Tetrahedron. Vol. 32, pp. 1917 to 1920. Pergamon Press 1976. Printed in Great Britain

DIASTEROTOPISM IN SULPHINYL CHLORIDES

R. P. GUPTA, J. S. PIZEY* and K. SYMEONIDES
Department of Chemistry, The University of Aston in Birmingham, Birmingham B4 7ET, England

(*Received in the UK* 29 *January* 1976; *Accepted for publication* 11 *March* 1976)

Abstract—A number of isopropyl-β-ketosulphinyl chlorides has been synthesised and their PMR spectra studied. Magnetic non-equivalence of the *alpha gem*-dimethyl groups is, in general, observed together with, in certain cases, magnetic non-equivalence of suitably positioned methylene and methine H atoms. This effect has been found to be temperature and solvent dependent and is probably due to both the intrinsic diastereomerism of the groups and to the presence of rotational conformers.

In view of the interest[1] shown in the optical stability of the chlorosulphinyl group we wish to publish our observations on the chemical shift of potentially diastereotopic groups or atoms in some β-ketosulphinyl chlorides and related compounds.

We have synthesised a number of β-ketosulphinyl chlorides,[2] a new class of compound, by treating the isopropyl ketone with thionyl chloride under controlled conditions and have examined the PMR and IR spectra of the products. The sulphoxide absorption, ν_{so} in the IR is a strong band at $1150 \pm 5\,\mathrm{cm}^{-1}$ and hence is of the same order as found for aliphatic sulphinyl chlorides. This would indicate that electronic interaction between the sulphoxide group and the carbonyl group is negligible. In addition molecular models suggest that the two groups are too far apart for steric interaction to occur. We have studied the PMR spectra of the β-ketosulphinyl chlorides in some detail and the relevant chemical shifts are given in Table 1.

The chiral properties of the sulphoxide group are well known but it is only recently that the optical stability of the chlorosulphinyl group has been noted.[1] It is evident from the above results that diastereotopic shifts are general for suitably positioned hydrogen atoms or methyl groups in β-ketosulphinyl chlorides although the relative chemical shifts are variable and depend on the structure of the molecule, the solvent, and the concentration of the compound in the solvent. This latter point is shown by the results in Table 2.

2 - Methyl - 3 - oxopentane - 2 - sulphinyl chloride (**2**), for example, shows a diastereotopic shift of 4 Hz for protons H_A and H_B in benzene as a solvent whereas in carbon tetrachloride the effect is not seen. It is interesting to note that the chiral effect of the chlorosulphinyl group in **2** is transmitted across the carbonyl group making the anisochronous nature of the geminal protons observable in benzene. Van der Vlies[3] has suggested that a phenyl group is necessary for a large diastereotopic shift; or alternatively an aromatic solvent such as benzene should be used. We have shown in Tables 1 and 2 that these conditions are unnecessary. Thus in certain cases quite large shifts are found for purely aliphatic sulphinyl chlorides in the absence of any solvent, e.g. **4** in Table 2. This substantiates the previous work by Mikolajczyk[1a] and Canalini.[1b] Nevertheless it is evident from our work that the relative chemical shifts found in our compounds are generally greater or more readily observed when benzene rather than carbon tetrachloride is used as a solvent.

The relative chemical shift of Me_A and Me_B in 2,4 - dimethyl - 3 - oxopentane - 2 - sulphinyl chloride (**4**) is both temperature and solvent dependent. Thus variable studies of $\Delta_{Me_B-Me_A}$ in benzene at a concentration of 50:50 show a linear decrease with temperature and extrapolation of the straight line obtained to the point when $\Delta_{Me_B-Me_A}$ was zero gave a temperature of 347°. This high temperature suggests that magnetic non-equivalence in the molecule is due to both intrinsic asymmetry and conformational preference. As might be expected the separation of the two lines of each doublet for R^1 and R^2, the α'-methyl groups, also decreases with increase in temperature. If the concentration in benzene is decreased to 25:75, compound:solvent, then the two doublets disappear and a triplet appears at τ9.10, at a concentration of 5:95 the triplet appears at τ9.11. The spectrum of **4** in carbon disulphide at 31° gives $\Delta_{Me_B-Me_A}$ a value of 7 Hz and $\Delta_{R^2 R^1}$ a value of 0Hz, whereas the spectrum at −70° shows $\Delta_{Me_B-Me_A}$ to be unchanged and line-splitting now occuring in the peak for R^1 and R^2 giving a value of approximately 1 Hz. Furthermore a study of the diastereotopic shifts in a mesitylene–benzene solvent shows a change in relative chemical shift with changing solvent composition. From these results it may be seen that the relative chemical shift of both the possible diastereotopic R and Me groups is temperature and solvent dependent and hence is due not only to the intrinsic diastereomerism of the group but is also due to conformational preferences. In the case of aromatic solvents complexing would readily occur with the carbonyl group to give rotational conformers.

The compound 2 - methyl - 3 - oxo - 4 - phenylpentane - 2 - sulphinyl chloride (**5**) possesses two chiral centres and hence the methyl groups, Me_A and Me_B, will be anischronous and should, in theory, give four singlets (Fig. 1). The spectrum is given in Fig. 1. Double decoupling experi-

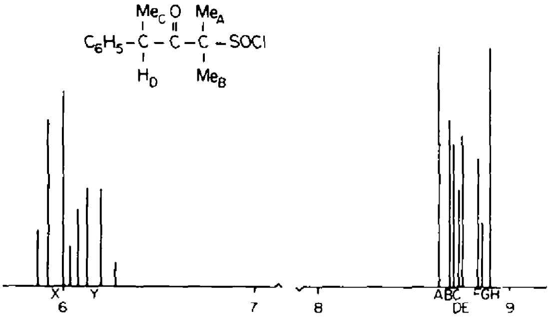
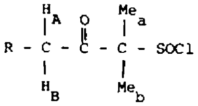


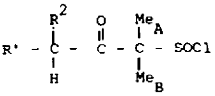
Fig. 1.

Table 1. Chemical shifts[a], τ, of β-ketosulphinyl chlorides



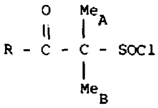
$$R-\underset{H_B}{\overset{H_A}{C}}-\overset{O}{\overset{\|}{C}}-\underset{Me_b}{\overset{Me_a}{C}}-SOCl$$

No.	R	Solvent[b]	H_A	H_B	$\Delta_{H_B-H_A}$ Hz.	Me_A	Me_B	$\Delta_{Me_B-Me_A}$ Hz.
1	H	CCl_4	7.7s	7.7s	0	8.35s	8.42s	7
	H	C_6H_6	8.0s	8.0s	0	8.70s	8.77s	7
	H	-	7.7s	7.7s	0	8.40s	8.40s	0
2	CH_3	CCl_4	7.77q	7.77q	0	8.40s	8.42s	2
	CH_3	C_6H_6	7.80q	7.84q	4	8.67s	8.74s	7
3	C_6H_5	CCl_4	6.16s	6.16s	0	8.40s	8.52s	12
	C_6H_5	C_6H_6	6.32s	6.34s	2	8.57s	8.68s	11



$$R'-\underset{H}{\overset{R^2}{C}}-\overset{O}{\overset{\|}{C}}-\underset{Me_B}{\overset{Me_A}{C}}-SOCl$$

No.	R'	R^2	Solvent[b]	R'	R^2	$\Delta_{R^2-R'}$, Hz.	H	ΔHHz	Me_A	Me_B	$\Delta_{Me_B-Me_A}$ Hz.
4	CH_3	CH_3	CCl_4	8.90d	8.90d	0	6.97sp	0	8.30s	8.38s	8
	CH_3	CH_3	C_6H_6,50%	9.00d	9.07d	7	7.10sp	0	8.52s	8.60s	8
	CH_3	CH_3	-	8.90d	8.90d	0	6.86sp	0	8.30s	8.38s	8
5[c]	C_6H_5	CH_3	CCl_4	2.8m	8.63d	0	5.84q6.01q	17	8.44s	8.68s	24
									8.46s	8.55s	9
	C_6H_5	CH_3	C_6H_6,50%	-	8.65d, 8.69d	4	5.95q 6.15q	20	8.59s	8.87s	28
									8.61s	8.67s	6
	C_6H_5	CH_3	-	-	8.65d	0	5.72q 5.84q	12	8.45s	8.72s	27
									8.47s	8.56s	9



$$R-\overset{O}{\overset{\|}{C}}-\underset{Me_B}{\overset{Me_A}{C}}-SOCl$$

No.	R	Solvent[b]	Me_A	Me_B	$\Delta_{Me_B-Me_A}$ Hz.
6	C_6H_5	CCl_4	8.22s	8.22s	0
	C_6H_5	C_6H_6	8.43s	8.51s	8
	C_6H_5	-	8.22s	8.22s	0
7	p-MeC_6H_4	C_6D_6	8.38s	8.45s	7
	p-MeC_6H_4	CCl_4	8.20s	8.20s	0
	p-MeC_6H_4	-	8.22s	8.22s	0
8	α-$C_{10}H_7$	CCl_4	8.42s	8.42s	0
	α $C_{10}H_7$	C_6H_6	8.25s	8.30s	5

[a] s, singlet: d, doublet; q, quarter; sp, septet; m, multiplet.

[b] unless otherwise stated the compound:solvent ratio in approx. 25:75.

[c] further details in Table 3.

Table 2. Relative chemical shifts of *alpha gem*-dimethyl groups

No.	$\Delta_{Me_B-Me_A}$ Hz						
	neat	CCl_4			C_6H_6		
		50%	75%	95%	50%	75%	95%
1	0	0	7	9	0	6	9
4	8	8	8	8	8	8	9
5	27	25	24	24	28	27	28
6	0	0	0	0	8	8	10
7	0	0	0	0	4	7	9
10	15	16	17	17	7	P	7
13	24	24	24	25	23	23	23

Table 3. Chemical shifts (τ) of **5** in benzene

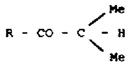
Line	Group	Chemical Shift
X	H_{D1}	5.95q
Y	H_{D2}	6.15q
A, H	Me_{A1} Me_{B1}	8.59s 8.87s
B, E	Me_{A2} Me_{B2}	8.60s 8.67s
C, F	Me_{C1}	8.61, 8.68d
D, G	Me_{C2}	8.65, 8.72d

ments in benzene at 100 MHz enabled the spectrum to be solved giving the chemical shifts shown in Table 3.

The quartets H_{D1} and H_{D2} are of unequal intensity as are the doublets for Me_{C1} and Me_{C2}, but the ratios H : Me are the same in each case. As would be expected the ratio $Me_{A1}:Me_{B1}$ and $Me_{A2}:Me_{B2}$ is one. The ratios $Me_{C1}:Me_{C2}$ and $H_{D1}:H_{D2}$ vary with temperature. A similar phenomenon appears to occur when carbon tetrachloride is used as a solvent but the peaks are insufficiently split to compare the ratios with those found in benzene. The large relative chemical shift, $\Delta_{Me_{B1}-Me_{B2}}$, of 26 Hz is unusual for this type of compound. The difference in intensity of the two quartets, H_{D1} and H_{D2}, in both benzene and carbon tetrachloride is presumably due to a conformational preference whilst the variation in ratio of the two quartets with temperature and solvent is accordance with our postulate of rotational conformers with some solvent interaction.

We have also similarly examined the relative chemical shifts within the two series of closely related compounds, ketones (Table 4) and chlorocompounds (Table 5).

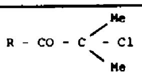
Table 4. Chemical shifts (τ) of ketones



$$R-CO-C\begin{matrix}\diagup Me\\ -H\\ \diagdown Me\end{matrix}$$

No		Solvent	Me_A	Me_B	$\Delta_{Me_B-Me_A}$ Hz.
9	$C_6H_5CH_2$	C_6H_6	9.13d		0
		CCl_4	9.03d		0
10	$C_6H_5C(Me)H$	CCl_4	8.98d	9.15d	17
		C_6H_6	9.09d	9.17d	8
		-	9.01d	9.16d	15
11	$C_6H_5C(Cl)Me$	CCl_4	8.86d	9.27d	41
		C_6H_6	8.91d	9.33d	42
12	EtC(Me)H	CCl_4	8.93d	8.94d	1
		C_6H_6	9.04d	9.07d	3

Table 5. Chemical shifts (τ) of chloro-compounds



$$R-CO-C\begin{matrix}\diagup Me\\ -Cl\\ \diagdown Me\end{matrix}$$

No	R	Solvent	Me_A	Me_B	$\Delta_{Me_B-Me_A}$ Hz.
13	$C_6H_5C(Cl)H$	CCl_4	8.40	8.64	24
		C_6H_6	8.49	8.72	23
		-	8.43	8.66	23
14	Me_2CH	CCl_4	8.33	8.33	0
15	C_6H_5	C_6D_6	8.47	8.47	0
16	p-MeC_6H_4	C_6D_6	8.22	8.22	0
17	$C_6H_5C(Me)H$	CCl_4	8.43	8.59	16
		C_6H_6	8.50	8.66	16

It is of interest to note that within these closely related groups of compounds, using the same solvents and concentrations, the relative chemical shifts, if shown, of the *alpha gem*-dimethyl groups adjacent to the chlorosulphinyl group are fairly constant and depend on the structure of the chiral group. Thus the sulphinyl chloride group exerts an effect in our aliphatic compounds ≅7 Hz, i.e. in **1**, **2** and **4**. A relative chemical shift between these two methyl groups is also shown by **6** and **7**. The chiral group $C_6H_5C(Me)H$—in both **10** and **17** has an effect ≅16 Hz. In **5** an additional effect may be seen (-SOCl and $C_6H_5C(Me)H$-) and the relative chemical shift is in the order of 24 Hz. It should also be noted that the relative chemical shift in **13** > **10** which suggests an electronic influence operating whilst **11** > **13** > **10** suggesting the relative chemical shift is controlled by both steric and electronic factors.

A study of the ortho-hydrogen atoms in α-methylpropiophenone-α-sulphinyl chloride (**6**) and α-methyl-p-methylpropiophenone-α-sulphinyl chloride (**7**) shows, as expected, the absence of any diastereotopic shift for either hydrogen. The use of a lanthanide shift reagent showed that the difference in relative shifts of the ring protons in the presence of the shift reagent is greater but the splitting, J_{H_o,H_m}, is the same at 8 Hz. The difference in chemical shift of Me_A and Me_B changes from 8 Hz to 10 Hz in the presence of the shift reagent.

A number of α-chloro-α-sulphenyl chlorides of similar structure have been synthesised and the relative chemical shifts shown by groups adjacent or near to the chiral centre are similar to those shown by the sulphinyl chlorides. Further details will be published in a later paper.

EXPERIMENTAL

^{1}H PMR spectra were obtained at 308°K and 100 MHz, unless otherwise stated, using a Varian HA100D PMR spectrometer operating in the internally locked frequency sweep mode. The double resonance experiments were facilitated by the use of an Airmec type 422 oscillator. The solutions were made approximately up to a 25% V/V ratio, compound : solvent, except where otherwise stated.

The sulphinyl chlorides were obtained by treating the appropriate ketone with thionyl chloride under standard conditions.[2] The α-chloro-α-sulphenyl chlorides were made by treating ketones containing two $\alpha\alpha$-hydrogen atoms with thionyl chloride, exact synthetic conditions will be published shortly.

The chloro-compounds were prepared by treating the appropriate ketone with sulphuryl chloride.[2,4]

Analytical data and absorption spectra for all new compounds agree with the proposed structures.

REFERENCES

[1a] M. Mikolajczyk and J. Drabowicz, *Z. Naturforsch.* **26b**, 1372 (1971); [b] G. Canalini, G. Maceagnini and F. Taddei, *Tetrahedron Letters* 3035 (1971); [c] J. F. King and R. P. Beatson, *Chem. Commun.* 663 (1970).

[2] J. S. Pizey and K. Symeonides, *Int. J. Sulphur Chem.* **9**, 1 (1974).

[3] C. van der Vlies, *Rec. Trav. Chim.* **84**, 1289 (1965).

[4] D. P. Wyman, P. R. Kaufman and W. R. Freeman, *J. Org. Chem.* **29**, 2706 (1964).