Tetrahedron Vol. 34, pp. 2655–2661
© Pergamon Press Ltd., 1978. Printed in Great Britain

0040-4020/78/0901-2655/$02.00/0

CYCLOHEXENE-SULFUR DICHLORIDE ADDUCTS. STEREOCHEMICAL CONSIDERATIONS.

GENRICH A. TOLSTIKOV,* N. N. NOVITSKAYA, R. G. KANTYUKOVA and L. V. SPIRIKHIN
Institute of Chemistry, Bashkir Branch of Acad. Sci. USSR, Ufa, U.S.S.R.

and

NICOLAI S. ZEFIROV* and VLADIMIR A. PALYULIN
Department of Chemistry, Moscow State University, Moscow 117234, U.S.S.R.

(*Received in UK 20 January 1978; Accepted for publication 30 March 1978*)

Abstract—The reaction of sulfur dichloride with cyclohexene produces two isomeric *trans*-adducts of *meso* and *dl* configurations. Derivatives of both series have been obtained and configurations have been assigned by means of pseudoasymmetry. General principles for the conformational analysis of systems which contain two inverting 6-membered rings have been discussed and the positions of conformational equilibria have been evaluated. The new conformational effect—stabilization of "heteroconformer"—has been found in the case of *dl*-bis(2-chlorocyclohexyl)sulfoxide.

Electrophilic addition of sulfenyl chlorides to olefins has been the subject of considerable study. Recent investigations have been focussed on (a) mechanistic aspects of these reactions,[1,2] (b) the problem of increasing the effective electrophilicity of sulfenyl chlorides[2,3] and (c) conformational study of adducts.[4,5] The addition sulfur dichloride to double bonds has received less attention. However this reaction has been used for synthesis of polycyclic and cage compounds.[6] The addition of SCl_2 to cyclohexene has been reported in a patent[7] and in our preliminary communications.[8,9] The purpose of this paper is to summarize the results of stereochemical investigations (partially re-investigations) of this reaction.

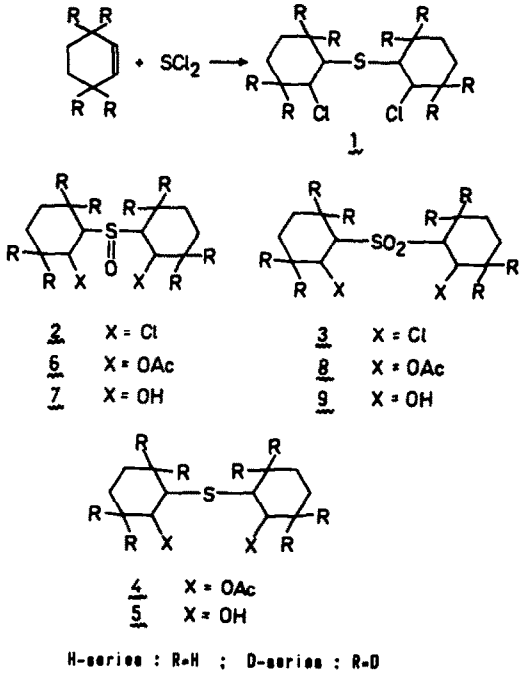

Chart 1.

RESULTS

Although only a single adduct of SCl_2 and a cyclohexene had been previously isolated[7] we have reported that two isomeric adducts (liquid, **1A**, and solid, **1B**; Chart 1) were formed in this reaction.[8,9] PMR data show that the major isomer is **1A**, but it is unstable and undergoes the irreversible conversion into **1B** upon heating or on standing.

The presence of asymmetric C atoms in the structures of adducts **1** and their derivatives requires the existence of *meso* and *racemic* diastereomers. An oxidation of adducts **1** produces either isomeric sulfoxides **2** or sulfones **3**, *giving in that way the two configurational series of derivatives.* The interconversions experimentally observed and stereochemical correlations are summarized in Chart 2. Acetolysis of the adducts proceeds cleanly but non-stereoselectively to give the same mixture of acetates **4** starting both from **1A** and from **1B**. The individual acetates **4A** and **4B** have been separated and purified. Similarly a hydrolysis of either **1A** or **1B** gives the same mixture of **5**. The individual **5A** and **5B** have been obtained by a hydrolysis of pure acetates **4A** and **4B** correspondingly. The treatment of both **5A** and **5B** with $SOCl_2$ produces the mixture of two isomeric adducts, **1A** and **1B**. The acetoxy (**4**) and hydroxy (**5**) derivatives have been in turn oxidized to the cor-

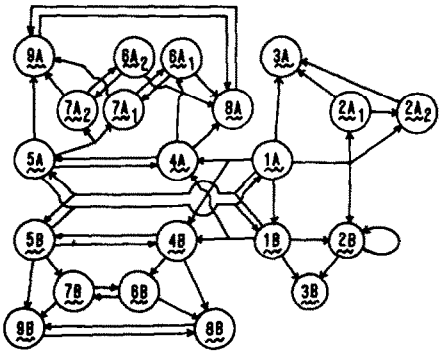

Chart 2. Graph of interconversions of the compounds obtained.

responding sulfoxides or sulfones (Chart 2) using the efficient and mild reagent—t-amylhydroperoxide + $MoCl_5$.[10]

Oxidation of the sulfides of **B**-series gave *always only a single isomer of corresponding sulfoxides*. An oxidation of the sulfides of **A**-series gave *sometimes a pair of isomeric sulfoxides*, but one of the isomers was sharply predominant. For example an oxidation of **5A** gave a mixture of $7A_1$ and $7A_2$ in approximate ratio of 1:10. However an oxidation of **4A** yielded a single isomer $6A_1$ which has been transformed into the *minor* sulfoxide $7A_1$. In contrast an aectylation of $7A_2$ gave the sulfoxide $6A_2$ which has not been isolated from the crude products of oxidation of **4A**. Analogous remarkable specifity of the oxidation reaction and drastic dependence on the substituents has been reported in literature.[8,10]

Oxidation of **1A** produces three sulfoxides, $2A_1$, $2A_2$ and **2B**, which evidences that oxidation occurs partially with configurational isomerization. Similar rearrangement seems to have been previously observed for polycyclic systems.[10] In order to acquire an unambiguous configurational correlation we investigated the epimerization reactions of sulfoxide groups.[11] The treatment of $2A_1$ with triethyloxonium fluoroborate gave the epimeric sulfoxide $2A_2$; the sulfoxide **2B** was recovered unchanged after that treatment.

In a view of the complexity of ^{1}H NMR spectra of the compounds investigated we have prepared in certain cases the partially deuterated derivatives (Chart 1, D-series) to simplify an interpretation. The ^{1}H NMR data are listed in Tables 1 and 2.

DISCUSSION

The stereochemical investigation of this reaction has to include three main problems: (1) the determination of the *cis-trans* configuration of the compounds, (2) configurational assignment of **A** and **B** series to *meso* and *dl* diastereomers and (3) the evaluation of the parameters of conformational equilibria.

The first problem may be solved by inspection of J_{12} values. The PMR spectra of 1,2-disubstituted cyclohexanes have been extensively studied and this information has been of assistance in interpretation. The *cis* 1,2-disubstituted cyclohexanes adopt *ae* or *ea* conformation with J_{12} in a range of 2–4 Hz. *trans*-Compounds have J_{12} coupling constants in a range of 2–4 Hz for the *aa*-conformation but of 9–12 Hz for the *ee*-conformation and average values in the cases of intermediate positions of conformational equilibrium. Hence in the cases of intermediate positions of conformational equilibrium. Hence large values of J_{12} ($\geq$6 Hz) can serve as an unambiguous criterion of the *trans*-configuration. The data of Table 1 show that many of the compounds examined have large coupling constants (up to 11 Hz) which assign to them *trans*-structures. Similarly the data of Table 2 show the large width of multiplets relevant (up to 24–26 Hz between the outer peaks) which also evidences the *trans* arrangement of the substituents. In some cases values of J_{12} are relatively small (Tables 1 and 2) but chemical correlations (Chart 2) lead to a clear-cut conclusion that such lowering is caused by a conformational origin (*ee* $\rightleftarrows$ *aa*, *vide infra*) and *not* by a configurational change (*trans* $\rightarrow$ *cis*). *trans*-Structure of **4** has also been supported with the addition of SCl_2 to cyclohexene in acetic acid in presence of $LiClO_4$.[2,3] This reaction gave the acetates **4** which were identical with ones obtained by acetolysis of adduct **1**. Thus, *all compounds investigated have the* trans-*structures and their isomerism has not* cis-trans *nature.*

The *trans*-structures of the adducts **1** are in agreement with stereospecific *trans*-addition of sulfenyl chlorides to olefins.[1,2] However the *trans*-structures of the products of their acetolysis (**4**) and hydrolysis (**5**) as well as the non-stereospecific course of these reactions (in a sense *meso* vs *dl*; see Chart 2) have to be explained. We believe that the stereochemical result observed is due to the participation of the sulfide group in the rate determining ionization step under the solvolytic conditions.[12] The adducts **1** possess the *trans*-orientation of S and Cl atoms required for such participation via formation of an episulfonium ion (e.g. **10**, Chart 3). The rear-side attack at this ion, e.g. **10**, by nucleophiles should give two isomeric compounds of *trans*-structure (Chart 3): an

Table 1. The coupling constants and mole fractions of the conformers (CCl_4)

Compound	$J^{12}=J^{1'2'}$ (Hz)	First method (Appendix 1) $n_{ee,ee}$ (%)	n_{het} (%)	$n_{aa,aa}$ (%)	Second method $J_{obs}=\sum n_i J_i$ (5) n_{aa}(%)	$K_{aa/ee}$
D-1A	6.0	23	41	36	56	1.28
D-1B	6.5	29	42	29	50	1.0
D-$2A_1$*	11.0	(100)	0	0	0	0
$2A_2$*#	4.5	9	32	59	75	3.0
D-3A*	6.5	29	42	29	50	1.0
D-3B*	10.0	88	11	1	6	0.07
D-4A	8.5	59	32	9	25	0.33
D-4B	8.5	59	32	9	25	0.33
D-5A	10.5	100	0	0	0	0
D-5B	10.5	100	0	0	0	0
$6A_2$#	8.5	59	32	9	25	0.33

*in $CDCl_3$, #undeuterated; double resonance.

Table 2. The experimental characteristics of the compounds of H-series

Compound	m.p. °C	Chemical shifts, δ, ppm (the width of multiplets between the outer peaks, Hz) H_1, H_1'	H_2, H_2' or H_2''	Solvent (PMR)	R_f
1A	(liq)	2.86(17.5)	3.98(17.5)	CCl_4	0.9[j]
1B	72-73[c]	2.86(17)	3.88(17)	CCl_4	0.9[j]
$2A_1$	128-129[d]	2.74(24)	3.95(23)	CCl_4	0.4[j]
$2A_2$	96-97[e]	3.25(16.5)	4.41(16)	$CDCl_3$	0.62[j]
2B[a]	103-105[d]	2.72(25) 2.98(12)	3.98(25) 4.50(12)	CCl_4	0.56[j]
3A	91-92[f]	3.50(18)	4.55(17.5)	CCl_4	0.8[j]
3B	176-177[f]	3.80(24)	4.16(24)	$CDCl_3$	0.8[j]
4A	73.5-74[f]	2.68(20)	4.53(20)	CCl_4	0.86[k]
4B	93-94[f]	2.74(20)	4.52(20)	CCl_4	0.86[k]
5A	66-68[d]	2.44(24)	3.12(23)	CCl_4	0.50[k]
5B	88-89[d]	2.28(24)	3.12(23)	CCl_4	0.50[k]
$6A_1$	125-126[g]	2.86(26)	4.88(24)	CCl_4	0.45[k]
$6A_2$	106-108[g]	3.03(23)	5.10(22)	CCl_4	0.45[k]
6B[a]	94-95[g]	3.05(25) 3.05(25)	4.86(24) 5.11(24)	$CDCl_3$	0.45[k]
$7A_1$	200-201[h]	3.16(26)	4.03(24)	$Py(D_5)$	0.27[k]
$7A_2$	126-127[h]	3.03(26)	4.0(24)	$CDCl_3$	0.42[k]
7B[a]	136-138[h]	2.42(25) 2.80(25)	3.67(24) 3.95(24)	$CDCl_3$	0.36[k]
8A	143.5-145[g]	3.18(25.5)	5.10(24)	CCl_4	0.6[k]
8B	164.5-165.5[g]	3.32(26)	4.95(24)	CCl_4	0.6[k]
9A	123-124[i]	3.21(25)	3.92(24)	$CDCl_3$	0.42[k]
9B[b]	207-208[h]	3.42(25)	3.73(24)	DMFA(D_7)	0.48[k]

[a] dl-sulfoxide, $\delta_{H_1} \neq \delta_{H_1'}$; [b] chemical shift at 125°; at room temperature an unresolved multiplet of H_1, H_1', H_2 and H_2'' ; [c] from Et_2O-light petroleum; [d] from hexane; [e] from heptane; [f] from EtOH; [g] from Et_2O; [h] from acetone; [i] from acetone-hexane; [j] CCl_4-acetone(4:1); [k] benzene-EtOH(9:1).

attack at C_2 leads to the *trans*-product of initial configurational series but an attack at C_1 leads also to the *trans*-product but of alternative configurational series (Chart 3). Participation of sulfur in a common intermediate also explains the facile rearrangement of **1A** into **1B** (reaction of "cyclometathesis"[13] or "diotropic"[14] type).

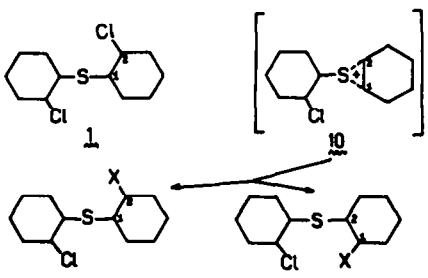

Chart 3.

Let us consider the problems of the configurational isomerism and conformational equilibria. There are two types of the internal motions of the nuclear framework of molecules of the compounds under investigation: (i) a ring reversal of 6-membered rings and (ii) the internal rotation about C–S bonds, which leads to the existence of rotameric conformations. Independent ring reversal results in the existence of four principle conformers (Chart 4): two "homoconformers" with the identical positions of the substituents in both rings (*aa,aa* and *ee,ee*) and two "heteroconformers" with different orientations of the substituents in cyclohexane rings (*aa,ee* and *ee,aa*). It has to be kept in mind that Chart 4 represents the bare essentials of the conformational

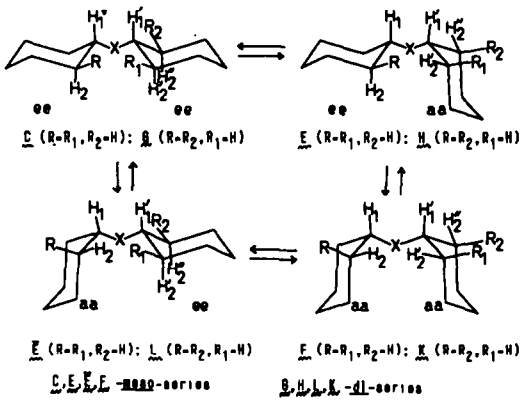

Chart 4. Interconversion of cyclohexane rings for the compounds of *meso* and *dl*-series.

equilibria because there are sets of rotameric conformations (due to the rotation about C–S bonds) correspond to each of the conformation depicted. Thus, the general picture of conformational equilibria is quite complicated.

Consider firstly the compounds with achiral group X (Chart 4, X = S and SO_2). In this case the heteroconformers **E** and $\bar{\mathbf{E}}$ (Chart 4) are the pair of enantiomers and the heteroconformers **L** and **H** can be interchanged by symmetry operation C_2 and must be equivalent. Thus, there exist three diastereomeric conformations due to the ring reversal in a conformational equilibrium. These three conformers can be determined in principle by low temperature NMR measurement (*vide infra*). The conformations **C** and **F** of *meso*-series have the σ plane which passes through the S atom. Therefore the cyclohexane rings in both these conformations, **C** and **F**, are enantiotopic and the protons H_1 and H_1' (as well as H_2 and H_2') must have the same chemical shift. The conformations **G** and **K** of *dl*-series have the C_2 axis and the rings are equivalent. With these two exceptions (**C** and **F** or **G** and **K**) all other conformations (including the majority of the rotameric ones) have not any elements of symmetry and therefore they have the diastereotopic cyclohexane rings. However this situation does not lead to the chemical-shift non-equivalence of protons of cyclohexane rings due to (i) the existence of the mentioned conformations with either enantiotopic (**C** and **F**) or equivalent (**G** and **K**) cyclohexane rings and (ii) rapid conformational transitions on the NMR time scale. Thus the NMR cannot be used as a tool for making configurational assignment.†

The classical criterion for distinguishing between the *meso* and *dl* isomers involves the resolution of racemic mixture.[15] However this operation is often difficult to carry out. The modern criterion includes the use of pseudoasymmetry for this purpose.[9,16] The S atom of sulfoxides obtained may be regarded as a center of pseudoasymmetry and the oxidation into sulfoxides creates a new chiral unit quite naturally.

The oxidation of *meso*-sulfide can produce two *meso*-sulfoxides. Also the above analysis of the interrelation of 6-membered rings can be applied to the *meso*-sulfoxides: they have σ plane, the rings must be enantiotopic and undistinguishable in NMR spectra. However, the conformations **L** and **H** for *dl*-sulfoxides become non-equivalent and non-entiotopic; thus, there exist now *four* conformers in the conformational equilibrium. The conformations **G** and **K** in this case have no elements of symmetry and the rings must be diastereotopic.

Thus, the criteria of configurational assignment may be summarized as follows: (1) an oxidation of *meso*-sulfides can provide two isomeric *meso*-sulfoxides, while an oxidation of *dl*-sulfide must provide a single *dl*-sulfoxide; (2) the protons H_1 and H_1' (as well as H_2 and H_2' or H_2'') show the chemical-shift equivalence for all compounds of *meso*-series as well as for sulfides and sulfones of *dl*-series; however they are diastereotopic and hence anisochronous in the NMR spectra of *dl*-sulfoxides.

The experimental data (Tables 1 and 2) show the realization of above criteria. Thus, the oxidation of sulfides **1A** and **5A** (Chart 2) results in two sulfoxides ($\mathbf{2A_1}$, $\mathbf{2A_2}$ and $\mathbf{7A_1}$, $\mathbf{7A_2}$) while the oxidation of corresponding sulfides of **B**-series results in only a single sulfoxide. While the single sulfoxide $\mathbf{6A_1}$ has been isolated after the oxidation reaction, the second isomer, $\mathbf{6A_2}$, has been obtained by acetylation of $\mathbf{7A_2}$.

In PMR spectra of sulfoxides **2B**, **6B** and **7B** the protons H_1 and H_1' (as well as H_2 and H_2') have different chemical shifts, while the chemical shifts of the corresponding protons of sulfoxides of **A**-series are equal. Thus, combination of the above criteria permits us to conclude that *the compounds of A-series belong to* meso-*series, and those of B-series to* dl-*series.*

Let us return to the conformational problems. The compounds investigated may be regarded as the *trans*-1,2-disubstituted cyclohexanes and hence the basic problem is the evaluation of the factors which determine the relative stability of diaxial vs diequatorial conformers.[4] Although steric reasons favor the *ee*-conformation, the experimental data show the increased content of *aa*-form especially for the substituents which are the elements of low periods (Br, S).[4] This "phenomenological conformational effect" (see Ref. 17) has been rationalized in terms of either electrostatic interactions or an orbital-overlap mechanism.[4]

The above discussion reveals the complexities of the conformational problem for the compounds investigated: conformational equilibrium must generally include four principle conformers, **G**, **H**, **L**, **K** (Chart 4) and vicinal coupling constants observed for each ring can be expressed by eqns (1) and (2):

$$J^{12}_{obs} = n_G J^G_{aa} + n_H J^H_{aa} + n_K J^K_{ee} + n_L J^L_{ee} \quad (1)$$

$$J^{1'2'}_{obs} = n_G J'^G_{aa} + n_H J'^H_{aa} + n_K J'^K_{ee} + n_L J'^L_{ee} \quad (2)$$

where n_i is the mole fraction of i-conformer. It is evident that simple PMR analysis cannot provide the description of such equilibrating system (*vide infra*). Thus, it is expedient now to discuss the particular case of the equilibrium for three conformers (*vide supra*). In fact, this case is very important because it includes the majority of the compounds studied. In this case the eqns (1) and (2) are transformed into eqn (3):

$$J^{12}_{obs} = J^{1'2'}_{obs} = n_{ee,ee} J^{ee,ee}_{aa} + n_{aa,aa} J^{aa,aa}_{ee} + n_{bot}\left(\frac{J^{bot}_{aa} + J^{bot}_{ee}}{2}\right). \quad (3)$$

†Of course *meso* and *dl* compounds have the different chemical shifts but this criterion cannot be used for the unambiguous assignment.

Hence, the coupling constant observed, J_{12}, is the function of the mole fractions of two homoconformers, $n_{ee,ee}$ and $n_{aa,aa}$, and of one of heteroconformer, n_{het}.

First of all we have obtained *the experimental evidence for the presence of three conformers* in the equilibria discussed. At room temperature the 180 MHz proton spectrum of **D-1A** consists of two AX doubletes with $J_{12} = 6$ Hz (Table 1). At the $-90°$ (in CS_2) when the ring reversal is frozen the spectrum contains two doublets of equatorial protons H–CCl (δ 4.38 and 4.25 ppm, both $J_{12} = 2.5$ Hz), two doublets of equatorial protons H–CS (δ 3.08 and 3.03 ppm, both $J_{12} = 2.5$ Hz), two doublets of axial protons H–CCl (δ 3.69 and 3.56 ppm, both $J_{12} = 10.5$ Hz) and two doublets of axial protons H–CS (δ 2.52 and 2.50 ppm, both $J_{12} = 10.5$ Hz). Thus, low temperature spectrum of **D-1A** shows the separate resonances of three individual conformers **C**, **E** and **F** (Chart 4). It should be noted that $J_{aa}^{homo} = J_{aa}^{het}$ and $J_{ee}^{homo} = J_{ee}^{het}$. We shall accept the equality of the relevant coupling constants in *homo* and *hetero*-conformers: it is reasonable assumption because the conformational change of one ring should not strongly influence the geometry of the second ring. With this assumption the eqn (3) transforms into eqn (4)

$$J_{obs}^{12} = n_{ee,ee}J_{aa} + n_{aa,aa}J_{ee} + n_{het}(J_{aa} + J_{ee})/2. \quad (4)$$

The low temperature constants $J_{aa} = 10.5$ Hz and $J_{ee} = 2.5$ Hz have been chosen as the "standard" values (see Ref. 4).

Of course the one equation with two independent variables cannot be solved and one needs other assumptions. Firstly, the zero-order approximation assumes *that ring reversal in the molecule is completely independent*, i.e. that the factors which stabilize (or destabilize) the *aa*-conformation in *aa,aa*-homoconformer have the same magnitude in *aa,ee*-heteroconformer. In other words, one assume a non-existance of any specific effects for the heteroconformation as compared with a homoconformation (*vide infra*). Thermodynamically this means that the enthalpies, ΔH, are equal for the conformational transitions *ee,ee* → *ee,aa* and *ee,aa* → *aa,aa*. The content of the conformers has been calculated (Appendix 1) using this zero-order approximation and the data presented in Table 1.

Secondly, it is easy to calculate the values n_{ee} or n_{aa} (Table 1, eqn (5); n_i is the content of cyclohexane rings of particular conformation). Using this approach one calculates, in fact, the mole fractions of *dieq* or *diax* 6-membered rings regardless the conformer to which they belong. For example, if one obtains 50% *dieq* rings, this can mean the variety of the equilibria with the content of the heteroconformer from 0% (but 50:50 of homoconformers!) up to 100% (but 0% of other conformers). Thus, one question may be posed: what range of n_{het} can be expected at the particular value of J_{obs}^{12}? Mathematical details of this problem are shown in Appendix 2. Inspection of it shows the n_{het} goes to zero as J_{obs}^{12} approaches either J_{aa} or J_{ee}. For instance, the compounds **4** have $J_{obs}^{12} = 8.5$ Hz and the range of n_{het} is 0–0.5. However, the compound **D-3B** has the $J_{obs}^{12} = 10$ Hz (Table 1) and the content of heteroconformer cannot exceed 12.5%.

The results of Table 1 show interesting regularities, some expected, some surprising. The chlorosulfides, **D-1**, have the increased content (up to 56%) of *diax* 6-membered rings. In general this trend is in accordance with the data for analogous *trans*-1,2-disubstituted cyclohexanes;[4] however the effect observed is slightly diminished. Moreover this effect is sharply diminished for the acetoxy compounds, **D-4**, where a predominance for the *dieq* rings is observed (see Ref. 4). The strong preference for the *dieq* conformation for hydroxy compounds **D-5** is generally expected, considering the conformational behaviour of related 2-substituted cyclohexanoles.[4] The $-\Delta G$ value for CH_3SO_2 group (2.5 kcal/mol[18]) is much larger than the ones for CH_3SO (1.2 kcal/mol[18]) and RS (CH_3S 1.0 kcal/mol[18]; C_6H_5S 1.1 kcal/mol[19]) groups. However the corresponding *trans* - (2 - chlorocyclohexyl)phenylsulfone has an increased content (up to 60%) of the *diax* conformation.[20] In the case of sulfones **D-3** *the conformational characteristics depend on the configurational series* (Table 1). Assuming the equilibrium of *trans* - (2 - chlorocyclohexyl)-phenylsulfone as the reference,[20] one may qualify the conformational behaviour of *meso* **D-3A** as "normal" and of racemic **D-3B** as "exceptional".

The comparison of sulfoxides $2A_1$ and $2A_2$ (Table 1) show an unexpected drastic difference in conformational behavior of the compounds belonging to the same configurational series: while for $2A_2$ *aa,aa* conformer dominated, $2A_1$ has both rings in *dieq* conformation.

Thus, if one takes into account the trends mentioned, namely (i) the diminished content of *diax* conformation as compared with reference compounds and (ii) dependence of equilibria on the configurational series, one comes to the qualitative conclusion that, at least for some cases, (a) *the rotameric conformations are important and must be taken into account* and (b) *the assumption that rings are completely independent is not good approximation for the sulfones and sulfoxides.*

To gather further evidence on this matter, we examined the PMR spectrum of sulfoxide **D-2B**. In principle, the conformational equilibrium of this compound must include four conformers, and coupling constants observed must be determined by eqns (1) and (2). The PMR data for this compound are of exceptional interest. The PMR spectrum of **D-2B** ($CDCl_3$, 25°) contains *two* doublets (δ 2.89 and 3.94 ppm) with $J_{obs}^{12} = 4$ Hz and *two* doublets (δ 3.10 and 4.58 ppm) with $J_{obs}^{1'2'} = 11.0$ Hz. Thus at room temperature the 6-membered rings have different arrangements of substituents: *one ring has the diaxial and the another one has the diequatorial conformation*, and the conformational equilibrium is sharply shifted to the heteroconformer/s. Thus, one may postulate *the new phenomenological conformational effect* (see Ref. 17) *of additional stabilization of heteroconformer/s* of type **E**, **H** and **L** (Chart 4). The origin of this effect is probably connected with the existence of such rotameric conformations (rotation about C–S bonds) in which the mutual orientation of dipoles of C–Cl and S=O bonds in *ee,ee* or *aa,aa* conformations are so unfavorable, that it leads to a change in the conformation of one rings (it has to be emphasized that the rings are different in principle!). Similarly, extraordinary difference of conformational behavior of $2A_1$ and $2A_2$ (it has to emphasized that in that case the rings are effectively enantiotopic and only average coupling constant can be observed!) probably connected with the difference in population of rotameric conformations and hence with difference in the *gauche*-interaction of the substituents.

CONCLUSION

We have attempted to show that (1) the addition of SCl_2 to cyclohexene proceeds stereospecifically to give

the *trans*-adducts, (2) the nucleophilic substitution of Cl atoms in the adducts proceeds also to give the *trans*-compounds, (3) two configurational series of the compounds, namely *meso* and *dl* series, have been obtained and the unambiguous configurational assignment has been achieved using the pseudoasymmetry as the means for that purpose, (4) the conformational behavior of the compounds obtained has been discussed in comparison with related "reference" cyclohexanes and the new conformational effect of stabilization of heteroconformer/s has been found. We believe, that the present stereochemical consideration may be useful in general, because the similar types of structures are often obtained by addition reactions (e.g. nitrosochlorination[21]), by symmetrization reactions of alcoxymercurials,[22] etc.

We have proposed that this new conformational effect and related conformational features may be understood in terms of rotameric preferences about C–SO bonds. More experimental data, including precise molecular mechanics calculations of the rotameric conformations and their populations, will be used to provide a more detailed analysis of the origin/s of this effect.

EXPERIMENTAL

PMR spectra were recorded using Tesla BS-487B (80 MHz) spectrometer with HMDS as internal reference. IR spectra were obtained using UR-20 spectrometer (neat films, Nujol mulls and KBr pellets): for all compounds investigated the ordinary characteristic absorption bands corresponding to functional groups were observed. Analytical data of the compounds investigated were in accordance with formulas proposed (±0.3 for C and H, ±0.4 for Cl and S). 3,3,6,6-Tetradeuterocyclohexene was prepared in accordance with Ref. 23. The reactions were monitored with thin layer chromatography on alumina (Table 2).

Bis(2-chlorocyclohexyl)sulfides **1A** *and* **1B**

A stirred soln of cyclohexene (34 g) in CH_2Cl_2 (100 ml) was treated with a soln of SCl_2 (21 g) in CH_2Cl_2 (30 ml) at −25 to −30° by dropwise addition over a period of an hr. The mixture was then allowed to warm up to room temp. (for 1 hr) after which the solvent was removed *in vacuo*. The liquid was separated from crystals to give **1A** (26–27 g). To obtain reproducible results, liquid **1A** was used for synthesis just after preparation (after 3–4 days at 0° **1A** converts completely into **1B**). Crystals (25–26 g) were recrystallized three times from ether–light petroleum to give **1B**.

Oxidation of **1A**

A soln of **1A** (25 g) in dry benzene (200 ml) was refluxed allowing benzene to distill with simultaneous treatment with a soln of t-amylhydroperoxide (10.7 g, 92%) and $MoCl_5$ (15–20 mg) in dry benzene (10 ml) by dropwise addition over a period of an hr. The end of oxidation was determined by TLC. The mixture was washed with water, dried and concentrated. Fractional crystallization of this material (from hexane) gave 8.5 g of **2A**$_1$, then 3.4 g of individual **2B** and 3.5 g of a mixture of **2A**$_1$ and **2B** (*ca.* 3:1). The evaporation of mother liquor followed by fractional cristallization of the residue (from heptane) and preparative-layer chromatography resulted in the isolation of **2A**$_2$ (0.9 g).

The same general procedure has been used for oxidation of (i) sulfides into sulfoxides (yields 85–95%): **1B** → **2B**, **4A** → **6A**$_1$, **4B** → **6B**, **5A** → **7A**$_1$ + **7A**$_2$ (crystallization from acetone afforded **7A**$_1$ (5%) and **7A**$_2$ (72%) was isolated from mother solution), **5B** → **7B**; (ii) sulfoxides into sulfones (yields 80–95%): **2A**$_1$ → **3A**, **2A**$_1$ → **3A**, **2B** → **3B**, **6A**$_1$ → **8A**, **6A**$_2$ → **8A**, **6B** → **8B**, **7A**$_1$ → **9A**, **7A**$_2$ → **9A** and **7B** → **9B**. The same procedure with double quantity of t-amylhydroperoxide has been used for oxidation of sulfides into sulfones (yields 80–95%): **1A** → **3A**, **1B** → **3B**, **4A** → **8A**, **4B** → **8B**, **5A** → **9A**, **5B** → **9B**.

Interconversion of chlorosulfoxides

A soln of **2A**$_1$ (1 g) and equimolar quantity of $Et_3O^+BF_4^-$ (3.7 mmol) in CH_2Cl_2 was allowed to stand at room temp. for 24 hr and then was concentrated. Dioxane (2 ml) was added to a residue and the soln was neutralized with 25% NaOH aq, extracted with benzene and dried ($MgSO_4$). The usual work-up gave 0.8 g of **2A**$_2$ identical to those prepared by oxidation of **1A**.

Sulfoxide **1B** was recovered unchanged after similar treatment.

Bis(2-acetoxycyclohexyl) sulfides **4A** *and* **4B**

1A or **1B** (25.9 g) were dissolved in glacial AcOH (200 ml) at 98–100° and anhyd NaOAc (18 g) was added. The mixture was stirred for 30 min, poured into 2 l. of water, allowed to stand for 7–8 hr at 0° and filtered to give 28.7 g of a mixture of **4A** and **4B**. Crystallization of the residue resulted in the isolation of **4A** (2 g), m.p. 73.5–74° (from EtOH). The residue was a mixture (*ca.* 17 g, m.p. 58–63°) of **4B** and **4A** (*ca.* 1:1.5).

Bis(2-hydroxycyclohexyl) sulfide **5A**

A water–EtOH (1:1, 100 ml) soln of **4A** (3 g) and KOH (2.3 g) was refluxed for 15 min, neutralized, evaporated *in vacuo*, extracted with ether, filtered, concentrated and recrystallized (from hexane) to give 2.2 g (96%) of **5A**. Analogously the following conversions were performed (yields 75–95%): **4B** → **5B**, **8A** → **9A**, **8B** → **9B**, **6A**$_1$ → **7A**$_1$, **6A**$_2$ → **7A**$_2$, **6B** → **7B**.

Bis(2-acetoxycyclohexyl)sulfoxide **6A**$_2$

Acetylation of 0.2 g of **7A**$_2$ with 0.5 ml Ac_2O and 15 ml pyridine for 48 hr at room temp. followed by usual work-up and crystallization (from ether) afforded 0.2 g of **6A**$_2$. The same procedure was used for acetylation of other hydroxyl containing compounds (yields 70–95%): **7A**$_1$ → **6A**$_1$, **7B** → **6B**, **5A** → **4A**, **5B** → **4B**, **9A** → **8A**, **9B** → **8B**.

Hydrolysis of **1**

A water–acetone (1:3, 40 ml) soln of **1A** or **1B** was refluxed for 10 min, neutralized and evaporated *in vacuo*. The residue was extracted with ether, the extracts were filtered and concentrated to give 1 g of a mixture of **5A** and **5B** (*ca.* 2:3, m.p. 63–66°).

Interaction of **5A** *and* **5B** *with* $SOCl_2$

To a soln of **5A** or **5B** (0.1 g) in $CHCl_3$ (5 ml) a soln of $SOCl_2$ (0.2 ml) in $CHCl_3$ (2 ml) was added dropwise and mixture was allowed to stand for 1 hr. Concentration gave 0.11 g of a mixture of **1A** and **1B** (*ca.* 1:1).

Acknowledgement—One of us (N.S.Z.) is indebted to Prof. S. Wolfe for his kind invitation and generous support to visit the Queen's University, Kingston, Canada, where there was the greatest opportunity to discuss many stereochemical ideas. We are also grateful to Drs B. Schlegel, D. J. Mitchell and D. Klayman for their help in the translation of the manuscript.

REFERENCES

[1]V. R. Kartashov, I. V. Bodrikov, E. V. Skorobogatova and N. S. Zefirov, *Zh. Org. Khim.* **12**, 297 (1976); *Int. J. Sulf. Chem.* **9**, 213 (1977); E. A. Vorob'eva, M. Z. Krimer and V. A. Smit, *Izv. Akad. Nauk SSSR, Ser. Khim.* 1318, 2743 (1976); V. A. Smit, M. Z. Krimer and E. A. Vorob'eva, *Tetrahedron Letters* 2451 (1975); G. Capozzi, O. Delucchi, V. Luccini and G. Modena, *Ibid.* 2603 (1975); G. H. Schmid and D. Garratt, *The Chemistry of Double Bonded Functional Groups* (Edited by S. Patai), Vol. 2. Wiley, New York (1977).

[2]N. S. Zefirov, N. K. Sadovaja, A. M. Maggerramov, I. V. Bodrikov and V. R. Kartashov, *Tetrahedron* **31**, 2948 (1975); and Refs. therein.

[3]N. S. Zefirov, N. K. Sadovaja, A. M. Maggerramov and I. V. Bodrikov, *Zh. Org. Chim.* **13**, 245 (1977); I. V. Bodrikov, T. S. Ganzhenko and N. S. Zefirov, *Ibid.* **13**, 2476 (1977).

[4]N. S. Zefirov, L. G. Gurvich, A. S. Shashkov, M. Z. Krimer and E. A. Vorob'eva, *Tetrahedron* **32**, 1211 (1976); and Refs. therein.

[5]N. S. Zefirov, *Zh. Org. Khim.* **6**, 1761 (1970); G. M. Underwood, C. T. Watts and C. A. Kingsbury, *J. Org. Chem.* **36**, 1553 (1973).
[6a]Reviews: N. S. Zefirov and S. V. Rogozina, *Usp. Khim.* **42**, 423 (1973); N. V. Averina and N. S. Zefirov, *Ibid.* **45**, 1077 (1976); E. Kühle, *Synthesis* 561 (1970); [6b]P. H. McCabe and W. Routledge, *Tetrahedron Letters* 85 (1976); S. Braverman and D. Segev, *J. Am. Chem. Soc.* **96**, 1245 (1974); B. J. Corey and E. Block, *J. Org. Chem.* **31**, 1663 (1966); N. N. Novitskaja, R. V. Kunakova, E. E. Zaev, G. A. Tolstikov and L. V. Spirikhin, *Zh. Org. Khim.* **9**, 636 (1974); **11**, 1434 (1975).
[7]Badische Anilin- und Soda-Fabric, *Ger. Pat.* 840 691 (1952); *Chem. Abst.* **48**, 1413 (1954).
[8]N. N. Novitskaja, R. G. Kantyukova and G. A. Tolstikov, *Zh. Obchsh. Khim.* **44**, 2732 (1974).
[9]G. A. Tolstikov, N. N. Novitskaja, R. G. Kantyukova, L. V. Spirikhin, V. A. Palulin and N. S. Zefirov, *Zh. Org. Khim.* **13**, 894 (1977).
[10]N. N. Novitskaja, R. V. Kunakova, L. K. Yuldasheva and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.* 384 (1976); G. A. Tolstikov, *Reactions of Hydroperoxide Oxidation* (Russ.), Nauka, Moscow (1976).
[11]F. Lautenschlager, *J. Org. Chem.* **31**, 1679 (1966); C. R. Johnson and D. McCants, *J. Am. Chem. Soc.* **87**, 5404 (1965).
[12]W. H. Muller and P. E. Butler, *Ibid.* **90**, 2075 (1968).
[13]N. S. Zefirov and S. S. Trach, *Zh. Org. Khim.* **11**, 225 1785 (1975); **12**, 7, 697 (1976).
[14]M. T. Reetz, *Tetrahedron* **29**, 2189 (1973).
[15]S. N. Lewis and W. D. Emmons, *J. Org. Chem.* **31**, 3572 (1966).
[16]M. Raban, S. K. Lauderback and D. Kost, *J. Am. Chem. Soc.* **97**, 5178 (1975).
[17]N. S. Zefirov, *Tetrahedron Reports* No. 47, 3193 (1977).
[18]E. L. Eliel and D. Kandasamy, *J. Org. Chem.* **41**, 3899 (1976).
[19]O. A. Subbotin, V. A. Palyulin, S. I. Kozhushkov and N. S. Zefirov, *Zh. Org. Khim.* **14**, 209 (1978).
[20]A. A. Bayramov, I. G. Mursakulov, M. M. Guseinov and N. S. Zefirov, *Ibid.* **13**, 1339 (1977).
[21]P. P. Kadzyauskas and N. S. Zefirov, *Usp. Khim.* **37**, 7 (1968); M. M. Rogic, T. R. Demmin, R. Fuhrmann and F. W. Koff, *J. Am. Chem. Soc.* **97**, 3241 (1975).
[22]T. G. Traylor and S. Winstein, *J. Org. Chem.* **23**, 1796 (1958).
[23]J. R. Campbell, *Ph. D. Thesis*, Queen's University, Kingston, Canada (1969); N. S. Zefirov and V. N. Chekulaeva, *Vestn. Mosk. Univ. Khim.* **23**, 117 (1968); *Chem. Abst.* **70**, 28426 (1969).

APPENDIX 1

The zero-order approximation assumes that the enthalpies for the conformational equilibria *aa,aa* ⇄ *aa,ee* and *aa,ee* ⇄ *ee,ee* are equal (eqn 6). The equilibrium constants in this case must obey eqn (7). So far as the heteroconformer is a *dl*-pair (e.g. enanthiomers **E** and $\bar{\mathbf{E}}$, Chart 4), it is favorable with entropy factor $S = R \ln 2$. Thus the eqn (7) transforms into eqns (8) and (9).

$$\Delta H_{ee,ee/aa,aa}/2 = \Delta H_{aa,ee/aa,ee} = \Delta H_{aa,ee/aa,aa} \quad (6)$$

$$\frac{\exp(\Delta S_{ee,ee/aa,aa}/R)}{\exp(\Delta S_{aa,ee/aa,ee}/R)} \cdot K_{ee,ee/aa,ee} = K_{aa,ee/aa,aa} \quad (7)$$

$$2K_{ee,ee/aa,ee} = K_{aa,ee/aa,aa} \quad (8)$$

$$n_{het}^2 = 2n_{aa,aa} \cdot n_{ee,ee} \quad (9)$$

$$n_{aa,aa} + n_{ee,ee} + n_{het} = 1. \quad (10)$$

The mole fractions of the conformers can be found from eqns (4) and (9) taking into account the eqn of material balance (10). Thus, these eqns are transformed into eqns (11) and (12):

$$n_{het}^2 + 2n_{het} - 4ab = 0 \quad (11)$$

$$n_{aa,aa} = a - n_{het}/2 \quad (12)$$

where $a = (J_{aa} - J_{obs})/(J_{aa} - J_{ee})$ and $b = (J_{obs} - J_{ee})/(J_{aa} - J_{ee})$. The value of n_{het} is found as a positive root of eqn (11) and $n_{aa,aa}$ from eqn (12).

APPENDIX 2

The starting point of the analysis of the permitted values of n_{het} as a function of J_{obs} is the eqn (4). The eqns (4) and (10) give the eqn (13). In this eqn $K \geqslant 0$ and $0 \leqslant n_{het} \leqslant 1$.

$$K_{ee,ee/aa,aa} = \frac{n_{ee,ee}}{n_{aa,aa}} = \frac{J_{obs} - J_{ee} - n_{het}(J_{aa} - J_{ee})/2}{J_{aa} - J_{obs} - n_{het}(J_{aa} - J_{ee})/2}. \quad (13)$$

Let us introduce the parameter $J_{crit} = (J_{aa} - J_{ee})/2$. In the case $J_{obs} = J_{crit}$, $K = 1$ and n_{het} can adopt any value in the range from 0 to 1. For standard coupling constants $J_{aa} = 10.5$ and $J_{ee} = 2.5$ Hz, $J_{crit} = 6.5$ Hz. For J_{obs} less than this value the range of permitted values of n_{het} may be found from eqn (14); for $J_{obs} > J_{crit}$ this range may be found from eqn (15). Eqns (14) and (15) was derived from eqn (13) taking into account that $K \geqslant 0$.

$$n_{het} < \frac{J_{obs} - J_{ee}}{J_{crit}} \quad (14)$$

$$n_{het} < \frac{J_{aa} - J_{obs}}{J_{crit}} \quad (15)$$

Thus, when the difference between J_{obs} and J_{crit} is large, the uncertainty of n_{het} is small and vice versa as has been discussed in the text.