.42-7.35 (m,2H); 7.2-7.1 (m,2H); 5.35 (q,J=2Hz,1H); 2.7-2.45 (m,1H); 2.33 (s,3H); 1.87 (d,J=2Hz,3H). ^{13}C NMR: 138.4 (4°); 137.9 (4°); 129.2 (3°); 126.5 (3°); 82.7 (4°); 79.4 (4°); 64.5 (3°); 21.1 (1°); 3.7 (1°). MS (CI): 178 (M^++18,5); 177 (M^++17,12); 176 (M^++16,11); 161 (M^++1,7); 160 (M^+,43); 143 (100).

The (E)-allylic alcohols were prepared from the above substituted propargylic alcohols by reduction with lithium aluminium hydride [24] and were found to be pure (>99%; GLC or HPLC).

2-Methyl-4(E)-hexen-3-ol (**1c**): bp_{18}= 52-54°C; (Lit.[25]: bp_{25}= 58°C).

2,2-Dimethyl-4(E)-hexen-3-ol (**1d**): bp_{12}= 55-57°C; (Lit.[26]: bp_{33-35}= 63-65°C).

1-(4-Methylphenyl)-2(E)-buten-1-ol (**1f**): mp= 45-46°C(pentane); IR: 3340, 1660 and 980 cm^{-1} ^1H NMR: 7.35-7.25 (m,2H); 7.25-7.15 (m,2H); 5.88-5.66 (m,2H); 5.2-5.1 (m,1H); 2.35 (s,3H); 2.04 (br s,1H); 1.72 (dd,J=6 and 1Hz,3H). ^{13}C NMR: 140.4 (4°); 138.9 (4°); 133.6 (3°) ; 129.0 (3°); 126.7 (3°); 126.0 (3°); 74.8 (3°); 21.0 (1°); 17.6 (1°). MS (EI): 162 (M^+,12); 161 (10); 147 (26); 144 (34); 143 (13); 129 (100); 128 (72); 127 (23); 119 (52); 116 (36); 105 (22); 91 (70).

2(E)-Undecen-4-ol (**1g**): $bp_{0.01}$ = 56-57°C; IR: 3360, 1670 and 975 cm^{-1}. ^1H NMR 5.70 (dqd, J=15, 7 and 1Hz,1H); 5.54 (ddq,J=15, 7 and 2Hz,1H); 4.05 (dt,J=7 and 7Hz,1H); 2.45 (br s,1H); 1.62 (dd,J=7 and 2Hz,3H); 1.45-1.16 (m,12H); 0.9 (t,J=7Hz,3H). ^{13}C NMR: 134.3 (3°); 126.5 (3°); 73.4 (3°); 37.2 (2°); 31.8 (2°); 29.5 (2°); 29.2 (2°); 25.4 (2°); 22.6 (2°); 17.5 (1°); 14.0 (1°). MS (CI): 170 (M^+,46); 100 (100).

2-Methyl-3(E)-dodecen-5-ol (**1h**): $bp_{0.03}$ = 67-72°C; IR: 3440, 1675 and 980 cm^{-1}. ^1H NMR: 5.66 (ddd,J=16, 6.5 and 1Hz,1H); 5.45 (ddd,J=16, 7 and 1.5Hz,1Hz); 4.07 (m,1H); 2.31 (dhd, J=6.5, 6.5 and 1Hz,1H); 2.0 (br s,1H); 1.7-1.2 (m,12H); 1.0 (d,J=6.5Hz,6H); 0.88 (t, J=7.5Hz,3H). ^{13}C NMR: 138.9 (3°); 130.0 (3°); 73.2 (3°); 37.4 (2°); 31.8 (2°); 30.6 (3°); 29.5 (2°); 29.2 (2°); 25.4 (2°); 22.6 (2°); 22.3 (1°); 22.2 (1°); 14.0 (1°). MS (CI): 198 (M^+,33); 197 (100).

The (Z)-allylic alcohols were prepared by partial hydrogenation of the substituted propargylic alcohols with Lindlar catalyst [27] and were found to be pure 97-99% with 3-1% of the corresponding (E)-allylic alcohols (GLC or HPLC).

3(Z)-Penten-2-ol (**1'b**): bp_{60}= 58-60°C; (Lit.[28]: bp= 120-121°C).

2-Methyl-4(Z)-hexen-3-ol (**1'c**): bp_{20}= 50-52°C; (Lit.[25]: bp_{30}= 60°C).

2,2-Dimethyl-4(Z)-hexen-3-ol (**1'd**): bp_{12}= 53-54°C. IR 3340,1440 and 750 cm^{-1}. ^1H NMR: 5.67 (dqd,J=11, 7 and 1Hz,1H); 5.46 (ddq,J=11, 9 and 2Hz,1H); 4.11 (dd,J=9 and 1Hz,1H); 1.68 (dd,J=7 and 2Hz,3H); 1.49 (br s,1H); 0.9 (s,9H). ^{13}C NMR: 132.8 (3°); 126.1 (3°); 67.1 (3°); 35.4 (4°); 25.5 (1°); 13.0 (1°). MS (CI): 128 (M^+,55); 111 (100).

1-(4-Bromophenyl)-2(Z)-buten-1-ol (**1'e**): oil; IR: 3360, 1590, 1485 and 740 cm^{-1}. ^1H NMR: 7.42-7.32 (m,2H); 7.20-7.10 (m,2H); 5.65-5.40 (m,3H); 1.92 (br s,1H); 1.7 (dd,J=6.5 and 1Hz,3H). ^{13}C NMR 142.6 (4°); 132.4 (3°); 131.4 (3°); 127.5 (3°); 126.6 (3°); 121.0 (4°); 68.6 (3°); 13.3 (1°). MS (CI) 246 (M^++18,7); 244 (M^++18,7); 228 (M^+,35); 226 (M^+,38); 212

(11); 211 (60); 210 (13); 209 (100).

1-(4-Methylphenyl)-2(Z)-buten-1-ol (**1'f**): $bp_{0.01}$ = 75°C; IR: 3350, 1655, 1440, 980 and 780 cm^{-1}. ^1H NMR: 7.35-7.25 (m,2H); 7.25-7.15 (m,2H); 5.74-5.58 (m,2H); 5.58-5.50 (m,2H); 2.34 (s,3H); 2.24 (br s,1H); 1.76 (d,J=5Hz,3H). ^{13}C NMR: 140.8 (4°); 136.4 (4°); 133.1 (3°); 128.7 (3°); 125.6 (3°); 125.0 (3°); 68.7 (3°); 20.7 (1°); 12.9 (1°). MS (EI): 162 (M^+,19); 147 (50); 129 (62); 128 (40); 119 (55); 115 (38); 105 (24); 93 (57); 92 (50); 91 (100).

2(Z)-Undecen-4-ol (**1'g**): $bp_{0.02}$ = 52-53°C; IR: 3350, 1640 and 740 cm^{-1}. ^1H NMR: 5.6 (dqd, J=12.5, 7 and 1Hz,1H); 5.45 (ddq,J=12.5, 11 and 2Hz,1H); 4.5 (dt,J=7 and 7Hz,1H); 1.8 (br s 1H); 1.7 (dd,J=7 and 2Hz,3H); 1.51-1.20 (m,12H); 0.9 (t,J=7Hz,3H). ^{13}C NMR: 133.6 (3°); 125.7 (3°); 67.2 (3°); 37.3 (2°); 31.7 (2°); 29.5 (2°); 29.2 (2°); 25.2 (2°); 22.5 (2°); 13.9 (1°); 13.1 (1°); MS (CI): 188 (M^++18,60); 171 (M^++1,23); 170 (M^+,100); 153 (78).

2-Methyl-3(Z)-dodecen-5-ol (**1'h**): $bp_{0.04}$ = 70-72°C. IR: 3340, 1405 and 765 cm^{-1}. ^1H NMR: 5.21 (dd,J=10.5 and 9Hz,1H); 5.17 (dd,J=10.5 and 8Hz,1H); 4.40-4.30 (m,1H); 2.57 (dh,J=9 and 6.5Hz,1H); 1.55 (br s,1H); 1.55-1.30 (m,2H); 1.30-1.10 (m,10H); 0.92 (d,J=6.5Hz,3H); 0.88 (d,J=6.5Hz,3H); 0.82 (t,J=7Hz,3H). ^{13}C NMR: 139.2 (3°); 130.2 (3°); 67.8 (3°); 37.6 (2°); 31.7 (2°); 29.5 (2°); 29.2 (2°); 28.9 (3°); 23.2 (2°); 23.1 (2°); 22.6 (2°); 14.0 (1°). MS(CI): 198 (M^+,27) ; 197 (100).

The *N,N-dialkylamidosulfenyl chlorides* **2a,b,c** were prepared following a previously described procedure [1b].

Preparation of allylic sulfinamides **3,3'(a-v)**.

Procedure A: Using N,N-dimethylamidosulfenyl chloride **2a** or 4-morpholinesulfenyl chloride **2b**.

A solution of substituted allylic alcohol **1** or **1'**(5 mmol) and triethylamine (10 mmol) in anhydrous ether (20 mL) was stirred at -78°C under argon. A solution of N,N-dialkylamidosulfenyl chloride (5 mmol) in ether (10 mL) was rapidly added. A solid precipated out immediately. The mixture was stirred at -78°C for 15 min then warmed to room temperature. After stirring 1hr, the mixture was filtered through a small amount of Kieselgel and the solid washed with ether (2x20 mL). After evaporation of the solvent under reduced pressure, the crude product was left at room temperature under argon for the time indicated in **Table 1**. Purification of the sulfinamides **3+3'** was performed by flash chromatography (Kieselgel Merck 230-400 mesh) using ether:acetone (100:0 to 80:20) as eluent.

Procedure B: Using bis(1-methylethyl)-amidosulfenyl chloride **2c**.

To a stirred solution of substituted allylic alcohol (5 mmol) in anhydrous ether (10 mL) cooled at 0°C, a solution of n-butyl lithium in hexane (5 mmol) was added dropwise and the solution was stirred at room temperature for 1h. After cooling at -78°C, a solution of chloride **2c** (5 mmol) in ether(10 mL) was added dropwise. After stirring at -78°C for 15 min, the mixture was allowed to warm to room temperature and left during the time indicated in **Table 1**. After addition of water, the organic layer was separated and the aqueous phase extracted with ether (3x10 mL). The combined organic extracts were washed with brine and dried over potassium carbonate. After filtration and evaporation of the solvent under reduced pressure, the crude sulfinamide was purified as above.

The yields, ratios of diastereoisomers and spectral data are given in **Tables 1, 3, 4** and **5**. The ratios **3:3'** cannot be determined by HPLC due to decomposition.

Most of these allylic sulfinamides can be stored under argon at -18°C for several months, without noticeable decomposition or modification of diastereoisomeric ratios.

Samples of the above purified mixtures of diastereoisomeric sulfinamides (**3:3'**,**m** and **o**) were carefully chromatographed on a column of silicagel with ether : acetone (100:0→80:20) as eluent. Some pure fractions (^1H NMR;250 MHz) were twice crystallised from ether: **3'm**: mp. 110°C; **3o**: mp. 78-79°C (unstable at exposure to air); **3'o**: mp. 101°C (not suitable for single crystal X-ray analysis).

Table 3.: ^{1}H NMR data for allylic sulfinamides 3 and 3'.

	diastereoisomer 3	Common signals	diastereoisomer 3'
a	5.81(ddd,J=17.5,11 and 7Hz,1H) 5.3-5.2(m,2H) 2.66(s,6H) 1.42(d,J=7Hz,3H)	3.6-3.45(m,2H)	6.0(ddd,J=16.5,11 and 7.5Hz,1H) 5.45-5.32(m,2H) 2.68(s,6H) 1.25(d,J=7Hz,3H)
b	5.85(ddd,J=17,11 and 8Hz,1H) 5.36-5.24(m,2H) 1.44(d,J=7Hz,3H)	3.88-3.72(m,8H) 3.6-3.4(m,2H) 3.2-3.1(m,8H)	6.0(ddd,J=17,11 and 7.5Hz,1H) 5.5-5.38(m,2H) 1.3(d,J=7Hz,3H)
c	5.81(ddd,J=17,11 and 7.5Hz,1H) 5.3-5.2(m,2H) 1.42(d,J=7Hz,3H) 1.34(d,J=7Hz,6H) 1.13(d,J=7Hz,6H)	3.85-3.66(m,4H) 3.55(m,2H)	6.06(ddd,J=17,11 and 7.5Hz,1H) 5.4-5.3(m,2H) 1.35(d,J=7Hz,6H) 1.25(d,J=7Hz,3H) 1.18(d,J=7Hz,6H)
d	5.72(dqd,J=15.5,7.5 and 1Hz,1H) 5.42(dqd,J=15.5,7.5 and 1.5Hz,1H) 2.75(s,6H) 1.4(d,J=7Hz,3H)	3.45-3.25(m,2H) 1.8-1.7(m,2H)	5.81(dqd,J=15.5,7 and 1Hz,1H) 5.58(ddq,J=15.5,7.5 and 1.5Hz,1H) 2.76(s,6H) 1.2(d,J=7Hz,3H)
e	5.72(dqd,J=15.5,7 and 1Hz,1H) 5.44(ddq,J=15.5,8 and 1.5Hz,1H) 1.4(d,J=7Hz,3H)	3.88-3.73(m,8H) 3.55-3.35(m,2H) 3.35-3.1(m,8H) 1.83-1.73(m,6H)	5.84(dqd,J=15.5,6.5 and 1Hz,1H) 5.59(ddq,J=15.5,8 and 1.5Hz,1H) 1.29(d,J=7Hz,3H)
f	5.66(dqd,J=15.5,7 and 1Hz,1H) 5.4(ddq,J=15.5,7 and 1.5Hz,1H) 1.7(dd,J=7 and 1Hz,3H) 1.39(d,J=7Hz,3H) 1.33(d,J=7Hz,6H) 1.1(d,J=7Hz,6H)	3.75-3.65(m,4H) 3.45-3.3(m,2H)	5.72(dqd,J=15,7 and 1Hz,1H) 5.5?(ddq,J=15,7 and 1.5Hz,1H) 1.75(d,J=7Hz,3H) 1.3(d,J=7Hz,6H) 1.19(d,J=7Hz,3H) 1.12(d,J=7Hz,6H)
g	5.51(dd,J=15.5 and 7Hz,1H) 5.2(ddd,J=15.5,8 and 1Hz,1H) 2.65(s,6H) 1.28(d,J=7Hz,3H) 0.89(d,J=5Hz,6H)	3.3-3.13(m,2H) 2.33-2.13(m,2H)	5.62(ddd,J=15.5,6.5 and 1Hz,1H) 5.39(ddd,J=15.5,7 and 1Hz,1H) 2.66(s,6H) 1.22(d,J=7Hz,3H) 0.99(d,J=5Hz,6H)
h	5.53(ddd,J=15.5,8 and 1Hz,1H) 5.22(ddd,J=15.5,8 and 1Hz,1H) 1.29(d,J=7Hz,3H)	3.75-3.52(m,8H) 3.4-3.2(m,2H) 3.18-2.78(m,8H) 2.3-2.1(m,2H) 0.91(d,J=7Hz,12H)	5.65(ddd,J=15.5,7 and 1Hz,1H) 5.38(ddd,J=15.5,7 and 1Hz,1H) 1.18(d,J=7Hz,3H)
i	5.59(ddd,J=15.5,7 and 1Hz,1H) 5.31(ddd,J=15.5,7 and 1Hz,1H) 1.4(d,J=7Hz,3H) 1.33(d,J=7Hz,6H) 1.12(d,J=7Hz,6H) 0.99(d,J=7Hz,6H)	3.85-3.65(m,4H) 3.5-3.3(m,2H) 2.45-2.25(m,2H)	5.71(dd,J=15.5 and 7Hz,1H) 5.53(dd,J=15.5 and 7Hz,1H) 1.35(d,J=7Hz,6H) 1.23(d,J=7Hz,3H) 1.16(d,J=7Hz,6H) 1.02(d,J=7Hz,6H)
j	5.66(dd,J=16 and 1Hz,1H) 5.24(dd,J=16 and 8Hz,1H) 2.72(s,6H) 1.37(d,J=7Hz,3H) 1.02(s,9H)	3.4-3.2(m,2H)	5.76(dd,J=16 and 1Hz,1H) 5.45(dd,J=16 and 7.5Hz,1H) 2.74(s,6H) 1.23(d,J=7Hz,3H) 1.03(s,9H)

Table 3. (continued)

k	5.66(dd,J=16 and 1Hz,1H) 5.26(dd,J=16 and 8Hz,1H) 1.4(d,J=7Hz,3H) 1.03(s,9H)	3.81-3.69(m,8H) 3.5-3.3(m,2H) 3.25-3.05(m,8H)	5.78(dd,J=16 and 1Hz,1H) 5.43(dd,J=16 and 7.5Hz,1H) 1.18(d,J=7Hz,3H) 1.04(s,9H)
l	5.66(dd,16 and 1Hz,1H) 5.3(dd,J=16 and 8Hz,1H) 3.75(h,J=6.5Hz,2H) 3.5(dq,J=8 and 7.5Hz,1H) 1.39(d,J=7.5Hz,3H) 1.33(d,J=6.5Hz,6H) 1.12(d,J=6.5Hz,6H) 1.00(s,9H)		
m			7.47-7.38(m,2H) 7.31-7.22(m,2H) 6.58(d,J=16Hz,1H) 6.27(dd,J=16 and 8Hz,1H) 3.86-3.7(m,4H) 3.7-3.55(m,1H) 3.28-3.1(m,4H) 1.4(d,J=7Hz,3H)
n	6.58(d,J=16Hz,1H) 6.13(dd,J=16 and 8Hz,1H) 2.78(s,6H) 2.36(s,3H) 1.5(d,J=7Hz,3H)	7.4-7.3(m,4H) 7.22-7.15(m,4H) 3.43(m,2H)	6.65(d,J=16Hz,1H) 6.28(dd,J=16 and 7.5Hz,1H) 2.82((s,6H) 2.35(s,3H) 1.35(d,J=7.5Hz,3H)
o	6.49(d,J=16Hz,1H) 6.05(dd,J=16 and 7.5Hz,1H) 2.34(s,3H) 1.5(d,J=7.5Hz,3H)	7.32-7.2(m,4H) 7.18-7.04(m,4H) 3.84-3.68(m,8H) 3.7-3.5(m,2H) 3.3-3.08(m,8H)	6.59(d,J=16Hz,1H) 6.2(dd,J=16 and 7.5Hz,1H) 2.32(s,3H) 1.39(d,J=7.5Hz,3H)
p	6.47(d,J=16Hz,1H) 6.05(dd,J=16 and 7.5Hz,1H) 3.8-3.6(m,3H) 2.35(s,3H) 1.51(d,J=7Hz,3H) 1.35(d,J=7Hz,6H) 1.1(d,J=7Hz,6H)	7.4-7.2(m,4H) 7.15-7.05(m,4H)	6.6(d,J=16Hz,1H) 6.3(dd,J=16 and 7.5Hz,1H) 3.82(h,J=7Hz,2H) 3.65(dq,J=7.5 and 7Hz,1H) 2.05(s,3H) 1.35(d,J=7Hz,9H) 1.2(d,J=7Hz,6H)
q	5.61(dtd,J=16,7 and 1Hz,1H) 5.32(ddt,J=16,7 and 1.5Hz,1H) 2.75(s,6H) 1.32(d,J=7Hz,3H)	3.4-3.25(m,2H) 2.11-1.95(m,4H) 1.3-1.19(m,20H) 0.85(t,J=7Hz,6H)	5.75(dtd,J=16,7 and 1Hz,1H) 5.42(ddt,J=16,7.5 and 1.5Hz,1H) 2.77(s,6H) 1.17(d,J=7Hz,3H)
r	5.61(dtd,J=16,7 and 1Hz,1H) 5.35(ddt,J=16,7 and 1Hz,1H) 1.3(d,J=7Hz,3H)	3.8-3.7(m,8H) 3.37(m,2H) 3.21-3.02(m,8H) 2.15-2.02(m,4H) 1.45-1.16(m,20H) 0.85(t,J=7Hz,6H)	5.75(dtd,J=16,7 and 1Hz,1H) 5.5(ddt,J=16,7.5 and 1.5Hz,1H) 1.1(d,J=7Hz,3H)

Table 3. (continued)

s	5.62(dt,J=15.5 and 7Hz,1H) 5.36(dd,J=15.5 and 7Hz,1H) 1.41(d,J=7Hz,3H) 1.34(d,J=7Hz,6H) 1.12(d,J=7Hz,6H)	3.7(h,J=7Hz,2H) 3.4(qd,J=7 and 7Hz, 2H) 2.15-1.96(m,4H) 1.5-1.2(m,20H) 0.9(t,J=7Hz,6H)	5.74(dt,J=15.5 and 6.5Hz,1H) 5.51(dd,J=15.5 and 7Hz,1H) 1.35(d,J=7Hz,6H) 1.23(d,J=7Hz,3H) 1.16(d,J=7Hz,6H)
t	5.5(dt,J=15.5 and 7Hz,1H) 5.26(ddt,J=15.5,10.5 and 1.5Hz, 1H) 2.70(s,6H) 0.93(d,J=7Hz,6H)	3.1-2.9(m,2H) 2.1-1.95(m,6H) 1.48-1.18(m,20H) 0.8(t,J=7Hz,6H)	5.66(dt,J=15 and 7Hz,1H) 5.38(ddt,J=15,10 and 1.5Hz,1H) 2.67(s,6H) 0.87(d,J=7Hz,6H)
u	5.6(dt,J=15.5 and 7Hz,1H) 5.28(ddt,J=15.5,10.5 and 1Hz,1H)	3.86-3.66(m,8H) 3.28-3.04(m,10H) 2.25-2.03(m,6H) 1.48-1.16(m,20H) 1.05-0.9(m,18H)	5.76(dt,J=15.5 and 7Hz,1H) 5.5(ddt,J=15.5,10 and 1.5Hz,1H)
v	5.54(dt,J=15.5 and 7Hz,1H) 5.2(ddt,J=15.5,10.5 and 1.5Hz,1H) 3.87-3.6(m,2H) 3.25(dd,J=10.5 and 3Hz,1H) 1.34(d,J=7Hz,6H) 1.08(d,J=7Hz,6H) 0.99(d,J=7Hz,3H) 0.95(d,J=7Hz,3H)	2.1-1.98(m,6H) 1.5-1.2(m,20H) 0.89(t,J=6.5Hz,6H)	5.7(dt,J=15.5 and 6.7Hz,1H) 5.49(ddt,J=15.5,10 and 1Hz,1H) 3.76(h,J=6.5Hz,2H) 3.05(dd,J=10 and 3.5Hz,1H) 1.33(d,J=6.5Hz,6H)) 1.14(d,J=6.5Hz,6H) 0.96(d,J=4Hz,3H) 0.93(d,J=7Hz,3H)

Table 4: ^{13}C NMR data for allylic sulfinamides.

3'e: 129.8 (3°); 125,8 (3°); 66.6 (2°); 59.0 (3°); 45.9 (2°); 17.9 (1°); 14.4 (1°).
3l: 144.9 (3°); 121.1 (3°); 58.5 (3°); 45.4 (3°); 33.1 (4°); 29.3 (1°); 23.0 (1°); 15.6 (1°).
3'm: 135.1 (4°); 132.2 (3°); 131.5 (3°); 127.9 (3°); 125.3 (3°); 121.5 (4°); 66.7 (2°); 60.0 (3°); 46.0 (2°); 14.0 (1°).
3'p: 137.3 (4°); 135.8 (4°); 133.2 (3°); 129.0 (3°); 128,3 (3°); 124,9 (3°); 59.7 (3°); 45.4 (3°); 23.9 (1°); 23.0 (1°); 21.0 (1°); 14.6 (1°).
3's: 135.3 (3°); 126.0 (3°); 59.0 (3°); 45.2 (3°); 32.6 (2°); 31.6 (2°); 28.9 (2°); 28.8 (2°); 23.8 (1°); 22.9 (1°); 22.4 (2°); 14.7 (1°); 13.9 (1°).
3'v: 137.5 (3°); 121.1 (3°); 71.0 (3°); 45.5 (3°); 32.7 (2°); 31.7 (2°); 29.1 (2°); 29.05 (2°); 29.0 (2°); 27.9 (3°); 23.2 (1°); 22.5 (2°); 21.5 (1°); 18.4 (1°); 14.0 (1°).

Table 5: Other spectroscopic and analytical data for allylic sulfinamides.

Compound	IR (cm^{-1})	MS (m/e, rel. int. %)	Formulae	Analyses (C,H,N)	calc.	found.
3+3'a	1640,1460,1420 915,840	165(M^++18,30);148(M^++1,100)	$C_6H_{13}NOS$			
3+3'b	1630,1450,1415 970,730	207(M^++18,25);190(M^++1,80) 105(100)	$C_8H_{15}NO_2S$	50.75 51.02	7.99 8.45	7.40 7.32
3+3'c	1640,1470,1400 920,745	204(M^++1,80);102(100)	$C_{10}H_{21}NOS$	59.07 59.20	10.41 10.22	6.89 6.75
3+3'd	1640,1070,970	162(M^++1,100)	$C_7H_{15}NOS$	52.14 51.87	9.37 9.52	8.68 8.87

Table 5. (continued)

3+3'e	1655,1120,1075 970	204(M^++1,25);102(100)	$C_9H_{17}NO_2S$	53.20 52.99	8.40 8.65	6.90 6.96
3+3'f	1630,1130,1060 965	218(M^++1,30);132(100)	$C_{11}H_{23}NOS$			
3+3'g	1630,1110,1055 970	189(M^++1,80);142(67);129(77); 114(100)	$C_9H_{19}NOS$			
3+3'h	1630,1110,1070 970	232(M^++1,75);105(100)	$C_{11}H_{21}NO_2S$	57.11 57.38	9.15 9.39	6.05 6.21
3+3'i	1630,1120,1050 965		$C_{13}H_{27}NOS$	63.61 63.70	11.09 10.97	5.70 5.58
3+3'j	1635,1060,970	204(M^++1,32);143(70),128(100); 126(98)	$C_{10}H_{21}NOS$			
3+3'k	1635,1110,1065 970	246(M^++1,100)	$C_{12}H_{23}NO_2S$	58.74 58.40	9.45 9.41	5.71 5.61
3l	1635,1110,1065 970	260(M^++1,100);134(85);102(88)	$C_{14}H_{29}NOS$	64.81 64.50	11.27 11.20	5.40 5.26
3'm	1650,1115,1070 970	363(M^++18,14);361(M^++18,14) 346(M^++1,30);344(M^++1,29); 211(88);209(100)	$C_{14}H_{18}BrNO_2S$	48.83 48.68	5.27 5.22	4.07 3.93
3+3'n	1650,1130,1060 970	255(M^++18,38);238(M^++1,100)	$C_{13}H_{19}NOS$	65.79 66.04	8.07 8.15	5.90 5.76
3'o	1635,1110,1055 970	280(M^++1,10);145(100)	$C_{15}H_{21}NO_2S$	64.48 64.26	7.57 7.77	5.01 5.19
3+3'p	1620,1130,1030 975	294(M^++1),10);145(100)	$C_{17}H_{27}NOS$	69.58 69.11	9.27 9.44	4.77 4.61
3+3'q	1635,1170,1060 960	263(M^++18,12);246(M^++1,100)	$C_{13}H_{27}NOS$	63.62 63.34	11.09 11.21	5.71 5.79
3+3'r	1655,1115,1070 970	288(M^++1,100)	$C_{15}H_{29}NO_2S$	62.67 62.45	10.17 10.27	4.87 4.91
3+3's	1650,1135,1070 960	302(M^++1,100)	$C_{17}H_{35}NOS$	67.71 67.52	11.70 11.78	4.64 4.79
3+3't	1635,1050,965	274(M^++1,15);102(100)	$C_{15}H_{31}NOS$	65.88 66.10	11.43 11.62	5.12 5.61
3+3'u	1650,1110,1060 965	316(M^++1,100)	$C_{17}H_{33}NO_2S$	64.72 64.51	10.54 10.47	4.44 4.69
3+3'v	1650,1120,1060 965	330(M^++1,100)	$C_{19}H_{39}NOS$	69.24 69.57	11.93 12.03	4.26 4.45

Single crystal X ray analysis for compound ***3'm.***

Rough formula: $C_{14}H_{18}BrNO_2S$, M= 344.28; monoclinic, space group $P2_{1/n}$; a= 13.994 (6) Å,

b= 9.502 (4) Å, c= 11.715 (5) Å, β= 98.04 (4)°, V= 1542 Å^3, Z =4, D_m= 1.50 g.cm^{-3}, D_c= 1.48 g.cm^{-3}. Graphite monochromated MoK$_\alpha$ radiation (0.7107 Å), μ= 27.12 cm^{-1}.

A crystal about 0.57x0.57x0.30 mm was mounted on a four circle Phillips PW 1100 diffractometer. Data collection performed with θ-2θ scan technique up to θ= 26° provided 6696 reflexions corresponding to two asymetric units ±h, ±k, l, out of which 1218 with $I \geqslant 3\sigma(I)$ were used in refinement by full matrix least-square procedure. The structure solved by direct methods using SHELX86 [29] and was refined with SHELX76 [30] programs, weights being in the form $w = 1/\sigma^2(F)+2.6\ 10^{-3}F^2$. Absorption corrections were not applied.
In a first step the structure was refined to R =6.4% all atoms considered with anisotropic thermal factors. However the abnormally short (1.05 Å) C_2=C_3 distance and the high equivalent isotropic thermal factor of C_3 with the presence of a pic close to C_3 in the difference-Fourier synthesis led to consider the presence of disorder, unity occupation factor for C_3 being inconvenient. The refinement of the disordered part of the molecule (see **Fig 2**) required constraints on the phenyl rings which were refined in rigid blocks with theoretical angles and distances of 1.395 Å between the carbons, the other atoms of the disordered fragment being free to vary. Anisotropic thermal factors were introduced for all the atoms except the disordered ones. All hydrogens were introduced in theoretical positions with a conventionnal distance of 1 Å from bound atom and isotropic thermal factor set to equal to 10% larger than that of the latter. The refinement led to R = 6.1%, R_w= 7.7%. The last Fourier-synthesis showed a maximum electron density of 0.77 e.Å^{-3} in the area of bromine.
The interatomic distances and angles, the anisotropic thermal factors, the coordinates of the H-atoms and the F_o, F_c listing have been deposited at the Cambridge Crystallographic data Center.

4-Methyl-1-[[1'-methyl-3'(4"-methylphenyl)-2'(E)-propenyl]-sulfinyl]-benzenes **4:4'**.
Following the procedure described for allenyl phenyl sulfoxides [31] (without the treatment with methyl iodide), the alcohol **1'f** was converted with 4-methyl benzenesulfenyl chloride into the crude sulfoxides mixture **4:4'** = 55:45.
^{1}H NMR:
major diastereoisomer: 6.3 (d,J=16Hz,1H); 5.78(dd,J=16 and 3Hz,1H); 1.43(d,J=7Hz,3H).
minor diastereoisomer: 6.28 (d,J=16Hz,1H); 5.82(dd,J=16 and 3Hz,1H); 1.4(d,J=7Hz,3H).
common signals: 7.6-7.4(m,8H); 7.2-7.0(m,8H); 3.6.5-3.45(m,2H); 2.32(s,6H).

2-Cyclohexen-1-ol and *4,4-dimethyl-2-cyclohexen-1-ol* [32] were prepared by reduction of the corresponding enones with a solution of DIBAL-H in toluene according to a general procedure [33].

[(1'S,(S)S*]-4-[2'-cyclohexen-1'-ylsulfinyl]-morpholine* **6a**.
Following the general procedure A (72h), the sulfinamide **6a** was obtained (50%) as a single diastereoisomer. IR: 1640, 1450, 1070, 920, 725,and 690 cm^{-1}; ^{1}H NMR: 6.16(dtd, J=10.5 ,4 and 2Hz,1H); 5.86(ddt,J=10.5, 4 and 2Hz,1H); 3.9-3.7(m,4H); 3.52-3.41(m,1H); 3.3-3.1(m,4H); 2.15-2.05(m,2H); 1.95-1.55(m,6H).^{13}CNMR: 133.4 (3°); 121.1 (3°); 66.5 (2°); 56,7 (3°); 45.6 (2°); 24.3 (2°); 22.9 (2°); 19.7 (2°). MS (CI): 233 (M$^+$+18,2); 217 (M$^+$+2,45); 216 (M$^+$+1,100); 134 (50); 120 (60).

[(1'R,(S)S*]-4-[6,6'-dimethyl-2'-cyclohexen-1'-ylsulfinyl]-morpholine* **6b**.
Following the general procedure A (96h), the sulfinamide **6b** was obtained (62% yield) as a single diastereoisomer. IR: 1454, 1070, 920 and 730 cm^{-1}. ^{1}H NMR: 6.0(dtd,J=10, 3.5 and 2Hz, 1H); 5.70(ddt,J=10, 4 and 2Hz, 1H); 3.8-3.7(m,4H); 3.25-3.2(m,1H); 3.2-3.1(m,4H); 2.2-2.0(m,2H); 1.65-1.5(m,1H); 1.5-1.3(m,1H) 1.09(s,3H); 1.07(s,3H). ^{13}C NMR: 131.4 (3°); 120.0 (3°); 66.8 (2°); 66.3 (3°); 45.7 (2°); 34.5 (4°); 31.3 (2°); 28.2 (1°); 23.5 (1°); 22.3 (1°). MS (CI): 244 (M$^+$+1,90); 196 (55); 126 (85); 105 (100). Analysis: Found: C, 58.87; H, 8.62; N, 5.81; $C_{12}H_{21}NO_2S$ requires C, 59.20; H, 8.64; N, 5.76.

Methyl [(1S,(S)S*]-2-cyclohexenesulfinate* **7**.
Following a general procedure [21], the sulfinamide **6a** afforded after flash-chromatography (90%) a mixture of the two diastereoisomeric methyl sulfinates **7** and **7'** in the ratio

90:10.
IR: 1660, 1450, 1120, 990, 700 cm^{-1};
^1H NMR: **7** : 6.08(dtd,J=10,4. 5 and 1.5Hz,1H); 5.67(ddt,J=10, 4 and 2Hz,1H); 3.81(s,3H), 3.30-3.20(m,2H).
7': 6.17(dtd,J=10, 4 and 2Hz,1H); 5.76(ddt,J=10, 4 and 2Hz,1H); 3.79(s,3H); 3.40-3.30(m,2H).
common signals: 2.17-2.02(m,4H); 2.02-1.60(m,8H).
^{13}C NMR: **7** : 134.1 (3°); 119.2 (3°); 62.4 (1°); 54.6 (3°); 24.4 (2°); 21.1 (2°); 19.1 (2°).
7': 134.5 (3°); 119.0 (3°); 61.5 (1°); 54.0 (3°); 24.3 (2°); 21.4 (2°); 19.5 (2°).
MS(CI): 178 (M^++18,100); 161 (M^++1,100)

Methyl [(1R,(S)S*]-(6,6-dimethyl-2-cyclohexene)sulfinate.*
Obtained (48% yield) as a single diastereoisomer; IR: 1645, 1450, 1120, 990 and 700 cm^{-1}; ^1H NMR: 6.02(dtd,J=10.5, 3.5 and 2Hz,1H); 5.70(ddt,J=10.5, 4 and 2Hz,1H); 3.76(s,3H); 3.07-3.0(m,1H); 2.16-2.02(m,2H); 1.64-1.46(m,1H); 1.46-1.32(m,1H); 1.14(s,3H); 1.12(s,3H); ^{13}C NMR: 131.8 (3°); 118.6 (3°); 72.6 (1°); 54.0 (3°); 34.7 (4°); 31.1 (2°); 28.5 (1°); 24.5 (1°); 22.4 (2°); MS (CI): 206 (M^++18,9); 189 (M^++1,25); 142 (100); 141 (41); 125 (75).

[(1'S,(S)S*]-1-(2'-cyclohexen-1'-sulfinyl)-4-methyl-benzene* **5a**.
To a solution of methyl sulfinates **7**:**7'** (320 mg) in THF (12mL) cooled to -78°C was added dropwise an ethereal solution of 4-methylphenylbromomagnesium (1.2 equivalent). After stirring at -78°C for 2h, the reaction mixture was quenched with water and extracted with ether (2x5mL). The usual work up and a chromatography on silica gel Merck (ether:pentane, 1:1) gave a mixture of the sulfoxides **5a**:**5'a** (91% yield) with a ratio 89:11 (HPLC).
IR: 1640, 1595, 1490, 1450, 1045, 810 and 730 cm^{-1};
^1H NMR **5a** : 6.18(dtd, J=10, 4 and 2Hz,1H); 5.81-5.71(m,1H).
5'a: 6.08(m,1H); 5.2-5.1(m,1H).
common signals: 7.62-7.52(m,4H); 7.4-7.3(m,4H); 3.4-3.3(m,2H); 2.43(s,6H); 2.12-2.0(m,4H); 1.9-1.65(m,6H); 1.65-1.45(m,2H).
These NMR data are similar to those already reported [20a].
MS(CI): 238 (M^++18,20); 221 (M^++1,100); 205 (35).

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