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Properties of some derivatives of 3,3-disubstituted propa-1,2-dienesulfinic acids [1]

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Summary – The title acids are formed by *in situ* acidic hydrolysis of the corresponding *N*-morpholinosulfinamides **1**. They undergo disproportionation to give thiosulfonates **2** and the unusual compounds **3**. Anhydrous protonation of two allenic *t*-butyl sulfinates **6** affords the α,β-unsaturated γ-sultines **7**.

α-allenic sulfinamides / α-allenic sulfinic acids / α-allenic esters / bis-allenic thiosulfonates / γ-sultines

Introduction

It has previously been shown that several 4-(alka-1,2-dienylsulfinyl)morpholines, with or without a substituent at the 1 position, can be readily hydrolyzed into the transient allenic sulfinic acids, which fragment with rearrangement to give acceptable yields (53-72%) of the corresponding alkynes [2] (fig 1). However, starting from some 4-(1,3,3-trisubstituted propa-1,2-dienylsulfinyl) morpholines **1** (R^1 = nC_4H_9, R^2, R^2 = -$(CH_2)_5$; R^1 = CH_2-C_6H_4-*p*-CH_3 R^2 = CH_3; R^1 = nC_8H_{17}, R^2 = CH_3), poor yields (25-33 %) of the corresponding alkynes were obtained [2].

Since several substituted allenic sulfinamides have been smoothly converted by treatment with methanol/boron trifluoride etherate into their corresponding allenic sulfinic methyl esters with good yields [1b], it was reasonably expected that the hydrolysis of these sulfinamides under similar conditions to the corresponding substituted allenic sulfinic acids should be straightforward. However, the γ,γ-disubstituted allene group is presumably reluctant to be protonated in the manner necessary for loss of sulfur dioxide [3], thus allowing the unstable allenic sulfinic acids to undergo other transformations peculiar to their function, in particular the known disproportionation [4].

We report herein some of our results in this area with an unexpected sequence of reactions involving certain 3,3-disubstituted propa-1,2-dienesulfinic acids.

Results

The two sulfinamides **1a,b** were easily prepared (88 and 93%) from the corresponding α-acetylenic alcohols by the reaction with morpholine-4-sulfenyl chloride in the presence of triethylamine [2], and were chosen for the simple structure of their allenic chain, which would facilitate the structural determination of their hydrolysis products. Due to a possible participation of the acetoxy group, we have also studied the properties of a third allenic sulfinamide **1c**.

We have previously reported many examples of the hydrolytic desulfinylation of allylic [3, 5], allenic [2] and propargylic [6] sulfinamides leading to olefins, acetylenic and allenic compounds, respectively, generally with appreciable yields. When similarly treated with either water/boron trifluoride etherate or methanesulfonic acid in THF, the sulfinamides **1a,b,c** gave the results summarized in figure 2 and table I; the oily **2a,b,c** and crystalline **3a,b** were separated by flash chromatography on silica gel. As might well be expected, we did not detect the minor amounts of acetylenic compounds corresponding to the hydrolytic desulfinylation in figure 1, and our efforts focused on the isolation and structure determination of the major products **2** and **3**. The ^1H NMR of the crude products showed the presence of other compounds, which could not be purified by flash chromatography and this explains the relatively low yields of the pure compounds unstable **2** and stable **3**.

Compounds **2a,b,c** were easily characterized by their spectroscopic data and **2a** gave a positive thiosulfonate test [7]. The good yield of compound **2c** may be due to the presence of the neighboring acetoxy group. The substituted propa-1,2-dienesulfinic acids, formed *in situ* by hydrolysis of the sulfinamides **1**, have thus disproportionated via the classical intermediates shown in figure 3

* Correspondence and reprints

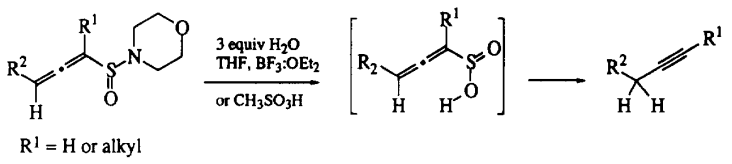
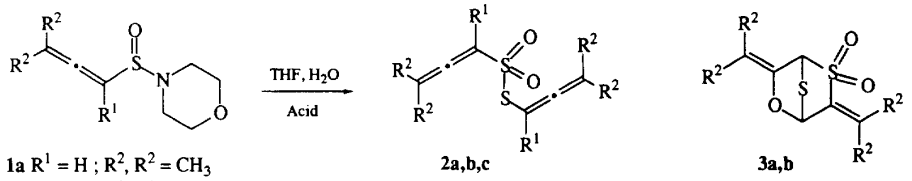


Fig 1



1a R^1 = H ; R^2, R^2 = CH_3
1b R^1 = H ; R^2, R^2 = -$(CH_2)_5$-
1c R^1 = CH_2OAc ; R^2, R^2 = -$(CH_2)_5$-

Fig 2

Table I. Reaction of sulfinamides **1** with water and Lewis or Brönsted acids.

Entry	Substrate	Conditions	isolated products (% yields)	
1	**1a**	THF; H_2O (3 equiv); BF_3:OEt_2 (1.5 equiv) 0°C (30 min) then RT (2.5 h)	**2a** (17)	**3a** (20)
2	**1a**	THF; H_2O (1.05 equiv); BF_3:OEt_2 (2 equiv) 0°C (30 min) then RT (2.5 h)	**2a** (11)	**3a** (56)
3	**1a**	THF; H_2O (3 equiv); CH_3SO_3H (1 equiv) 0°C (2 h)	**2a** (25)	**3a** traces*
4	**1b**	THF; H_2O (3 equiv); BF_3:OEt_2 (1 equiv) 0°C (2 h)	–	**3b** (50)
5	**1b**	THF; H_2O (3 equiv); CH_3SO_3H (1 equiv) 0°C (2 h)	**2b** (34)	–
6	**1c**	THF; H_2O (3 equiv); CH_3SO_3H (1 equiv) 0°C (2 h)	**2c** (67)	–

* The ^{1}H NMR spectrum of the crude product showed the presence of other unidentified compounds.

[8]. The substituted propa-1,2-dienesulfonic acids could not be isolated in our experiments.

Similarly to the above transformation **1** → **2**, when 4-[(4-methylphenyl)sulfinyl]morpholine **4** underwent acidic hydrolysis, it afforded the known thiosulfonate **5**, which was isolated in low yield.

The crystalline compounds **3a** and **3b** gave acceptable analytical data for $C_{10}H_{14}O_3S_2$ and $C_{16}H_{22}O_3S_2$, respectively, and were characterized by their ^{1}H and

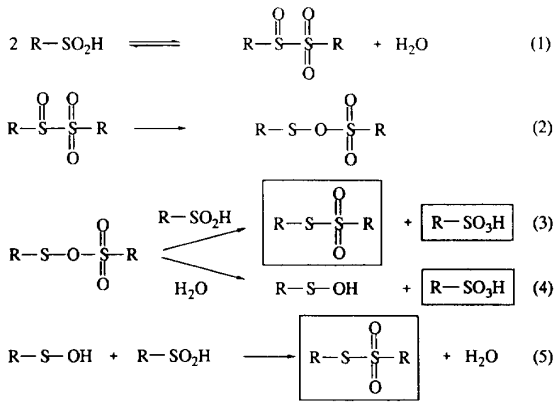


Fig 3

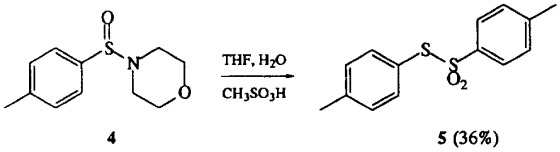


Fig 4

^{13}C NMR data. Final evidence for the structure of compound **3b** was obtained from a single crystal X-ray analysis (fig 5). Significant bond lengths and angles are presented in table II.

The presence of three oxygen atoms in structure **3** strongly suggests that these compounds originate from the highly reactive intermediate bis-allenic sulfinyl sulfones I, which, in the presence of water, are in equilibrium with the starting sulfinic acids (equation 1). The results of entries 1 and 2 (table I) show that the yield of compound **3a** increases as the amount of water in the reaction medium is decreased. To explain the surprising formation of compounds **3**, we propose the following reaction sequence. A [3,2]-sigmatropic rearrangement [9] of the sulfinylsulfone I could give the intermediate II, which is set up for attack of the allenic sulfenate on the neighboring sulfene group [10] with participation of a lone pair from the oxygen atom. The resulting zwitterion should, as shown in formula III, easily lead to the final products **3a,b**. Although this hypothesis is purely

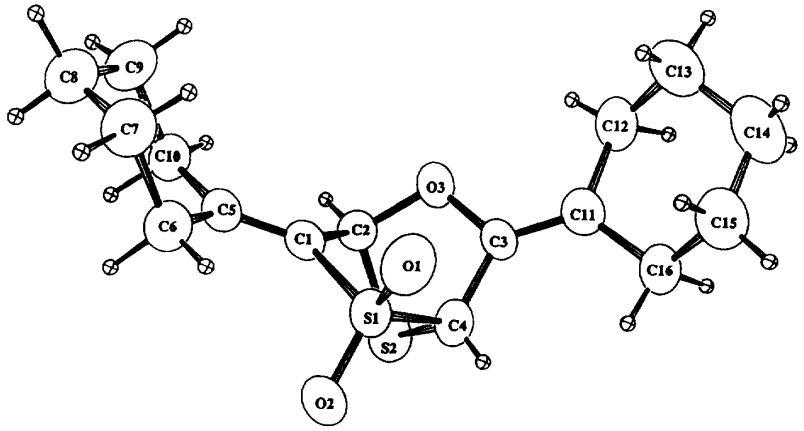


Fig 5. ORTEP drawing of **3b**.

Table II. Selected bond lengths (Å) and angles (°) for **3b**.

S(1)–O(1)	1.440 (5)	O(1)–S(1)–O(2)	116.8 (3)
S(1)–O(2)	1.426 (4)	O(1)–S(1)–C(1)	111.3 (3)
S(1)–C(1)	1.784 (6)	O(1)–S(1)–C(4)	110.7 (3)
S(1)–C(4)	1.774 (7)	O(2)–S(1)–C(1)	111.9 (3)
S(2)–C(2)	1.837 (6)	O(2)–S(1)–C(4)	111.5 (3)
S(2)–C(4)	1.808 (7)	C(1)–S(1)–C(4)	92.0 (3)
O(3)–C(2)	1.412 (7)	C(2)–S(2)–C(4)	78.1 (3)
O(3)–C(3)	1.416 (7)	C(2)–O(3)–C(3)	108.9 (5)
C(1)–C(2)	1.490 (8)	S(1)–C(1)–C(2)	106.5 (4)
C(1)–C(5)	1.324 (8)	S(1)–C(1)–C(5)	123.2 (5)
C(2)–H(2)	0.980 (6)	C(2)–C(1)–C(5)	130.1 (6)
C(3)–C(4)	1.468 (9)	S(2)–C(2)–O(3)	105.5 (4)
C(3)–C(11)	1.318 (8)	S(2)–C(2)–C(1)	104.2 (4)
C(4)–H(4)	0.770 (6)	S(2)–C(2)–H(2)	117.0 (4)
C(5)–C(6)	1.496 (9)	O(3)–C(2)–C(1)	112.0 (5)
C(5)–C(10)	1.506 (9)	O(3)–C(2)–H(2)	106.0 (4)
		C(1)–C(2)–H(2)	112.0 (4)
		O(3)–C(3)–C(4)	106.7 (5)
		O(3)–C(3)–C(11)	119.7 (6)
		C(4)–C(3)–C(11)	133.5 (6)
		S(1)–C(4)–S(2)	103.7 (3)
		S(1)–C(4)–C(3)	110.0 (5)
		S(1)–C(4)–H(4)	99.0 (5)
		S(2)–C(4)–C(3)	104.8 (5)
		S(2)–C(4)–H(4)	120.0 (5)
		C(3)–C(4)–H(4)	118.0 (5)
		C(1)–C(5)–C(6)	123.4 (6)
		C(1)–C(5)–C(10)	122.5 (6)
		C(6)–C(5)–C(10)	114.0 (6)
		C(3)–C(11)–C(12)	125.6 (6)
		C(3)–C(11)–C(16)	121.3 (6)
		C(12)–C(11)–C(16)	113.1 (6)

Numbers in parentheses are estimated standard deviations in the least significant digits.

speculative, it is hoped that further studies of the reactivity of other bis-α-unsaturated sulfinyl-sulfone systems will provide clear proof for this sequence of three unusual reactions I → II → III → **3**.

The experiments reported in table I also gave some other unidentified products. Bearing in mind the acidic conditions of certain experiments (entries 3, 5, 6), it seemed likely that the allenic group of either the starting sulfinamide or the intermediate sulfinic acid could be protonated thus leading to an α,β-unsaturated γ-sultine, in a manner similar to the previously reported

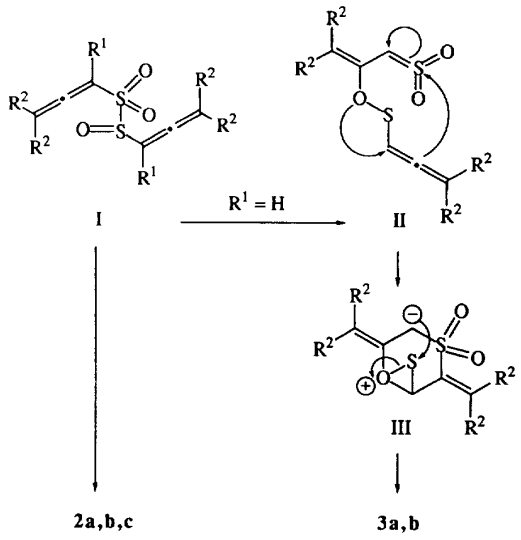
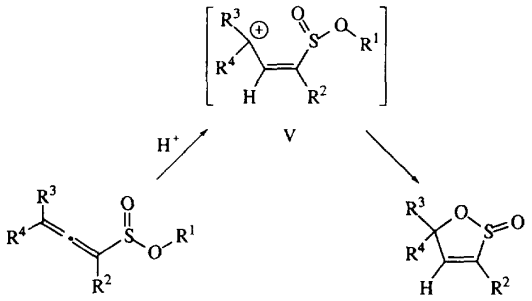


Fig 6

transformation of the propargylic allenesulfinic ester IV into the sultine VI by trifluoroacetic acid [11].

We therefore decided to prepare an authentic sample of the sultine **7a** for comparison of its ^{1}H NMR spectrum with that of the crude hydrolysis product of sulfinamide **1b**. It was conceivable that the precedent transformation IV → VI [11] could be extended to analogous allenic *t*-butyl sulfinates such as **6a**. This ester was easily obtained (78%) by treatment of the corresponding *N*-morpholinosulfinamide **1b** with *tert*-butanol and boron trifluoride etherate, following a slightly modified general procedure [1b]. When treated with trifluoroacetic acid in dichloromethane at room temperature, the sulfinate **6a** was smoothly converted into the α,β-unsaturated γ-sultine **7a** (74%). The ^{1}H NMR data of pure sultine **7a** enabled us to ascertain the absence of this compound from the crude hydrolysis product of allenic sulfinamide **1b** (entry 5).

The presence of two γ-alkyl substituents on the allenic chromophore and a *tert*-alkyl ester group seemingly plays an important role in the cyclizations IV → VI and **6a** → **7a**, and it is hoped that further studies of



IV $R^1 = C(CH_3)_2\text{-}C{\equiv}CH$; $R^2 = H$; $R^3 = R^4 = CH_3$ — VI (ref. 11)

6a $R^1 = C(CH_3)_3$; $R^2 = H$; $R^3, R^4 = -(CH_2)_5-$ — **7a** (74%)

6b $R^1 = C(CH_3)_3$; $R^2 = CH_3$; $R^3 = 4\text{-}CH_3C_6H_4$; $R^4 = H$ — **7b** (57%)

Fig 7

the acidic cyclization of other analogous allenic *t*-butyl sulfinates will provide a viable route to some substituted sultines. Considering the formula of the intermediate V, it seemed likely that such a carbocation could be stabilized by the presence of an adjacent aromatic ring. We therefore prepared the *tert*-butyl sulfinate **6b** from a previously described *N*-morpholinosulfinamide [2]. The ester **6b** was converted into a mixture of *cis* and *trans* isomers of sultine **7b** by treatment with trifluoroacetic acid in dichloromethane.

Conclusion

The above investigations have involved the acidic hydrolysis of some sulfinamides, providing *in situ* 3,3-disubstituted propa-1,2-dienesulfinic acids, which were found to preferently undergo disproportionation. These results are probably limited to allenic derivatives bearing certain γ-substituent(s) that lessen the classical retro-ene reaction that occurs with elimination of sulfur dioxide. In fact, the unexpected formation of the compounds **3** underscores the lack of information which still surrounds the reactivity of α-unsaturated sulfinic acids.

The anhydrous acidic treatment of allenic *t*-butylsulfinates **6** can be considered as an extension of a known procedure [11] but seems to be limited to substrates that can form stabilized carbocations V. It is hoped that this procedure will be considered complementary to the reported synthesis of α,β-unsaturated γ-sultines starting with alk-2-yn-1-ols [12].

Experimental section

Typical hydrolytic procedure with water and boron trifluoride etherate

Water (0.76 mL, 42 mmol) was added to the sulfinamide **1a** (2.8 g, 14 mmol) [2] in THF (28 mL) at 0°C. Boron trifluoride etherate (3.6 g, 2.6 mL, 21 mmol) was then slowly added and the mixture was stirred for 30 min. After removing the cooling bath and stirring for 2.5 h at room temperature, the mixture was poured into cold aqueous sodium hydrogen carbonate and extracted with ether (3 × 50 mL). The extracts were washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure. Flash chromatography on silica gel (pentane/ether) afforded first **2a** (0.25 g, 17% yield) and then **3a** (0.3 g, 20% yield).

S-(3-Methylbuta-1,2-dienyl) 3-methylbuta-1,2-diene-1-thiosulfonate **2a**

This oily product is unstable on standing at room temperature and its spectra must be determined immediately.

IR (film) : 1 950 (allene), 1 325 (SO_2), 1 125 (SO_2) cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz) : δ 6.19 (h, J = 2.6 Hz, 1H); 5.94 (h, J = 2.4 Hz, 1H); 1.90 (d, J = 2.6 Hz, 6H); 1.81 (d, J = 2.4 Hz, 6H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 208.9 (s, $=C=$); 203.4 (s, $=C=$); 108.4 (s); 101.0 (s); 100.9 (d, CH-SO_2); 79.6 (d, $=C$H-S); 20.0 (q); 19.7 (q).

MS (CI, NH_3) : m/z 248 (M^+ + 18, 100); 231 (M^+ + 1, 2.5); 167 (26); 101 (59).

Anal calc for $C_{10}H_{14}O_2S_2$: C, 52.14; H, 6.13. Found : C, 52.25; H, 6.12.

3,6-Diisopropylidene-2-oxa-5,7-dithiabicyclo [2.2.1]heptane 5,5-dioxide **3a**

Mp 145-146°C (ether/pentane).

IR (film) : 1 660, 1 440, 1 380, 1 370 (SO_2), 1 290, 1 250, 1 200, 1 190, 1 150 (SO_2), 1 110, 1 080, 985 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz) : δ 6.35 (d, J = 1.1 Hz, >CH-O); 5.35 (d, J = 1.1 Hz, >CH-SO_2); 2.12 (s, 3H); 1.98 (s, 3H); 1.84 (s, 3H); 1.75 (s, 3H).

The protons at 6.35 and 5.35 ppm were assigned by ^1H-^{13}C NMR correlation.

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 140.5 (s); 139.1 (s); 135.0 (s); 111.6 (s); 83.0 (d, >CH-O); 67.9 (d, >CH-SO_2); 21.8 (q); 20.4 (q); 19.9 (q); 17.6 (q).

MS (CI, NH_3) : m/z 264 (M^+ + 18, 42); 247 (M^+ + 1, 100); 183 (53); 165 (33).

Anal calc for $C_{10}H_{14}O_3S_2$: C, 48.76; H, 5.73. Found : C, 48.78; H, 5.65.

S-(Cyclohexylideneethenyl) cyclohexylideneethene-1-thiosulfonate **2b**

Prepared in the conditions summarized in entry 5; oil.

IR (film) : 1 950 (allene), 1 330 (SO_2), 1 130 (SO_2) cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz) : δ 6.22-6.14 (m, 1H); 5.96-5.88 (m, 1H); 2.40-2.12 (m, 8H); 1.82-1.46 (m, 12H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 206.1 (s); 200.6 (s); 114.8 (s); 107.7 (s); 100.1 (d); 79.2 (d); 30.8 (2t); 30.4 (2t); 26.7 (2t); 26.6 (2t); 25.6 (t); 25.4 (t).

MS (CI, NH_3) : m/z 328 (M^+ + 18, 31); 311 (M^+ + 1,9); 141 (100).

3,6-Dicyclohexylidene-2-oxa-5,7-dithiabicyclo [2.2.1]heptane 5,5-dioxide **3b**

Mp 166°C (ethanol).

IR (film) : 2 925, 1 645, 1 445, 1 295, 1 180, 1 175, 1 145, 1 140, 1 110, 975 cm^{-1}.

^{1}H NMR ($CDCl_3$, 250 MHz) : δ 6.40 (d, J = 1 Hz, >C*H*-O); 5.36 (d, J = 1 Hz, >C*H*-SO_2); 2.56 (t, J = 6 Hz, 2H); 2.34 (t, J = 6 Hz, 2H); 2.40-2.10 (m, 4H); 1.90-1.40 (m, 12H).

A COSY spectrum of compound **3b** showed coupling between the two protons at 6.40 and 5.36 ppm.

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 147.2 (s, =*C*-O); 136.7 (s, =*C*-SO_2); 132.4 (s); 119.2 (s); 82.2 (d, >*C*H-O); 66.6 (d, >*C*H-SO_2); 32.0 (t); 31.1 (t); 30.8 (t); 27.6 (t); 27.5 (t); 27.3 (t); 26.9 (t); 26.5 (t); 26.2 (t); 25.6 (t).

MS (CI, NH_3) : m/z 344 (M^+ + 18, 34); 327 (M^+ + 1, 56).

Anal calc for $C_{16}H_{22}O_3S_2$: C, 58.86; H, 6.79. Found : C, 58.91; H, 6.96.

X-ray structure determination

$C_{16}H_{22}O_3S_2$: Mr = 326.48, monoclinic, $P2/n$, a = 21.333 (3), b = 6.436 (3), c = 11.939 (9) Å, β = 103.81 (9)°, V = 1 592 (3) Å^3, Z = 4, D_x = 1.362 Mg m^{-3}, λ(MoKα) = 0.70926 Å, μ = 3.27 cm^{-1}, F(000) = 640, T = 294 K, final R = 0.071 for 1 741 observations.

The sample (0.35 × 0.35 × 0.50 mm) is studied on an automatic diffractometer CAD4 Enraf-Nonius with graphite monochromatized MoKα radiation. The cell parameters are obtained by fitting a set of 25 high-θ reflections. The data collection ($2\Theta_{max}$ = 50°, scan $\omega/2\Theta$ = 1, t_{max} = 60 s, range hkl : h 0.24 k 0.7 l −14.14, intensity controls without appreciable decay (0.2 %) gives 3 230 reflections of which 1 741 are independent (R_{int} = 0.023) with $I > 3\sigma(I)$.

After Lorenz and polarization corrections, the structure was solved with direct methods which reveal many non-hydrogen atoms of the molecule. The remaining atoms were found after successive scale factors and Fourier difference calculations. After isotropic (R = 0.12), then anisotropic refinement (R = 0.095), the hydrogen atoms are found using Fourier difference (between 0.48 and 0.26 eÅ^{-3}). The whole structure was refined by the full-matrix least-square techniques (use of F magnitude; x, y, z, β_{ij} for S, O and C atoms and x, y, z for H atoms; 257 variables and 1 741 observations; $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04\ F_o^2)^2]^{-1/2}$) with the resulting R = 0.073, R_w = 0.071 and S_w = 1.77 (residual $\Delta\rho < 0.48$ eÅ^{-3}).

Atomic scattering factor were taken from *International Tables for X-ray Crystallography* [13]. All the calculations were performed on a Digital Micro VAX 3100 computer with the MOLEN package [14]. Relevant crystal data are given in table III.

4-[(1-Acetoxymethyl-2-cyclohexylideneethenyl)sulfinyl] morpholine **1c**

1-(3-Acetoxyprop-1-ynyl)cyclohexan-1-ol [15] was converted into the allenic sulfinamide **1c** following a general procedure [16] (87% yield).

IR (film) : 1 955, 1 740, 1 445, 1 370, 1 255, 1 220, 1 110, 1 100, 1 060, 1 025 cm^{-1}.

^{1}H NMR ($CDCl_3$, 250 MHz) : δ 4.70 (d, J = 12.8 Hz, 1H); 4.65 (d, J = 12.8 Hz, 1H); 3.76 (t, J = 4.8 Hz, 4H); 3.18 (dt, J = 12.2 Hz and 4.8 Hz, 2H); 3.11 (dt, J = 12.2 Hz and 4.8 Hz, 2H); 2.29-2.22 (m, 4H); 2.08 (s, 3H); 1.83-1.50 (m, 6H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 198.3 (s); 170.2 (s); 114.9 (s); 104.4 (s); 66.8 (t); 59.9 (t); 45.4 (t); 30.8 (t); 30.7 (t); 27.2 (t); 25.5 (t); 20.8 (q).

MS (CI, NH_3) : m/z 314 (M^+ + 1, 100).

Table III. Crystal data for compound **3b**.

Formula	$C_{16}H_{22}O_3S_2$
Mol Wt	326.48
Cryst Syst	Monoclinic
Space group	$P2/n$
a	21.333 (3)
b	6.436 (3)
c	11.939 (9)
α	–
β	103.81 (9)
γ	—
V	1 592 (3)
Z	4
ρ calc g cm^{-3}	1.362
F(000)	696
μ(MoKα) cm^{-1}	3.27
T (°K)	294
Crystal size (mm)	0.35 * 0.35 * 0.50
Radiation	Mo Ka
Max 2Θ (°)	50°
Scan	$\omega/2\Theta$ = 1
t_{max} (for one measure), s	60
Variance of standards	0.2%
Range of hkl	0.24; 0.7; −14.14
Reflections measured	3 230
Reflections observed ($I > 3\sigma(I)$)	1 741 (3σ)
R_{int} (from merging equiv refl)	0.023
R (isotropic)	0.12
R (anisotropic)	0.095
Fourier Difference	0.48 – 0.28
N(obs)/N(var)	1 741/257
Final R	0.073
Rw	0.071
$w = 1/\sigma(F_o)^2) = [\sigma^2(I) + (0.04\ F_o^2)^2]^{-1/2}$	
Sw	1.77
Max residual e Å^{-3}, Δ/σ	0.48, 0.61

Anal calc for $C_{15}H_{23}NO_3S$: C, 60.58; H, 7.80; N, 4.71. Found : C, 60.43; H, 7.74; 4.67.

S-[(1-Acetoxymethyl-2-cyclohexylidene)ethenyl] (1-acetoxy-2-cyclohexylidene)ethene-1-thiosulfonate **2c**

Oil.

IR (film) : 1 950, 1 745, 1 440, 1 370, 1 325 (SO_2); 1 220, 1 135 (SO_2); 1 030 cm^{-1}.

^{1}H NMR ($CDCl_3$, 250 MHz) : δ 4.88 (s, 2H); 4.76 (s, 2H); 2.35-2.18 (m, 8H); 2.09 (s, 3H); 2.08 (s, 3H); 1.84-1.50 (m, 12H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 206.1 (s); 201.0 (s); 170.0 (s); 169.9 (s); 129.0 (s); 115.7 (s); 108.3 (s); 107.5 (s); 64.5 (t); 60.0 (t); 30.4 (t); 30.3 (t); 26.8 (t); 26.6 (t); 25.4 (t); 25.3 (t); 20.7 (q).

MS (CI, NH_3) : m/z 472 (M^+ + 18, 22); 331 (100).

S-(4-Methylphenyl) 4-methylbenzene-1-thiosulfonate **5**

When treated with methanesulfinic acid (1 equiv) and water (3 equiv) in THF at 0°C for 30 min, and then 18°C for 2 h, 4-[(4-methylphenyl)sulfinyl]morpholine **4** [17] afforded, after the usual work up and flash chromatography, the known thiosulfonate **5** [18] (36% yield, mp 72-73°C) which was separated from other unidentified products.

^{1}H NMR ($CDCl_3$, 250 MHz) : δ 7.5-7.45 (m, 2H); 7.28-7.23 (m, 2H); 7.26-7.20 (m, 2H); 7.18-7.12 (m, 2H); 2.44 (s, 3H); 2.40 (s, 3H).

1,1-Dimethylethyl 2-cyclohexylideneethene-1-sulfinate **6a**

Boron trifluoride etherate (1.49 g, 1.3 mL, 10.5 mmol) was added to a solution of 4-[(cyclohexylideneethene)sulfinyl] morpholine [2] (1.7 g, 7 mmol) and *tert*-butanol (5.18 g, 70 mmol) in dichloromethane (14 mL) at 0°C. The cooling bath was removed and after stirring at room temperature (*ca* 10°C) for 4.5 h, the reaction mixture was poured into cold water and extracted with dichloromethane (3 × 30 mL). The extracts were washed with water. The usual workup and flash chromatography on silica gel (pentane/ether) afforded the pure sulfinate **6a** (1.26 g; 78% yield).

Mp 33°C.

IR (film) : 1 960, 1 450, 1 370, 1 180, 1 125 (S=O), 860, 790 cm^{-1}.

^{1}H NMR ($CDCl_3$, 250 MHz) : δ 5.84 (q, J = 2 Hz, 1H); 2.25-2.12 (m, 4H); 1.68-1.44 (m, 6H); 1.40 (s, 9H).

When the $CDCl_3$ solution was left at room temperature for 4 weeks, the ^{1}H NMR spectrum showed complete transformation into the sultine **7a**.

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 198.1 (s); 112.0 (s); 102.5 (d); 82.0 (s); 30.5 (t, 2C); 29.6 (q, 3C); 27.0 (t); 25.6 (t).

MS (CI, NH_3) : m/z 246 (M^+ + 18, 58); 229 (M^+ + 1, 82); 190 (98); 173 (39); 142 (100); 141 (74); 139 (59); 126 (59); 125 (49); 124 (88).

Anal calc for $C_{12}H_{20}O_2S$: C, 63.12; H, 8.83. Found : C, 63.01; H, 8.90.

1,1-Dimethylethyl 1-methyl-3-(4-methylphenyl)propa-1,2-diene-1-sulfinate **6b**

In the same way as the preparation of **6a**, but operating at 0°C for 45 min, the 4-[[1-methyl-3-(4-methylphenyl)propa-1,2-dienyl]sulfinyl]morpholine (diastereoisomeric ratio 65:35) [2] was converted into the sulfinate **6b** (62% yield).

IR (film) : 1 935, 1 510, 1 450, 1 370, 1 250, 1 170, 1 130 (S=O), 860, 790, 710 cm^{-1}.

^{1}H NMR ($CDCl_3$, 250 MHz) : δ 7.26-7.17 (m, 4H); 7.12 (2d, J = 8 Hz and 8.1 Hz, 2 × 2H); 6.56 (q, J = 3 Hz, 1H); 6.55 (q, J = 3 Hz, 1H); 2.34 (s, 2×3H); 2.08 (d, J = 3 Hz, 2 × 3H); 1.47 (s, 9H); 1.46 (s, 9H).

Ratio of diastereoisomers ≈ 70:30.

After standing at room temperature for one month, ^{1}H NMR of the $CDCl_3$ solution gave a spectrum corresponding to the sultines **7b**.

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 202.2 and 201.8 (s); 138.1 and 138.0 (s); 129.3 and 129.7 (s); 129.4 and 129.5 (d); 127.2 and 127.3 (d); 114.6 and 114.7 (s); 101.2 and 101.0 (d); 82.7 and 82.2 (s); 29.7 and 29.6 (q); 21.2 (q); 9.4 and 9.0 (q).

MS (CI, NH_3) : m/z 282 (M^+ + 18, 14); 265 (M^+ + 1, 15); 226 (100); 209 (24); 160 (25); 143 (15).

1-Oxa-2-thiaspiro[4.5]dec-3-ene 2-oxide **7a**

Trifluoroacetic acid (279 mg, 0.19 mL, 2.44 mmol) was added to a solution of sulfinate **6a** (558 mg, 2.44 mmol) in dichloromethane (5 mL). After standing at room temperature for 4 h, the usual workup with water and dichloromethane, then flash chromatography on silica gel afforded the sultine **7a** (310 mg, 74% yield).

IR (film) : 3 070, 2 950, 2 870, 1 600, 1 445, 1 320, 1 300, 1 255, 1 205, 1 125 (S=O), 1 105, 1 015, 955, 920, 905, 850, 830, 800, 765, 745, 630, 580 cm^{-1}.

^{1}H NMR ($CDCl_3$, 250 MHz) : δ 6.84 (d, J = 6.3 Hz, 1H); 6.60 (d, J = 6.3 Hz, 1H); 2.07-1.28 (m, 10H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 144.1 (d, C_4); 134.2 (d, C_3); 101.9 (s, C_5); 38.5 (t); 35.9 (t); 24.6 (t); 22.7 (t); 22.6 (t).

MS (CI, NH_3) : m/z 190 (M^+ + 18, 11); 173 (M^+ + 1, 100); 155 (21); 137 (6); 124 (5).

Anal calc for $C_8H_{12}O_2S$: C, 55.79; H, 7.02. Found : C, 55.62; H, 6.97.

3-Methyl-5-(4-methylphenyl)-5H-1,2-oxathiole 2-oxide **7b**

As for the above-described transformation **6a** → **7a**, the sulfinate **6b** (0.264 g, 1 mmol) was treated with trifluoroacetic acid (1.1 equiv) in dichloromethane at 0°C then at room temperature for 15 h. The crude product showed the presence of starting material (18%) and two diastereoisomeric products (ca 55:45). Flash chromatography on silica gel (pentane/ether) afforded first the *cis* isomer (39 mg) and then the *trans* isomer (60 mg).

cis **7b**

^{1}H NMR ($CDCl_3$, 250 MHz) : δ 7.34-7.28 (m, 2H); 7.22-7.17 (m, 2H); 6.27 (dq, J = 2 Hz and 1.6 Hz, =C*H*–); 6.16 (dq, J = 2 Hz and 2 Hz, >C*H*-O); 2.35 (s, 3H); 2.18 (dd, J = 2 Hz and 1.6 Hz, 3H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 145.7 (s); 139.1 (s); 133.2 (s); 133.1 (d, C_4); 129.5 (d, 2C); 127.6 (d, 2C); 96.8 (d, C_5); 21.2 (q); 10.7 (q).

trans **7b**

IR (film) : 2 910, 1 650, 1 610, 1 510, 1 440, 1 130, 1 120, 1 040, 890, 820, 770, 740, 710 cm^{-1}.

^{1}H NMR ($CDCl_3$, 250 MHz) : δ 7.24-7.19 (m, 2H); 7.19-7.13 (m, 2H); 6.67 (qd, J = 2.25 Hz and 1.5 Hz, >C*H*-O); 6.32 (qd, J = 1.65 Hz and 1.5 Hz, =C*H*-); 2.36 (s, 3H); 2.20 (dd, J = 2.25 Hz and 1.65 Hz, 3H).

Irradiation of the protons of vinylic methyl showed J_{H_4,H_5} = 1.5 Hz, J_{H_4,CH_3} = 1.65 Hz, J_{H_5,CH_3} = 2.25 Hz.

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 147.2 (s); 139.4 (s); 132.6 (s); 132.2 (d, C_4); 129.6 (d, 2C); 127.0 (d, 2C); 95.0 (d, C_5); 21.2 (q); 10.8 (q).

MS (CI, NH_3) : m/z 226 (M^+ + 18, 86); 209 (M^+ + 1, 100); 144 (41); 129 (25).

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Supplementary material

- Complete table of bond distances in Å (1 page)
- Complete table of bond angles in degrees (2 pages)
- Tables of torsional angles in degrees (1 page)
- Table of positional parameters and their estimated standard deviations (2 pages)
- Table of general displacement parameter expressions -B's (2 pages)
- Values of 10*Fobs and 10*Fcalc (11 pages)

These data have been deposited with the British Library, Document Supply Center at Boston Spa, Wetherby, West Yorkshire, LS23 7BQ UK, as supplementary publication n°

SUP 90366 and is available on request from the Document Supply Center.

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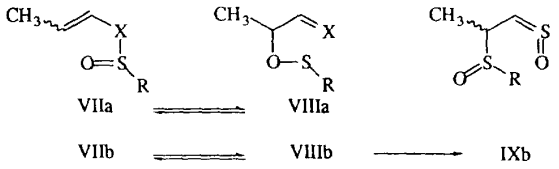

Fig 8

a) X = S; R = CH_3; nC_3H_7; CH_2-CH=CH_2 (scheme 38)

b) X = S = O; R = CH_3; nC_3H_7; CH_2-CH=CH_2 (scheme 39)

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