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STEREOCHEMICAL COURSE OF THE [2,3]-SIGMATROPIC REARRANGEMENT OF SUBSTITUTED PROPARGYL N,N-DIALKYLAMIDOSULFOXYLATES. X-RAY MOLECULAR STRUCTURE OF [S^*,(S)R^*]-4-[(1,4,4-TRIMETHYL-1,2-PENTADIENYL)SULFINYL]-MORPHOLINE.[1]

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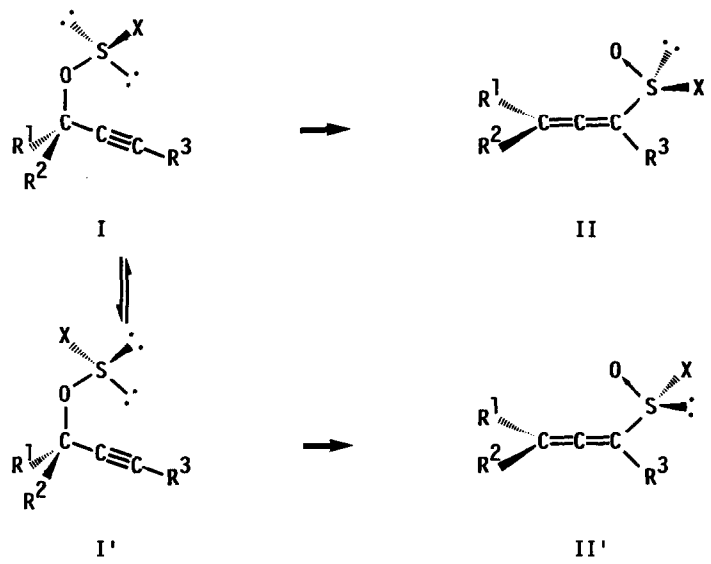
Summary By the reaction with three N,N-dialkylamidosulfenyl chlorides **2** bearing representative sizes for the R group on the nitrogen atom, several substituted secondary propargylic alcohols (**1a-f**) have been converted into the corresponding pairs of diastereoisomeric allenic sulfinamides **3a-n** and **3'a-j,l,m**. Their ratios have been determined by ^{1}H NMR spectroscopy and were found to depend essentially on the sizes of both the R^1 and R groups of the starting materials. The stereochemistry of one pure diastereoisomer **3m** has been determined by a single crystal X-ray analysis.
When treated with p.toluenesulfenyl chloride, the alcohol **1f** led to a major α-allenic sulfoxide **5** which was found to be identical to that prepared by unambiguous procedures from the major α-allenic sulfinamide **3m**.

The [2,3]-sigmatropic rearrangement of propargyl trichloromethanesulfenates Ia to allenic trichloromethyl sulfoxides IIa was discovered in 1967 by Braverman and Stabinsky [2] and this transformation has become a versatile synthetic approach to allenic chloromethyl-[3], methyl-[4] and aryl-[5] sulfoxides (IIb,c,d). Since then some of these functionalized allenes (IIb and d) have received growing interest in organic synthesis [3,6,7e]. There is however, relatively little information concerning the diastereoselectivity of the [2,3]-sigmatropic rearrangement of substituted propargylic arenesulfenates [5b,7]. The very reasonable transition states Id and I'd have recently been hypothesized by Okamura and co-workers [8] for rationalizing the diastereoselectivity of the [2,3] rearrangements (II ⟵ I ⇌ I' ⟶ II') for compounds X= C_6H_5, R^1= 2,6,6-trimethyl-1-cyclohexen-1-yl; R^2=H and R^3=H, Me, Et, iPr, tBu. The rearrangement would occur preferentially via the less hindered conformation Id to give the major isomer IId since the phenyl and the large substituent R^1 are anti to one another. However it was not actually proved in their paper [8] whether or not the two series of diastereoisomers described correspond in their relative configuration to those depicted in **scheme 1**.



I II I' II'

a) X= CCl_3 (ref. 2)
b) X= CH_2Cl (ref. 3)
c) X= CH_3 (ref. 4)
d) X= Aryle (ref. 5)
e) X= O-R (ref. 9)
f) X= NR_2 (ref. 10)

Scheme 1

Concerning the stability of the substituted α-allenic aryl sulfoxides, it has been reported that some representative isomers can be equilibrated to a ca 1:1 mixture of the two allenes II, II'd in somewhat forcing conditions.[7a,b]

The classic [2,3]-sigmatropic rearrangement of propargyl sulfenates (I, X=alkyl or aryl) has been extended to sulfoxylates (I, X= O-alkyl) [9] and recently to 4-morpholinesulfenates (I, X= $N(C_2H_4)_2O$) [10] which are characterized by the interesting presence of three contiguous heteroatoms. The rearrangement of the twelve propargylic 4-morpholinesulfenate esters so far examined have been generally of low diastereoselectivity except for two compounds **3** (R^1= nBu; R^2= nPent.; R_2= $(C_2H_4)_2O$) and (R^1= iPr; R^2= nHex.; R_2= $(C_2H_4)_2O$) which afforded a ratio **3**:**3'** of 85:15 and 90:10 respectively.[10]

As our former pairs of diastereoisomeric substituted 4-(1',2'-alkadienesulfinyl) morpholines have been found to be stable to equilibration at room temperature, the wish to obtain a deeper understanding of the factors influencing the stereochemistry of this [2,3]-sigmatropic rearrangement led us to explore the influence of the substituents R^1, R^2 and particularly R upon the ratios of the diastereoisomeric allenic sulfinamides **3** and **3'**.

This task was aided by the easy access [11] to dimethylamidosulfenyl chloride **2a** (R= Me) and bis (1-methylethyl)amidosulfenyl chloride **2c** (R= iPr). Reaction of the chlorides (**2a,b,c**) with representative secondary alkynols (**1a-f**) in the presence of triethylamine in ether at low temperature readily affords the corresponding α-allenic sulfinamides **3** and **3'** (Table 1), the more interesting observations being the following:

- Samples of **3** and **3'** did not equilibrate under normal laboratory conditions during prolonged period (>1 year). Furthermore, when treated with excess piperidine in ether at room temperature for 24 h, the sulfinamides **3**+**3'm** were found to be stable and their ratio

unchanged; no acetylenic alcohol **1f** was detected in contrast to certain α-allenic sulfoxides [7a]. The tabulated ratios **3**:**3'** must therefore be considered as unambiguous.

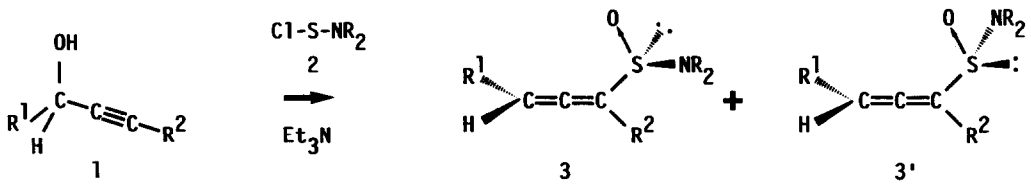


TABLE 1

Entry		R^1	R^2	R_2	chemical yield(%)		ratios **3** : **3'**	
1	**1a**	Me	Me	Me_2	66	**3a**	60 : 40	**3'a**
2		Me	Me	$[(CH_2)_2]_2O$	98	**3b**	65 : 35	**3'b**
3		Me	Me	iPr_2	72	**3c**	70 : 30	**3'c**
4	**1b**	nHept	Me	Me_2	31	**3d**	65 : 35	**3'd**
5		nHept	Me	$[(CH_2)_2]_2O$	75	**3e**	75 : 25	**3'e**
6		nHept	Me	iPr_2	57	**3f**	80 : 20	**3'f**
7	**1c**	nHept	iPr	$[(CH_2)_2]_2O$	77	**3g**	75 : 25	**3'g**
8	**1d**	nHept	tBu	$[(CH_2)_2]_2O$	85	**3h**	75 : 25	**3'h**
9	**1e**	iPr	Me	Me_2	41	**3i**	75 : 25	**3'i**
10		iPr	Me	$[(CH_2)_2]_2O$	77	**3j**	85 : 15	**3'j**
11		iPr	Me	iPr_2	72	**3k**	> 95 : 5 <	
12	**1f**	tBu	Me	Me_2	55	**3l**	70 : 30	**3'l**
13		tBu	Me	$[(CH_2)_2]_2O$	76	**3m**	85 : 15	**3'm**
14		tBu	Me	iPr_2	48	**3n**	>95 : 5 <	

The ratios **3**:**3'** were determined by ^1H NMR.

- When the groups R on nitrogen are small or medium-sized (Me or morpholino), the rearrangements of the intermediate N,N-dialkylamidosulfenate esters (If) are rapid (1-2h) in contrast to the N,N-diisopropylamidosulfenate esters which require 24-48 h for complete conversion.
- The results of entries 5, 7, 8 show that the same ratio of diastereoisomeric sulfinylmorpholines **3**:**3'** is formed starting with alcohols nHept-CH(OH)-C≡C-R^2 bearing

substituents of various sizes R^2 (Me, iPr, tBu).[12]

- When R^2= R = Me (entries 1, 4, 9, 12), the increasing bulk of the group R^1 has a small influence upon the diastereoisomeric ratios of sulfinamides **3:3'**. For the series R^2 = Me, R_2 =-$(CH_2)_2$-O-$(CH_2)_2$- (entries 2, 5, 10, 13), the diastereoselectivity of the [2,3]-sigmatropic rearrangement is notably improved from 65:35 to 85 : 15. In each of the four series (entries 1-3, 4-6, 9-11 and 12-14), the large N,N-diisopropyl group leads to the best diastereoselectivity. The comparison of the results of entries 3, 6, 11 and 14 show that the rearrangement become entirely stereoselective when both groups R^1 and R are large (entries 11, 14).

The major diastereoisomer **3m** was purified by careful chromatography and crystallisations. Final evidence for its structure was obtained from a single crystal X-ray analysis. The X-ray analysis is of interest since, to our knowledge, there is very little information concerning X-ray data of sulfinamides.[13] The perspective view with the atom numbering scheme is given in **Fig. 1**. The fractional coordinates with equivalent isotropic thermal factors for non-H atoms are given in **Table 2**

TABLE 2 Fractional atomic coordinates ($x10^4$) for non-H atoms and equivalent isotropic thermal parameters ($Å^2$,$x10^3$) with esd's in parentheses:

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

	X	Y	Z	U_{eq}
S	8480 (1)	1440 (1)	1410 (1)	93 (1)
N	8607 (2)	1702 (3)	3252 (3)	69 (4)
O_1	7144 (3)	1795 (3)	311 (3)	138 (7)
O_2	8448 (3)	2840 (3)	6454 (3)	112 (6)
C_1	7951 (3)	-1041 (3)	-581 (4)	75 (6)
C_2	6669 (3)	-2045 (3)	-2628 (4)	78 (6)
C_3	5410 (3)	-3044 (3)	-4681 (4)	76 (6)
C_4	5310 (3)	-3521 (3)	-6474 (4)	69 (5)
C_5	6855 (4)	-2570 (6)	-5549 (5)	136 (12)
C_6	4088 (4)	-2910 (5)	-7413 (5)	129 (10)
C_7	4765 (5)	-5621 (5)	-8336 (6)	137 (12)
C_8	7165 (3)	908 (3)	2586 (4)	81 (6)
C_9	7582 (4)	989 (4)	4288 (5)	112 (9)
C_{10}	9823 (3)	3606 (4)	7083 (4)	96 (7)
C_{11}	9489 (3)	3629 (3)	5491 (4)	80 (6)
C_{12}	9113 (4)	-1739 (4)	232 (5)	97 (8)

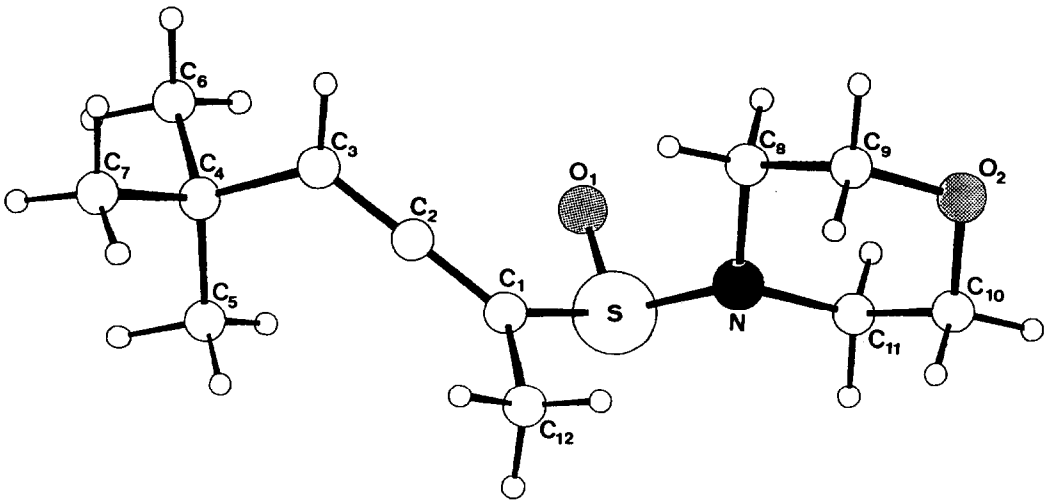
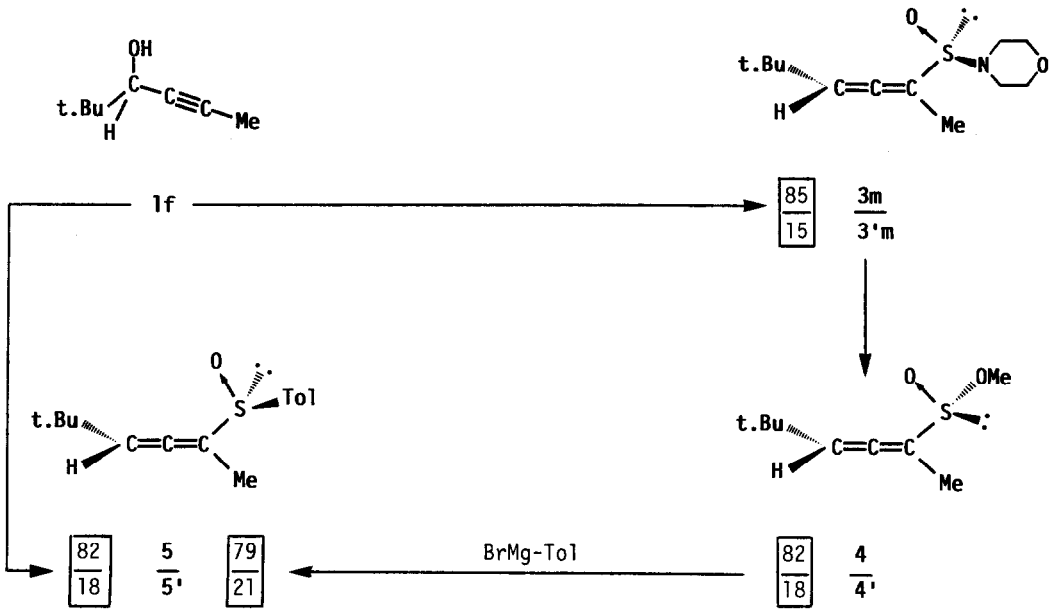


Fig. 1 ORTEP drawing of the molecule **3m** in S^*, (S) R^* configuration showing the direction of the free pair on sulfur.

The distances and angles found in compound **3m** are consistent with expected values. We point out the following representative values relative to the allenic group and the contiguous sulfur atom: S-N: 1.673 Å(3); S-O_1:1.465 Å(3); S-C_1:1.805 Å(3); C_1-C_2:1.302 Å(3); C_2-C_3:1.299 Å(3); N-S-O_1:112.0°(2); N-S-C_1:96.2°(2); O_1-S-C_1:107.0°(2); C_1-C_2-C_3:178.6°(4). The C_1-C_2-C_3 angle is flat within experimental error; therefore the presence of heavy substituent has little influence on it.

As the major diastereoisomer of substituted sulfinamides **3** offers unique opportunities for the regio- and stereo-controlled manipulation of sulfur functionality, we have tried to establish the validity of the transition states Id⟷I'd during the formation of an α-allenic p.tolylsulfoxide by the following experiments. Reaction of p.toluenesulfenyl chloride with the alkynol **1f** in the presence of triethylamine in the usual conditions affords the α-allenic sulfoxides **5**:**5'** in a ratio 82:18 near to that observed for the corresponding α-allenic sulfinamides **3m**:**3'm** (85:15). Treatment of these sulfinamides **3m**:**3'm** [14] with methanol in toluene in presence of 1.5 equivalents of boron trifluoride etherate at 0°C provides the methyl α-allenic sulfinates (82:18), the relative configurations of which are given in formula **4**:**4'** since this esterification procedure should proceed almost completely stereospecifically with inversion of configuration at the sulfinyl function [15]. Finally, the sulfinates **4**:**4'** were converted by a well established procedure i.e. treatment with p.tolyl magnesium bromide into the corresponding sulfoxides **5**:**5'** with a ratio 79:21 very close to that of the same sulfoxides prepared directly by the treatment of alcohol **1f** with p.toluenesulfenyl chloride.



Scheme 2 (only the formulae of the major diastereoisomers have been represented)

One can therefore conclude that the aforementioned results are of particular interest because they provide strong evidence in support of the hypothesized transition states I(d or f)⟵⟶I'(d or f) and the less hindered conformation I(d or f) explains readily the formation of the major diastereoisomers II(d or f). It seems very likely that the hitherto unsuspected facets of the chemistry of α-allenic sulfinamides reported here, and earlier by us [10,1b], should have some interesting consequences in the synthetic applications of these compounds.

EXPERIMENTAL SECTION

Boiling and melting points are uncorrected. The ^{1}H NMR spectra were recorded at 250 MHz in $CDCl_3$ on a Cameca 250 or a Brucker 250 spectrometer; ^{1}H chemical shifts are given in δ (ppm) from internal TMS. The ^{13}C NMR spectra were recorded in $CDCl_3$ on a Brucker AL 100 MHz spectrometer; ^{13}C chemical shifts are given in δ (ppm) from TMS with the solvent peaks as internal standard.

The mass spectra were recorded on a Nermag R-10-10B spectrometer with electronic impact (70eV) or chemical ionisation with NH_3 (CI). The Infra Red spectra were recorded on a Varian 599 spectrophotometer. Elemental analyses were carried out by the Service de Microanalyse de l'Université P. et M. Curie, 4 place Jussieu, 75005 Paris.

The substituted propargyl alcohols (**1a-f**) were prepared according to Brandsma [16] from freshly distilled commercial aldehydes and lithium derivatives of propyne, 3-methyl-1-butyne [17] and 3,3-dimethyl-1-butyne.

3-pentyn-2-ol (**1a**): bp_{20}= 59°C (Lit.[18]: bp_{20}= 58-62°C).

2-undecyn-4-ol (**1b**): $bp_{0.3}$ = 78-79°C. IR: 3360 (br) and 2210 cm^{-1}. ^1H NMR: 4.35 (tq, J=6 and 2Hz,1H); 1.85 (d,J=2Hz,3H); 1.8 (br s.,1H); 1.75-1.6 (m,2H); 1.5-1.15 (m,10H); 0.9 (t,J=7Hz, 3H). ^{13}C NMR: 80.6 (4°); 80.3 (4°); 62,4 (3°); 38.0 (2°); 31.7 (2°); 29.2 (2°); 29.1 (2°); 25.1 (2°); 22.5 (2°); 13.9 (1°); 3.3 (1°). MS (CI): 186 (M^++18,100); 168 (M^+,18).

2-methyl-3-dodecyn-5-ol (**1c**): bp_1 = 100-102°C. IR: 3370 (br) and 2240 cm^{-1}. ^1H NMR: 4.38 (t,J=6.5 and 2Hz,1H); 2.6 (hd,J=7 and 2Hz,1H); 2.0-1.9 (br s,1H); 1.7-1.6 (m,2H); 1.5-1.2 (m,10H); 1.17 (d,J=7Hz,6H); 0.89 (t,J=7Hz,3H). ^{13}C NMR: 90,8 (4°); 80.5 (4°); 62.6 (3°); 38.1 (3°); 31.7 (2°); 29.2 (2°); 29.1 (2°); 25.1 (2°); 22.9 (2°); 22.6 (2°); 20.4 (2°); 14.0 (1°). MS (CI): 214 (M^++18,100); 197 (M^++1,21); 196 (80).

2,2-dimethyl-3-dodecyn-5-ol (**1d**): $bp_{0.04}$ = 78°C. IR: 3350 and 2220 cm^{-1}. ^1H NMR: 4.36 (t, J=7Hz,1H); 1,8 (br s,1H); 1.74-1.56 (m,2H); 1.54-1.25 (m,10H); 1.22 (s,9H); 0.89 (t,J=7Hz, 3H). ^{13}C NMR: 93.5 (4°); 79.8 (4°); 62.5 (3°); 38.1 (2°); 37.4 (4°); 31.7 (2°); 30.9 (1°); 29,2 (2°); 29.1 (2°); 25.1 (2°); 22.6 (2°); 14.0 (1°). MS (CI): 228 (M^++18,100); 211 (M^++1,11); 210 (M^+,48).

2-methyl-4-hexyn-3-ol (**1e**): bp_{22}= 73-74°C (Lit.[19] bp_{25}=74°C).

2,2-dimethyl-4-hexyn-3-ol (**1f**): bp_{15} = 60°C; IR: 3400 and 2215 cm^{-1}. ^1H NMR: 3.92 (q,J=2Hz, 1H); 1.9 (br s,1H); 1.86 (d,J=2Hz,3H); 0.97(s,9H). ^{13}C NMR: 81.3 (4°); 78.9 (4°); 71.4 (3°); 35.6 (4°); 25.1 (1°); 3.3 (1°). MS (CI): 144 (M^++18,100); 126 (M^+,44).

The *N,N'-dithiobis[N-methyl]-methanamine* [20,21a](crude yield: 85%; ^1H NMR: 2.6 (s,12H), *N,N'-dithiobis-morpholine* [21b](crude yield: 80%; ^1H NMR: 3.80-3.55 (m,8H); 2.90-2.70 (m,8H) and *N,N'-dithiobis[N-(1-methylethyl)]-2-propanamine* [22] (crude yield: 90%; ^1H NMR: 3.35 (h,J= 7Hz,4H); 1.1 (d,J= 7Hz,24H) were prepared following a slightly modified general procedure [21b].

To a rapidly stirred and cooled (0°C) two phase system composed of water (90 mL), sodium hydroxide (10,6g; 0.265 mol), hexane (38 mL) and amine (0.20 mol) was slowly added a solution of sulfur monochloride (9.2 mL; 0.115 mol) in hexane (26 mL). The cooling bath was removed and the mixture stirred for 2 h at room temperature. The organic layer was separated and the aqueous phase extracted with dichloromethane (2x 20 mL). The combined organic extracts were washed with water (2x 20 mL) then with brine. Drying over potassium carbonate followed by evaporation of the solvents under reduced pressure gave the crude disulfide which was used without further purification.

The N,N-dialkylamidosulfenyl chlorides (**2a,b,c**) were prepared following a slightly modified general procedure described for bis(ethyl)-amidosulfenyl chloride [23]:

A solution of sulfuryl chloride (10 mL; 16.8g; 0.125 mol) in carbon tetrachloride (5 mL) was added dropwise with stirring to a solution of N,N'-bis[dialkylamino]disulfide (0.1 mol) in carbon tetrachloride (10 mL) maintained at 60°C. The reaction mixture was then heated to 60°C for 2 h. The solvent and unreacted sulfuryl chloride were removed in vacuo and the residue was distilled:

Dimethylamidosulfenyl chloride (**2a**)(75% yield: bp_{45}=55°C (Lit.[24] bp_{45}= 55°C); ^1H NMR: 3.15 (s,6H) [23]. *4-morpholinesulfenyl chloride* (**2b**)(85% yield): $bp_{0.1}$ = 44°C (Lit.[23] : $bp_{0.6}$ = 58-60°C); for ^1H and ^{13}C NMR data, see ref 25. *Bis(1-methylethyl)-amidosulfenyl chloride* (**2c**) (81% yield): $bp_{0.01}$= 39-40°C; ^1H NMR: 4.05 (h,J= 7Hz,2H); 1.2 (d,J= 7Hz,12H) [26]. These three chlorides can be stored at -18°C for several weeks.

α-*allenic sulfinamides* **3,3'(a-n)**. General procedure.

A solution of substituted propargyl alcohol **1** (10 mmol) and triethylamine (10 mmol) in anhydrous ether (25 mL) was stirred at -78°C under argon. A solution of N,N-dialkylamidosulfenylchloride **2** (10 mmol) in ether (20 mL) was rapidly added. A solid precipitated out immediately; the mixture was stirred at -78°C for 15 min then warmed to room temperature. After stirring 1 h, 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. When the groups R on nitrogen were methyl or parts of the morpholino ring, the rearrangements of the

intermediate amidosulfenates (If) were rapid (1-2h) [27] whereas the N,N-diisopropylamidosulfenates required 24-48 h for complete conversion [27].

Purification of the products **3, 3'** was performed by flash-chromatography (Kieselgel Merck 230-400 mesh) using dichloromethane-acetone (100:0 to 80:20) as eluent. The yields and spectral data are given in the **Tables 1, 3, 4, 5.** The ratios **3 : 3'** of these sulfinamides cannot be determined by HPLC, due to decomposition. Most of these sulfinamides can be stored at -18°C for several months. Solutions of sulfinamides **3+3'f,g,h,m** in ether or in deuteriochloroform have been stored at -18°C during one year without noticeable decomposition or modification of diastereoisomeric ratios.

TABLE 3. ^{1}H NMR data for α-allenic sulfinamides **3** and **3'**.

	Diastereoisomer **3**	common signals for **3** and **3'**	Diastereoisomer **3'**
a	5.65(qq,J=7.5 and 3 Hz,1H) 2.71(s,6H)	1.85-1.75(m,12H)	5.74(qq,J=7.5 and 3Hz,1H) 2.74(s,6H)
b	5.67(qq,J=7 and 3 Hz,1H) 1.84(d,J=3 Hz,3H) 1.80(d,J=7 Hz,3H)	3.8-3.7(m,8H) 3.2-3.0(m,8H)	5.75(qq,J=7 and 3 Hz,1H) 1.83(d,J=3 Hz,3H) 1.79(d,J=7 Hz,3H)
c	5.62(qq,J=7 and 3 Hz,1H) 3.72(h,J=6.9 Hz,2H)	1.85-1.70(m,12H) 1.35(d,J=6.9 Hz,12H) 1.15(d,J=6.9 Hz,12H)	5.67(qq,J=7 and 3 Hz,1H) 3.75(h,J=6.9 Hz,2H)
d	5.67(tq,J=6.7 and 3 Hz,1H) 2.71(s,6H)	2.1-2.05(m,4H) 1.81(d,J=3 Hz,6H) 1.50-1.20(m,20H) 0.90(t,J=6.5 Hz,6H)	5.75(tq,J=6.7 and 3 Hz,1H) 2.73(s,6H)
e	5.77(tq,J=7 and 3 Hz,1H)	3.85-3.75(m,8H) 3.25-3.10(m,8H) 2.20-2.10(m,4H) 1.85(d,J=3 Hz,6H) 1.50-1.20(m,20H) 0.90(t,J=7 Hz,6H)	5.84(tq,J=7 and 3 Hz,1H)
f	5.72(tq,J=7 and 3 Hz,1H) 3.77(h,J=7Hz,2H)	2.20-2.10(m,4H) 1.82(d,J=3 Hz,6H) 1.70-1.20(m,20H) 1.36(d,J=7 Hz,12H) 1.16(d,J=7 Hz,12H) 0.88(t,J=7 Hz,6H)	5.76(tq,J=7 and 3 Hz,1H) 3.81(h,J=7 Hz,2H)
g	5.87(td,J=7 and 2 Hz,1H) 1.15(d,J=7 Hz,3H) 1.11(d,J=7 Hz,3H)	3.84-3.7(m,8H) 3.24-3.07(m,8H) 2.4(hd,J=7 and 2 Hz, 2H) 2.22-2.1(m,4H) 1.54-1.2(m,20H) 0.89(t,J=7 Hz,6H)	5.95(td,J=7 and 2 Hz,1H) 1.13(d,J=7 Hz,3H) 1.12(d,J=7 Hz,3H)
h	5.79(t,J=7 Hz,1H) 1.19(s,9H)	3.84-3.74(m,8H) 3.35-3.02(m,8H) 2.24-2.10(m,4H) 1.56-1.22(m,20H) 0.89(t,J=7 Hz,6H)	5.96(t,J=7 Hz,1H) 1.2(s,9H)

TABLE 3. (continued)

i	5.70(dq,J=6.6 and 3 Hz,1H) 2.71(s,6H) 2.45(dh,J=6.6 and 6.6 Hz,1H) 1.06(d,J=6.6 Hz,6H)	1.83(d,J=3 Hz,6H)	5.78(dq,J=6.6 and 3 Hz,1H) 2.74(s,6H) 2.46(dh,J=6.6 and 6.6 Hz,1H) 1.08(d,J=6.6 Hz,1H)
j	5.76(dq,J=6 and 3 Hz,1H)	3.82-3.70(m,8H) 3.20-3.10(m,8H) 2.48(h,J=7 Hz,2H) 1.87(d,J=3 Hz,6H) 1.10-1.00(m,12H)	5.82(dq,J=6 and 3 Hz,1H)
k	5.75(dq,J=6.5 and 3 Hz,1H) 3.77(h,J=7 Hz,2H) 2.54-2.4(hd,J=6.5 and 7Hz,1H) 1.83(d,J=3 Hz,3H) 1.36(d,J=7 Hz,6H) 1.16(d,J=7 Hz,6H) 1.06(d,J=7 Hz,3H) 1.05(d,J=3 Hz,3H)		
l	5.68(q,J=3 Hz,1H) 2.72(s,6H) 1.09(s,9H)	1.83(d,J=3 Hz,6H)	5.73(q,J=3 Hz,1H) 2.74(s,6H) 1.11(s,9H)
m	5.77(q,J=3 Hz,1H) 1.1(s,9H)	3.85-3.75(m,8H) 3.22-3.12(m,8H) 1.87(d,J=3 Hz,6H)	5.81(q,J=3 Hz,1H) 1.11(s,9H)
n	5.71(q,J=3 Hz,1H) 3.75(h,J=7 Hz,2H) 1.83(d,J=3 Hz,3H) 1.37(d,J=7 Hz,6H) 1.16(d,J=7 Hz,6H) 1.09(s,9H)		

TABLE 4. ^{13}C NMR data for α-allenic sulfinamides **3k,m,n**.

3k. 201.2 (4°); 108.7 (4°); 106.8 (3°); 45.7 (3°); 28.4 (1°); 23.8 (1°); 23.5 (1°); 22.5 (1°); 22.0 (1°); 14.3 (1°).
3m. 199.9 (4°); 111.7 (3°); 107.8 (4°); 66.7 (2°); 45.4 (2°); 32.9 (4°); 29.8 (1°); 13.6 (1°).
3n. 200.3 (4°); 110.8 (3°); 108.9 (4°); 45.5 (3°); 32.9 (4°); 29.8 (1°); 23.6 (1°); 23.3 (1°); 14.1 (1°).

TABLE 5. Other spectroscopic and analytical data for α-allenic sulfinamides **3-3'**.

compound	I.R. (cm^{-1})	M.S.(m/e, rel. int. %)	Formulae	analyses (C,H,N)	calc. found.
3+3'a	1965,1100,925	177(M^++18,22);170(M^++1,100)	$C_7H_{13}NOS$		
3+3'b	1960,1110,920	219(M^++18,10);202(M^++1,70); 134(31);105(99);102(100); 101(88)	$C_9H_{15}NO_2S$		
3+3'c	1960,1080,940	216(M^++1,2);102(100)	$C_{11}H_{21}NOS$		

TABLE 5. (continued)

3+3'd	1955,1105,930	261(M^++18,3);244(M^++1,100); 234(12)	$C_{13}H_{25}NOS$			
3+3'e	1950,1110,920	286(M^++1,100);183(20);105(29)	$C_{15}H_{27}NO_2S$	63.12 62.97	9.53 9.52	4.91 5.05
3+3'f	1950,1080,940	300(M^++1,100);284(12);218(17) 201(14);186(29);185(28);149(56) 148(70);134(44);133(84);132(58)	$C_{17}H_{33}NOS$	68.17 68.02	11.10 11.19	4.68 4.79
3+3'g	1955,1115, 1100,920	314(M^++1,100),134(20)	$C_{17}H_{31}NO_2S$	65.12 64.71	9.97 10.20	4.47 4.63
3+3'h	1950,1110, 1090,910	328(M^++1,90);316(80);288(100)	$C_{18}H_{33}NO_2S$	66.00 65.57	10.15 10.41	4.29 4.46
3+3'i		205(M^++18,10);188(M^++1,100)	$C_9H_{17}NOS$			
3+3'j	1950,1110,920	247(M^++18,21);230(M^++100)	$C_{11}H_{19}NO_2S$			
3k	1950,1085,940	244(M^++1,100);228(38)	$C_{13}H_{25}NOS$	64.15 63.68	10.35 10.45	5.75 5.94
3+3'l	1950,1100,930	219(M^++18,7);202(M^++1,100)	$C_{10}H_{19}NOS$			
3m	1960,1120,925	244(M^++1,100);228((5);190(4)	$C_{12}H_{21}NO_2S$	59.22 59.12	8.70 8.75	5.76 5.78
3n	1950,1085,940	258(M^++1,100);242(22)	$C_{14}H_{27}NOS$	65.32 65.19	10.57 10.69	5.44 5.50

[S,(SR*]-4-[(1,4,4-trimethyl-1,2-pentadienyl)-sulfinyl]-morpholine* **3m**.

A sample of the above purified mixture of diastereoisomeric sulfinamides **3m**: **3'm** (85:15) after storing at -18°C gave at room temperature a welcome crystalline mass. It was carefully chromatogaphed on a column of silicagel with ether as eluent; some fractions gave crystals grown at 5°C from an ether solution; mp 48°C.

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

Rough formula: $C_{12}H_{21}NO_2S$, M= 243,37; triclinic space group $P\bar{1}$;
a= 11.205(5), b= 10.501(5), c= 10.471(5)Å, α= 132.21(7), β= 124.70(6), γ= 81.10(5)°,
V= 696 Å^3, Z= 2, D_C= 1,16 g.cm^{-3}, graphite monochromated Cu K_α radiation (1.5418 Å),
μ= 18.63 cm^{-1}.

A crystal 0.25x 0.35x 0.50mm was mounted on a four circle Phillips PW 1100 diffractometer. Data collection performed with θ-2θ scan technique up to θ= 65° provided 5067 reflexions, out of which 2130 with $I \geq 3\sigma(I)$ were used in refinement by full matrix least-square procedure. The structure solved by direct methods using SHELX86 [28] was refined with the SHELX76 [29] programs, weights being in the form: $w = 1/\sigma^2_{(F)} + 2.10^{-6} F^2$.

Absorption corrections were not applied. Anisotropic thermal parameters were taken for all atoms except hydrogens which were introduced in theoretical positions, with thermal factor set equal to that of the bound atom. Constraints were introduced for the H-atoms of the three methyl groups. The refinement led to final values of R= 5.6%, R_ω= 5.7%.

The fractional coordinates with equivalent isotropic thermal factors of non-H atoms, the

anisotropic thermal factors, the coordinates of the H-atoms, the interatomic distances and angles have been deposited at the Cambridge Crystallographic Data Center.

[S,(SR*)]-Methyl (1,4,4-trimethyl-1,2-pentadiene)-1-sulfinates* **4:4'**.

Following the procedure of Hiroi and co-workers [15], the sulfinamides **3m:3'm** were converted into the methyl sulfinates **4:4'** which were purified by flash chromatography (Kieselgel Merck 60) using pentane: ether as eluent, (96% yield). The ratio **4:4'** cannot be determined by HPLC, due to decomposition.

IR: 1950, 1135, 985 and 970 cm^{-1}.
^1H NMR(400MHz) major diastereoisomer: 1.11 (s,9H)
minor diastereoisomer: 1.09 (s,9H); ratio **4:4'**= 82:18.
common signal: 5.72-5.69 (m,1H); 3.66 (s,3H); 1.93 (d,J= 3Hz,3H)
^{13}C NMR **4** : 200.2 (4°); 111.1 (3°); 110.9 (4°); 51.2 (1°); 32.8 (4°); 29.9 (1°); 10.1 (1°).
4': 200.1 (4°); 111.0 (3°); 110.8 (4°); 51.1 (1°); 32.9 (4°); 28.8 (1°); 10.1 (1°).
MS (CI): 206 (M^++18,100); 189 (M^++1,63); 109(47)
Analysis; Found: C, 57.00; H, 8.61. $C_9H_{16}O_2S$ requires: C, 57.41; H, 8.56.

[S,(SR*)]-1-Methyl-4-[(1,4,4-trimethyl-1,2-pentadienyl)sulfinyl]-benzene* **5:5'**.

A. A solution of sulfinates **4:4'** (5 mmol) in THF (10 mL) was stirred at -78°C under argon and treated with a freshly prepared ethereal solution of (4-methylphenyl)magnesium bromide (0.64 M; 8.6 mL). After 2 h at -78°C, the reaction mixture was quenched with saturated aqueous ammonium chloride. The usual work up afforded a crude product which was purified by flash chromatography using pentane: ether (100:0 to 20:80) as eluent; 94% yield. An analytical HPLC (SiO_2 Dupont B 5809) indicated a 79:21 mixture of diastereoisomers **5:5'**.

B. Following the procedure of Brandsma and Verkruijsse [30], the alcohol **1f** was converted with 4-methyl-benzenesulfenyl chloride into the crude sulfoxides mixture **5:5'** which was purified but not separated by flash chromatography (90% yield); ratio of diastereoisomers **5:5'**= 82:18 (HPLC)

IR: 1945; 1075; 1045 and 805 cm^{-1}.
^1H NMR(250MHz): major : 5.64 (q,J= 3Hz,1H); 1.72 (d,J= 3Hz,3H); 1.07 (s,9H).
minor : 5.59 (q,J= 3Hz,1H); 1.71 (d,J= 3Hz,3H); 1.12 (s,9H).
common signals: 7.54-7.48 (m,2H); 7.33-7.27 (m,2H); 2.41 (s,3H).
^{13}C NMR major: 199.7 (4°); 140.9 (4°); 139.8 (4°); 129.4 (3°); 124.3 (3°); 109,4 (4°); 108.7 (3°); 32.7 (4°); 21.1 (1°); 9.5 (1°).
minor: 199.3 (4°); 140.7 (4°); 140.2 (4°); 129.3 (3°); 124.2 (3°); 109.8 (4°); 109.0 (3°); 32.8 (4°); 25.1 (1°); 9.4 (1°).
common signals: 29.8 (1°).
MS (CI): 266 (M^++18, 41); 249 (M^++1, 100).
Analysis; Found: C, 72.39; H, 8.20; $C_{15}H_{20}OS$ requires C, 72.54; H,8.12.

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