Tetrahedron Vol. 41, No. 12, pp. 2419 to 2433, 1985
Printed in Great Britain.

0040-4020/85 $3.00 + .00

STEREOCHEMISTRY OF ORGANIC SULPHUR COMPOUNDS. Part. 17[#] CONFORMATIONAL ANALYSIS OF SOME ERYTHRO- AND THREO-THIO-DERIVATIVES OF β-FLUORINATED AND β-OXYGENATED ETHANES

J.C.CARRETERO, J.L.GARCIA RUANO* M.C.MARTINEZ and J.H.RODRIGUEZ

Departamento de Química Orgánica, Facultad de Ciencias, Universidad Autónoma de Madrid, Canto Blanco, 28049 Madrid, Spain.

F. ALCUDIA

Departamento de Química Orgánica, Facultad de Farmacia, Universidad de Sevilla, 41071 Sevilla, Spain.

(*Received in UK 2 January* 1985)

Abstract - The synthesis and conformational analysis of 2-fluoro, 2-hydroxy and 2-methoxy thioderivatives (thioethers, sulphoxides, sulphones and sulphonium salts) of 1,2-dimethyl and 1,2-diphenylethanes (erythro and threo) are reported. Steric effects in thioethers and electrostatic interactions in sulphonium salts are the main factors determining the stability rotamers. A balance of these factors controls the conformational equilibria in sulphoxides and sulphones. Electronic interactions between the π-aromatic electrons or the unshared β-heteroatomic electrons and the sulphur atom are suggested to explain large differences in rotamer populations induced by changes in the carbon sketelon or in the relative configuration of the sulphinylic sulphur.

INTRODUCTION

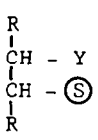
The conformational study of several thioderivatives of β-oxygenated acyclic compounds allowed us to determine the role played by electronic density as well as the unshared electron pairs of the oxygen in the heteroatomic interactions which contribute to the conformational equilibria of these compounds[1,2]. In the case of the trisubstituted ethanes it was possible to evaluate rotamer populations from $^{3}J_{H,H}$ values[1,3], obtained from computer analysis of their ^{1}H-nmr spectra, and by use of the values of $^{3}J_{H,H}$ for each conformation, calculated from adequate semi-empirical equations, such as the equation of Altona et al[4]. This evaluation could not be done for compounds with a tetrasubstituted ethane skeleton, because there was only one vicinal coupling constant. It was therefore only possible to know the relative population of the conformation with two protons in an anti relationship, with respect to the two remaining rotamers. Fortunately, in all cases studied (erythro- and threo-2-thioderivatives of 1,2-diphenylethanol[5,6]) it was possible to know which rotamer was predominant by considering the main role of steric effects on the conformational equilibria.

In compounds with this carbon skeleton, additional information could be obtained by replacing the OH group by F, based on the existing relationship between the values of $^{3}J_{F,H}$ and the stereochemistry of the coupled nuclei. Thus, a qualitative evaluation of the population of the rotamers in the conformational equilibria of these fluorocompounds could be determined. In addition, by comparison of the results obtained in the fluorinated compounds with the oxygenated ones, some insight

[#]Part 16. F. Alcudia, E.Brunet, L. Castillo, J.L.García Ruano, M.M. Llera y J.H. Rodríguez, An. Quím., 1985 (in the press).

could be gained into the participation of the rotamers that have their protons in a gauche relationship in β-oxygenated thioderivatives. On the other hand, this comparison would also permit us to know the influence of the electronegativity of these heteroatoms (F > O) on the interactions that they exhibit with the different sulphur functions. In this paper, the synthesis and conformational analysis of 2-fluoro-, 2-hydroxy- and 2-methoxy-thioderivatives of 1,2-dimethyl and 1,2-diphenylethane, with equal (threo-) and opposite (erythro-) relative configuration in two chiral carbons, were carried out. In all cases, the SMe, SOMe (two diastereomers designated as α and β), SO_2Me and $\overset{+}{S}Me_2$ functions were considered.

The sixty compounds studied in this paper will be designated in the following way:



Ⓢ = I(SMe), II(SOMe-α), III(SOMe-β), IV(SO_2Me) or V($\overset{+}{S}Me_2$)
R = Me or Ph
Y = OH, OMe or F
c = e (erythro) or t (threo)

The sulphur functions Ⓢ are indicated by Roman numerals (I=SMe, II=SOMe (α), III=SOMe (β), IV=SO_2Me and V=$\overset{+}{S}Me_2$). The sulphur configuration is identical to that of the Y bearing carbon in the α sulphoxides (II), whereas they are opposite in the β-sulphoxides (III). The Y function is indicated as a subscript of the Roman numeral. The relative configuration of the chiral carbons (erythro- or threo-) is indicated as the superscript, c(e or t) to the left of the Roman numeral. The nature of the carbon skeleton is also given by another superscript R to the right of the Roman numeral (Me= 1,2-dimethylethane; Ph=1,2-diphenylethane).

RESULTS AND DISCUSSION

The syntheses of all thioethers studied in this paper has been previously described[7]. S-Methylation and S-oxidation reactions respectively afforded the corresponding dimethylsulphonium salts and sulphones (see Experimental). The pairs of the epimeric sulphoxides (II and III), obtained by controlled oxidation of thioethers I as diastereomeric mixtures, could only be separated in the case of hydroxyderivatives, by chromatography or fractional crystallization. The syntheses of pure O-methylderivative diastereomers were carried out by independent O-methylation of previously separated hydroxysulphoxides. The obtention of the diastereomerically pure fluorosulphoxides has only been possible in the case of $^{e}II_{F}^{Ph}$. For all remaining cases the conformational study was performed by analysis of the mixture of epimers (II + III). From spectra of this mixture the corresponding parameters of each diastereomer were easily identified.

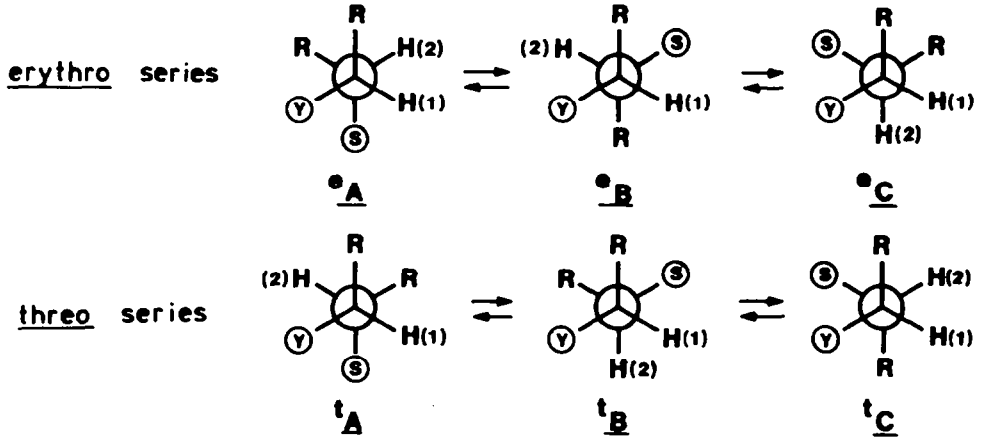


Fig.1. Conformational equilibria around the CH-CH bond in erythro and threo derivatives.

The staggered conformations, around the C-C bond, of erythro and threo series are given in Figure 1. The conformational analysis of these compounds was carried out from the $J_{1,2}$ values and, in the fluoroderivatives, also from $J_{2,F}$.

Taking into account that observed coupling constant values correspond to a weighted means between the different conformations, it was necessary to find out the limit values of ^3J in order to evaluate the conformational populations, Very different values for $^3J_{F,H}$ have been used in the literature for gauche- and anti- relationships between H and F[8,9]. In conformationally rigid cyclohexanes, values of 9 Hz (gauche)[10] and 38 Hz (anti)[11] have been reported. Nevertheless the values of these coupling constants could be modified by the electronegativity of substituents[12] or by the concentration and polarity of the solvent[13,14]. These facts suggested that the values observed in our compounds should only be used for qualitative predictions of the rotamer populations. In this sense, the values of 7 Hz and 40 Hz will be used in this paper for the two arrangements nuclei mentioned before. It should also be considered that in compounds with a 1,2-dimethylethane skeleton the corresponding values should be slightly larger than in 1,2-diphenylethane derivatives (Ph more electronegative than Me) and in all cases dihedral and bond angle distorsions probably contribute to the fact that limit values are not reached.

The situation is similar for $^3J_{H,H}$, although the effects of substituents and their relative orientations are better known. In this way, the Karplus equation, modified by Altona et al[4], accurately predicted the coupling constant values of ß-oxygenated thioderivatives with a trisubstituted ethane skeleton[15]. Using the parameters proposed by Altona[4] for tetrasubstituted ethanes, $J_{1,2}$ takes the values of 9.9 Hz, for the rotamers ^eB and ^tA (Fig. 1), 1.7, for ^eA and ^tC, and 3.3, for ^eC and ^tB (in the fluorinated thioderivatives these values are slightly smaller). The values obtained by Zefirov for trans-1-methoxy-2-methylthiocyclohexane[16] and the values observed by us for trans-2,3-dimethyl-1,4-oxathiane[17] (both systems are monoconformational) are in accordance with the J_{anti} calculated from the Altona equation[4]. Therefore we will consider as valid the calculated values for rotamers given in fig. 1 in compounds with a butane skeleton (a similar structure to that of the indicated cyclohexane and 1,4-oxathiane derivatives). Nevertheless, the values in the 1,2-diphenylethane derivatives should be slightly larger. Hence, we have found values of 11 Hz (see later) for $^3J_{anti}$ (~1 Hz larger than the calculated value and the observed one for the afore mentioned cyclic compounds). The J_{gauche} values should also be larger in the 1,2-diphenylethane series (~0.5 Hz) as could be deduced from the fact that supposedly identical conformational situations in both series, exhibit differences in coupling constants.

Table 1 gives the vicinal coupling constants used for the conformational analysis of thioethers and obtained from the analysis of their ^{1}H-nmr spectra. As a rule, the $J_{1,2}$ values suggest that A, B and C rotamers (Fig. 1) have a similar participation in the equilibria of butane thioderivatives, whereas in compound with a 1,2-diphenylethane skeleton the most sterically favoured rotamers, ^eB and ^tA, predominate. This difference in behaviour could be explained by considering steric factors, such as the larger size of the Ph group with respect to the Me one. Accordingly the increase in the participation of ^eB and ^tA in the 1,2-diphenylethane derivatives should be due to the decrease in contribution of ^eC and ^tB, which are the least sterically stabilized rotamers. This can be observed in the fluoroderivatives I_F from the $^3J_{F,H}$ values, which indicate that the ^eA and ^tC populations (H (2) and F in an anti- relationship) must be similar, whichever skeleton the compounds exhibit.

Table 1. $^3J_{1,2}$, $^3J_{2,F}$(*) and $^3J_{1,OH}$(#) values of the thioethers I.

solvent	Config.	Compound					
		I^{Me}_{OH}	I^{Me}_{OMe}	I^{Me}_{F}	I^{Ph}_{OH}	I^{Ph}_{OMe}	I^{Ph}_{F}
a	b	3.3	4.6	5.5(15.0)*	7.2	7.3	7.3(15.9)*
b	e	5.2	4.5	5.1(16.9)*	7.0(4.8)#	8.0	8.0(15.7)*
a	t	7.8	4.5	5.0(15.2)*	8.5(2.6)#	8.1	7.3(14.0)*
b	t	4.3	4.1	4.7(17.5)*	7.3(4.9)#	8.8	8.0(14.8)*

a = $CDCl_3$. b = DMSO-d_6. e = erythro. t = threo.

Differences in behaviour of the hydroxythioethers in $CDCl_3$ with respect to both the methoxy and fluorinated thioethers show the obvious role of intramolecular hydrogen bondings in stabilizing mainly ^eA and ^tA rotamers. Such differences disappear in DMSO-d_6 (where these associations are prevented). The relative contribution of the hydrogen bondings to the conformational stability must be larger in butane skeleton compounds (where the steric factors are less restrictive) than in 1,2-diphenylethane derivatives. On the other hand, intramolecular associations are easier (and therefore stronger) in the threo- than in the erythro- series. In these, rotamer ^eA exhibits the $(R/R)_{gauche}$ interaction (fig. 1), causing a partial removal of the R groups and consequently, of the OH and SMe groups, that minimize the hydrogen bondings (completely prevented when R=Ph). The above considerations clarify all data of table 1 relative to hydroxythioethers.

Electrostatic and electronic interactions between the heteroatomic functions ought not to play an important role in the conformational stabilities. This can be deduced in methoxy and fluoroderivatives from the small and normally non-systematic differences in $J_{1,2}$ values both with the solvent change and with the nature of the heteroatomic function.

Nevertheless, the steric interactions as such could not explain the following experimental facts: i) The participation of the rotamers $^eB^{Ph}$ and $^tB^{Ph}$ in their respective conformational equilibria, has to be similar (deduced from the corresponding $J_{1,2}$ values). ii) The population of $^tC^{Ph}$ has to be slightly lower than that of $^eA^{Ph}$ (deduced from the $J_{2,F}$ values). iii) The contribution of all conformations that present the $(R/SMe)_{gauche}$ interaction is lower in the 1,2-diphenylethane derivatives (R=Ph) than in the butane skeleton compounds (R=Me) (deduced by comparison of the coupling constants obtained in both series). iv) When the carbon skeleton changes from R=Me to R=Ph, the increase in the participation of ^tA (with the $(R/R)_{gauche}$ interaction) is larger than that of ^eB (with the $(R/SMe)_{gauche}$ interaction).

All these facts can only be explained assuming that in these compounds the $(Ph/SMe)_{gauche}$ interaction was more destabilizing than might be anticipated on steric grounds. It could be rationalized by considering the existence of an electrostatic repulsion between the aromatic π electrons and those on the sulphur atom. It can also be considered the existence of a gauche repulsive effect[20] between the two groups, owing to the spatial interaction between the orbitals containing the π (aromatic) and n (sulphur) electrons. This effect would be similar to the hockey-stick effect[21], proposed to explain the additional repulsion observed between heavy heteroatoms, which are in a gauche relationship.

The vicinal coupling constants obtained from the analysis of the ^{1}H-nmr spectra of sulphonium salts are given in Table 2. The different conformational behaviour of sulphonium salts with respect to that of the thioethers (see Tables 1 and 2) could be explained taking into account the characteristic differences between the

two sulphur functions. The steric hindrance of the $\overset{+}{S}Me_2$ group is larger than that of SMe[22] and the charge density of the sulphur atom has a different sign in the two functions mentioned. In the sulphonium salts there is an attractive electrostatic interaction between the sulphur and the other heteroatom which is absent in the thioethers.

Table 2. $^3J_{1,2}$ and $^3J_{2,F}$(*) values of the sulphonium salts V.

Solvent	Config.	Compound					
		V^{Me}_{OH}	V^{Me}_{OMe}	V^{Me}_{F}	V^{Ph}_{OH}	V^{Ph}_{OMe}	V^{Ph}_{F}
a	e	2.5	2.9	1.7(30.0)*	#	4.2	3.0(33.1)*
b	e	2.9	3.0	2.2(27.4)*	4.0	4.7	3.8(29.4)*
a	t	8.3	6.2	6.2(16.9)*	#	10.1	9.7(8.7)*
b	t	6.9	7.0	7.0(15.2)*	10.4	10.9	10.6(8.9)*

a = $CDCl_3$. b = DMSO-d_6. e = erythro. t = threo. # = unsoluble.

This favourable interaction will determine a special stability of the A and C rotamers, whereas from a steric viewpoint, the change of sulphur function from SMe to $\overset{+}{S}Me_2$ will destabilize all rotamers in the order A < B < C (see fig. 1). As a consequence of the contribution of both factors, the participation of the A rotamers is considerably larger in sulphonium salts than in thioethers. The population of the C rotamers in sulphonium salts is slightly higher than that in thioethers when R=Me (electrostatic interactions counteract the effect of steric ones) but it is lower when R=Ph (steric effects are predominant). All these conclusions can be drawn from the differences observed in the values of $J_{1,2}$ and $J_{2,F}$ in Tables 1 and 2. In compounds $^eV^{Me}$, the contribution of the ^eB rotamers ought to be negligible, despite being the sterically favoured rotamer, emphasizing the predominance of electrostatic interactions over steric ones in their conformational equilibria.

The electronegativity of the substituent Y (compare OH and OMe with F) induces variations that are compatible with the greater intensity of electrostatic interactions in the fluorderivatives. In the erythro compounds an important decrease in $J_{1,2}$ when Y=F is observed. This is a result of both the increase in the participation of ^eA and of the decrease in the magnitude of $J_{1,2}$ (due to the larger electronegativy of the fluorine). Meanwhile, in the threo compounds $J_{1,2}$ remains unaltered because the effects of both indicated factors counteract each other (in these salts the increase in the populations of ^tA makes larger $J_{1,2}$).

The influence of the solvent is also compatible with the main role played by the electrostatic interactions in the conformational equilibria of sulphonium salts. In DMSO-d_6, these interactions become less significant and the size of both the polar groups and the aromatic rings increases[21]. In the erythro series both effects favoured the increase in the population of ^eB (larger $J_{1,2}$ and lower $J_{2,F}$ values). In the threo- series, the situation is different. Upon considering the electrostatic interactions, the ^tB rotamers should be those conformations in which the relative destabilizacion in DMSO-d_6 is smaller. Meanwhile the increase in steric hindrance of the groups, in this solvent, would mainly augment the energy of ^tB and ^tC rotamers. In the butane derivatives where the steric effects are moderate, the increase in populations of ^tA, observed in DMSO-d_6 (larger $J_{1,2}$ values) is produced at the expense of ^tC rotamer (lower $J_{2,F}$ values). In 1,2-diphenylethane derivatives (larger steric interactions), the ^tB populations also decrease whereas the increase in population of ^tA is observed (larger $J_{1,2}$ values).

The coupling constant values of the sulphoxides are given in Table 3. Prior to the conformational study it was necessary to make their configurational assignment. In the case of $^eII^{Ph}_{OH}$ the unmistakable configurational assignment was made by X-ray

diffraction studies[22]. In this way it was possible to know the relative configuration of all β-oxygenated sulphoxides (erythro and threo) with a 1,2-diphenylethane skeleton by chemical correlations[2]. The different conformational behaviour of diastereomers could be used to assign their relative configuration. These differences determined that sulphoxides II had smaller $J_{1,2}$ values in erythro (RSR, SRS) and larger ones in threo (RRR, SSS) than in the corresponding epimers III. On the other hand, the $J_{1,2}$ values of the hydroxysulphoxides II_{OH} were independent of the dilution and the solvent polarity, while their epimers, III_{OH}, showed valuable changes, specially with the solvent polarity. This difference could be attributed to the intramolecular hydrogen bondings, which only would be effective in the sulphoxides III where the populations of intramolecular associated rotamers decreased in DMSO. On considering these criteria, the as yet undetermined relative configuration of sulphoxides, could be assigned, as indicated in Table 3.

Table 3. $^{2}J_{1,2}$, $^{3}J_{2,F}$(*) and $^{3}J_{1,OH}$(#) values obtained for sulphoxides II an III.

	Erythro		Threo	
Comp.	$CDCl_3$	DMSO-d_6	$CDCl_3$	DMSO-d_6
II^{Me}_{OH}	2.0	2.5	8.3	8.0
II^{Me}_{OMe}	2.3	2.4	8.8	7.4
II^{Me}_{F}	1.9 30.2*	2.0 32,0*	8.6 10.2*	7.7 12.5*
III^{Me}_{OH}	2.8	4.5	8.1	6.5
III^{Me}_{OMe}	4.0	4.1	5.5	5.7
III^{Me}_{F}	3.3 21.6*	3.8 22.4*	6.0 14.5*	6.4 13.8*
II^{Ph}_{OH}	2.6	3.0 4.4#	10.0 3.9#	10.8 4.8#
II^{Ph}_{OMe}	3.0	3.3	10.6	11.0
II^{Ph}_{F}	2.0 34.6*	2.6 35.5*	10.4 8.2*	10.9 9.0*
III^{Ph}_{OH}	7.4 2.2#	8.5 4.8#	9.5	8.3 3.7#
III^{Ph}_{OMe}	9.3	9.7	5.7	8.6
III^{Ph}_{F}	8.1 16.5*	8.7 16.2*	6.2 14.9*	9.1 12.0*

Some aspects of the conformational behaviour of hydroxy and methoxy sulphoxides with 1,2-diphenylethane skeleton have been established elsewhere[2]. Therefore in this paper we only consider the questions that permit the confirmation of some previously reported hypotheses and shed new light on other findings.

In the sulphinyl group, the sulphur atom bears a certain density of positive charge and therefore it could interact with the heteroatomic function of the β position, stabilizing A and C conformations, as happened in the sulphonium salts. This stabilizing interaction must be smaller than the one present in the sulphonium salts, where threre is a formal positive charge. So, on electrostatic grounds, the conformational equilibria of sulphoxides should be placed between those of the thioethers and the sulphonium salts.

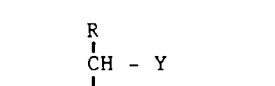
The vicinal coupling constants of methoxy and fluoroderivatives in thioethers, sulphoxides and sulphonium salts are compared in Table 4.

The most remarkable fact derives from the varying behaviour of the pairs of diastereomers, which reflects the existence of additional interactions depending on the configuration. These interactions will mean that A rotamers being more stable in sulphoxides II than in sulphonium salts. As a consequence, their contribution will be greater in the above mentioned sulphoxides and this can be deduced from the higher and lower $J_{1,2}$ values for threo, adn erythro derivatives respectively. In the fluorinated compounds of the erythro configuration, the $J_{2,F}$ value (related to the A population) is also greater than the corresponding value for the sulphonium salt, whereas it is lower in the threo-derivative, showing the scarce contribution of the ^{t}C romater.

This conformational behaviour could be explained, assuming the existence of a stabilizing interaction between the unshared electrons on the heteroatom (Y) and the unoccupied orbital d of the sulphur (n→d interaction) as it was proposed in a previously described series[2,3]. The efficiency of this interaction depends on

Table 4. $^3J_{1,2}$ and $^3J_{2,F}$(*) values of β-methoxy and β-fluoro thioethers, sulphoxides and sulphonium salts.

R	Ⓢ	Y			
		e_{OMe}	e_F	t_{OMe}	t_F
Me	SMe(I)	4.6	5.5(15.0)*	4.5	5.0(15.2)*
	SOMe(II)	4.0	3.3(21.6)*	5.5	6.0(14.5)*
	$\overset{+}{S}Me_2$(V)	2.9	1.7(30.0)*	6.2	6.2(16.9)*
	SOMe(III)	2.3	1.9(30.2)*	8.8	8.6(10.2)*
Ph	SMe(I)	7.3	7.3(15.9)*	8.1	7.3(14.0)*
	SOMe(II)	9.3	8.1(16.5)*	5.7	6.2(14.9)*
	$\overset{+}{S}Me_2$(V)	4.2	3.0(33.1)*	10.1	9.7(8.7)*
	SOMe(III)	3.0	2.0(34.6)*	10.6	10.4(8.2)*



e = erythro. t = threo.

the relative orientation of the interactive groups and it is larger when the relative configuration permits the arrangement depicted in Fig. 2. In this arrangement the Y group must be in a 1,3-parallel relationship with respect to the electron pair on the sulphur and with the sulphinylic oxygen in a perpendicular plane to the C_1-C_2-S one[2]. This favourable arrangement is only found in the A rotamers of the sulphoxides ^eII and ^tII and in the C ones of the sulphoxides ^eIII and ^tIII, although these latter romaters were destabilized by the existence of an $(R/O)_{1,3-p}$ interaction.

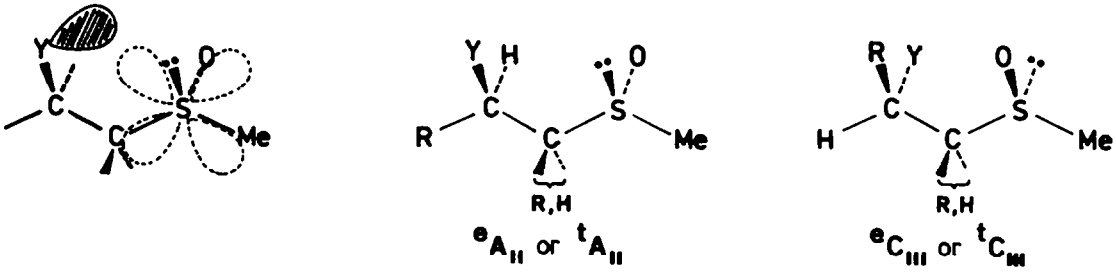


Fig.2.Conformations with the π→d° interaction and spatial arrangement that makes it possible.

The second anomaly, deduced from Table 4, consists of the unusually high population of the B rotamer in the sulphoxides III^{Ph}. From Fig. 3, where the most favourable spatial arrangement on steric grounds is depicted, it can be observed that the Ph group at C-1 has, with respect to the sulphur function, an analogous stereochemistry to that of the Y group in Fig. 2. A donor-acceptor interaction between the π electrons of the adequately oriented phenyl group and the unoccupied d orbital of the sulphur could also justify its large population. This π-d interacion would be similar to the n-d one discussed above.

In the light of the effect to changing solvent, on this interaction the larger $J_{1,2}$ value observed in DMSO-d_6 with respect to $CDCl_3$ ($\Delta J \simeq 3$ Hz) in the case of $^tIII^{Ph}_{OMe}$ and $^tIII^{Ph}_{F}$ could be explained. This influence of the solvent is greater than that observed in other compounds and therefore could not be due only to electrostatic and steric factors. Taking into account the spatial requirements for the donor-acceptor π→d interaction, any change in the relative orientation of the phenyl group could minimize the efficiency of this interaction. The steric hindrance increase of the aromatic rings, due to association with DMSO, will determine, in the ^tB conformation (which has a Ph/Ph) gauche interaction), a change in the relative stereochemistry of both phenyl groups. This change affects the spatial orientation of the groups involved in the donor-acceptor interaction and therefore decreases its efficiency. Thus the stability of the ^tB rotamer decreases

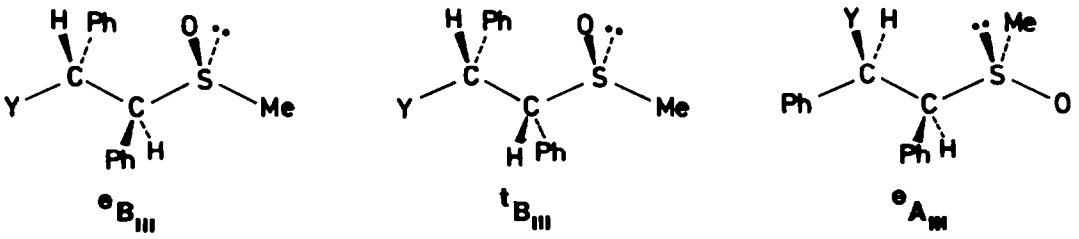


Fig. 3. Some of the favoured rotamers in sulphoxides ^{e}III and ^{t}III.

significantly. This fact determines a shift of the conformational equilibrium towards the ^{t}A rotamers (favourable on steric grounds) causing the increase in the $J_{1,2}$ value.

The solvent effect on the ^{e}B stability ought to be weaker than in the ^{t}B rotamer, since the phenyl groups are now in an anti relationship, and the Ph at C-1 could easily be oriented for the interaction with the sulphinyl group to be efficient, even in DMSO-d_6. On the other hand, ^{e}B is the most stabilized rotamer from the steric viewpoint, while ^{e}A presents the methyl group in an anti relationship with respect to the phenyl at C-2 (Fig. 3). This stereochemistry gives rise to an appreciable destabilization, according to the studies carried out by Kodama et al[23] in alkyl benzyl sulphoxides.

Finally,both the scarce influence of the changing solvent in the sulphoxides II, and the conformational behaviour of the hydroxysulphoxides can be explained as in other cases previously studied[2].

The coupling constants of sulphones used in their conformational analysis are given in Table 5. The $J_{1,2}$ values (small in erythro and large in threo compounds) suggest a preference for A rotamers in all cases. This is confirmed, in the fluorosulphones, from the $^{3}J_{2,F}$ values (29-31 Hz and 9-11.5 Hz for the erythro and threo sulphones, respectively). A comparative analysis of Tables 3 and 5 shows that the sulphones exhibit a conformational predominance for one rotamer larger than in the sulphoxides III and like sulphoxides II (stabilized by the donor-acceptor interaction). This conformational behaviour could be attributed to electrostatic and steric factors. The size of the SO_2Me group is larger than that of the SOMe one, determining the steric destabilization of B and C rotamers in relation to A (see Fig. 1) in the sulphones with respect to the sulphoxides. On

Table 5. $^{3}J_{1,2}$, $^{3}J_{2,F}$(*)and $^{3}J_{1,OH}$(#) values of the sulphones IV.

Solvent	Config.	IV^{Me}_{OH}	IV^{Me}_{OMe}	IV^{Me}_{F}	IV^{Ph}_{OH}	IV^{Ph}_{OMe}	IV^{Ph}_{F}
$CDCl_3$	Erythro	1.5	2.0	1.6(28.6)*	2.7	3.5	2.6(30.9)*
DMSO-d_6	Erythro	2.0(5.2)#	2.3	1.7(29.0)*	3.4(4.6)#	4.2	3.2(31.3)*
$CDCl_3$	Threo	8.4	7.8	8.2(10.5)*	9.7(2.4)#	10.1	9.8(8.8)*
DMSO-d_6	Threo	6.4	6.2	7.4(11.4)*	10.0(4.0)#	10.5	10.5(8.8)*

the other hand A rotamers must also be stabilized from a electrostatic viewpoint, according to the results obtained by Eliel et al[24]. Therefore, the larger participation of the A rotamers in compounds IV than in sulphoxides is in agreement with these facts.

In relation to the rotamer populations, around the C-S bond, Fig. 4 suggests that the electrostatic stabilization of A(1) rotamer ought to be greater than that of A(2) and A(3), because in the first the negative end of the C-F dipole is further from the negative end of the $-SO_2-$ dipole. Nevertheless, as the oxygen

size is smaller than that of the methyl group[20,25], the A(1) rotamer, with $(Y/Me)_{1,3-p}$ interaction, is sterically less favoured than A(2) and A(3), which exhibit the $(Y/O)_{1,3-p}$ interaction. In addition on steric grounds the A(1) rotamer will be less favoured in the erythro series than in the threo compounds, due to the relative orientation of the R group at C-2 with respect to the sulphur substituents.

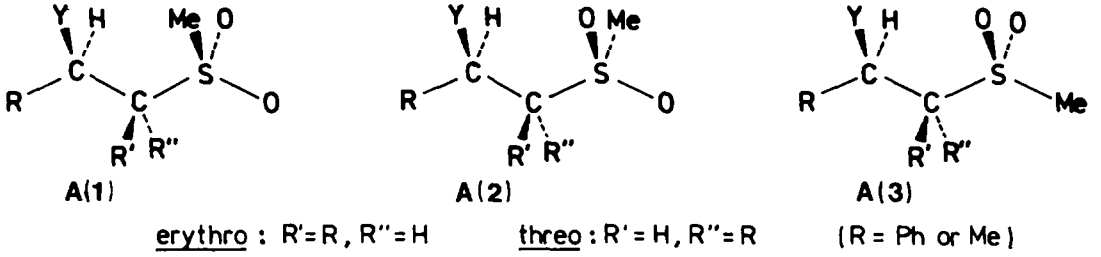


Fig. 4. The A rotamers around the C-S bond in sulphones.

In fluoro and methoxysulphones of erythro configuration there is a long-range coupling constant between H(2) and the methyl protons of the methylsulphonyl group. The $^4J_{2,Me}$ value ranges from 0.5 to 0.8 Hz and is slightly greater in the butane derivatives than in the 1,2-diphenylethane compounds.

In all cases the $^4J_{2,Me}$ value decreases in DMSO-d_6, becoming negligible in the series of 1,2-diphenylethane. Bearing in mind that a W planar arrangement between protons[26] involved is necessary and that this is only possible in $^eA(1)$, the $^4J_{2,Me}$ value could be used to evaluate its contribution to the equilibrium. Eliel[24] has indicated the value of 0.4 Hz as the result of equal rotamer contribution around the C-S bond. Therefore from the values observed in our sulphones the major contribution of rotamer $^eA(1)$ in the equilibrium $^eA(1) \rightleftharpoons {}^eA(2) \rightleftharpoons {}^eA(3)$ can be deduced. This result and the decreasing of the conformational preference with the solvent polarity can be rationalized by considering that the electrostatic interactions are more important than the steric ones. In the cases of threo-sulphones the longe-range coupling constant is not observed. This fact indicates that the contribution of $^tA(2)$ (the only rotamer of the threo series which can adopt the required W coplanar arrangement) ought to be scarce or nonexistent.

The fact that A(1) is the favoured rotamer can also be deduced from the longe-range coupling constant between the fluorine atom and methyl group ($^5J_{F,H}$), in the fluoroderivatives. In acyclic systems the values of 0.97 and 0.16 Hz have been observed when the nuclei involved in the coupling are in gauche and anti relationship, respectively[27]. The difference between these values was attributed to an important contribution of a direct interaction through the space between involved groups, which is only possible in the gauche arrangement. Assuming this fact, in our sulphones, the value of $^5J_{F,H}$ could indicate the major contribution of A(1), where the F and Me groups are near enought to give a sizeable interaction. In steroids[28] a longe-range coupling constant has been observed between F and Me groups where they are in a 1,3-syndiaxial arrangement ($^5J_{F,H}$ 2-4 Hz). This coupling constant decreases as the groups involved move away. In the threo-sulphones $^tIV_F^{Me}$ and $^tIV_F^{Ph}$, $^5J_{F,H} > 2$ Hz, whereas in the analogous erythro, $^5J_{F,H} < 1$ Hz. These findings suggest that the contribution of A(1) in the threo-sulphones is larger than in the erythro-sulphones, where this rotamer was still the predominant one, in accordance with the value of $^4J_{Me,2}$. Although there is no clear evidence, the conformational behaviour of methoxysulphones must be similar to that of fluoro-sulphones and therefore electrostatic interactions ought to be more significant than steric factors.

In the hydroxysulphones there is an additional factor that contribute to the

conformational equilibria shift. The intramolecular hydrogen bonding O-H...O-S stabilizes A(2) and A(3) with respect to A(1) (see Fig. 4), B and C (see Fig. 1). Hence, in the erythro series $^{4}J_{2,Me}$ does not appear in $CDCl_3$, whereas in DMSO-d_6, where the formation of intramolecular hydrogen bonds is prevented, $^{e}IV_{OH}$ shows $^{4}J_{2,Me} \sim 0.5$ Hz. On the one hand, the $J_{1,2}$ values increase in the erythro series on changing the solvent (from $CDCl_3$ to DMSO-d_6) and on the other, they decrease in the threo series (see Table 5). All these facts reflect the diminution of A rotamer population when the intramolecular associations are hindered. In $^{t}IV_{OH}$, it has been possible to observed the values of $^{3}J_{1,OH}$ in $CDCl_3$ and DMSO-d_6 (see Table 5), which reflect the existence of intramolecular hydrogen bondings in $CDCl_3$, which disappear in DMSO-d_6 (see above).

Finally, it is worth noting that the butane derivatives seem to show a certain trend for having both protons in gauche relationship, like the other groups (X, Y and R). This trend, contrary to steric predictions, is responsible for the decrease in the ^{e}B rotamer population in the erythro series and of ^{t}A in the threo one. Its repercussion on $^{3}J_{1,2}$ values is more important in the threo-series, since the most favoured conformations by the above mentioned interactions are the most affected, particulary in the case of sulphoxides, sulphones and sulphonium salts. The factor responsible for this behaviour is not evident.On the one hand, it could be attributed to the fact that the $(Y/Me)_{1,2\text{-}g}$ interaction were stabilizing, such as was proposed for the series of 1-fluoropropane[29] and 1-propanol[30]. Another contribution could be due to the bond angle distorsions that minimize the interactions present in ^{t}B and ^{t}C rotamers, such as had been proposed to explain the predominance of those rotamers which show the two methynic hydrogens in a gauche relationship in the 2,3-dimethyl butane[31]. The abnormally low values of $J_{1,2}$ in the threo derivatives, the large populations of ^{t}C in sulphoxides III and sulphonium salts, and its anomalous behaviour with the change of the solvent ($J_{1,2}$ increases instead of decreasing) may be the result of this trend.

The main new conclusions deduced from this paper could be summarized in the following points: a) The interaction between the Ph and SMe groups, when they are in a gauche relationship, is more destabilizing than could be expected from the steric view point. The electrostatic repulsion between the π electrons of the aromatic ring and the n ones of sulphur, or even the interaction between the mentioned orbitals, giving rise to and appearance of a repulsive gauche effect, could be the reason of the additional destabilization. b) The phenyl group can give a donor-acceptor stabilizing interaction with the d orbitals of sulphinylic sulphur, suitably orientated. c) The conformational equilibria around the C-SO_2Me bond in β-oxygenated and β-fluorinated sulphones is mainly controlled by electrostatic interactions. This, in turn, is adjusted by steric factors and, in the case of hydroxysulphones, by intramolecular hydrogen bonding. d) The electrostatic interactions due to OMe and F groups are very similar and they show analogous conformational behaviour. e) The 2-thioderivatives of 3-heterosubstituted butanes show a certain tendency to present that conformation with the four substituents of the CH-CH- system in gauche relationship.

EXPERIMENTAL

General: Silica gel used in column chromatography was Merck K-60 (70-230 mesh). Melting points were determined on a Buchi 594392 tipe S apparatus in open capillary tubes and are uncorrected. Distillation of liquid crude products was carried out in a Buchi GKR-50 ball oven and boiling temperatures (b.t.) refer to the apparatus temperature. Elemental analyses were performed by the "Instituto de Química Orgánica (CSIC)" in Madrid. Mass spectra (M.S.) were recorded in a HP-5985 spectrometer in the electron impact (EI) at 70 eV or chemical ionization (CI) (methane as reagent gas) ionization modes. Mass data are reported in mass unit (m/e) and the values in bracket regard the relative intensity from the base peak (as 100%). IR spectra were obtained on a Pye-Unicam SP-1100 spectrometer. ^{1}H-NMR spectra were

recorded on a Bruker WM-200-SY or a Varian XL-100-15 spectrometer in the FT mode on $CDCl_3$ solutions unless otherwise specified. Chemical shifts are in parts per million downfield from internal Me_4Si. The syntheses of all the sulphides studied in this paper[7], the sulphoxides ${}^{e}II^{Ph}_{OH}$, ${}^{t}II^{Ph}_{OH}$, ${}^{e}II^{Ph}_{OMe}$, ${}^{t}II^{Ph}_{OMe}$, ${}^{e}III^{Ph}_{OH}$, ${}^{t}III^{Ph}_{OH}$, ${}^{e}III^{Ph}_{OMe}$ and ${}^{t}III^{Ph}_{OMe}$[2], the sulphones ${}^{e}IV^{Ph}_{OH}$ and ${}^{t}IV^{Ph}_{OH}$[3,6] and the sulphonium salts ${}^{e}V^{Ph}_{OH}$ and ${}^{t}V^{Ph}_{OH}$[3,6] have been previously reported.

Sulphoxides. Hydroxy and fluorosulphoxides were obtained from the corresponding hydroxy and fluorosulphoxides by oxidation with sodium metaperiodate or m-chloroperbenzoic acid following general methods outlined in the literature[34]. Methoxysulphoxides were prepared by metylation of hydroxysulphoxides using the phase-transfer system Me_2SO_4/NaOH/TBAI reported by Herz[35].

erythro-2-Hydroxy-1-methyl sulphoxides ${}^{e}II^{Me}_{OH}$ and ${}^{e}III^{Me}_{OH}$. They were obtained by oxidation of erythro-3-methylsulphenyl-2-butanol (${}^{e}I^{Me}_{OH}$)[7] with sodium metaperiodate, as a hygroscopic syrup. Yield 94%, b.t. 90-95°/0.8 mm Hg. Found: C: 41.24; H:9.31; S: 21.89. $C_5H_{12}O_2S.0.5\ H_2O$ requires C: 41.35; H: 9.02; S: 22.08. Separation of the diastereomers was acomphished by column chromatography using chloroform-methanol-acetic acid (60:5:1) as eluent.

α-diastereoisomer (${}^{e}II^{Me}_{OH}$). It was crystallized from benzene-diethyl ether at -15°, m.p. 58-59°. IR (paraffinol) ν_{max}: 3400, 1155, 1030, 955 and 915 cm^{-1}. MS (EI) 136 (M^+ 3.2), 75 (19.4), 73(60.2), 64 (11.8) and 55 (100). ^{1}H-NMR δ : 1.24 (d, J=7.0 Hz, 3H, CH_3CS), 1.32 (d, J=6.5 Hz, 3H, CH_3CO), 2.62 (m, 1H, CHS), 2.64 (s, 3H, CH_3S), 3.9 (s, 1H, OH) and 4.5 (dq, J=2.0 and 6.5 Hz, 1H, CHO).

β-diastereoisomer (${}^{e}III^{Me}_{OH}$). It was obtained as a syrup after chromatography, b.t. 95-100°/1 mmHg. IR (film) ν_{max}: 3400, 1455, 1425, 1145, 1080, 940 and 905 cm^{-1}. MS (EI) m/e: 136(M^+ 7.7), 118 (3.3), 73 (44.5), 64 (18.7) and 55 (100). ^{1}H-NMR δ: 1.31 (d, J=6.4 Hz, 3H, CH_3CO), 1.32 (d, J=7.1 Hz, 3H, CH_3CS), 2.55 (m, 1H, CHS), 2.57 (s, 3H, CH_3S), 3.40(s,1H,OH) and 4.40 (dq, J=2.9 and 6.5 Hz, 1H, CHO).

threo-2-Hydroxy-1-methylpropyl methyl sulphoxides (${}^{t}II^{Me}_{OH}$ and ${}^{t}III^{Me}_{OH}$). They were prepared by the method described above for ${}^{e}II^{Me}_{OH}$ and ${}^{e}III^{Me}_{OH}$. Yield 96%, b.t. 140-150°/0.4 mmHg. Found:C:40.43; H: 9.28; S: 22.24. $C_5H_{12}O_2S.0.6\ H_2O$ requires C:40.84; H: 9.05; S: 21.81. Isolation of the diastereoisomers were carried out by column chromatography using chloroform-methanol-formic acid (90:8:1) as eluet.

α-diastereoisomer (${}^{t}II^{Me}_{OH}$). IR (film) ν_{max}: 3400, 1130, 1050, 1025 and 955 cm^{-1}. MS (EI) m/e: 136 (M^+ 15.2), 118 (4.3), 85 (13), 73(100), 65 (11.0) and 55 (76.1). ^{1}H-NMR δ: 1.20 (d, J=7.0 Hz, 3H, CH_3CS), 1.31 (d, J=6.3 Hz, 3H, CH_3CO), 2.59 (s,3H, CH_3S), 2.66 (dq, J=7.0 and 8.3 Hz, CHS), 3.90 (s, 1H, OH) and 4.10 (dq, J=6.3 and 8.3 Hz, 1H, CHO).

β-diastereoisomer (${}^{t}III^{Me}_{OH}$). IR (film) ν_{max}: 3380, 1115, 1030, 950 and 920 cm^{-1}. MS (EI) m/e: 136 (M^+ 11.7), 121 (5.0), 92 (6.7), 73 (100), 64 (13.3) and 55 (99.2). ^{1}H-NMR δ: 1.11 (d, J=7.0 Hz, 3H, CH_3CS), 1.30 (d, J=6.3 Hz, 3H, CH_3CO), 2.66 (s, 3H, CH_3S), 2.81 (dq, J=7.0 and 8.1 Hz, 1H, CHS), 4.18 (dq, J=6.3 and 8.1 Hz, 1H, CHO) and 4.40 (s, 1H, OH).

erythro- and threo-2-Methoxy-1-methylpropyl methyl sulphoxides (${}^{e}II^{Me}_{OMe}$, ${}^{e}III^{Me}_{OMe}$, ${}^{t}II^{Me}_{OMe}$ and ${}^{t}III^{Me}_{OMe}$. Their synthesis has been accomplished by independent methylation of the corresponding diastereomerically pure hydroxysulphoxides ${}^{e}II^{Me}_{OH}$, ${}^{e}III^{Me}_{OH}$, ${}^{t}II^{Me}_{OH}$ and ${}^{t}III^{Me}_{OH}$.

erythro-α-diastereoisomer (${}^{e}II^{Me}_{OMe}$). Yield 64%, b.t. 65-70°/0.25 mmHg. IR(film) ν_{max}: 2850, 1460 and 1055 cm^{-1}. MS (EI) m/e: 150 (M^+ 1.5), 87 (64.1), 86 (23.1), 71 (10.3), 59 (15.9) and 55 (100). ^{1}H-NMR δ: 1.15 (d, J=7.0 Hz, 3H, CH_3CS), 1.24 (d, J=6.4 Hz, 3H, CH_3CO), 2.56 (s, 3H, CH_3S), 2.64 (dq, J=2.3 and 7.0 Hz, 1H, CHS), 3.37 (s, 3H, CH_3O) and 4.03 (dq, J=2.3 and 6.4 Hz, 1H, CHO).

erythro-β-diastereoisomer (${}^{e}III^{Me}_{OMe}$). Yield 70%, b.t. 65-75°/0.25 mmHg. IR(film) ν_{max}: 2850, 1465, 1160, 1095 and 1045 cm^{-1}. MS (EI) m/e: 150 (M^+ 2.4), 87 (44.6), 86 (12.0), 59 (16.9) and 55 (100), ^{1}H-NMR δ: 1.29 (d, J=6.4 Hz, 3H, CH_3CO), 1.30 (d, J=7.2 Hz, 3H, CH_3CS), 2.56 (s, 3H, CH_3S), 2.70 (dq, J=4.0 and 7.2 Hz, 1H, CHS), 3.35 (s, 3H, CH_3O) and 3.73 (dq, J=4.0 and 6.4 Hz, 1H, CHO).

threo-α-diastereoisomer (${}^{t}II^{Me}_{OMe}$). Yield 58%, b.t. 70-75°/0.25 mmHg. IR (film) ν_{max}: 2850, 1470, 1160, 1130, 1100, 1045, 950 and 880 cm^{-1}. MS (EI) m/e: 150 (M^+ 1.7), 87 (52.4), 86 (28.2), 59 (18.7) and 55 (100). ^{1}H-NMR δ:1.24 (d, J=6.0 Hz, 3H, CH_3CO), 1.25 (d, J=7.2 Hz, 3H, CH_3CS), 2.54 (m, 1H, CHS), 2.57 (s, 3H, CH_3S), 3.37 (s. 3H, CH_3O) and 3.49 (dq, J=6.0 and 8.8 Hz, 1H, CHO).

threo-β-diastereoisomer ($^{t}III_{OMe}^{Me}$). Yield 65%, b.t. 65-70°/0.25 mmHg. IR (film) ν_{max}: 2840, 1460, 1100 and 1050 cm^{-1}. MS (EI) m/e: 150 (M^+ 0.4), 133 (19.4), 87 (40.0), 59 (28.2) and 55 (100). ^{1}H-NMR δ: 1.18 (d, J=7.2 Hz, 3H, CH_3CS), 1.28 (d, J=6.2 Hz, 3H, CH_3CO),2.53 (s, 3H, CH_3S), 3.03 (dq, J=5.5 and 7.2 Hz, 1H, CHS), 3.33 (s, 3H, CH_3O) and 3.69 (dq, J=5.5 and 6.2 Hz, 1H, CHO).

erythro- and threo-2-Fluor-1-methylpropyl methyl sulphoxides ($^{e}II_{F}^{Me}$, $^{e}III_{F}^{Me}$, $^{t}II_{F}^{Me}$ and $^{t}III_{F}^{Me}$). They were prepared by oxidation of erythro- and threo-2-fluor-1-methylpropyl methyl sulphides ($^{e}I_{F}^{Me}$ and $^{t}I_{F}^{Me}$) respectively with m-chloroperbenzoic acid. Separation of the diastereoisomers (α + β) in each reaction mixtures was not yet possible using chromatographyc and crystallization methods. The following data are refered to the diastereoisomers mixture.

erythro-α and β-diastereoisomers ($^{e}II_{F}^{Me}$ and $^{e}III_{F}^{Me}$). Yield 93%, b.t. 65-70°/0.25 mmHg. Found: C: 43.80; H: 8.30; S: 22.90. $C_{11}H_{11}FOS$ requires C: 43.45; H: 8.02; S: 23.20. IR (film) ν_{max}: 1390, 1150, 1080, 1040, 1000, 950 and 895 cm^{-1}. MS (EI) m/e: 138 (M^+ 14.7), 75 (18.7), 64 (31), 59 (10.4), 55 (58.2) and 47 (100). ^{1}H-NMR α-diastereoisomer ($^{e}II_{F}^{Me}$)δ: 1.25 (d, H=7.0 Hz, 3H, CH_3CS), 1.45 (dd, J=6.5 and 24.0 Hz, 3H, CH_3CF), 2.57 (d, J=0.7 Hz, 3H, CH_3S), 2.75 (ddq, J=1.8, 7.0 and 30.2 Hz, 1H, CHS) and 5.27 (ddq, J=1.8, 6.5 and 48.2 Hz, 1H, CHF). β-diastereoisomer ($^{e}III_{F}^{Me}$)δ : 1.31 (d, J=7.0 Hz, 3H, CH_3CS), 1.49 (dd, J=6.5 and 24.0 Hz, 3H, CH_3CF), 2.56 (d,J=1.5 Hz, 3H, CH_3S), 2.80 (ddq, J=3.5, 7.0 and 21.6 Hz, 1H, CHS) and 5.19 (ddq, J=3.5, 6.5 and 47.7 Hz, 1H, CHF).

threo-α and β-diastereoisomers ($^{t}II_{F}^{Me}$ and $^{t}III_{F}^{Me}$). Yield 96%, b.t. 75-80°/0.20 mmHg. Found: C: 43.53; H: 7.87; S: 23.45. $C_6H_{11}FOS$ requires C: 43.45; H: 8.02; S: 23.20.IR (film) ν_{max}: 1300. 1090, 1040, 940 and 895 cm^{-1}. MS (EI) m/e: 138 (M^+ 15.3), 75 (15.6), 64 (31.9), 55 (59.1) and 47 (100). ^{1}H-NMR α-isomer ($^{t}II_{F}^{Me}$) δ: 1.28 (d, J=7.2 Hz, 3H, CH_3CS), 1.49 (dd, J=6.5 and 24.5 Hz, 3H, CH_3CF), 2.60 (d, J=0.7 Hz, 3H,CH_3S), 2.73 (ddq, J=7.2, 8.6 and 10.2 Hz, 1H, CHS) and 4.83 (ddq, J=6.5, 8.6 and 47.6 Hz, 1H, CHF). β-isomer ($^{t}III_{F}^{Me}$ δ:1.28 (d, J=7.2 Hz, 3H, CH_3CS), 1.47 (dd, J=6.5 and 24.7 Hz, 3H, CH_3CF), 2.59 (d, J=1.5 Hz, 3H, CH_3S), 3.06 (ddq, J=6.0, 7.2 and 14.5 Hz, 1H, CHS) and 5.01 (ddq, J=6,0, 6.5 and 47.1 Hz, 1H, CHF).

erythro- and threo-2-Fluor-1,2-diphenylethyl methyl sulphoxides ($^{e}II_{F}^{Ph}$, $^{e}III_{F}^{Ph}$, $^{t}II_{F}^{Ph}$ and $^{t}III_{F}^{Ph}$). They were obtained by oxidation of erythro- and threo-2-fluor-1,2-diphenylethyl methyl sulphides[7] ($^{e}I_{F}^{Ph}$ and $^{t}I_{F}^{Ph}$) respectively with m-chloroperbenzoic acid. A mixture of the two possible diastereoisomers (α + β) was formed in each case.

erythro-α and β-diastereoisomers ($^{e}II_{F}^{Ph}$ and $^{e}III_{F}^{Ph}$). Yield 96%. The mixture α:68%, β:32% crystallizes from cyclohexane, m.p. 96-99°. Found: C:68.54; H:5.79; S:12.40. $C_{15}H_{15}FOS$ requires C: 68.68; H: 5.76; S: 12.22. IR(KBr) ν_{max}: 3040, 2920, 1600, 1495, 1450, 1060, 1045, 900, 755 and 705 cm^{-1}. MS (CI) m/e: 263 (M^+ +1, 30.6), 227 (5.9), 199 (100) and 180 (36.8). ^{1}H-NMR β isomer δ: 2.17 (d, J=1.4 Hz, 3H, CH_3S), 3.81 (dd, J=8.1 and 16.5 Hz, 1H, CHS), 6.20 (dd, J=8.1 and 46.5 Hz, 1H, CHF) and 7.25 (m, 10H, C_6H_5).

Pure erythro-α-diastereoisomer ($^{e}II_{F}^{Ph}$) could be isolated by crystallization of the reaction mixture using cyclohexane as solvent, m.p. 106-108°. Found: C: 68.74; H: 6.11; S: 12.43. $C_{15}H_{15}FOS$ requires C: 68.68; H: 5.76; S: 12.22. IR (KBr) ν_{max}: 3060, 1490, 1450, 1060, 1035, 950 and 700 cm^{-1}. MS (CI) m/e: 263 (M^+ +1, 22.8), 227 (6.0), 199 (100) and 180 (34.5). ^{1}H-NMR δ: 2.35 (s, 3H, CH_3S), 3.75 (dd, J=2.0 and 34.6 Hz, 1H, CHS), 6.44 (dd, J=2.0 and 46.1 Hz, 1H, CHF) and 7.3 (m, 10H, C_6H_5).

threo-α and β-diastereoisomers ($^{t}II_{F}^{Ph}$ and $^{t}III_{F}^{Ph}$). Yield 94%. The reaction mixture was purified by column chromatography using chloroform-methanol (30:1) as eluent yielding the sulphoxides as a syrup. IR (film) ν_{max}: 3100, 3060, 1510, 1465, 1320, 1150, 1065, 765 and 705 cm^{-1}. MS (CI) m/e: 263(M^+ +1, 0.6), 227 (5.5), 199 (100) and 180 (19.8). ^{1}H-NMR α-isomer ($^{t}II_{F}^{Ph}$) δ: 2.24 (s, 3H, CH_3S), 3.89 (dd, J=8.2 and 10.4 Hz, 1H, CHS), 6.13 (dd, J=10.4 and 46.0 Hz, 1H, CHF) and 7.25 (m, 10H, C_6H_5). β-isomer ($^{t}III_{F}^{Ph}$) δ: 2.51 (d, J=1.2 Hz, 3H, CH_3S), 4.43 (dd, J=6.2 and 14.9 Hz, 1H, CHS), 6.31(dd, J=6.2 and 45.3 Hz, 1H, CHF) and 7.25 (m, 10H, C_6H_5).

Sulphones. Sulphones with butane or 1,2-diphenylethane skeleton were prepared from the suitable sulphides by oxidation with an excess of sodium metaperiodate or m-chloroperbenzoic acid, following the generally methods outlined in the literature[34].

erithro-2-Hydroxy-1-methylpropyl methyl sulphone ($^{e}IV_{OH}^{Me}$). Obtained from $^{e}I_{OH}^{Me}$ using $NaIO_4$ as oxidant. Cuantitative yield. Crystallized from benzene-diethyl ether at -15°, m.p. 53-54°. Found: C: 39.16; H: 8.32; S: 21.17. $C_5H_{12}O_3S$ requires C: 39.46; H: 7.95; S: 21.06. IR(paraffinol) ν_{max}: 3520, 1300, 1130, 975, 920, 820 and 790 cm^{-1}. MS(CI) m/e: 153 (M^+ +1, 69.7), 135 (69.7) and 81 (47.8). ^{1}H-NMR δ : 1.30 (d, J=6.5 Hz, 3H, CH_3CO), 1.45 (d, J=7.4 Hz, 3H, CH_3CS), 2.61 (s, 1H, OH), 2.87 (m,

1H, CHS), 2.94 (s, 3H, CH_3S) and 4.61 (dq, J=1.5 and 6.5 Hz, CHO).

threo-2-Hydroxy-1-methylpropyl methyl sulphone ($^{t}IV^{Me}_{OH}$). Obtained from $^{t}I^{Me}_{OH}$ using $NaIO_4$ as oxidant. Yield 96%, b.t. 150-160°/0.3 mmHg. Found: C: 39.55; H: 8.23; S: 20.75. $C_5H_{12}O_3S$ requires C: 39.46; H: 7.97; S: 21.06. IR (film) ν_{max}: 3520, 1295, 1140, 1120, 965 and 765 cm^{-1}. MS (CI) m/e: 153 (M^+ +1, 100), 135 (77,3) and 81 (40.3). ^{1}H-NMR δ: 1.33 (d, J=6.4 Hz, 3H, CH_3CO), 1.36 (d, J=7.2 Hz, 3H, CH_3CS), 2.93 (m, 1H, CHS), 3.00 (s, 3H, CH_3S), 3.09 (s, 1H, OH) and 4.19 (dq, J=6.4 and 8.4 Hz, 1H, CHO).

erythro-2-Methoxy-1-methylpropyl methyl sulphone ($^{e}IV^{Me}_{OMe}$).Obtained from $^{e}I^{Me}_{OMe}$ using $NaIO_4$ as oxidant. Cuantitative yield, b.t. 95-100°/1.5 mmHg. Found: C: 43.05 H: 8.56; S: 19.68. $C_6H_{14}O_3S$ requires C: 43.35; H: 8.44; S: 19.28. IR (film) ν_{max}: 2840, 1295, 1130, 1115 and 1090 cm^{-1}. MS(CI) m/e: 167 (M^+ +1, 100) and 81 (14.6). ^{1}H-NMR δ : 1.23 (d, J=6.5 Hz, 3H, CH_3CO), 1.44 (d, J=7.4 Hz, 3H, CH_3CS), 2.86 (s, 3H, CH_3S), 3.30 (m, 1H, CHS), 3.36 (s, 3H, CH_3O) and 4.12 (dq, J=2.0 and 6.5 Hz, 1H, CHO).

threo-2-Methoxy-1-methylpropyl methyl sulphone ($^{t}IV^{Me}_{OMe}$). Obtained from $^{t}I^{Me}_{OMe}$ with $NaIO_4$ as oxidant. Cuantitative yield, b.t. 95-100°/2 mmHg. Found: C: 43.00; H: 8.62; S: 18.87. $C_6H_{14}O_3S$ requires C: 43.35; H: 8.49; S: 19.28. IR (film) ν_{max}: 2850, 1305, 1145, 1110, 965 and 765 cm^{-1}. MS(CI) m/e: 167 (M^+ +1, 100), 135 (53.2), 87 (12.4) and 81 (30.5). ^{1}H-NMR δ: 1.26 (d, J=6.3 Hz, 3H, CH_3CO), 1.34 (d, J=7.3 Hz, 3H, CH_3CS), 3.00 (s, 3H, CH_3S), 3.04 (m, 1H, CHS), 3.37 (s, 3H, CH_3O) and 3.70 (dq, J=6.3 and 7.8 Hz, 1H, CHO).

erythro-2-Methoxy-1,2-diphenylethyl methyl sulphone ($^{e}IV^{Ph}_{OMe}$). Obtained from $^{e}I^{Ph}_{OMe}$ using m-chloroperbenzoic acid as oxidant. Yield 95%. Crystallized from cyclohexane, m.p. 83-84°. Found: C: 65.92: H: 6.46; S: 11.33. $C_{16}H_{18}O_3S$ requires C: 66.18; H: 6.25; S: 11.04. IR (KBr) ν_{max}: 3090, 3050, 2960, 1610, 1500, 1460, 1380, 1310, 1230, 1130, 1110, 950, 765, 720 and 700 cm^{-1}. MS (CI) m/e: 291 (M^+ +1, 3.1), 259 (100), 211 (68.1), 195 (20.0) and 180 (42.0). ^{1}H-NMR δ:2.8 (d, J=0.5 Hz, 3H, CH_3S), 3.4 (s, 3H, CH_3O), 4.1 (d, J=3.5 Hz, 1H, CHS), 5.4 (d, J=3.5 Hz, 1H, CHO) and 7.3 (m, 10H, C_6H_5).

threo-2-Methoxy-1,2-diphenylethyl methyl sulphone ($^{t}IV^{Ph}_{OMe}$). Obtained from $^{t}I^{Ph}_{OMe}$ using m-chloroperbenzoic acid as oxidant. Cuantitative yield. Crystallized from cyclohexane, m.p. 148-149°. Found: C:65.80; H: 6.45; S: 11.28. $C_{16}H_{18}O_3S$ requires C: 66.18; H: 6.25; S: 11.04. IR (KBr) ν_{max}: 3060, 2960, 1500, 1460, 1300, 1140, 1100, 965, 750 and 700 cm^{-1}. MS(CI) m/e: 291 (M^+ +1, 5.5), 259 (100), 211 (65.7) and 180 (41.9). ^{1}H-NMR δ:3.17 (s, 3H, CH_3S), 3.30 (s, 3H, CH_3O), 4.37 (d, J=10.1 Hz, 1H, CHS), 4.96 (d, J=10.1 Hz, 1H, CHO) and 7.15 (m, 10H, C_6H_5).

erythro-2-Fluor-1-methylpropyl methyl sulphone ($^{e}IV^{Me}_{F}$). Prepared from $^{e}I^{Me}_{F}$ using m-chloroperbenzoic acid as oxidant. Yield 94%, crystallized from benzene-diethyl ether, m.p. 56-58°. Found: C: 39.12; H: 7.33; S: 20.56. $C_5H_{11}FO_2S$ requires C: 38.95; H: 7.19; S: 20.79. IR (paraffinol) ν_{max}: 1310, 1130, 1000, 965, 900, 820, and 780 cm^{-1}. MS (CI) m/e : 155 (M^+ +1, 100), 135 (24.9) and 81 (28.5). ^{1}H-NMR δ: 1.45 (dd, J=6.5 and 24.0 Hz, 3H, CH_3CF), 1.51 (d, J=7.3 Hz, 3H, CH_3CS), 2.85 (dd, J=0.8 and 1.3 Hz, 3H, CH_3S), 2.90 (m. 1H, CHS) and 5.44 (ddq, J=1.6, 6.5 and 53.3 Hz, 1H, CHF).

threo-2-Fluor-1-methylpropyl methyl sulphone ($^{t}IV^{Me}_{F}$).Prepared from $^{t}I^{Me}_{F}$ with m-chloroperbenzoic acid as oxidant. Yield 98%, b.t. 90-95°/0.20 mmHg. IR (film) ν_{max}: 1295, 1140, 1105, 1070, 1030, 970, 905, 845 and 765 cm^{-1}. MS (CI) m/e: 155 (M^++1, 92.9) and 135 (100). ^{1}H-NMR δ: 1.36 (d, J=7.3 Hz, 3H, CH_3CS), 1.49 (dd, J=6.4 and 25.1 Hz, 3H, CH_3CF), 3.00 (d, J=2,3 Hz, 3H, CH_3S), 3.19 (ddq, J=7.3, 8.2 and 10.5 Hz, 1H, CHS) and 5.01 (ddq, J=6.4, 8.2 and 47.3 Hz, 1H, CHF).

erythro-2-Fluor-1,2-diphenylethyl methyl sulphone ($^{e}IV^{Ph}_{F}$). Obtained from $^{e}I^{Ph}_{F}$ using m-chloroperbenzoic acid as oxidant. Cuantitative yield. Crystallized from cyclohexane-carbon tetrachloride (1:1), m.p. 115-116°. Found: C: 64.62; H: 5.29; S: 11.47. $C_{15}H_{15}FO_2S$ requires C: 64.73; H: 5.43; S: 11.52. IR(KBr) ν_{max}: 3000, 2950, 1505, 1460, 1310, 1135, 1060, 960, 820, 720 and 705 cm^{-1}. MS (EI) m/e: 278 (M^+ 0.3), 190 (100), 180(10.5), 179 (59.9), 178 (54.5) and 109 (25.4). ^{1}H-NMR δ:2.77 (s, 3H, CH_3S), 4.23 (dd, J=2.6 and 30.9 Hz, 1H, CHS), 6.60 (dd, J=2.6 and 46.5 Hz, 1H, CHF) and 7.3 (m, 10H, C_6H_5).

threo-2-Fluor-1,2-diphenylethyl methyl sulphone ($^{t}IV^{Ph}_{F}$). Prepared from $^{t}I^{Ph}_{F}$ with m-chloroperbenzoic acid as oxidant. Cuantitative yield. Crystallized from cyclohexane-carbon tetrachloride (1:1), m.p. 116-117°. Found: C: 64.79; H: 5.63; S: 11.27. $C_{15}H_{15}FO_2S$ requires C: 64.73; H: 5.43; S: 11.52. MS (CI) m/e: 279 (M^+ +1, 0.3), 259 (80.3), 199 (100), 181 (60.6) and 180 (55.3). ^{1}H-NMR δ: 3.09 (d, J=1.9 Hz, 3H, CH_3S), 4.54 (dd, J=8.8 and 9.8 Hz, 1H, CHS), 6.21 (dd, J=9.8 and 46.1 Hz, 1H, CHF) and 7.2 (m, 10H, C_6H_5).

Sulphonium salts. Sulphonium p-toluenesulphonates and sulphonium tetrafluorborates were obtained by methylation of the corresponding sulphides with an excess of methyl p-toluensulphonate and methyl iodide/silver tetrafluorborate respectively. Purification of resulting compounds (except $^{e}V^{Me}_{OH}$ and $^{t}V^{Me}_{OH}$) was not possible owing to their hygroscopic character. However, in all cases, the spectroscopic data and the synthetic procedure were in accordance with the structures.

erythro-2-Hydroxy-1-methylpropyl dimethyl sulphonium p-toluenesulphonate ($^{e}V^{Me}_{OH}$). Yield 93%, m.p. 68-85°. Found C: 50.65; H: 7.32: S: 20.87. $C_{13}H_{22}S_2O_4$ requires C: 50.95; H: 7.24; S: 20.92. IR (paraffinol) ν_{max}: 3300, 1215, 1185, 1125, 1035, 1010 and 815 cm^{-1}. ^{1}H-NMR δ: 1.19 (d, J=6.3 Hz, 3H, CH_3CO), 1.34 (d, J=6.8 Hz, 3H, CH_3CS), 2.33 (s, 3H, CH_3-C_6H_4), 2.92 (s, 3H, CH_3S), 3.13 (s, 3H, CH_3S), 3.92 (dq, J=2.5 and 6.8 Hz, 1H, CHS), 4.2 (s, 1H, OH), 4.41 (dq, J=2.5 and 6.3 Hz, 1H, CHO) and 7.16-7.80 (m, 4H, AA'BB' system, C_6H_4).

threo-2-Hydroxy-1-methylpropyl dimethyl sulphonium p-toluenesulphonate ($^{t}V^{Me}_{OH}$). Yield 95%, m.p. 60-95°. Found: C: 50.87; H: 6.87; S: 20.68. $C_{13}H_{22}S_2O_4$ requires C: 50.95; H: 7.24; S: 20.92. IR (paraffinol) ν_{max}: 3400, 1225, 1195, 1130, 1040, 1015, 820 and 685 cm^{-1}. ^{1}H-NMR δ: 1.28 (d, J=6.5 Hz, 6H, CH_3CS and CH_3CO), 2.33 (s, 3H, CH_3-C_6H_4), 2.81 (s, 1H, OH), 2.82 (s, 3H, CH_3S), 2.95 (s, 3H, CH_3S), 3.74 (m, 1H, CHS), 3.80 (m, 1H, CHO) and 7.16-7.80 (m, 4H, AA'BB' system, C_6H_4).

erythro-2-Methoxy-1-methylpropyl dimethyl sulphonium p-toluenesulphonate ($^{e}V^{Me}_{OMe}$). Cuantitative yield. IR (film) ν_{max}: 1220, 1200, 1130, 1040, 1020, 820 and 685 cm^{-1}. ^{1}H-NMR δ: 1.17 (d, J=6.3 Hz, 3H, CH_3CO), 1.36 (d, J=7.0 Hz, 3H, CH_3CS), 2.33 (s, 3H, CH_3-C_6H_4), 2.96 (s, 3H, CH_3S), 3.12 (s, 3H, CH_3S), 3.28 (s,3H, CH_3O), 3.91 (dq, J=2.9 Hz and 6.3 Hz, 1H, CHO), 4.18 (dq, J=2.9 and 7.0 Hz, 1H, CHS) and 7.16-7.80 (m, 4H, AA'BB' system, C_6H_4).

threo-2-Methoxy-1-methylpropyl dimethyl sulphonium p-toluenesulphonate ($^{t}V^{Me}_{OMe}$). Yield 95%. IR (film) ν_{max}: 1230, 1200, 1130, 1040, 1020, 820, 755 and 685 cm^{-1}. ^{1}H-NMR δ: 1.29 (d, J=6.3 Hz, 3H, CH_3CO), 1.46 (d, J=6.7 Hz, 3H, CH_3CS), 2.33 (s, 3H, CH_3-C_6H_4), 2.92 (s, 3H, CH_3S), 3.13 (s, 3H, CH_3S), 3.31 (s, 3H, CH_3O), 3.49 (m, 1H, CHO), 3.87 (m, 1H, CHS) and 7.16-7.80 (m, 4H, AA'BB' system, C_6H_4).

erythro-2-Methoxy- 1,2-diphenylethyl dimethyl sulphonium tetrafluorborate ($^{e}V^{Ph}_{OMe}$). Yield 91%. IR(KBr) ν_{max}: 3020, 1600, 1500, 1460, 1300, 1090, 750 and 710 cm^{-1}. MS (CI) m/e: 273 (M^+ -BF_4, 5.3) and 211 (80.3). ^{1}H-NMR δ: 2.46 (s, 3H, CH_3S), 2.99 (s, 3H, CH_3S), 3.30 (s, 3H, CH_3O), 4.69 (d, J=4.2 Hz, 1H, CHS), 5.04 (d, J=4.2 Hz, 1H, CHO) and 7.16 (m, 10H, C_6H_5).

threo-2-Methoxy-1,2-diphenylethyl dimethyl sulphonium tetrafluorborate ($^{t}V^{Ph}_{OMe}$). Yield 95%. IR (KBr) ν_{max}: 3060, 1500, 1460, 1440, 1090, 770 and 710 cm^{-1}. MS (CI) m/e: 273 (M^+-BF_4, 1.4) and 211 (22.7). ^{1}H-NMR δ: 2.44 (s, 3H, CH_3S), 3.29 (s, 3H, CH_3S), 3.30 (s, 3H, CH_3O), 4.84 (d, J=10.1 Hz, 1H, CHS), 5.04 (d, J=10.1 Hz, 1H, CHO) and 7.3 (m, 10H, C_6H_5).

erythro-2-Fluor-1-methylpropyl dimethyl sulphonium p-toluenesulphonate ($^{e}V^{Me}_{F}$). Yield 63%. IR (film) ν_{max}: 1225, 1200, 1130, 1040, 1015, 820 and 695 cm^{-1}. ^{1}H-NMR δ: 1.29 (dd, J=6.3 and 24.3 Hz, 3H, CH_3CF), 1.34 (d, J=7.0 Hz, CH_3CS), 2.33 (s, 3H, CH_3-C_6H_4), 2.93 (s, 3H, CH_3S), 3.12 (s, 3H, CH_3S), 4.30 (ddq, J=1.7, 7.1 and 30.0 Hz, 1H, CHS), 5.20 (ddq, J=1.7, 6.3 and 49.0 Hz, 1H, CHF) and 7.16-7.80 (m, 4H, AA'BB' system, C_6H_4).

threo-2-Fluor-1-methylpropyl dimethyl sulphonium p-toluenesulphonate ($^{t}V^{Me}_{F}$). Yield 73%. IR (film) ν_{max}: 1220, 1200, 1130, 1020, 825 and 685 cm^{-1}. ^{1}H-NMR δ: 1.38 (d, J=6.9 Hz, 3H, CH_3CS), 1.42 (dd, J=6.2 and 25.0 Hz, 3H, CH_3CF), 2.33 (s, 3H, CH_3-C_6H_4), 2.90 (s, 3H, CH_3S), 3.09 (s, 3H, CH_3S), 4.12 (ddq, J=6.2, 6.9 and 16.9 Hz, 1H, CHS), 4.80 (double quintuplet, J=6.2 and 47.3 Hz, 1H, CHF) and 7.16-7.80 (m, 4H, AA'BB' system, C_6H_4).

erythro-2-Fluor-1,2-diphenylethyl dimethyl sulphonium tetrafluorborate ($^{e}V^{Ph}_{F}$). Yield 79%. IR (film) ν_{max}: 2950, 1720, 1460, 1070, 760 and 710 cm^{-1}. ^{1}H-NMR δ: 2.79 (s, 3H, CH_3S), 3.23 (s, 3H, CH_3S), 5.39 (dd, J=3.0 and 33.1 Hz, 1H, CHS), 6.36 (dd, J=3.0 and 47.7 Hz, 1H, CHF) and 7.4 (m, 10H, C_6H_5).

threo-2-Fluor-1,2-diphenylethyl dimethyl sulphonium tetrafluorborate ($^{t}V^{Ph}_{F}$). Yield 68%. IR (film) ν_{max}: 2940, 1680, 1600, 1500, 1460, 1030, 760 and 700 cm^{-1}). ^{1}H-NMR δ: 2.58 (s, 3H, CH_3S), 3.16 (d, J=2.7 Hz, 3H, CH_3S), 5.46 (dd, J=8.7 and 9.6 Hz, 1H, CHS), 6.1 (dd, J=9.6 and 47.0 Hz, 1H, CHF) and 7.5 (m, 10H, C_6H_5).

Dedicatory

We would like to dedicate this paper to the memory of the late Prof. Dr. Juan Borges del Castillo.

Ackowledgements

We are indebted to the Comisión Asesora de Investigación Científica y Técnica (CAICYT) for financial support.

REFERENCES

1. F.Alcudia, E.Brunet, J.L. García Ruano, J.H.Rodríguez and F. Sánchez, J.Chem. Research, (M)1982, 2810; (S)1982, 284.
2. F.Alcudia, E.Brunet, J.L.García Ruano, M.C.Martínez and J.H. Rodríguez, Tetrahedron, 40, 2023 (1984).
3. F.Alcudia, E.Brunet, J.L.García Ruano, M.A.Hoyos, P.Prados and J.H.Rodríguez, Org.Magn.Reson., 21, 643 (1983).
4. C.A.G.Hassnot, F.A.A.H. de Leeuw and C.Altona, Tetrahedron, 36, 3403 (1980).
5. F.Alcudia, F.Fariña, J.L.García Ruano, J.H.Rodríguez and F.Sánchez, J.Chem.Soc. Perkin II, 1979, 564.
6. F.Alcudia, J.L.García Ruano, J.H.Rodríguez and F.Sánchez, An.Quím., 75, 375 (1979).
7. J.C.Carretero, J.L.García Ruano, M.C.Martínez and J.H.Rodríguez, J.Chem.Research (in press).
8. L.Phillips and V. Wray, J.Chem.Soc.(B), 1971, 1618.
9. T.Tsushima, K.Kawada, J.Nishikawa, T.Sato, K.Tori, T.Tsuji and S.Misaki, J.Org. Chem., 49, 1163 (1984).
10. S.Rozen and M.Brand, Tetrahedron Lett., 1980, 4543.
11. T.N.Wade, J.Org.Chem., 45, 5328 (1980).
12. S. Hamman, C.Beguin, C.Charlon and C.Lund-Duc, Org.Magn.Reson., 21, 361 (1983).
13. R.J. Abraham and R.H. Kepm, J.Chem.Soc.(C), 1971, 1240.
14. M.Barfield and M.D.Johuston, Chem.Rev., 73, 53 (1973).
15. F.Alcudia, E.Brunet, J.L.García Ruano and J.H.Rodríguez, Tetrahedron (in press).
16. N.S.Zefirov, L.G.Gorvich, S.A.Sahohkov, M.Z.Krimer and E.A. Vorob'era, Tetrahedron, 32, 1211 (1976).
17. J.C.Carretero, J.L.García Ruano and J.H.Rodríguez, Tetrahedron Lett., 1984, 3029.
18. C.A. Kingsbury and R.A. Aerbach, J.Org.Chem., 36, 1737 (1971).
19. N.B.Moniz, C.F.Parauski Jr. and T.H.Hall, J.Am.Chem.Soc., 88, 190 (1966).
20. E. Juaristi, J.Chem.Educ., 56, 438 (1970).
21. H.S. Zefirov, J.Org.Chem., USSR, 6, 1768 (1970); H.S.Zefirov U.S.Balgoveshcheusky, I.V. Kazimickid and N.S. Sorova, Tetrahedron, 27, 311 (1971).
22. J.A. Hirsch, Top.Stereochem., 1, 199 (1967).
23. The specific solvation of the S-O group by aromatic solvents (R.R. Fraser, T. Durst, M.R.McClory, R.Vian and Y.Y. Wigfield, Int.Sulfur.Chem.A., 1, 133 (1971) suggest that the size of the Ph group must increase in DMSO.
24. M.A.Hoyos, S.Martínez and S.García Blanco, Acta Crystallogr. C39, 118 (1983).
25. Y.Kodama, S.Zuski, K.Mishihala and K. Nishio, J.Chem.Soc.Perkin II, 1980, 1306.
26. M.K.Kaloustian, N.Dennis, S.Mager, S.A.Evans, F.Alcudia and E.L.Eliel, J.Am. Chem.Soc., 98, 956 (1976).
27. G.W. Buchanan and J.B.Stothers, Chem.Commun., 1967, 1250.
28. M.Borfield, A.M.Dean, C.J.Fallick, R.J.Spear, S.Sternhel and P.W.Westerman, J.Am.Chem.Soc., 97, 1482 (1975).
29. A. de Marco and G.Gath, Org.Magn.Reson., 3, 599 (1971).
30. H.L.Holland, Tetrahedron Lett., 1978, 881.
31. E.Hirota, J.Chem.Phys., 37, 283 (1962).
32. A.A. Abdorakhmanov, R.A. Ragimora and L.H. Imanov, Phys.Lett.(A), 32, 123 (1970).
33. N.L.Allinger, J.Hirsch, M.Miller, I.Tyminski and F.Van-Catledge, J.Am.Che.Soc., 90, 199 (1968).
34. See E.Block in "The Chemistry of functional group". Supplement E, Part 1, p. 539, S.Patai, Ed. J.Wiley and Sons, 1980 and references cited therein.
35. A.Herz and G.Marke, Angew.Chem., Int.Ed. in Eng., 12, 345 (1973).