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ORGANIC SYNTHESIS WITH SULFONES XXXVIII

ON THE MECHANISM OF THE STEREOSPECIFIC HYDROGENOLYSIS OF VINYLIC SULFONES BY SODIUM DITHIONITE.

Marc JULIA *, Hélène LAURON, Jean-Pierre STACINO and Jean-Noël VERPEAUX,
Laboratoire de Chimie, Ecole Normale Supérieure, 24, rue Lhomond, 75231 PARIS CEDEX 05. FRANCE.

Yves JEANNIN* and Yves DROMZEE, Laboratoire de Chimie des Métaux de Transition.
Université Pierre et Marie Curie, 4 place Jussieu, 75230 Paris Cedex 05. FRANCE.

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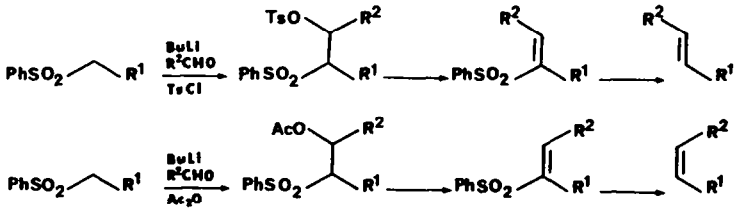
ABSTRACT : *The stereospecific hydrogenolysis of vinylic sulfones by sodium dithionite in a protic medium proceeds by addition of HSO_2^- to give an intermediate which could be isolated after alkylation in situ to a 1,2-bissulfone. The mechanism is therefore of the β-addition-elimination type. In the case of E-2-benzenesulfonyl-2-butene and ethyl iodide a single crystalline diastereoisomer was obtained and shown to have the threo configuration by X-ray crystallography. The addition step follows the syn and the elimination step the anti stereochemistry, thus accounting for the overall retention of configuration observed.*

INTRODUCTION

A stereoselective synthesis of 1,2-disubstituted olefins has recently been reported : antielimination of the readily available threo β-tosyloxysulfones led to the Z vinyl sulfones whereas convergent elimination of either the threo or the erythro β-acetoxysulfones led to the E vinyl sulfones (1). Stereospecific hydrogenolysis of the benzenesulfonyl residue could be carried out with sodium dithionite (2) with retention of configuration, the E sulfone leading to the Z olefin and vice versa.



We were led to try sodium dithionite because at about that time, this reagent had been recommended for the reduction of carbonyl groups (3). Besides, we knew from previous work (4) that saturated phenylsulfones are more rapidly reduced by sodium amalgam in methanol than saturated ketones, so we hoped that dithionite might reduce sulfones. Although it turned out that this was not a sound reason, since the mechanisms of the reduction reactions are quite different, the results were satisfactory in that the new reaction has preparative interest (5).

ELECTRON TRANSFER MECHANISM ?

A number of other reducing conditions had been tried without success ; indeed hydrogenolysis occurred, but mixtures of E and Z olefins were formed from both isomers of the vinylic sulfone. This was not really surprising since the reagents used : sodium amalgam in methanol, electrolysis, sodium or lithium in liquid ammonia, lithium in ethylamine, are known to transfer electrons to the substrate. Vinyl radicals are intermediates, and these are known to equilibrate very rapidly (6), apparently faster than the second electron is tranferred. The vinyl anions are configurationally stable (7).

This made it unlikely that the stereospecific hydrogenolysis with sodium dithionite could take place via successive electron transfers since it was hard to believe that this rather weak reducing agent could possibly reduce a vinyl radical to the corresponding anion faster than lithium in ethylamine. Moreover it has been found that sodium dithionite does not reduce saturated or allylic phenylsulfones. The half-wave reduction potentials of vinylic or allylic phenyl sulfones are roughly equal (8). It would appear therefore that the reduction does not proceed by way of an electron transfer.

ADDITION-DESULFONYLATION-ELIMINATION MECHANISM ?

A "nucleophilic" reduction process was therefore considered. The dithionite anion behaves sometimes as the dimer of the radical anion of sulfur dioxide $S_2O_4^{2-} = 2\ SO_2^{\cdot-}$. Addition of $SO_2^{\cdot-}$ in the Michael sense to a vinylic sulfone would lead to a radical anion which does not seem to be appropriate for a stereospecific reduction process. Sodium dithionite is also known to behave as a source of the dianion of sulfur dioxide -dioxosulfate (2-)- or sometimes its protonated form HSO_2^-, and presumably sulfur dioxide.

$$S_2O_4^{2-} = SO_2 + SO_2^{2-}$$

$$S_2O_4^{2-} + H_2O = SO_2 + HSO_2^- + OH^-$$

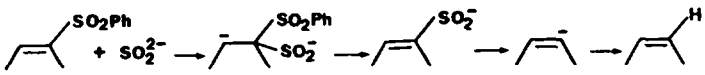
In the reduction of pyridinium salts (9), of carbonyl groups (10) or of electron deficient olefins (11), intermediate adducts have been isolated.
Sulfinate salts are known to undergo ready desulfonylation (analogous to decarboxylation) :

$$RSO_2^- = R^- + SO_2$$

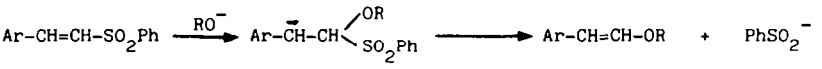
The species $H^+ + SO_2^{2-}$ or HSO_2^- could therefore behave as a hydride ion, in other words, sulfur dioxide dianion would be the two electron carrier necessary for converting H^+ into H^-. The overall reduction process is equivalent to a nucleophilic substitution process by a hydride ion on a vinylic substrate (12).
This can proceed in two ways :

α-addition-elimination

The group to be substituted ($PhSO_2^-$ here) would have to be a better leaving group than the incoming nucleophile (SO_2^{2-} here).



Reactions of this type can proceed either in a concerted way (13) or stepwise. In fact, we had come across a case of nucleophilic substitution of vinylic sulfones by alkoxides (14). This was however limited to styrylsulfones and apparently depended on the stabilization of the intermediate carbanion by the aromatic ring.

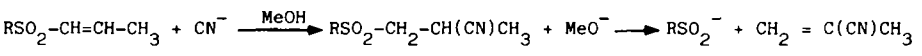


Since sodium dithionite very readily reduces simple (i.e. non styryl) vinyl sulfones, it probably does not proceed by such a mechanism.

β-addition-elimination

In this mechanism, the Michael addition of SO_2^{2-} to the vinylic sulfone, accompanied by protonation in the protic medium used would lead to an intermediate A which might be expected to expel both sulfur dioxide and an arenesulfinate ion, thus leading to the olefin (scheme I).

This seemed all the more reasonable since it is in agreement with several facts. It is known (15) that the sulfonyl group in vinylic sulfones can be displaced by cyanide ion :

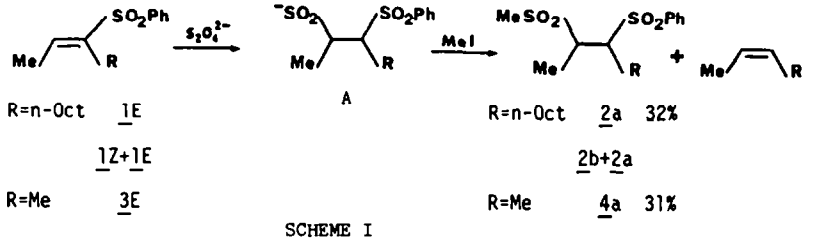


1-Tosyl isoprene can be converted into the isomeric 4-tosyl isoprene by sodium p-toluenesulfinate in ethanol (16) through addition-elimination. It is also known that β-halosulfinate salts readily undergo 1,2-elimination leading to the alkene (17) ; moreover this has been shown to be a very stereospecific process, with the threo compound leading to the Z olefin and the erythro isomer leading to the E olefin : antielimination is strictly followed. This could be explained by desulfonylation leading to a β-halogeno carbanion which would then eliminate the halide ion. In order to account for the strict stereochemistry observed (17b) a concerted process may have to be invoked. Alternatively, Walborsky (18) suggested an intramolecular displacement of the leaving group by the sulfinate ion, leading with inversion, to a β-sultine. An analogous displacement by a carboxylate anion, leading to a γ-lactone is known (19) ; β-sultines are known to lose sulfur dioxide easily, in the syn fashion, to give olefins with retention of configuration (20).

Ample precedent therefore exists for a β-addition elimination process in the hydrogenolysis of vinylic sulfones with sodium dithionite in a protic solvent.

TRAPPING OF THE INTERMEDIATE

The isolation of the intermediate sulfone sulfinate salt was not successful in hot aqueous DMF ; its decomposition might be more rapid than its formation. However, when the reaction of 3-benzenesulfonyl, 2-E-undecene 1E with sodium dithionite, sodium bicarbonate and a phase transfer catalyst in refluxing water/cyclohexane was interrupted by addition of methyl iodide, a new compound was indeed formed. This compound proved to be the expected disulfone 2 isolated in a 32 % yield, together with 10 % of Z olefin and 55 % of unchanged starting 1E. Remarkably, practically a single diastereoisomer was formed : 95 % of 2a and 5 % of the isomeric compound 2b. Repeating the experiment with a starting sulfone rich in the Z isomer (1Z/1E=75/25) led mainly to this isomeric disulfone 2b. A similar experiment with another vinylic sulfone 3E led again to a single diastereoisomer of the corresponding disulfone 4a.



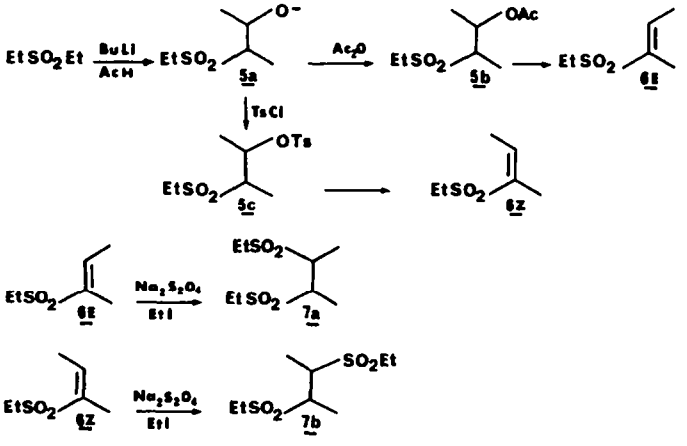
SCHEME I

This agrees with the suggested mechanism. We have so far failed to isolate the sulfone sulfinate salt itself ; this would be necessary to check that it is easily converted into the corresponding olefin.

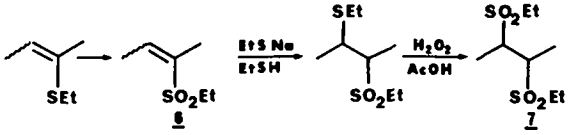
The addition step appears to be highly stereoselective and even stereospecific. The overall hydrogenolysis takes place with retention of configuration. This demands either anti addition followed by syn elimination or syn addition followed by anti elimination. The analogy with the result obtained by Kempe and Norin (17a) would suggest that the elimination step follows the anti stereochemistry. If it is true, the addition step must be syn. Since this type of addition is not common, we tried to confirm this with some experimental evidence. It was not easy to ascertain the threo or erythro structure of the adducts 2a, 2b or 4a. However, the problem was simplified by selecting a pair of disulfones with two similar sulfonyl residues and two similar alkyl "legs" so that the relationship between the diastereoisomers was now a meso/dl one. A similar structural identification has been carried out in an another case (21).

STEREOCHEMISTRY OF THE ADDITION AND ELIMINATION STEPS

We decided to prepare 2-ethylsulfonyl-2-butene 6E and Z and treat each of these vinylic sulfones with sodium dithionite, trapping the sulfinate salts with iodoethane, and studying the resulting 2,3-bis ethylsulfonyl butanes 7.

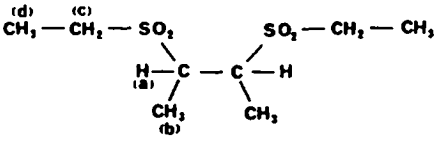


The procedure previously described with phenyl sulfones (1) is perfectly suitable with ethyl sulfones. The stereoconvergent elimination from both acetoxysulfones 5b led to 6E in a yield as high as 85-90%. Separation of the threo and erythro tosyloxysulfones 5c could be achieved by chromatography. The elimination step gave sulfone 6Z together with about 10% of 6E. Pure Z isomer has been obtained by flash chromatography. Iodoethane appears to be a little less effective than iodomethane in trapping the sulfone sulfinate salt, and the disulfones 7a and 7b were formed in a yield of only 10 %. 7a is a crystalline solid, whereas 7b in an oil. Because of this rather poor yield, and the tedious extraction procedure to get the pure disulfones 7 (involving a very careful chromatography to separate the disulfone from a mixture of other polar compounds, namely adogen and diethyl sulfone formed by alkylation of ethylsulfinate), it was decided to prepare disulfones 7a and 7b on a larger scale in a different way :



2- Ethylthio 2-butene is easily obtained from butanone ethylthioacetal (22), and oxidised to vinylic sulfone 6 as a mixture of E and Z isomers. Addition of ethanethiol, followed by oxidation with hydrogen peroxide gave a 60/40 mixture of disulfones 7A and 7B, from which 7A crystallised spontaneously. Complete separation of both isomers could be achieved by flash chromatography of the liquid residue and ether washing of the crystals. 7A was identified as the previously obtained 7a by its melting point and NMR spectrum. 7B was identified as 7b by TLC and NMR spectroscopy.

The ^1H NMR spectra of compounds 7a and 7b are quite different.



NMR spectrum of 7a and 7b. Solution in $CDCl_3$ - 250 MHz.

	H_a	H_b	H_c	H_d	J_{ab}	J_{cd}
7a	3.90	1.58	3.08	1.44	7Hz	7.5Hz
7b	3.66	1.68	3.22*	1.43	7Hz	7.5Hz

* symmetrical 10 line multiplet.

In disulfone 7a, the two diastereotopic protons H_c are equivalent, giving a nice quartet at 3.08 ppm. In 7b, this is no longer true, and selective decoupling shows that H_c and $H_{c'}$ appear at different chemical shifts ($\Delta\delta$ = 0.1ppm) with a coupling constant $J_{cc'}$ = -14Hz. The signal for H_c is basically an AB system, each of the four peaks being split into a quartet. This however does not greatly assist in the assignment of the disulfone configurations.

A few years ago, Shevlin studied the stereochemistry of similar disulfones : 2,3-bis benzenesulfonylbutane, and gave (21) the chemical shifts of protons H_a and H_b : δH_a = 3.88ppm and δH_b = 1.43ppm for the dl ; δH_a = 3.66ppm and δH_b = 1.55ppm for the meso.

These values suggest that 7a is the dl isomer, and 7b the meso. However, stronger evidence was needed. Kinetic resolution allowed structural assignment of the two 2,3-bis benzenesulfonyl butanes (21).
Each isomer was treated with a chiral amine, and the reaction was stopped before all the disulfone had reacted to give, via elimination, the vinylic sulfone. The recovered meso disulfone was optically inactive, but the recovered dl disulfone showed optical activity. Unfortunatly in our case, the optical rotations of recovered 7a and 7b, after reaction with (R) α-phenylethylamine, were too small for a definite conclusion to be drawn.

An X-ray structure determination of the crystalline isomer 7a showed unambiguously the dl configuration.

The addition of the HSO_2^- moiety must therefore have taken place in the syn mode, and the last step was an anti-elimination. The syn addition raises interesting questions which will be the subject of further investigation.

CRYSTAL STRUCTURE

The lattice is triclinic ; the space group is $P\bar{1}$ from statistical tests. Lattice constants are : a=10.645(9)Å, b=8.608(1)Å, c=13.958(3)Å, α=72.88(1)°, β=85.41(4)°, γ=87.90(4)° V=1218(1)Å^3. The experimental density is 1.39g.cm^{-3}, which leads to two molecules $C_8H_{18}O_4S_2$ per asymmetrical unit and a computed density of 1.32.

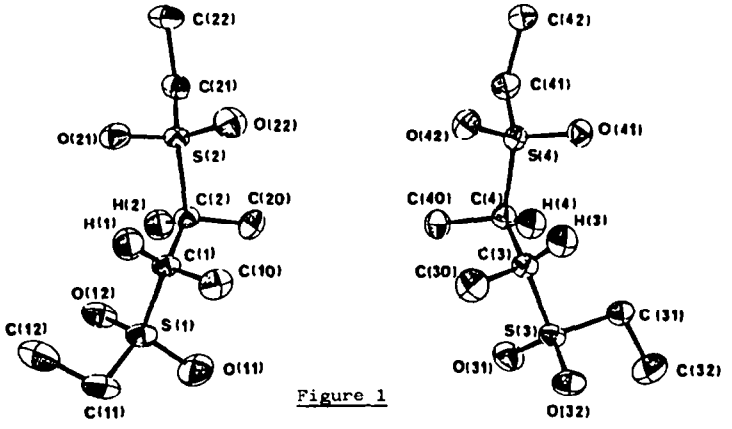


Figure 1

A crystal of parallepiped shape measuring 0.2/0.2/0.9mm was set on an automatic diffractometer. 3210 independent reflections were recorded at room temperature with MoKα radiation. 2888 reflections with $F > 3\sigma(F)$ were kept for computations carried out with SHELX 76 program. Two sulfur atoms were found from a Patterson map. Subsequent Fourier series led to the solution. Reliability factors were :

$$R = \sum(||F_o| - |F_c||) / \sum|F_o| = 0.048$$

$$R_w = \sum w^{0.5}(||F_o| - |F_c||) / \sum w^{0.5}|F_o| = 0.041$$

$$R_g = \left[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2\right]^{0.5} = 0.040$$

The unit cell contains four molecules symmetrically paired through the centre of symmetry. All molecules have the threo geometry. For clarity the two molecules of the

asymmetrical unit are represented in fig. 1 in a different way from that of the actual crystal packing, with the interatomic vectors C(1)-C(2) and C(3)-C(4) on one side. S(1)-S(2) and S(3)-S(4) on the other side symmetrical with respect to an arbitrary plane chosen perpendicular to the figure plane. These two molecules differ in the orientation of one $SO_2C_2H_5$ group. Indeed, the S(1)-C(11) and S(2)-C(21) bonds are roughly parallel to C(1)-C(2), while only the S(4)-C(41) bond is roughly parallel to C(3)-C(4).

vector 1	vector 2	angle	vector 1	vector 2	angle
S(1)-C(11)	C(1)-C(2)	13.2°(2)	C(1)-S(1)	C(11)-C(12)	105.7°(4)
S(2)-C(21)	C(1)-C(2)	17.9°(2)	C(2)-S(2)	C(21)-C(22)	4.4°(2)
S(4)-S(41)	C(3)-C(4)	10.6°(3)	C(3)-S(3)	C(31)-C(32)	6.5°(2)
S(3)-S(31)	C(3)-C(4)	104.1°(3)	C(4)-S(4)	C(41)-C(42)	8.9°(2)

Also C(2)-S(2) is nearly parallel to C(21)-C(22), and similarly C(3)-S(3) to C(31)-C(32), and C(4)-S(4) to C(41)-C(42).

As far as bonds are concerned the only interesting point is related to the eight carbon-sulfur bond lengths which seem to be of two types : those involving the asymmetrical carbon atom are systematically longer than those involving the carbon of the ethyl group by 0.04A ; this difference between average values is significantly larger than the standard deviation.

EXPERIMENTAL

NMR spectra were recorded on Cameca 250MHz (proton n.m.r.) and Bruker WH90 (^{13}C n.m.r.). All samples were run as solution in deuteriochloroform. Chemical shifts are recorded as δ values in ppm with respect to internal Me_4Si. Mass spectra were obtained using a Nermag R-10-10B instrument with electron ionisation at 70eV or chemical ionisation with ammonia or methane.
Melting points were determined on a Buchi apparatus. Silica gel sheets (Kieselgel 60, F_{254} Merck) were used for analytical TLC. Chromatographic separations were carried out on 70-230 mesh Merck silica gel or on "60H for thin layer chromatography" silica gel for flash chromatography.
New compounds (namely disulfones) have been submitted to microanalysis and gave satisfactory results.
Solvents were purified by standard methods and distilled before use.

Preparation of vinylic sulfones.

Sulfones 1E, 1Z and 3E have been prepared and reported recently (23).

Preparation of sulfones 6E and 6Z

2-Hydroxy, 3-ethylsulfonyl butane 5a

To a solution of diethylsulfone (6.10g - 50 mmol) in THF (200 ml) at -60°C, was added n-butyllithium (42 ml of a 1.2M solution in hexane - 50.4 mmol). The mixture was stirred for half an hour and freshly distilled acetaldehyde (3 ml - 65 mmol) was added. The reaction mixture was then stirred for one hour at -50°C before being quenched at low temperature with a saturated aqueous solution of ammonium chloride. After extraction with dichloromethane (3 times), washing with brine and drying of the organic phase, the hydroxysulfone 5a was obtained (7.14 g, 86%) as a mixture of diastereoisomers.

erythro : ^1H NMR 1.29(d,J=6.5Hz,3H) ; 1.41(t,J=7.5Hz,3H) ; 1.45(d,J=7Hz,3H) ; 2.97(q, J=7Hz, d,J=1.5Hz,1H) ; 3.10(q,J=7.5Hz, 2H) ; 4.60(q,J=6.5Hz,d,J=1.5Hz, 1H).

threo ^1H NMR· 1.32(d,J=6.5Hz,3H) ; 1.33(d,J=7Hz,3H) ; 1.40(t, J=7.5Hz,3H) ; 3.05(q,J= 7Hz,d,J=8Hz,1H) ; 3.17(q, J=7.5Hz,2H) ; 4.22(q,J=6.5Hz ; d,J=8Hz,1H).

The structure assignment was made according to Truce and Klinger (24).

2-Acetoxy, 3-ethylsulfonyl butane 5b

A solution of crude hydroxysulfone 5a (3.65 g, 22 mmol) in acetic anhydride and five drops of concentrated sulfuric acid was warmed to 90°C for half an hour. The mixture was poured onto crushed ice. The pH was brought up to 6 with sodium hydrogen carbonate. The aqueous layer was extracted with dichloromethane (3 times). The organic layer was washed with brine, dried and evaporated, giving the acetoxysulfone 5b : 4.10 g 89%. Separation of the diastereoisomers was achieved by flash chromatography (pentane - ethylacetate mixture).

erythro m.p. (ether 71°C).

^{1}H NMR 1.38(d,J=6.5Hz,3H) ; 1.40(t,J=7Hz,3H) ; 1.50(d, J=7.5Hz,3H) ; 2.10(s, 3H) ; 2.95 to 3.20(m,3H) ; 5.60(q,J=6.5Hz,d,J=2.5Hz,1H).
Analysis $C_8H_{16}O_4S$.

threo : oily

^{1}H NMR 1.37(d,J=6.5Hz,3H) ; 1.39(d,J=7Hz,3H) ; 1.43(t,J=7.5Hz,3H) ; 2.10(s,3H) ; 3.13(q,J=7.5Hz,2H) ; 3.37(q,J=7Hz,d,J=5Hz,1H) ; 5.40(q,J=6.5Hz,d, J=5Hz, 1H).

2-Ethylsulfonyl 2-butene E 6E

Powdered sodium hydroxide (380 mg, 9.5 mmol) was added to a solution of acetoxysulfone 5b (500 mg, 2.40 mmol) in dioxane (10 ml). The suspension was stirred at room temperature for 20 hours. After evaporation of the solvent and addition of a saturated aqueous solution of ammonium chloride (30 ml), the residue was extracted with dichloromethane. The organic phase was dried, washed and evaporated to give the crude vinylic sulfone 6E (250 mg, 70%) which was purified by column chromatography.

^{1}H NMR 1.29(t,J=7.5Hz,3H) ; 1.89(d,J=7Hz,q,J=1Hz,3H) ; 2.04((br. s,3H) ; 2.98(q,J= 7.5Hz,2H) ; 6.84(q,J=7Hz,q,J=1.5Hz,1H).

^{13}C NMR 7.03(CH_3) ; 11.62(CH_3) ; 14.08(CH_3) ; 45.99(CH_2) ; 134.61 (C) ; 137.65 (CH).

m/e : 148($M^{+\cdot}$), 95, 71, 55.

Analysis : $C_6H_{12}O_2S$.

2-Tosyloxy, 3-ethylsulfonyl butane 5c.

Condensation of the anion of diethylsulfone with acetaldehyde in THF, following the procedure described above, gave 50 mmol of the lithium salt of 5a, which was allowed to react with tosyl chloride (10.32 g, 50 mmol) for 15 hours at -30°C. After the usual extraction procedure, a mixture of both diastereoisomers of sulfone 5c was obtained (13.59 g, 85%). Purification (some vinylic sulfone was formed) and separation of the isomers was achieved by columm chromatography (20 % of ethylacetate in pentane).

erythro ^{1}H NMR :1.25(d,J=7Hz,3H) ; 1.35(d,J=7Hz,3H) ; 1.35(t,J=7Hz,3H) ; 2.49(s,3H) ; 3.02(q, J=7Hz,2H) ; 3.13(q,J=7Hz,d,J=3Hz,1H) ; 5.36(q,J=7Hz,d,J=3Hz,1H) ; 7.4 to 7.9 (m,4H).

Threo ^{1}H NMR : 1.33(d,J=6.5Hz,3H) ; 1.35(t,J=7Hz,3H) ; 1.41(d,J=7.5Hz,3H) ; 2.49(s,3H) ; 3.02 (q,J=7Hz,2H) ; 3.50(q,J=7.5Hz,d,J=3.5Hz,1H) ; 5.14(q,J=6.5Hz,d,J=3.5Hz,1H) ; 7.4 to 7.9 (m,4H).

The structure assignment was made according to Truce and Klinger (23), by comparison of the chemical shifts of the proton α to sulfonyle or tosylate groups.

m/e : 320 (H^+), 277, 173, 155.

2-Ethylsulfonyl-2-butene 6Z

To a solution of tosyloxysulfone 5c threo (1.87 g, 5.85 mmol) in ethanol (67 ml) was added sodium hydroxide (16.2 ml of a 0.4 M solution in ethanol, 6.48 mmol). The mixture was stirred at room temperature for half an hour. A white precipitate of sodium tosylate appeared. After concentration, hydrolysis with a saturated solution of ammonium chloride and extraction with dichloromethane, crude vinylic sulfone 6Z was obtained together with some isomer 6E (less than 10 %) and starting tosyloxy sulfone 5c (about 8 %). Pure sulfone 6Z was obtained by flash chromatography (550 mg. 63 %).

^{1}H NMR 1.36(t,J=7.5Hz,3H) ; 2.08(br,3H) ; 2.12(d,J=7.5Hz,q, J=1Hz,3H) ; 3.02(q,J=7.5Hz, 2H) ; 6.40(q,J=7.5Hz,q,J=1Hz, 1H).

^{13}C NMR 6.70(CH_3) ; 14.86(CH_3) , 20.43(CH_3) ; 48.07(CH_2) ; 134.87(C) ; 138.56(CH).

m/e = 148(M^+), 95, 77, 55.

Preparation of 2.3-bis benzenesulfonyl butane 7A and 7B
2-Ethylthio- 2-butene E and Z

This sulfide was prepared by pyrolysis of butanone ethylthioacetal with phosphoric acid and immediate distillation (21).

^{1}H NMR 1.22(t,J=7.5Hz) and 1.24(t,J=7.5Hz)3H ; 1.68(d,J=7Hz,q,J=1Hz) and 1.74(q,J=6.5Hz,q,

J=1.5Hz)3H ; 1.88(d,q,J=1Hz) and 1.99(d,q, J=1.5Hz)3H ; 2.67(q,J=7.5Hz) and 2.70(q, J=7.5Hz)2H ; 5.62(q,J=7Hz ; q,J=1Hz) and 5.50(q,J=6.5Hz,q,J=1.5Hz)1H.

2-Ethylsulfonyl- 2-butene E and Z 6

Oxidation of the vinylic sulfide (28g. 240 mmol) by hydrogen peroxide (63 ml of a 10M solution - 630 mmol) in acetic acid (480 ml) gave after 3 days at room temperature a crude mixture of vinylic sulfones 6E and 6Z. Distillation (76°C/0.05 mmHg) yielded the pure compound (18g, 50 %) ; 6E/6Z ≃ 50/50.

2.3-Bisethylsulfonyl butane 7

Vinylic sulfone 6 (as a mixture of isomers, 5g, 34 mmol) was dissolved in ethanethiol (7.5 ml). Sodium ethylate (0.7 ml of a 1M solution in ethanol) was then added and the mixture was stirred for 15 hours. Acetic acid (20 ml) was then added and the excess of ethanethiol was removed under vacuum. Hydrogen peroxide (12 ml of a 10 M solution) was added and the mixture was warmed to 85°C for 3 hours. The mixture was cooled, poured into water (170ml) and extracted with dichloromethane (3 times). The organic layer was washed with aqueous sodium hydrogen carbonate, dried and evaporated, yielding crude 7 as a mixture of diastereoisomers (8g, 97%). Some isomer 7A crystallized spontaneously. Washing with diethylether and recrystallization from ether gave pure 7A (1.8g). The ether mother liquors were evaporated, and the residue was purified by flash chromatography (pentane/dichloromethane). 1g of the residue gave about 350 mg of isomer 7A which eluted first (70 % of dichloromethane) and then about 500 mg of isomer 7B (90% of CH_2Cl_2).
isomer 7A, d,l.
mp : 72.5°C.

^1H NMR 1.44(t,J=7.5Hz,6H) ; 1.58(d,J=7Hz,6H) ; 3.08(q,J=7.5Hz, 4H) ; 3.90(q,J=7Hz,2H).

^{13}C NMR 6.77(CH_3) ; 10.13(CH_3) ; 46.32(CH_2) ; 52.53(CH).

m/e chemical ionisation NH_3 : 260(M+18). 243(M+1).
Analysis : $C_8H_{18}O_4S_2$.

A crystal, suitable for X-ray structure determination has been obtained by very slow crystallization from water.

isomer 7B meso
colourless oil

^1H NMR 1.43(t,J=7.5Hz,6H) ; 1.68(d,J=7Hz,6H) ; 3.22(m*,4H) ; 3.66(q,J=7Hz,2H).

^{13}C NMR 6.18(CH_3) ; 13.63(CH_3) ; 46.51(CH_2) ; 59.26(CH).

m/e chemical ionisation NH_3 : 260(M+18) ; 243(M+1).
Analysis : $C_8H_{18}O_4S_2$.

General procedure for trapping the intermediate sulfone-sulfinate salt

The vinylic sulfone (3 mmol) was dissolved in a solution of adogen 464 (3g ; 6 mmol) in cyclohexane (15 ml) ; to this solution were added water (15 ml), sodium dithionite (0.522g - 3 mmol) and sodium hydrogen carbonate (0.63g - 7.5 mmol). After 15 minutes refluxing under nitrogen, the reaction was stopped by cooling in ice, iodomethane, or iodoethane (12 equivalents) was added and the mixture was stirred at room temperature for 3 hours (CH_3I) or 10 hours (CH_3CH_2I). Water was then added, the organic phase separated and the aqueous layer extracted twice with dichloromethane. After drying ($MgSO_4$), the solvents were evaporated and the residue chromatographed on silica gel. The olefins were eluted with pentane, unchanged vinylic sulfones with dichloromethane and the bissulfones with dichloromethane /ether mixtures. This fraction was flash chromatographed on silica gel (pentane/increasing concentration of ethyl acetate) to separate small amounts of methylphenyl sulfone (resp. diethylsulfone) formed by alkylation of benzenesulfinate (resp. ethylsulfinate) with iodomethane (resp. iodoethane) and 1-decanol (from the adogen) from the bissulfone.

2-Methylsulfonyl- 3-phenylsulfonyl undecane threo 2a yield 32% from vinylic sulfone 1E colourless oil.
TLC pentane/ethylacetate (85/15) r_f=0.14.

^1H NMR 0.86(t,J=7Hz,3H) ; 1.0 to 1.3(m,12H) ; 1.59(d,J=7Hz,3H) ; 1.90(m,2H) ; 2.94(s,3H) ; 3.86(t,J=5.5Hz,d,J=1Hz,1H) ; 3.93(q,J=7Hz,d,J=1Hz,1H) ; 7.6 to 8.0(m,5H).

^{13}C NMR 10.3(CH_3) ; 14.2(CH_3) ; 39.7(CH_3) ; 56.1(CH), 61.2(CH) ; 129.2(CH) ; 128.3(CH) ; 134.0(CH) ; 137.9(C).

m/e chemical ionisation CH_4 : 375(M+1) ; 295 ; 233.
Analysis : $C_{18}H_{30}O_4S_2$.

* The shape of this 10 peak multiplet has been discussed above.

2-Methylsulfonyl- 3-phenylsulfonyl undecane erythro 2b

Obtained together with some 2a from a mixture of 1E and 1Z, purified by chromatography and recrystallised from ether. mp : 57°C. TLC pentane/ethyl acetate (85/15) r_f=0.20.

^{1}H NMR 0.86(t,J=7Hz,3H) ; 1.0 to 1.4(m,12H) ; 1.67(m,2H) ; 1.90 (d,J=7.5Hz,3H) ; 3.29(s, 3H) ; 3.34(q,J=7.5Hz,d,J=1Hz,1H) ; 4.0(d,J=9Hz,d,J=5Hz,d,J=1Hz,1H) ; 7.6 to 8.0(m, 5H).

m/e chemical ionisation CH_4 : 375(M+1) ; 295, 233.
Analysis : $C_{18}H_{30}O_4S_2$.

2-Methylsulfonyl- 3-phenylsulfonyl butane threo 4a

yield 31% from vinylic sulfone 3E. mp (dichloromethane/pentane) : 98°C.

^{1}H NMR 1.40(d,J=7Hz,3H) ; 1.62(d,J=7.5Hz,3H) ; 2.97(s,3H) ; 3.95(q,J=7Hz,d,J=1Hz,1H) ; 3.99 (q,J=7.5Hz,d,J=1Hz,1H) ; 7.65 to 8.0(m,5H).

^{13}C NMR 9.62(CH_3) ; 9.94(CH_3) ; 39.46(CH_3) ; 55.51(CH) ; 56.42(CH) ;128.59(CH) ; 129.24 (CH) ; 134.09(CH) ; 136.75(C).

m/e chemical ionisation CH_4 : 277(M+1) ; 221 ; 197 ; 143 ; 141.
Analysis : $C_{11}H_{16}O_4S_2$.

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