Translated from *Uspekhi Khimii*, 54, 803-836 (1985) U.D.C. 547.818:542:543:422

Thiadecalins and Condensed Thiacyclohexanes of the 2-Thiabicyclo[4.3.0]nonane Series

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The latest advances in the chemistry of condensed bicyclic thiacyclohexanes of the type of thiadecalins and their analogues are examined. The results of studies on the methods of synthesis, chemical reactions, and the conformational and configurational analysis of thiadecalins, their analogues, and derivatives are surveyed.
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I. INTRODUCTION

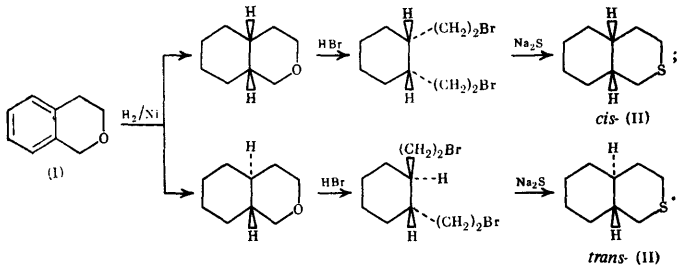
Particularly vigorous development of thiacyclohexane chemistry has occurred in the last two decades, as shown by the list of literature references quoted in this review. Major advances have been achieved in the development of synthetic methods in the synthesis of derivatives (sulphoxides, sulphones, sulphamides, sulphonium salts, and oxosulphonium salts), and in the study of the reactions and stereochemical characteristics of the structures of both the sulphides themselves and their derivatives. Whereas the original development of this field was in many respects due to the problem of the identification and utilisation of petroleum sulphides,[1,2] the shift of recent studies towards stereochemistry indicates the undoubted theoretical interest of the condensed thiacyclohexanes, primarily as thioanalogues of decalin. At the same time the search among them for substances with properties of practical value holds out much promise. It is known that certain derivatives of sulphoxides have been recommended as surfactants, flotation agents, oxidation and corrosion inhibitors, insecticides, solvents, and rare metal extractants.[3-11] The S-methylsulphonium salts play an important role in processes occurring in the living organism.[12] Among sulphonium salts, biologically active compounds[13] are being sought and thioanalogues of steroids are being synthesised.[14]

II. METHODS OF SYNTHESIS

1. *cis*- and *trans*-2-Thiadecalins derived from 1-(2-Bromoethyl)-2-Bromomethylcyclohexane

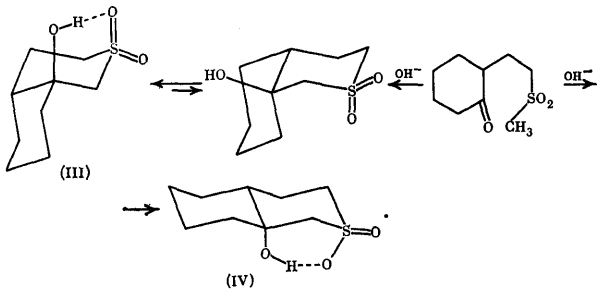
The synthesis of even the simplest condensed thiacyclohexanes is complicated by the fact that each of them can exist in two stereoisomeric forms. The synthesis of *cis*- and *trans*-2-thiadecalins (II) from isothiochroman (I) involves the preparation of 3-oxocyclo[4.4.0]decanes, the resolution of the stereoisomers, their conversion into the dibromides, and their subsequent cyclisation with sodium sulphide[15] (see the formula below).

Together with 1-thiadecalin, 2-thiadecalins (II) have been isolated from petroleum by extraction with an aqueous solution of mercury acetate.[1]

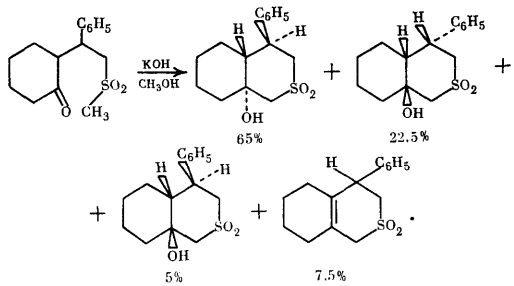


2. The Sulphones of *cis*- and *trans*-9-Hydroxy-2-Thiadecalins derived from 2-(2-Methanesulphonylethyl)cyclohexanone

The intramolecular cyclisation of 2-(2-methanesulphonylethyl)cyclohexanone under the conditions of base catalysis proceeds via the α-sulphonylcarbanion and leads to *cis*-9-hydroxy-2-thiadecalin 2,2-dioxide (III) and its *trans*-isomer (IV).[16] In the *cis*-isomer the conformation with the axial hydroxy-group is fixed by the intramolecular hydrogen bond:[16]



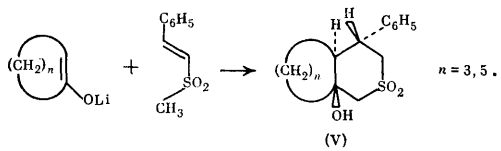
The cyclisation of 2-(α-methanesulphonylmethyl)benzylcyclohexanone under analogous conditions takes place with formation of 9α-hydroxy-4β-phenyl-*trans*-9β-hydroxy-4α-phenyl-*cis*-, and 9β-hydroxy-4β-phenyl-*cis*--2-thiadecalins 2,2-dioxides† and of the hydration product:[17]



The initial ketosulphones are obtained from 1-pyrrolidino or 1-morpholino-cyclohexene and αβ-unsaturated sulphones.[18] The cyclisation products have been separated by preparative chromatography and the configurational assignments have been made on the basis of ^{1}H NMR and infrared spectra; the *cis*-elimination reactions have also been achieved for the *O*-acetyl derivatives.[16,17]

3. Cyclisation of the Lithium Enolates of Cycloalkanes and Methyl Styryl Sulphone

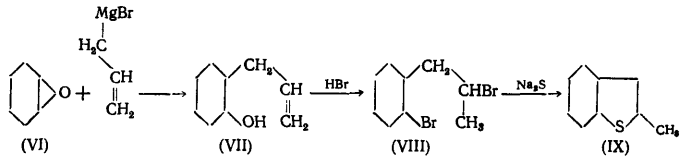
Derivatives of sulphones of 2-thiadecalin and its analogues, differing in the size of the condensed alicyclic 3-thiabicyclo-[4.3.0]nonane and 3-thiabicyclo[4.5.0]undecane# can be obtained by cyclising methyl styryl sulphone with the lithium enolates of cycloalkanes on heating in the 1:2 tetrahydrofuran (THF)–dimethylformamide (DMF) mixture. The yields of the final products (V) are 76–100%. The structural assignments have been made by means of ^{1}H NMR:[19]



(V)

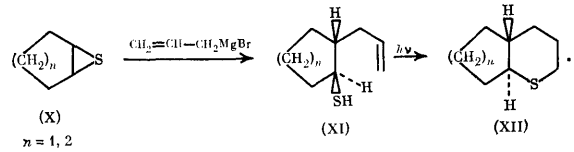
4. *trans*-1-Thiadecalins and *trans*-2-Thiabicyclo[4.3.0]-nonanes derived from Cycloalkene Sulphides and Allylmagnesium Bromides

Up to 1970 it was not possible to synthesise *trans*-1-thiadecalin. It seemed that the same method could be used for its synthesis as that for the synthesis of 2-thiadecalins but the synthesis of the corresponding dibromo-derivatives presents certain difficulties. Thus the interaction of epoxycyclohexane (VI) with allylmagnesium bromide and the subsequent reaction of 2-allylcyclohexanol (VII) with hydrogen bromide lead solely to 1-bromo-2-(2-bromopropyl)cyclohexane (VIII) whose cyclisation with sodium sulphide gives rise to a mixture of stereoisomers of 2-methyl-1-thiahydrindan (IX):[20]



(VI) (VII) (VIII) (IX)

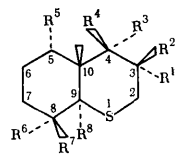
However, later the same workers[21–23] proposed the synthesis of *trans*-1-thiadecalins (XII) by the interaction of cyclo-olefin sulphides (X) with allylmagnesium bromide and subsequent intramolecular cyclisation of the allylcycloalkanethiols (XI) formed in this process:



(X) (XI) (XII)

1-Thiahydrindans or 2-thiabicyclo[3.3.0]octanes arise in the given reaction as side products.[21–23] The cyclisation of 2-allylcyclohexanethiol (XI, n = 2) with formation of a mixture of 1-thiadecalin (XII) and 2-methyl-1-thiahydrindan in proportions of 2:1 has been observed even after its prolonged storage; after ultraviolet irradiation, 1-thiadecalin is formed in a large amount, while on treatment with 75% sulphuric acid the product is 2-methyl-1-thiahydrindan. When crotylmagnesium bromide is used, a mixture consisting of two pairs of isomers, namely those of 4-methyl- 1-thiadecalin and 2,3-dimethyl-1-thiahydrindan, is formed in the same reaction.[22]

Despite the difficulties indicated, associated with the formation of side products, it has been possible to obtain 1-thiadecalin,[21] 4-methyl-1-thiadecalin,[22] 9-methyl-1-thiadecalin,[23] and 2-thiabicyclo[4.3.0]nonane.[24] Although the configurations of the intermediate and final products have not been investigated, the above sulphides have been described as the *trans*-isomers on the assumption that reactions involving the ring opening in the *cis*-sulphides are stereospecific and are accompanied by the formation of mercaptans with the *trans*-configuration, while no change in configuration takes place in the heterocyclisation reaction.[23] This hypothesis proved to be correct. The method proposed[21–23] has been used in another study[25] for the synthesis of 3-, 4-, 5-, 8-, and 9-monomethyl-substituted *trans*-1-thiadecalins (XII)–(XX); their configurations as well as the configurations of the initial sulphides and intermediate *trans*-2-allylcyclohexanethiols have been established by ^{13}C NMR.



(XII) all R = H; (XIII)*R^1 = 3α-CH_3; (XIV) R^3 = 3β-CH_3; (XV) R^3 = 4α-CH_3; (XVI) R^4 = 4β-CH_3; (XVII) R^5 = 5α-CH_3; (XVIII) R^6 = 8α-CH_3; (XIX) R^7 = 8β-CH_3; (XX) R^8 = 9-CH_3.

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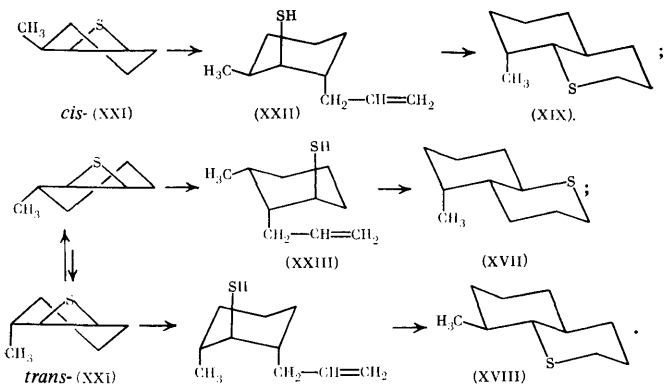
† The symbol β denotes substituents located on the same side of the ring as the hydrogen atom at C(10), while the symbol α denotes substituents on the opposite side of the ring in relation to this hydrogen atom.

#Since there is no uniformity in the literature quoted below in the names used for the same compounds, we adopted as a basis the term "thiadecalins" and, in the absence of trivial names, the term "thiabicycloalkanes".

*The substituents R not indicated here and henceforth are H atoms.

It has been shown[25] that the use of azobisisobutyronitrile (0.1 M) as the initiator of the intramolecular radical cyclisation of *trans*-2-allylcyclohexanethiols reduces to a minimum the formation of 1-thiahydrindans and thus leads to better results compared with initiation by ultraviolet irradiation.[21-24]

We shall now consider the stereochemistry of the reaction of 3-methylcyclohexene sulphide (XXI) with allylmagnesium bromide.[25] The reaction of the *cis*-isomer of compound (XXI) is accompanied by the opening of the three-membered ring with formation of compound (XXII) as an intermediate [with the *trans*-configurations at C(1) and C(2)], whose subsequent cyclisation yields only 8β-methyl-*trans*-1-thiadecalin (XIX) (in 90% yield).

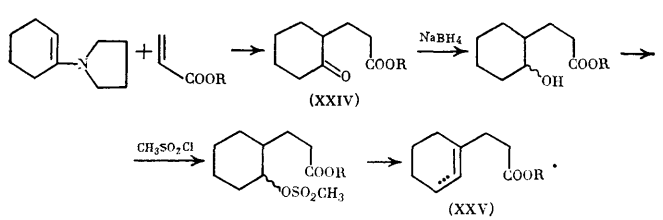


If a mixture of the *cis*- and *trans*-isomers of compound (XXI) (38 and 62% respectively) is used in the reaction, then the same thiadecalin (XIX) (63%) is obtained as the main product after cyclisation despite the fact that *trans*-(XXI) predominated in the initial mixture. By virtue of its greater stability, *trans*-(XXI) reacts with allylmagnesium bromide only partially and only two products, (XVII) and (XVIII), are formed from it in comparable amounts (11 and 13%). The attack on the preferred conformer of *trans*-(XXI), leading to compound (XVII), is probably difficult for steric reasons.[25]

The *trans*-1-thiadecalins (XIII) and (XIV), arising in the cyclisation of the corresponding mercaptans, have been detected in proportions of 1:30, which can be accounted for by the addition of the thiol to the double bond in the *trans*-position in the usual manner.[25]

5. The *cis*- and *trans*-1-Thiadecalins derived from 3-(2-Oxocyclohexyl)propionates

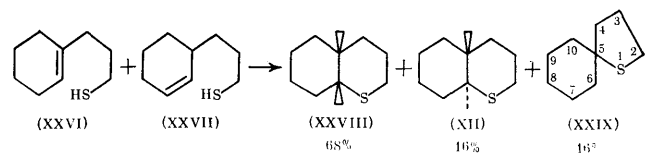
Method (a). It is known[26] that the condensation of pyrrolidinocyclohexenes with acrylates leads to 3-(2-oxocyclohexyl)propionates (XXIV), which can be converted into the isomeric 3-cyclohex-1-enyl or 3-cyclohex-2-enyl propionates (XXV):[25,27,28]



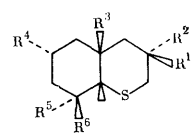
The latter are converted into 1- and 3-(3-mercaptopropyl)-cyclohexenes in accordance with the scheme[14,25]

$$-COOR \xrightarrow{LiAlH_4} -CH_2OH \xrightarrow{CH_3SO_2Cl} -CH_2OSO_2CH_3 \xrightarrow[KSCN]{} -CH_2SCN \xrightarrow{LiAlH_4} -CH_2SH .$$

The radical heterocyclisation of (3-mercaptopropyl)cyclohexenes (XXVI) and (XXVII) takes place preferentially with formation of *cis*-1-thiadecalins.[21] Thus, on heating with azobisisobutyronitrile in benzene, compounds (XXVI) and (XXVII) give rise to mixtures of *cis*-1-thiadecalin (XXVIII) (68%), *trans*-1-thiadecalin (XII) (16%), and 1-thia-spiro[4.5]-decane (XXIX) (16%). The predominance of the *cis*-1-thiadecalin (XXVIII) in the mixture is associated with the fact that the thioradicals add to cyclohexenes preferentially with formation of axially substituted thiacyclohexanes:[14,25,26,29]

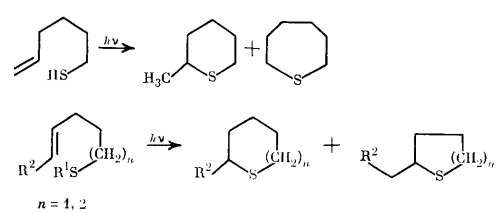


The mixtures of the products (XII), (XXVIII), and (XXIX) were separated by precipitation and recrystallisation of the complexes with $HgCl_2$ and by preparative gas–liquid chromatography (GLC). The configurations of the products were determined with the aid of ^1H and ^{13}C NMR. The 3-, 6-, 8-, and 10-monomethyl-*cis*-1-thiadecalins (XXX)–(XXXV) were isolated and characterised in this way.[25]



(XXVIII) all R = H; (XXX) $R^1 = 3\beta\text{-}CH_3$; (XXXI) $R^2 = 3\alpha\text{-}CH_3$; (XXXII) $R^3 = 10\text{-}CH_3$; (XXXIII) $R^4 = 6\alpha\text{-}CH_3$; (XXXIV) $R^5 = 8\alpha\text{-}CH_3$; (XXXV) $R^6 = 8\beta\text{-}CH_3$.

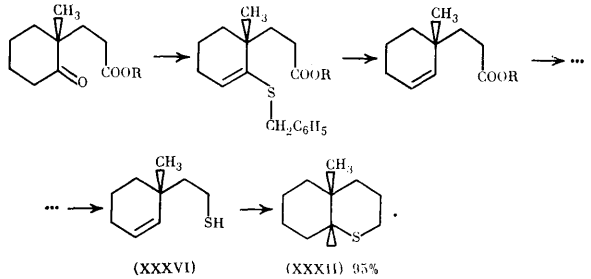
The formation of condensed thiepans can be expected in this reaction on the grounds that the photochemical cyclisation of unsaturated acyclic mercaptans or sulphides yields five-, six-, and seven-membered thiacycloalkanes:[30,31]



However, condensed thiepans were not isolated in the above reaction, which can be accounted for by the high steric requirements of the latter.[25]

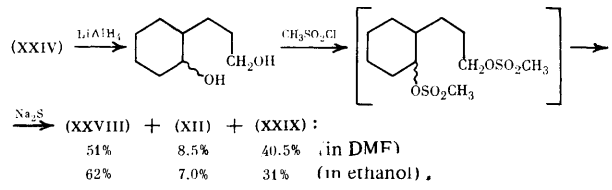
Method (b). A method described previously for 4-thia-5β-cholestanes has been used successfully in the synthesis of 10-methyl-*cis*-1-thiadecalin (XXXII).[14] 3-(1-Methyl-2-oxocyclohexyl)propionate is converted into the *S*-benzyl derivative of the thioenol by heating with benzylmercaptan in benzene. Subsequent desulphurisation of the *S*-benzyl derivative of the thioenol on activated Raney nickel leads to 3-(1-methyl-2-cyclohexenyl)propionate, which, as shown above, is subsequently converted in four stages into the

mercaptan (XXXVI) and is cyclised in the presence of azobisisobutyronitrile into 10-methyl-*cis*-1-thiadecalin (XXXII):[25]



(XXXVI) (XXXII) 95%

Method (c). The reduction of 3-(2-oxocyclohexyl)propionate (XXIV) with lithium aluminium hydride affords a mixture of the *cis*- and *trans*-diols which are treated with methanesulphonyl chloride and are converted, without isolating the bismethanesulphonates, into the *cis*- and *trans*-1-thiadecalins (XXVIII) and (XII) by heating with sodium sulphide in DMF or 50% methanol.[25] This makes it possible to reduce the number of intermediate stages:



(XXIV) → (XXVIII) + (XII) + (XXIX):

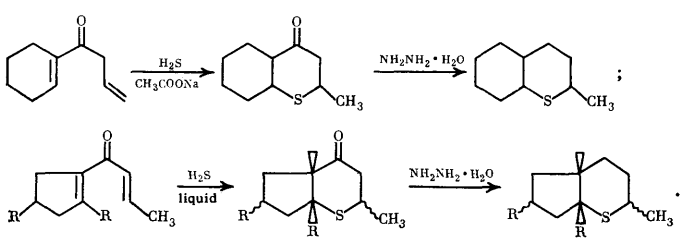
51%	8.5%	40.5%	(in DMF)
62%	7.0%	31%	(in ethanol).

1-Thiaspiro[4.5]decane (XXIX) is formed as a side product in a considerable amount. The methyl-substituted 3-(2-oxocyclohexyl)propionates behave analogously.[25]

The preferential formation of *cis*-1-thiadecalins and spirans of the type of compounds (XXVIII) and (XXIX) in the reaction considered is caused by the ready elimination of the axial methanesulphonyl group with subsequent addition of the mercapto-group to the double bond formed. The overall result of the reaction is very close to that obtained in the cyclisation of 3-(3-mercaptopropyl)cyclohexenes [see methods (a) and (b)].

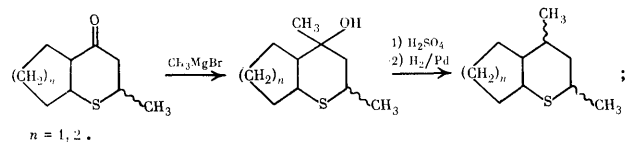
6. 2-Methyl-1-Thiadecalins derived from 2-Methyl-1-Thia-4-Decalones

The initial 2-methyl-1-thia-4-decalones can be synthesised by the familiar reaction of ketodienes with hydrogen sulphide.[32–34] A mixture of the isomers of 2-methyl-1-thia-4-decalone is formed from 1-(3-butenoyl)cyclohexene and hydrogen sulphide in the presence of sodium acetate.[35,36] The keto-group in the thiadecalones can be reduced by hydrazine hydrate with formation of 2-methyl-1-thiadecalins as a mixture of stereoisomers, which is a significant disadvantage of the method as a whole.[37–39] A mixture of the four isomeric 2-methylthiadecalins were separated chromatographically.[39]



2-Thiabicyclo[4.3.0]nonanes are obtained in accordance with an analogous scheme from the corresponding cyclopentene derivatives.[37,38] The cyclisation of ketodienes containing the planar cyclopentane ring proceeds with more difficulty and the introduction of the methyl group into the five-membered ring gives rise to additional steric hindrance. The reaction can be achieved after a considerable increase of the hydrogen sulphide concentration, which is attained by employing liquid hydrogen sulphide. The formation of derivatives of the *trans*-series in the form of five-membered derivatives is virtually ruled out.[37]

The interaction of the above ketosulphides with Grignard reagents makes it possible to synthesise 2,4-dialkyl-2-thiabicycloalkenes:[40]

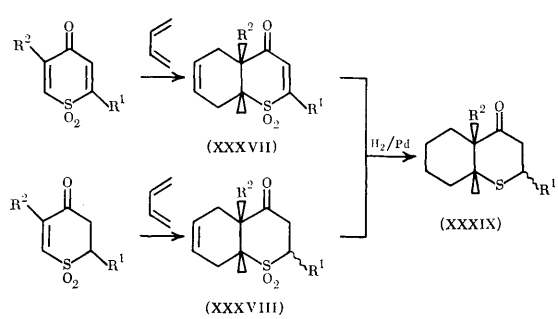


$n = 1, 2$.

Mixtures of 2-thiabicycloalkenes containing the double bond in the α-, β-, and γ-positions relative to the heteroatom are formed from cyclic carbinols on dehydration with sulphuric acid. It has been noted that the hydrogenation of these 2-thiabicycloalkenes in the presence of 5% Pd/C at 50 °C and a hydrogen pressure of 50–70 atm proceeds with difficulty and does not go to completion.[40,41]

7. The Diels–Alder Condensation of Thiopyrone and Dihydrothiopyrone Sulphones with Dienes

The Diels–Alder reaction of 4-thiopyrone and 2,3-dihydro-4-thiopyrone 1,1-dioxides with butadiene constitutes a convenient method of synthesis of the thermodynamically less stable *cis*-isomers. The condensation of 4-thiopyrone 1,1-dioxide with butadiene proceeds slowly even at room temperature, while on heating in an autoclave at 100 °C in dioxan it gives rise to 5,8,9,10-tetrahydrothiochroman-4-one 1,1-dioxide in 40% yield.[42] This method was later employed in other investigations.[36,43] Thus the corresponding oxosulphones (XXXVII) have been obtained from 2-methyl- and 2,5-dimethyl-4-thiopyrone 1,1-dioxides and butadiene. 2,5-Dimethyldihydrothiopyran-4-one 1,1-dioxide gives rise to a mixture of the stereoisomeric products (XXXVIII) differing in the position of the CH_3 group at C(2).[36] 2,3-Dihydrothiopyran-4-one 1,1-dioxide reacts with butadiene in benzene to form the condensation product in quantitative yield:[43]

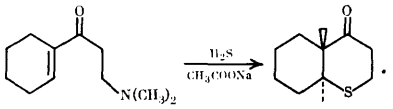


(XXXVII) (XXXVIII) (XXXIX)

The bicyclic sulphones obtained give rise to mixtures of stereoisomers (XXXIX) on reduction in the presence of palladium in dioxan or platinum in an acid medium, incomplete reduction of the keto-group to the hydroxy-group being observed in the latter case.[36] In the presence of acids, the *cis*-isomers of the oxosulphones ($R^2 = H$) isomerise to the corresponding *trans*-isomers as a result of inversion at the C(10) atom in the enolisation process.[43]

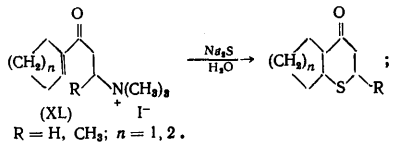
8. Thia-4-Decalones and 2-Thiabicyclo[4.3.0]-5-Nonanones Derived from 1-(3-Dimethylaminopropanoyl)cycloalkenes and Their Methiodides

On reaction with hydrogen sulphide in the presence of sodium acetate and subsequent heat treatment, 1-(3-dimethylaminopropanoyl)cyclohexene cyclises to form *trans*-1-thia-4-decalone (in 50% yield):[44]



1-(3-Dimethylaminobutanoyl)cyclohexene reacts analogously with hydrogen sulphide to form up to 78% of 2-methyl-1-thia-4-decalone.[44]

It has been shown[45] that the methiodides (XL) can be used instead of the Mannich bases. On heating to 50–60 °C in an atmosphere of nitrogen in the presence of sodium sulphide in an aqueous medium, these compounds are converted into 1-thia-4-decalones or 2-thiabicyclo[4.3.0]-5-nonanones:[45]



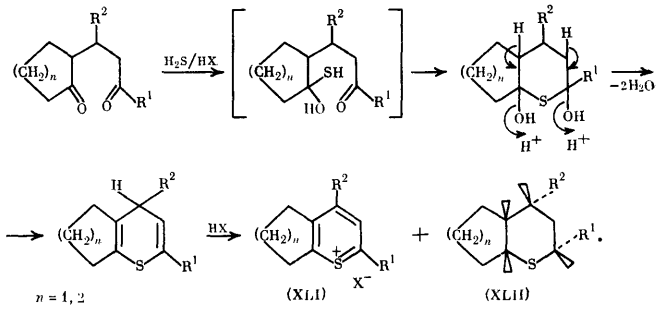
(XL)

$R = H, CH_3$; $n = 1, 2$.

The configuration has been assigned[44,45] only for *trans*-1-thia-4-decalone.

9. Aryl-Substituted *cis*-1-Thiadecalins and 2-Thiabicyclo-[4.3.0]Nonanes

(a) *Synthesis from 1-aryl- and 1,3-diaryl-3-(2-oxocycloalkyl)-1-propanones.* The configurationally and conformationally homogeneous aryl-substituted *cis*-1-thiadecalins and 2-thiabicyclo[4.3.0]nonanes have become available as a result of the reaction of 1-aryl- and 1,3-diaryl-3-(2-oxocycloalkyl)-1-propanones with hydrogen sulphide in acid media.[46–49] On interaction with hydrogen sulphide in the presence of acids at room temperature, the 1,5-diketones ($R^1 = Ar$) undergo heterocyclisation with formation of condensed 4*H*-thiopyrans as intermediates. On treatment with protic acids (fluoroboric,[46] hydrobromic,[47,48] hydrochloric,[48] and trifluoroacetic[49]), the latter disproportionate to form the corresponding 2-aryl-5,6-polymethylenethiopyrylium salts (XLI) and 3-aryl-2-thiabicyclo[4.3.0]nonanes or 2-aryl-*cis*-1-thiadecalins (XLII, $R^1 = C_6H_5$ or $C_6H_4OCH_3$-4; $R^2 = H$; $n = 1$ or 2) in proportions of 2:1.



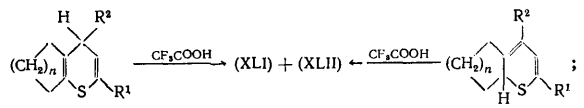
$n = 1, 2$ (XLI) (XLII)

Diaryl-substituted 2-thiabicyclo[4.3.0]nonanes and *cis*-1-thiadecalins ($R^1 = C_6H_5$ or $C_6H_4OCH_3$-4; $R^2 = C_6H_5$ or $C_6H_4OCH_3$-4; $n = 1$ or 2) can be obtained from the corresponding 1,5-diketones only in trifluoroacetic acid, which functions simultaneously as the solvent and a reactant in the above reaction.[49] Complete disproportionation of the intermediate 2,4-diaryl-5,6-polymethylene-4*H*-thiopyrans is not observed in the presence of the other acids enumerated and 3,5-diaryl-2-thiabicycloalkenes, in which an angular double bond is retained, are isolated as the reaction products together with the salts.[47,48]

It has been established by ^1H and ^{13}C NMR that *cis*-1-thiadecalins having the 2α-R^1-4α-R^2-configuration are formed.[50,51] It may be that the aryl-substituted 2-thiabicyclo[4.3.0]nonanes obtained by the same method have the same configuration. Despite the fact that the yields of the required products do not exceed 30%, the presence of only one stage and stereospecificity are undoubted advantages of the method.

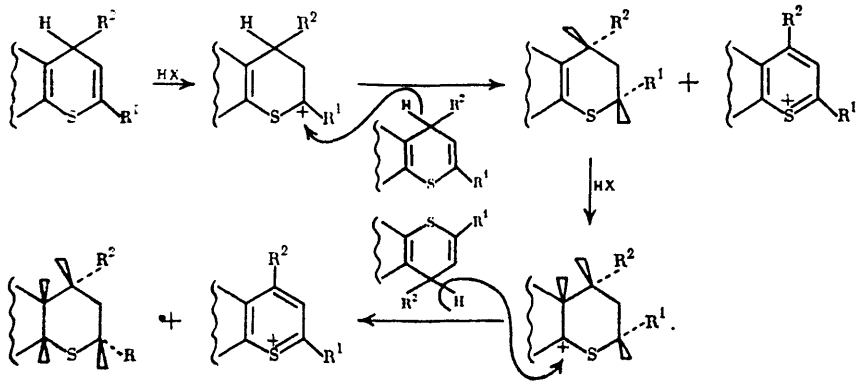
(b) *Disproportionation of 5,6-polymethylene-4H(6H)-thiopyrans and 2-thiabicycloalkenes.* The disproportionation of 5,6-polymethylene-4*H*(6*H*)-thiopyrans as a method of synthesis of condensed thiacyclohexanes can be of independent importance, since the initial compounds of the type stated can be obtained in reactions of 1,5-diketones with hydrogen sulphide in ethanol under the catalytic influence of hydrogen chloride[52] and from 5,6-polymethylenethiopyrylium salts on interaction with Grignard reagents[53] or on reduction with lithium aluminium hydride.[54,55]

2-Aryl and 2-aryl-4R-5,6-polymethylene-4*H*(6*H*)-thiopyrans disproportionate into the trifluoroacetates (XLI) and the thiacyclohexanes (XLII) in the presence of trifluoroacetic acid, which is an effective protonating and solvating agent:[51,56]



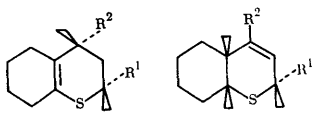
$R^1 = C_6H_5$, $C_6H_4OCH_3$-4; $R^2 = H$, C_6H_5, $C_6H_4OCH_3$-4, $C_6H_3(OCH_3)_2$-3,4, CH_3, C_2H_5, $CH_2C_6H_5$;
$n = 1, 2$; $X^- = CF_3COO^-$

Thiadecalins and 2-thiabicyclo[4.3.0]nonanes arise in this reaction as a result of the ionic reduction of thiopyran with participation of a protic acid and with intermolecular transfer of a hydride ion from another thiopyran molecule to the tertiary carbonium ion generated following the protonation of the double bond of the heterocycle, as shown in the scheme below:[49,56]



The sterically less hindered double bond in the 2,3-position is reduced first in 4*H*-thiopyrans and this is followed by the reduction of the angular double bond. The same *cis*-1-thiadecalins or 2-thiabicyclo[4.4.0]nonanes are obtained from the 6*H*-isomers as from the 4*H*-isomers. The mechanism of the disproportionation of the 6*H*-isomers has been described.[56]

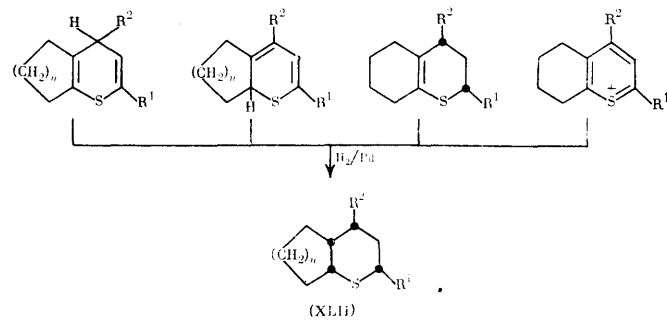
The degree of disproportionation of 5,6-polymethylene-4*H*(6*H*)-thiopyrans depends on the degree of their substitution and the nature of the protic acid. The reduction of only one double bond of the heterocycle with formation of thiabicycloalkenes is observed for the 2,4-diaryl-substituted derivatives in reactions with perchloric, hydrochloric, hydrobromic, and fluoroboric acids.[48,54]



By virtue of the hydride mobility of the α-hydrogen atoms, the condensed dihydrothiopyrans obtained in this way can also disproportionate on refluxing in trifluoroacetic acid, producing thereby thiopyrylium salts and thiacyclohexanes in proportions of 1 : 2.[57,58]

(c) *The ionic hydrogenation of 5,6-polymethylene-4H(6H)-thiopyrans and 2-thiabicyclo[4.4.0]decanes.* The reduction of the above bicyclic sulphides with trifluoroacetic acid and triethylsilane with sulphide : silane : acid ratios of 1 : 3 : 5 makes it possible to synthesise quantitatively 2α-R^1-4α-R^2-*cis*-1-thiadecalin (XLII).[51] Like disproportionation, the ionic reduction of 5,6-polymethylene-4*H*(6*H*)-thiopyrans and 2-thiabicycloalkenes gives rise to 2-thiabicycloalkanes having exclusively the *cis,cis,cis*-configuration.

(d) *The liquid-phase hydrogenation of condensed 4H(6H)-thiopyrans, dihydrothiopyrans, thiopyrylium salts, and 4H-thiopyran 1,1-dioxides.* Aryl-substituted 1-thiadecalins and 2-thiabicyclononanes of type (XLII) are formed on hydrogenation of the corresponding unsaturated heterocyclic compounds in the presence of 10% Pd/C. The *cis*-addition of hydrogen to the multiple bonds has been noted:



(XLII)

Thiopyrans and dihydrothiopyrans are hydrogenated at 100 °C at an initial hydrogen pressure of 50 atm,[48,49] while the reduction of 2,4-diphenyl-5,6-tetramethylenethiopyrylium tetrafluoroborate requires more severe conditions (a temperature of 100 °C and a hydrogen pressure of 100 atm).[60] The yields of the thiacyclohexanes (XLII) obtained from thiopyrans and dihydrothiopyrans are 75–80%, while the yields of the same compounds derived from 5,6-polymethylenethiopyrylium salts are 60%.

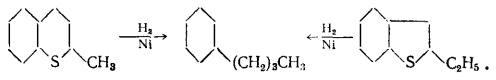
The hydrogenation of 5-oxo-2,4-diphenyl-5,6,7,8-tetrahydrothiochromene and 2,4-diphenyl-5,6-tetramethylene-4*H*-thiopyran 1,1-dioxide under the same conditions (100 °C, 50 atm) in the presence of 10% Pd/C involves the reduction of only the double bonds of the heterocycle, while the sulphonyl and carbonyl groups are unaffected.[61,62]

III. STRUCTURE AND PROPERTIES

The complexes with mercury(II) chloride, sulphoxides, sulphones, sulphimides, sulphonium salts, and ylides constitute the traditional list of derivatives of open-chain sulphides or saturated cyclic sulphides. The properties of condensed thiacyclohexanes have much in common with those

of the sulphides but any chemical reactions are very intimately related with the stereochemistry of these interesting systems. The stereochemical aspects of their study has in fact assumed a special importance in recent times.

The desulphurisation reaction in the presence of Raney nickel, which is widely used in the study of sulphides of of petroleum origin, has found hardly any applications in the chemistry of condensed thiacyclohexanes, namely as a result of the complexity of the system and the development of modern methods (^{1}H and ^{13}C NMR). The desulphurisation of condensed cyclic sulphides frequently does not even allow a conclusion concerning the size of the heterocycle[2] let alone the stereochemical features of the structure:



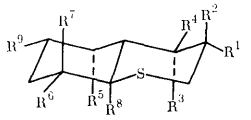
1. Complexes with Bivalent Mercury Salts

Another reaction, which has long been regarded as traditional in the study of sulphides, involves interaction with mercury salts and is used to isolate and identify thiacyclohexanes. Complexes of *cis*- and *trans*-1-thiadecalins, their alkyl derivatives, and 2-thiabicyclo[4.3.0]nonane with mercury(II) chloride, having the composition $R_2S.HgCl_2$, have been described.[21,22,24,25]

2. The Stereochemistry of *cis*- and *trans*-1-Thiadecalins

The study of the ^{13}C and ^{1}H NMR spectra of a large number of unsubstituted and methyl-substituted *cis*- and *trans*-1-thiadecalins permitted configurational and conformational assignments.[63] The signals were assigned by the method of double resonance, the parametrisation of the effects of substituents, and comparison with C- and N-analogues. The thiadecalins investigated were synthesised as described by Claus and Vierhapper.[25]

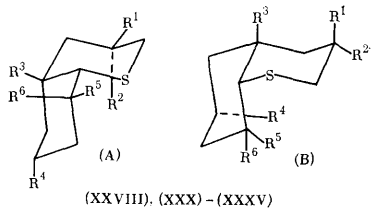
trans-1-Thiadecalins (XII)–(XX) are conformationally rigid systems for which ring inversion is ruled out. The nine expected signals have been detected in the ^{13}C NMR spectrum of *trans*-1-thiadecalin (XII). Analogous data have been obtained for methyl-substituted *trans*-1-thiadecalins. Without dwelling on the discussion of the spectra, which can be found in another communication,[63] one should note that the signals of the axial methyl groups in the spectra of the sulphides are to higher field than those of the equatorial CH_3 group. The lowest-field signals correspond to the C(9) and C(10) atoms.



(XII) – (XX)

Table 1 presents the parameters of the ^{13}C NMR spectra of unsubstituted *cis*- and *trans*-thiadecalins and some of their derivatives.[63,67,69,81,92]

At 30 °C the *cis*-1-thiadecalin (XXVIII) undergoes slow inversion, as shown by the broadening of five of the nine signals in the ^{13}C NMR spectrum. Two groups of signals are observed in the spectrum at −70 °C and can be assigned to conformers (A) and (B) (in proportions of 58:42).[63]

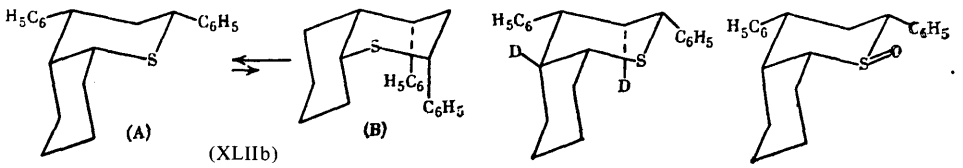


(XXVIII), (XXX) – (XXXV)

The ^{13}C NMR spectra of methyl-substituted *cis*-1-thiadecalins, namely the 3β-CH_3-derivative (XXX), the 10-CH_3-derivative (XXXII), and the 8β-CH_3-derivative (XXXV), also indicated the presence of two conformers. The conformational equilibrium has been investigated by low-temperature ^{13}C NMR.[63] Table 2 lists the ratios of the conformers, the equilibrium constants K, and the free energy differences ΔG^0.

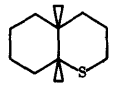
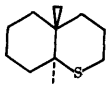
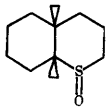
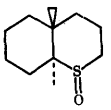
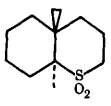
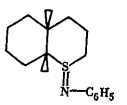
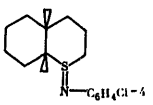
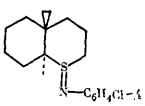
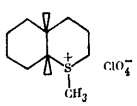
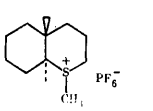
The 3α-CH_3-derivative (XXXI), the 6α-CH_3-derivative (XXXIII), and the 8α-CH_3-derivative (XXXIV) of *cis*-1-thiadecalin are conformationally homogeneous at room temperature, the first existing in the (B) conformation and the other two in the (A) conformation, in which the *syn*-axial interactions between the substituent and the methylene groups of the ring have been reduced to a minimum. For example, the (B) conformation is ruled out for the sulphide (XXXIV) by two *syn*-axial interactions of the CH_3 group with C(2) and C(4); in contrast to this, in the (A) conformation there is only one *gauche*-interaction of the CH_3 group in the heteroatom.

The configurational and conformational assignments for 2,4-diphenyl-1-thiadecalin, obtained as described in a number of communications,[49,56,59] have been made on the basis of the ^{1}H NMR study (80 MHz) of the disulphide itself, its 3,10-dideuterio-derivative, and the 1-oxide in the presence of $Eu(dpm)_3$.[50] It has been established that the disulphide has the *cis,cis,cis*-configuration and exists in the (A) conformation owing to the destabilisation of the other conformer by the *syn*-axial interaction of the phenyl groups with one another and with C(6) and C(8).



(XLIIb)

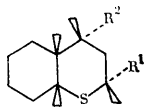
Table 1. ^{13}C NMR parameters of *cis*- and *trans*-1-thiadecalins and some derivatives in $CDCl_3$.

Compounds	Configuration and conformation*	T, °C	Chemical shifts δ, p.p.m.**									Refs.
			C (2)	C (3)	C (4)	C (5)	C (6)	C (7)	C (8)	C (9)	C (10)	
	*cis*-A *cis*-B	−70 −70	29.92 23.59	21.10 28.28	32.50 24 92	24.40 34.22	26.69 19.61	28.88 28.28	31.86 27.34	43.11 40.41	36.01 36.75	[63]
	*trans*-	30	30.04	28.23	34.40	34.56	26.34	26.76	32.58	47.01	44.27	[63]
	*cis*-A (β) *cis*-B (β)	−50 −50	51.48 40.25	19.09 15.68	31.22 25.90	25.25 32.11	27.36 20.46	20.63 27.36	26.20 21.48	64.65 56.22	38.72 23.40	[67]
	*trans*-(β) *trans*-(α)	+30 +30	46.45 51.47	15.71 21.75	32.89 32.89	33 84 33.14	25.53 25.39	26.06 25.45	27.74 27.01	59.57 67.11	31.27 38.74	[69]
	*trans*-	+30	51.59	23.15	32.06	32.78	24 78	25.17	20.29	65.06	39 83	[69]
	*cis*-A (β)	−45	48.44	19.95	30.80	(25.54)	27.13	21.19	(25.96)	63.57	32.23	[67]
	*cis*-B (α) *cis*-A, B (β) *cis*-A	30 30 −69	38.80 47.79 48.04	(23.36) 19.70 19.32	(23.07) 30.34 30.60	32.56 25 61 (25.53)	20.78 27.97 26.97	25.95 21.81 21.16	16.34 25.61 (25.79)	54.37 63.25 63.84	35.38 37.44 38.05	[81]
	*trans*-(α) *trans*-(β)	30 30	48.55 43.67	22.94 16.49	32.37 32.66	33.34 34.07	(25.54) (25.86)	(25.28) (25.24)	27.62 28.11	66.55 59.46	40.03 31.75	[81]
	*cis*-B (α) *cis*-A (β) *cis*-B (β)	+70 −68 −68	34.38 40.00 29.82	23.45 18.29 18.12	23.85 29.82 22.10	33.59 (25.75) 32.55	19.47 (25.94) 19.67	26.43 20.91 26.77	20.27 26.77 24.47	49.48 57.13 48.49	35.97 36.41 27.93	[92]
	*trans*-(α) *trans*-(β)	−30 +30	41.32 36.41	23.35 16.10	31.84 30.80	33.82 33.94	(25.48) (25.43)	(25.81) (26.75)	28.52 28.69	58.83 52.50	40.30 34.42	[92]

*β denotes that the substituent is located on the same side of the ring as the carbon atom at C(10) and α denotes that it is located on the opposite side of the ring relative to the hydrogen atom at C(10).
**The chemical shifts whose assignment is tentative are given in brackets.

In order to establish the configurations and preferential conformations, a study has been made of the ^{13}C NMR spectra at room temperature for 2-aryl- and 2,4-diaryl-1-thiadecalins (XLII) obtained in the disproportionation reactions and as a result of the ionic hydrogenation of condensed 2-aryl- and 2,4-diaryl-5,6-tetramethylene-4*H*(6*H*)-thiopyrans and the corresponding dihydrothiopyrans and also as a result of their hydrogenation. The signals were assigned with the

aid of spectra with incomplete decoupling from the protons and by comparing the experimental and theoretical spectra; the latter were calculated using the known parameters of the ^{13}C NMR spectra of unsubstituted *cis*- and *trans*-1-thiadecalins[63] and the increments for the equatorial phenyl group in the substituted cyclohexane.[64]



(XLII)

(a) $R^1 = C_6H_5$, $R^2 = H$; (b) $R^1 = R^2 = C_6H_5$; (c) $R^1 = C_6H_5$, $R^2 = C_6H_3OCH_3$-4; (d) $R^1 = C_6H_3OCH_3$-4, $R^2 = C_6H_5$; (e) $R^1 = C_6H_5$, $R^2 = C_6H_3(OCH_3)_2$-3,4

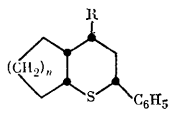
Table 2. Conformational transitions in mobile *cis*-1-thiadecalins*.[63]

Compound	(A), %	(B), %	K	ΔG^0, kcal mol^{-1}
cis-1-Thiadecalin (XXVIII)	58	42	1.4	+0.14
3β-Methyl-*cis*-1-thiadecalin (XXX)	95	5	19	+1.2
10-Methyl-*cis*-1-thiadecalin (XXXII)	33	67	0.49	−0.29
8β-Methyl-*cis*-1-thiadecalin (XXXV)	17	83	0.23	−0.65

*In $CHCl_3$ at −68 °C.

Compounds (XLII, a–e) belong to the *cis*-1-thiadecalin series. They all have the 2α-R^1-4α-R^2-configuration at C(2) and C(4) and are distinguished by a conformational rigidity, as already noted above for the sulphide (XLIIb).[50,51]

The dipole moments of certain aryl-substituted *cis*-1-thiadecalins (XLII, a, b, and e) and also 2-thiabicyclo[4.3.0]-nonanes (XLIIf, R = H) and (XLIIg, R = C_6H_5), measured by the Debye method in benzene at 20 °C, have been published.[65] The dipole moments vary from 1.51–1.96 D:



(XLII, a, b, e–g)

R	n	μ, D	n	μ, D
H	1	1.63	2	1.91
C_6H_5	1	1.51	2	1.82
$C_6H_3(OCH_3)_2$-3,4	—	—	2	1.96

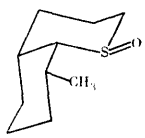
The scheme shows that the dipole moments of the corresponding 2-thiabicyclo [4.3.0]nonanes are smaller by 0.28–0.31 D than those of the *cis*-1-thiadecalins with the same substituents. On the other hand, a slight decrease (0.008 D) has been noted on passing from saturated systems to 5,6-polymethylene-4*H*-thiopyrans, which may be an indication of the equatorial position of the substituent. This is consistent with the structure of the aryl-substituted *cis*-1-thiadecalins (XLII, a–e) (with the aryl group in the equatorial position) and suggests that the aryl-substituted 2-thiabicyclo[4.3.0]nonanes have an analogous structure.

3. Sulphones and Sulphoxides

(a) *Methods of synthesis.* Certain sulphones have already been described above in the discussion of the methods of synthesis, since their formation uses sulphonyl-containing compounds as the starting materials for the synthesis of the heterocyclic system. The oxidation of condensed thiacyclohexanes, like that of thianes, results in the formation of *S*-oxides or, in the presence of an excess of the oxidant, of *SS*-dioxides. The oxidants employed are hydrogen peroxide,[21,22,24,38,66] *m*-chloroperbenzoic acid,[25,67] and t-pentyl hydroperoxide in the presence of MoCl or $Mo(CO)_6$.[68] The sulphones of 1-thiadecalin,[21,69] 4-methyl-1-thiadecalin,[22] 2-thiabicyclo[4.3.0]nonane,[24] 4-hydroxy-2-methyl-1-thiadecalin,[68] 2-methyl-1-thiadecalin,[68] 3-aryl- and 3,5-diaryl-2-thiabicyclo[4.3.0]nonanes,[59] and 2-aryl- and 2,4-diaryl-*cis*-1-thiadecalins[59] and the sulphoxides of 2-methyl-1-thiadecalins,[38,68] 6-methyl- and 8-methyl-*cis*-1-thiadecalins,[25] and 2-aryl- and 2,4-diaryl-*cis*-thiadecalins[49] have been described in the literature.

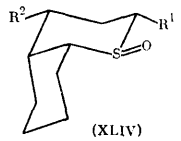
The sulphoxides with the α- and β-configurations are obtained in 55% yield by the oxidation of *trans*-1-decalin with a calculated amount of *m*-chloroperbenzoic acid.[69] A 79 : 21 mixture of the diastereoisomeric *cis*-1-thiadecalin 1-oxides with the α- and β-configurations is formed under identical conditions. The pure *cis*-1-thiadecalin 1β-oxide has been isolated by crystallising the crude product from an ether–petroleum ether mixture (yield 56%).[67]

The oxidation with *m*-chloroperbenzoic acid of the conformationally rigid 6α-methyl-*cis*-1-thiadecalin (XXXIII) and 8α-methyl-*cis*-1-thiadecalin (XXXIV), which exist in the (A) conformation,[63] leads solely to the β-sulphoxides in yields up to 90%, while the formation of the α-sulphoxides is ruled out by the powerful *syn*-axial interaction,[25,63] for example:



(XLIII) $S\alpha-CH_3$.

The formation of the sulphoxide having the β-configuration (with an equatorial S–O bond) is observed in the oxidation of the conformationally rigid 2α, 4α-diphenyl-*cis*-1-thiadecalin (XLIIb) with a calculated amount of hydrogen peroxide.[50] The sulphoxides (XLIV, a–d) have been obtained analogously and, although the configuration of the sulphur atom has not been assigned, one can state with confidence that the sulphinyl group in these compounds is equatorial:[49]

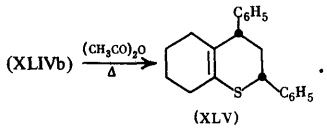


(XLIV)

(a) $R^1 = C_6H_5$, $R^2 = H$; (b) $R^1 = R^2 = C_6H_5$; (c) $R^1 = C_6H_5$, $R^2 = C_6H_4OCH_3$-4; (d) $R^1 = C_6H_4OCH_3$-4, $R^2 = C_6H_5$.

(b) *The Pummerer rearrangement.* Refluxing of 2α, 4α-diphenyl-*cis*-1-thiadecalin 1-oxide (XLIVb) in acetic anhydride under the conditions of the Pummerer reaction

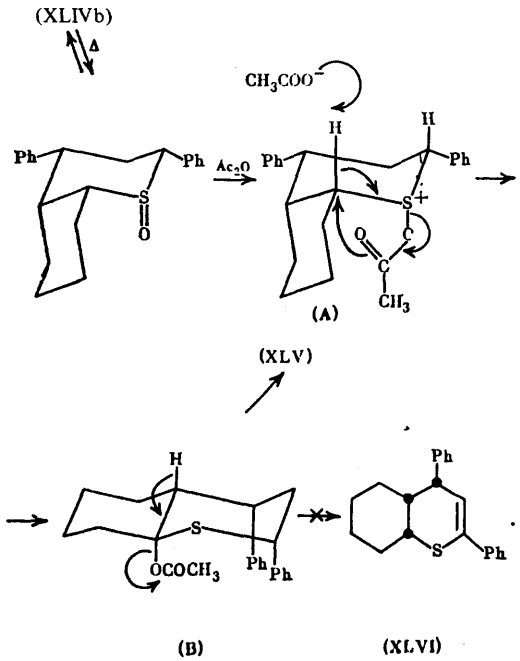
leads to the formation of *cis*-3,5-diphenyl-2-thiabicyclo[4.4.0]-$\Delta^{1,6}$-decane (XLV) as the product of the rearrangement:[70]



(XLV)

The structure of the sulphide (XLV) has been established by X-ray diffraction analysis (XDA). Both phenyl substituents occupy equatorial positions. Both rings have the distorted half-chair conformation.[70]

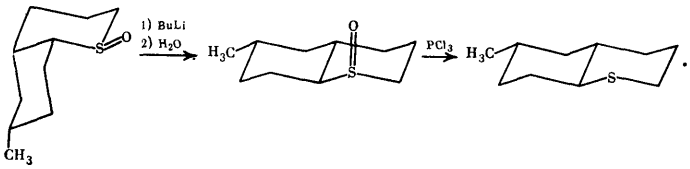
According to the generally accepted mechanism of the rearrangement of acyclic sulphoxides, the second of the two stages (*O*-acylation and deprotonation) is rate-limiting, the ylide formed being stabilised by the 3*d* orbital of the sulphur atom and being attacked by an external acetate anion. Despite the more acid character of the hydrogen atom at C(2) in the onium intermediate (A), the formation of *cis*,*cis*-3,5-diphenyl-2-thiabicyclo[4.4.0]dec-3-ene (XLVI) is not observed in the rearrangement of the sulphoxide (XLIVb):



This justifies the hypothesis that the rearrangement of the onium intermediate (A) to the 9-acetoxy-derivative (B) probably proceeds intramolecularly, as shown in the scheme, and leads to the final product (XLV) via *trans*-elimination. The absence of the isomer (XLVI) from the reaction products shows that the substituents at C(2) offers steric hindrance to the formation of the 2-acetoxy-derivative and hence of the isomer (XLVI).

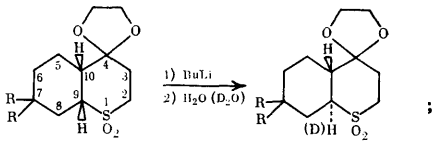
3-Methyl-2-thiabicyclo[4.4.0]dec-3-ene has been obtained under the conditions of the Pummerer rearrangement from a mixture of the four isomeric 2-methyl-1-thiadecalin 1-oxides, with 2β-methyl-*trans*-1-thiadecalins 1-oxide (89%) and 2α-methyl-*trans*-1-thiadecalin 1-oxide (7%) predominating, which should also be accounted for by the sensitivity of the reaction to steric factors.[71]

(c) *The CH-acid properties of sulphones and sulphoxides.* The *cis*,*trans*-isomerisation of sulphones and sulphoxides in the presence of BuLi and the subsequent reduction of the SO group by PCl_3 are used to obtain, for example, 6α-methyl-*trans*-1-thiadecalin, which is obtained in a low yield by other methods:[25,63]

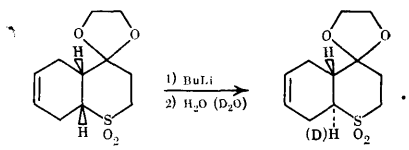


Calculations have shown that the *trans*-isomers of this sulphoxide are more stabel than the *cis*-isomers to the extent of 1.7 kcal mol^{-1}.[72] Their sulphoxide group is axial, as in thian 1-oxides.[73,74] Deuterio-derivatives, for example 9-methyl-*trans*-1-thiadecalin-2,2-d_2-1-oxide, can be obtained by the successive treatment of the sulphoxides with butyllithium and D_2O.[25]

The stereochemistry of the metallation of *cis*-sulphones (XLVIIa, R = H), (XLVIIb, $R_2 = OCH_2CH_2O$), and (XLVIII) by treatment with n-butyl-lithium in benzene at the normal temperature has been investigated. Hydrolysis of lithiosulphones leads to the *trans*-isomers (XLIX) and (L):[43,75]

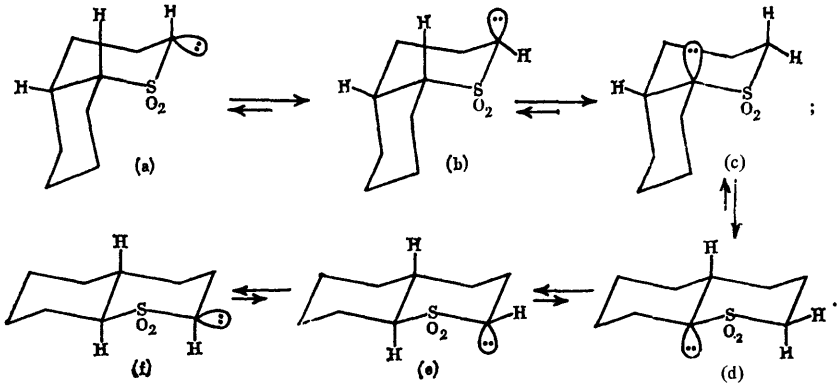


(XLVII a and b) (XLIX, a and b)



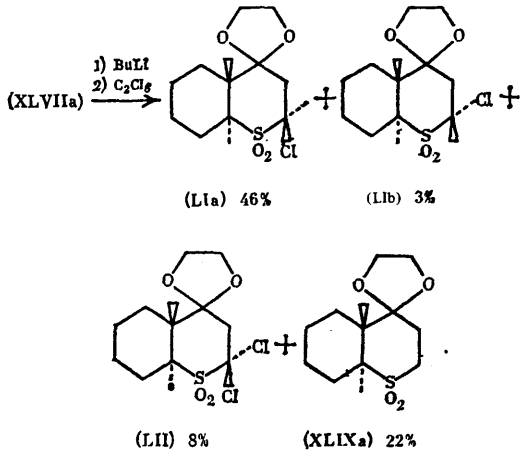
(XLVIII) (L)

The *cis*,*trans*-isomerisation, which involves the inversion of the configuration at C(9), is an intramolecular process, as shown by investigating the reaction using different reactant ratios. The structure of the final products has been confirmed by ^1H and ^{13}C NMR. It has been suggested,[43,75] that BuLi attacks the equatorial hydrogen atom at C(2), the α-sulphonyl carbanion (a) being in equilibrium with the anion (b) having the inverted configuration. Intramolecular proton transfer leads to the anion (c), which is converted into the anion (f) by proton shifts.



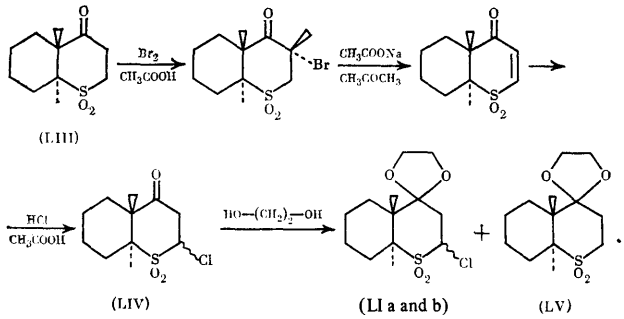
Refluxing of the sulphones (XLVII) and (XLVIII) with NaOD in a D_2O–dioxan mixture for 12 h yields trideuteriated sulphones with retention of the configuration at C(9), which can be explained by the short lifetime of the sulphonyl carbanion in a protic medium compared with the rate of inversion.[43] The mild conditions of the exchange (pH 8.5) in the experiment with the sulphone (XLVIIa) lead to the exchange of only the equatorial H(2) atom, which can be inferred from the disappearance of its signal (δ = 2.87) in the ^{1}H NMR spectrum. This is the first demonstration of a difference between the kinetic acidities of the equatorial and axial hydrogen atoms at C(2) in sulphones of type (XLVII).[43]

Chlorination of the lithiosulphonyl carbanions obtained from the *cis*-sulphone (XLVIIa) with hexachloroethane leads to a mixture of the *trans*-sulphones (LI, a and b), (LII), and (XLIXa). Products containing chlorine at C(9) were not detected:[75]



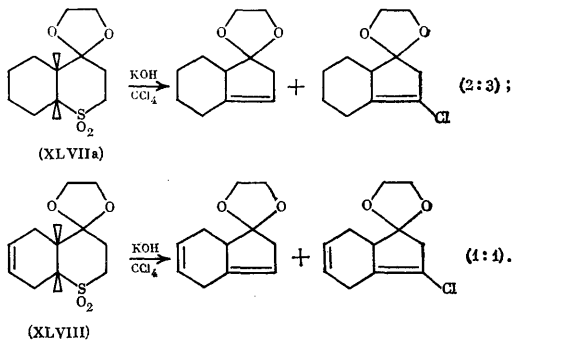
The sulphones (XLVIIb) and (XLVIII) behave analogously under the conditions indicated.

The *trans*-1-thiadecalone 1,1-dioxide (LIII) can be converted into the diastereoisomeric 2-chloro-*trans*-4-thiadecalone 1,1-dioxide (LIV) and further into the acetals (LI, a and b) in accordance with the scheme:



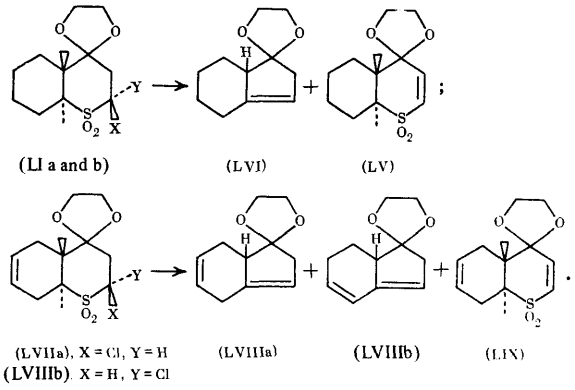
The chloro-derivatives (LI, a and b) are obtained in these reactions in low yields, which makes it preferable to halogenate the lithio-derivatives.[75] In addition, the formation of a considerable amount of the elimination products (LV) has been noted.

(d) *The Ramberg–Bäcklund reaction.* 4,4-Ethylenedioxy-*cis*-1-thiadecalin 1,1-dioxide (XLVIIa) and its unsaturated analogue (XLVIII) are converted via the Ramberg–Bäcklund reaction on treatment with KOH/CCl_4 into the acetals of hydrindenone and their chloro-derivatives:[76]



In the interaction of the α-halogenosulphones (LI, a and b) and (LVII) having the *trans*-configuration with potassium (sodium) t-butyloxide, the Ramberg–Bäcklund reaction can

compete with the 1,2-elimination of the hydrogen halide.[77] The more polar dimethyl sulphoxide (DMSO) favours the Ramberg–Bäcklund reaction while in the less polar dimethoxyethane (DME) the 1,2-elimination reaction predominates. It has been shown that the *trans*-sulphone (LVIIa) gives rise preferentially to the dienes (LVIIIa) and (LVIIIb), the latter as a result of the allyl rearrangement:[77]

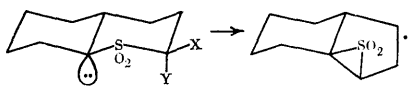


(LI a and b) (LVI) (LV)

(LVIIa), X = Cl, Y = H (LVIIIa) (LVIIIb) (LIX)
(LVIIIb), X = H, Y = Cl

The epimers of the *trans*-sulphones (LVII, a and b) behave differently in the reaction with potassium t-butoxide in DME: the isomer (LVIIa) with an equatorial halogen atom gives rise to the dienes (LVIII, a and b) while the isomer (LVIIb) with an axial halogen atom undergoes 1,2-elimination with formation of the vinyl sulphone (LIX).

It has been established[77] that the Ramberg–Bäcklund reaction, leading to an olefin, proceeds in the case of the *trans*-sulphones with the halogen in the equatorial position (X = Cl, Y = H) via the *Z*-episulphone (the sulphonyl group has the *Z*-configuration in relation to the angular hydrogen atom):

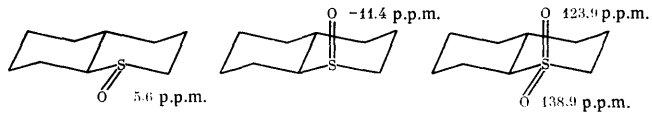


In conclusion one should note that the *cis*-configuration of the initial sulphone is more favourable for the Ramberg–Bäcklund reaction than the *trans*-configuration.[76,77]

(e) *The ^{13}C and ^{17}O NMR spectra of the sulphoxides and sulphones.* The study of the ^{13}C NMR spectrum of *cis*-1-thiadecalin 1β-oxide showed that it exists predominantly (to the extent of 65%) in the equatorial conformation.[67]

The ^{13}C NMR spectra of the 1α-oxide, 1β-oxide, and 1,1-dioxide of *trans*-1-thiadecalin have been described in a communication[69] which discusses the influence of the sulphinyl and sulphonyl groups on the chemical shifts of the carbon atoms (C_β and C_γ). The assignment of the signals to the axial and equatorial conformations of the diasteroisomeric sulphoxides has been based on the difference between the chemical shift of the C_β and C_γ atoms. Thus, of the two diastereoisomeric *trans*-1-thiadecalin 1-oxides, the isomers with the highest-field C_γ shift and the least low-field C_β shift have been assigned to the β-configuration (the S–O bond is axial) (Table 1). Compared with *trans*-1-thiadecalin, the introduction of the sulphonyl group into the molecule leads to the deshielding of the carbon atoms in the β-position [C(3) and C(9)], which can be explained by the influence of the inductive effect of the partially positively charged sulphur atom in the SO group and the β-effect of the oxygen substituent at the sulphur atom.[69]

The ^{17}O NMR spectra of the sulphoxides and the sulphone of *trans*-1-thiadecalin have been investigated. The β-isomer with the axial sulphinyl oxygen atom gives rise to a signal to a higher field than the α-isomer with an equatorial SO group ($\Delta\delta$ = 17 p.p.m.), which constitutes confirmation of the shielding by the γ-*gauche*-interaction with a CH_2 group:[78]

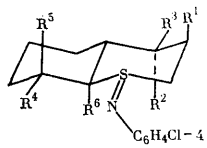


The scheme shows that the sulphonyl oxygen atoms are very highly deshielded compared with the sulphinyl oxygen atoms. The signal of the axial oxygen atom (δ = 123.9 p.p.m.) is in a higher field than the signal of the equatorial atom (δ = 138.9 p.p.m.).[78]

4. The *cis*- and *trans*-1-Thiadecalin 1-*N*-Arylimides

(a) *The synthesis of cis- and trans-1-thiadecalin 1-N-arylimides.* Sulphimides are a new class of thiadecalin derivatives. They can be regarded as isoelectronic analogues of sulphoxides. The methods of their synthesis, the mechanisms of their formation, and their structure and chemical properties have been described.[79–82] The reactions of the *cis*- and *trans*-1-thiadecalins with 4-chloroaniline and a slight excess of *N*-chlorosuccinimide (NCS) or t-butyl hypochlorite lead to the formation of the configurationally homogeneous crystalline *N*-4-chlorophenylsuphimides.[79,80] The sulphimides can be obtained also from the sulphoxides by treatment with P_2O_5 and 4-chloroaniline.[80] The configuration and the preferred conformation (in the case of mobile systems) in the series of *cis*- and *trans*-1-thiadecalin 1-*N*-4-chlorophenylimides have been determined by ^1H and ^{13}C NMR.[81]

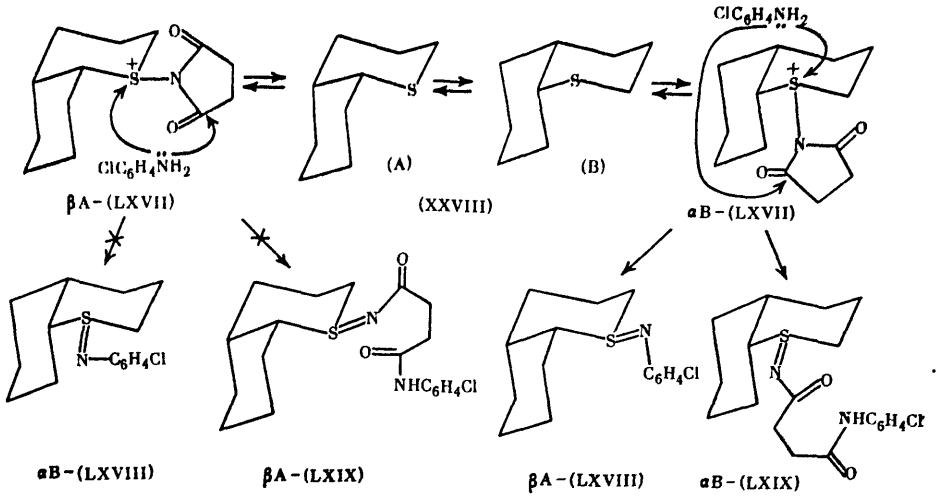
The sulphimides (LX)–(LXVI), having the α-configuration and an equatorial SN bond, have been found to form in the reactions of the *trans*-1-thiadecalins (XII), (XIV)–(XVI), and (XVIII)–(XX) with 4-chloroaniline and NCS or t-butyl hypochlorite.[79–80] The sulphimide α-(LXIV) has been obtained even from 8α-methyl-*trans*-1-thiadecalin (XVIII) despite the unfavourable mutual disposition of the equatorial methyl group and the SN bond.[80]



α-(LX) – α-(LXVI)

(LX): all R = H; (LXI): R^1 = 3β-CH_3; (LXII): R^2 = 4α-CH_3; (LXIII): R^3 = 4β-CH_3; (LXIV): R^4 = 8α-CH_3; (LXV): R^5 = 8β-CH_3; (LXVI): R^6 = 9-CH_3

The conformationally mobile *cis*-1-thiadecalin (XXVIII) reacts with 4-chloroaniline and NCS to form only the sulphimide β-(XLVIII), mainly in the (A) conformation, and the ring-opening product αB-(LXIX) with the α-configuration at the sulphur atom.[79,80] The proposed reaction mechanism is presented below taking into account the preferred conformations of the reaction products:

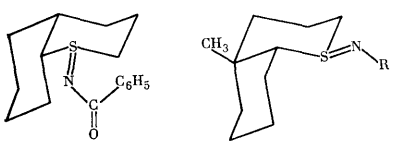


The corresponding succinimidylsulphonium chlorides are probably formed as intermediates. The substitution of the succinimidyl group in αB-(LXVII) by 4-chloroaniline takes place with inversion at the sulphur atom and leads to the sulphimide βA-(LXVIII); the product αB(LXIX) is formed from the same azasulphonium salt in a third reaction when the succinimidyl ring is opened as a result of attack on the carbonyl group, the configuration at the sulphur atom remaining unchanged.[80] The axial attack by 4-chloroaniline on the sulphur atom in the intermediate αB-(LXVII) may be facilitated by the capacity of the compound for inversion in the transition state.

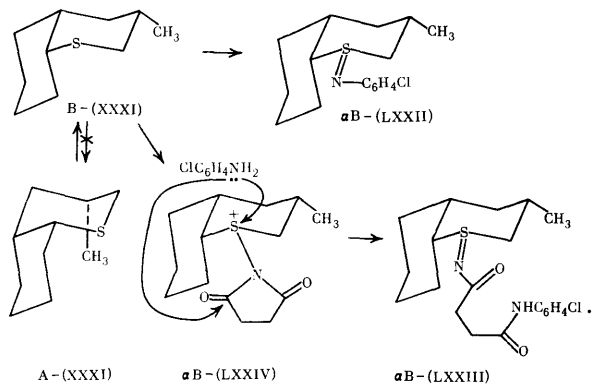
The absence of compounds αB-(LXVIII) and βA-(LXIX) from the reaction products has been explained[80] by the fact that the axial attack in the intermediate βA-(LXVII) should be hindered by the interaction with the methylene groups of the cyclohexane ring [C(5) and C(7)] and the counterion can also give rise to some hindrance. The hypothesis that azasulphonium salts may be formed in the reaction is based on the fact that the dimethyl sulphide and NCS give rise to a crystalline succinimidylsulphonium chloride.[83] Their formation is also indicated by open-chain products of the type of αB-(LXIX), which have been detected in amounts up to 30% in the analogous reactions of methyl-substituted *cis*-1-thiadecalins.

However, the results cannot be satisfactorily explained in terms of the mechanism described in all cases. Thus the reaction of *cis*-1-thiadecalin with *N*-bromobenzamide results in the formation of only benzoyl imide with the α-configuration [αB-(LXX)].

The reaction of 10-methyl-*cis*-1-thiadecalin with 4-chloroaniline/NCS or *N*-bromobenzamide yields in both cases the products (LXXI) with the β-configuration in the (A) conformation, although the initial sulphide itself exists in the (B) conformation to the extent of 67% (at −70 °C):[80]

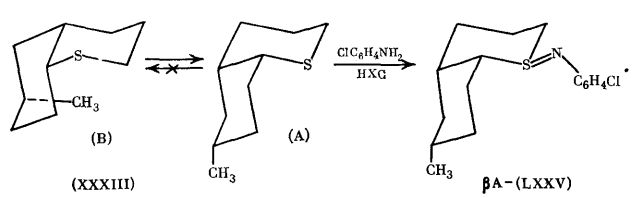


The analogous reaction of 3α-methyl-*cis*-1-thiadecalin (XXXI) led to the isolation of the imide αB-(LXXII) and the products of the ring opening in succinimide αB-(LXXIII) in high yields:[80]

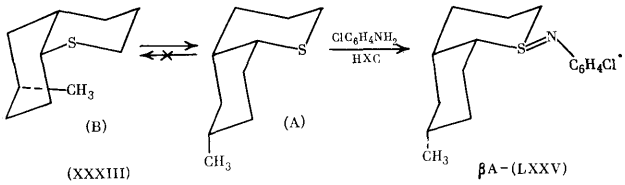


The axial attack on the intermediate αB-(LXXIV) should have led to the β-sulphimide in the (B) conformation with an axial SN bond, because ring inversion in the (A) conformation is prohibited by the *syn*-axial interaction between the CH_3 group and C(5). This attack is evidently less favourable than the competing attack on the azasulphonium salt αB-(LXXIV) at the carbonyl group, which results in the formation of the open-chain product αB-(LXXIII). The formation of the sulphimide αB-(LXXII) must be accounted for differently.

The sulphimide with the βA-(LXXV) configuration is formed in a high yield from 6α-methyl-*cis*-1-thiadecalin (XXXIII) for which ring inversion is forbidden by the *syn*-axial interaction between the methyl group and C(4):[80]



The sulphimide βA-(LXXVI) is obtained in a very low yield from 8α-methyl-*cis*-1-thiadecalins (XXXIV) for which the (A) conformation is preferred by virtue of the strong *syn*-axial interaction between the methyl group and C(2) and C(4):[80]

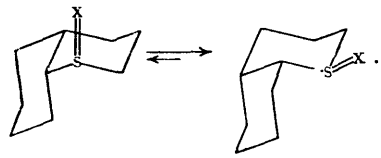


The facts described above do not make it possible to formulate a unique view concerning the mechanism of the formation of sulphimides in the reactions of thiadecalins with 4-chloroaniline and NCS examined above. As shown above, the reactions with alkyl-substituted *cis*-1-thiadecalin are sensitive to changes in the steric requirements and proceed differently with conformationally mobile and conformationally rigid sulphides. In the case of the conformationlly mobile compounds the reaction probably proceeds via the succinimidylsulphonium salts with the subsequent substitution of the succinimidyl component with inversion at the sulphur atom. It has been suggested that the sulphimides with conformationally rigid systems are formed with participation of *N*-chloroaniline, which rapidly reacts with the sulphides, removing them from the equilibrium mixture containing the sulphide, NCS, and the azasulphonium salt. The interaction of conformationally homogeneous *cis*-1-thiadecalins with 4-chloroaniline and t-butyl hypochlorite leads exclusively to sulphimides with an equatorial SN bond.[80] It has been suggested that the reaction in the presence of t-butyl hypochlorite also proceeds via *N*-chloroaniline. However, it is difficult to find a satisfactory explanation why the unsubstituted *cis*-1-thiadecalin (XXVIII) gives rise in this case to sulphimides having the α- and β-configurations in proportions of 1:2, while the reaction with NCS results in the formation of only the β-sulphimide [βA-(LXVIII)]. Finally, the reaction with *N*-bromobenzamide results in the formation of the α-benzoyl imide αB-(LXX).[79,80] The lack of data concerning the pyramidal inversion in *N*-arylsulphimides makes it impossible to infer whether the barrier to inversion is sufficiently low for the latter to play an appreciable role. However, according to the authors,[79,80] the isomerisation reactions accompanying the formation of the SN bond and leading to thermodynamically more stable products should be taken into account.

In contrast to the oxidation of thians to sulphoxides, where both isomers can be synthesised in an almost pure form or as a mixture depending on the oxidant and the oxidation conditions, the formation of sulphimide with an axial SN bond is difficult.[73] On the other hand the inversion of the configuration at the sulphur atom is known to occur in reactions of sulphoxides with arenesulphonylamides.[84,85]

A sulphimide with an axial SN bond has been obtained from *trans*-1-thiadecalin 1α-oxide with an equatorial SO bond on treatment with P_2O_5 and 4-chloroaniline (yield 10%).[80] The low yield of the reaction product can be explained by the fact that the axial attack by 4-chloroaniline on the sulphur atom in the intermediate formed from the sulphoxide and P_2O_5 is again difficult and the formation of a sulphide with an axial SN bond is an unfavourable process.[80]

(b) *The conformational equilibrium.* The conformational equilibrium for *N*-arylsulphimides and the sulphoxide of *cis*-1-thiadecalin has been investigated by the method of low-temperature ^{13}C NMR. The ratio of the equatorial (e) and axial conformers and the difference between their energies ΔG^0 have been determined.[67] The sulphoxide and sulphimides exist preferentially in the equatorial conformation:



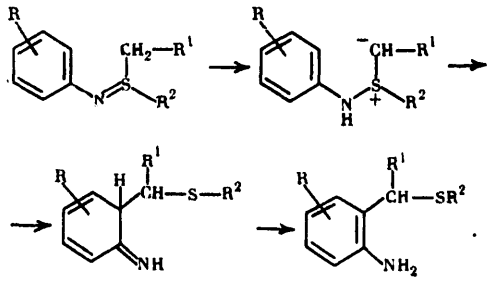
	(*e*), %	ΔG^0, kcal mol^{-1}
X = O	65	0.27
X = NC_6H_4Cl-4	>95	1.3
X = NC_6H_5	>95	1.3

A multiplicity of factors influence the observed conformational equilibrium: the *syn*-axial interactions between the axial substituent at the sulphur atom and the hydrogen atoms at C(3) and C(5), the *gauche*-interactions between the S=X group and the α-hydrogen atoms, the length of the S=X bond, the size of the heteroatom, and the polarity of the bond. At the same time, the interaction in one of the (B) conformations between the methylene groups at C(2) and C(8) is significant in *cis*-1-thiadecalin and its derivatives, which is responsible for some predominance of the (A) conformation in unsubstituted *cis*-1-thiadecalin. In contrast to thian 1-oxide, in which the SO group is preferentially axial, *cis*-1-thiadecalins 1β-oxide exists, as shown above, preferentially in the equatorial conformation, where the unfavourable interaction between C(2) and C(8) is ruled out. The above results for *cis*-1-thiadecalin 1β-oxide, *cis*-1-thiadecalin 1β-*N*-(4-chlorophenyl)imide, and the analogous 1β-*N*-phenylimide do not reveal an appreciable steric *gauche*-interaction of the substituent at the sulphur atom with the α-hydrogen atoms, and indicate at the same time the influence of the polarisation of the SX bond. In the axial conformation the SX group (X = O or N–R) is in the *gauche*-position relative to two C–C and two C–H bonds, while in the equatorial form the SX group is in the *gauche*-position relative to four C–H bonds. The dipole moments induced in these bonds by the S–X dipole should entail an increase of the fraction of the axial conformation with increase of the polarisation of the SX group by virtue of the higher polarisability of the C–C bond. Claus et al.[67] find this explanation to be the most correct.

(c) *The rearrangement of cis- and trans-1-thiadecalin 1-N-arylimides to 2-aryl-1-thiadecalins.* The configurationally and conformationally homogeneous *cis*- and *trans*-1-thiadecalin 1-*N*-(4-chlorophenyl)imides are capable of rearranging to the corresponding 2-(2-amino-5-chlorophenyl)-1-thiadecalins. The configurational assignments for the rearrangement products have been made by means of ^1H NMR.[82]

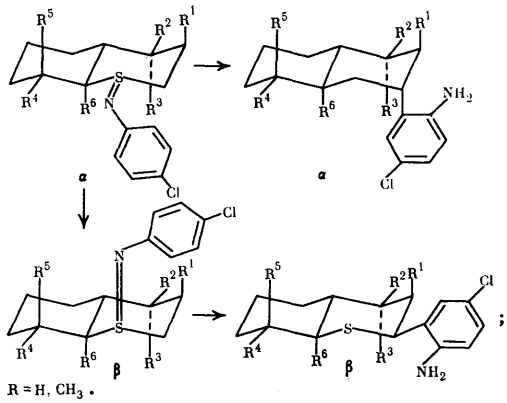
It is known[86–90] that the rearrangement of acyclic sulphimides proceeds via the azasulphonium ylide, which arises as a result of proton transfer to the nitrogen atom. This ylide is converted into cyclohexadienone imine and subsequently into the reaction product via the [2,3]-sigmatropic rearrangement. It has been shown that the rate of the

rearrangement is much higher than the rate of proton transfer:[82]



The rearrangement of 1-thiadecalin 1-*N*-arylimides proceeds with more difficulty than for the open-chain sulphimides and requires more severe conditions (heating in triethanolamine at 100–200 °C).[82] In the series of thiadecalins which are not sterically hindered the rearrangement proceeds with a high degree of stereoselectivity (>95%): sulphimides with an equatorial SN bond give rise to the rearrangement product with an axial aryl substituent, while sulphimides with an axial SN bond give rise to products with an equatorial aryl substituent. The results of the investigation confirm that the rearrangement proceeds via a cyclic transition state.

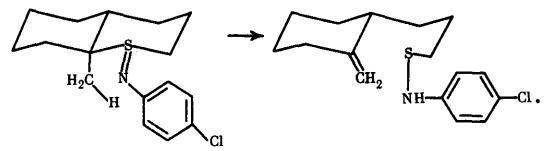
2α-Aryl-*trans*-1-thiadecalins are formed as the main products from the rigid *trans*-1-thiadecalin 1α-imides (with an equatorial bond) together with a smaller amount (<5%) of the 2β-isomers. With increase of the reaction temperature from 100° to 200 °C, the amount of the 2β-isomers increases to 25% (relative to the overall yield).



R = H, CH_3.

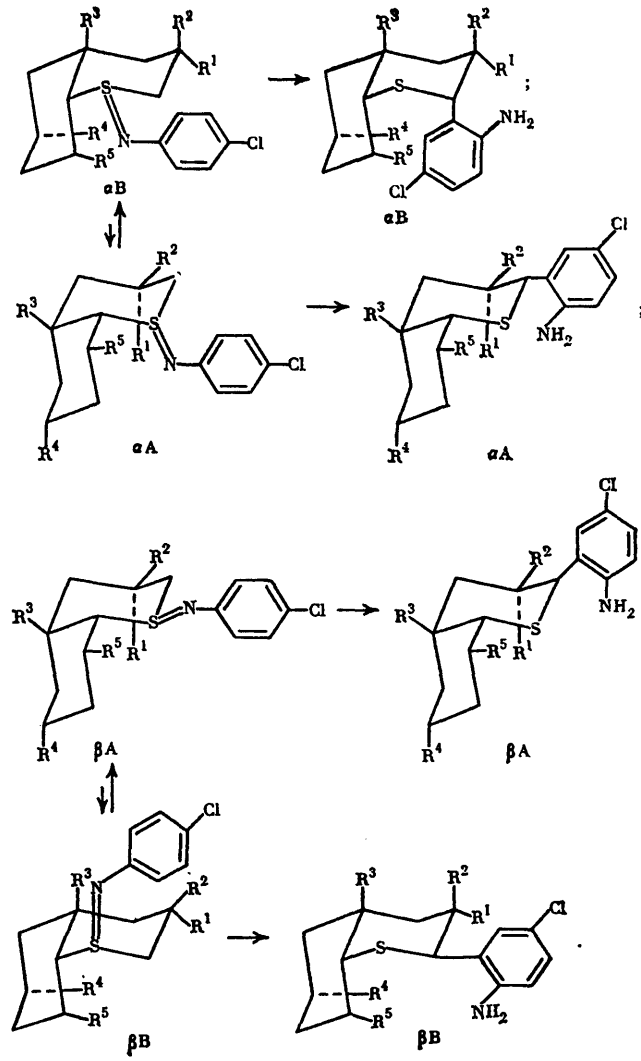
The mechanism of the rearrangement is analogous in broad outline to that of the rearrangement of acyclic sulphimides. However, the cyclic transition state in the formation of 2α-aryl-*trans*-1-thiadecalins from the 1α-imides is undoubtedly attained with more difficulty by virtue of the rigidity of the system and is more strained owing to the steric interaction between the axial hydrogen atoms at C(4) and C(9).[82] This should lead to an increase of the barrier to the rearrangement of the 1α-imide to 2α-aryl-1-thiadecalin compared with the flexible thiacyclohexane imides. In order to explain the formation of 2β-aryl-1-thiadecalines in the reactions considered one must assume the possibility of the inversion 1α-imide ⇌ 1β-imide, the inversion barrier being evidently comparable to the rearrangement barrier. It has been shown that the 1β-imide rearranges more readily to 2β-aryl-*trans*-1-thiadecalin.[82]

An unstable sulphenamide has been obtained from 9-methyl-*trans*-1-thiadecalin 1α-*N*-arylimide on heating in triethanolamine. The methyl group at C(9) in the molecule of the initial sulphenamide occupies an axial position and is close to the α-imide group, which favours the intramolecular proton transfer and the cleavage of the ring with formation of the sulphenamide:[83]



The cleavage and elimination side reactions occur also in other cases, but the indentification of the products is difficult owing to their low stability.[82]

The sulphimides of the unsubstituted and methyl-substituted *cis*-1-thiadecalins having the α- and β-configurations proceed differently under the rearrangement conditions.

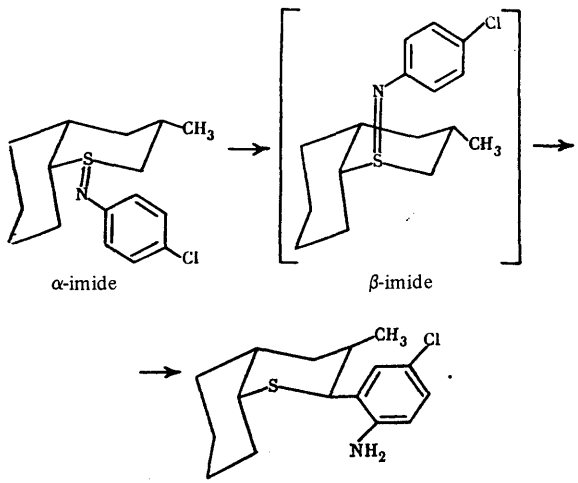


cis-1-Thiadecalin 1β-arylimide give rise to only one rearrangement product with the aryl group in the β-position, whose yield is 60%. The rearrangement of the isomeric

α-imide leads to a mixture of the α- and β-aryl-substituted products formed in proportions of 1 : 2 in an overall yield not exceeding 12%.

In the rearrangement of the α-imides, powerful *syn*-axial interactions between the aryl group and the methylene group in the 8-position must inevitably take place in the transition state, which is the cause of the formation of sulphenamides in a side reaction (the CH_2 group is in the β-position relative to the imide functional group) and of the decrease of the yield of the 2α-aryl-substituted products. The rearrangement product exists preferentially in the conformation with an equatorial aryl group at C(2).

Under the rearrangement conditions, 3α-methyl-*cis*-1-thiadecalin 1α-*N*-arylimide is converted into the 2β-aryl-substituted product, whose formation does not follow from the [2,3]-sigmatropic rearrangement of the initial sulphimide. Under the reaction conditions, the α-imide probably isomerises to the β-imide and the latter undergoes the [2,3]-sigmatropic rearrangement to the 2β-aryl-substituted product:[82]

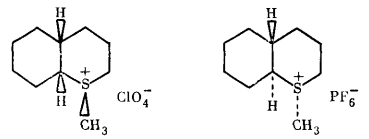


The β-sulphimides of the methyl-substituted *cis*-1-thiadecalins (the 3β-methyl-, 10-methyl-, 6α-methyl-, or 8α-methyl derivatives) give rise to 2β-aryl-substituted products on heating in triethanolamine (in 16–40% yield).

Thus the rearrangement of the *cis*- and *trans*-1-thiadecalin 1-*N*-arylimides proceeds with formation of the C(2)–aryl bond in the *cis*-position relative to the sulphimide functional group in the initial imide, i.e. suprafacially relative to the sulphimide fragment, whereupon assymetry is transferred from the sulphur atom to the C(2) carbon atom. The stereospecificity of the reaction is caused by the rigorous requirement for the retention of the orbital symmetry in the rearrangement.[82] Transfer of the aryl group to the angular position is not observed.

5. The *S*-Methylsulphonium Salts of *cis*- and *trans*-1-Thiadecalins

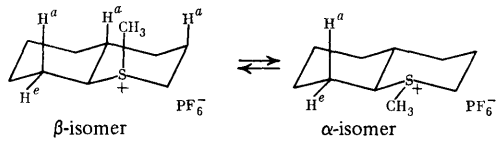
The *S*-methylsulphonium salts of *cis*- and *trans*-1-thiadecalins have been obtained by methylation with methyl iodide (with the subsequent exchange of I^- for ClO_4^-) or trimethyloxonium hexafluorophosphate.[91] 1β-Methyl-*cis*-1-thiadecalinium perchlorate constitutes a conformationally mobile system. The conformational equilibrium has been investigated by ^{13}C NMR at a low temperature in deuterioacetone (the ratio of the equatorial and axial conformers is 3 : 2).[91,92]



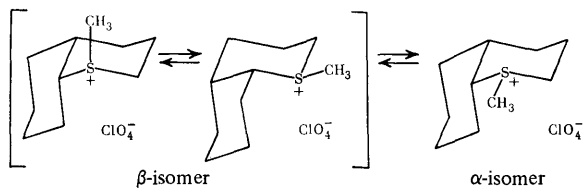
The reaction of *trans*-1-thiadecalin with trimethyloxonium hexafluorophosphate gives rise to the configurationally pure 1α-methyl isomer.[91]

The above *S*-methyl-*cis*- and *S*-methyl-*trans*-1-thiadecalinium salts undergo the pyramidal inversion at the sulphur atom on heating in deuterioacetonitrile, which makes it possible to detect diastereoisomers which are not formed on alkylation, for example, 1α-methyl-*cis*-1-thiadecalinium perchlorate or 1β-methyl-*trans*-1-thiadecalinium hexafluorophosphate.

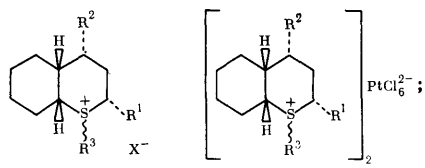
The free energy difference $-\Delta G^0_{SCH_3}$ for the two diastereoisomeric *S*-methyl derivatives of *trans*-1-thiadecalin with the equatorial and axial positions of the SCH_3 groups amounts to 0.80 ± 0.04 kcal mol^{-1}; the isomer with an axial methyl group is evidently destabilised by the *syn*-axial interaction with the hydrogen atoms at C(3), C(10), and C(8):[91,92]



The β-isomer of the *S*-methyl-*cis*-1-thiadecalinium salt exists as an equilibrium mixture of two conformers with the equatorial conformer predominating ($\Delta G^0 = -0.24$ kcal mol^{-1}). When this mixture is heated, the α-isomer is formed as a result of the inversion of the configuration at the heteroatom. The α-isomer of *S*-methyl-*cis*-1-thiadecalinium perchlorate is less favourable to the extent of 1.2 kcal mol^{-1}:[92]



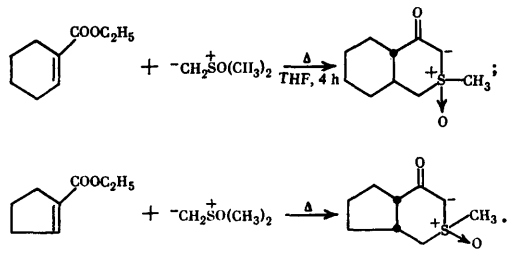
The corresponding sulphonium salts are obtained by alkylating 2α, 4α-diaryl-*cis*-1-thiadecalins with bromoacetic acid, methyl chloroacetate, acrylic acid, or methyl acrylate in the presence of hydrogen chloride.[13] The alkylation reaction usually yields a mixture of diastereoisomers with one of them predominating, but the configuration of this sulphur atom has not been determined:



$R_3 = CH_2COOH$, CH_2COOCH_3, CH_2CH_2COOH, $CH_2CH_2COOCH_3$; $X^- = Cl^-$, ClO_4^-.

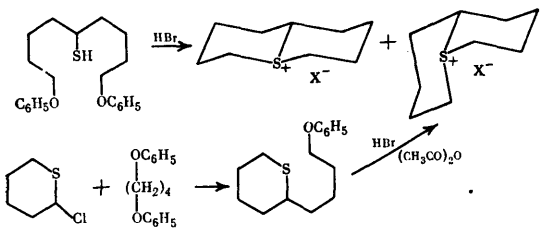
The oxosulphonium salts of condensed thiacyclohexanes are unknown. Our attempt to obtain the oxosulphonium salts by methylating 2,4-diaryl-*cis*-1-thiadecalin 1-oxides with

methyl iodide, i.e. by the method usually employed for the synthesis of acyclic oxosulphonium salts, was unsuccessful. However, oxosulphonium ylides, obtained by an indirect procedure involving the treatment of 1-ethoxycarbonylcycloalkenes with dimethylsulphoxonium methylide, have been described in the literature:[93,94]



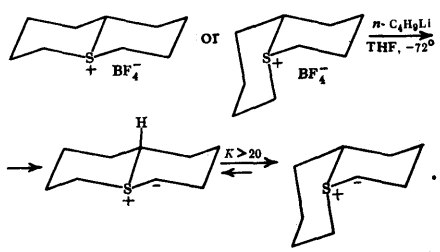
These oxosulphonium ylides are valuable intermediates in organic synthesis, for example, in the synthesis of cyclohexane derivatives with a specific configuration.[93]

The prospects for the use of sulphonium salts, and ylides based on them, as possible organic synthetic intermediates are responsible for the interest in 1-thioniabicyclo[4.4.0]-decane salts.[95-99] These are known under the name of Eastman's salts[95] and constitute a condensed heterocyclic system in the angular position of which the sulphonium centre is located. They were first obtained on heating 5-mercapto-1,9-diphenoxynonane with hydrobromic acid as a mixture of the *cis*- and *trans*-isomers in proportions of 2:3. The isomers were separated by preparative column chromatography on silica gel.[95] Eastman's salts can also be obtained from 2-chlorothiacyclohexane and phenoxybutylmagnesium chloride in the reaction involving subsequent treatment with hydrobromic acid:[96]

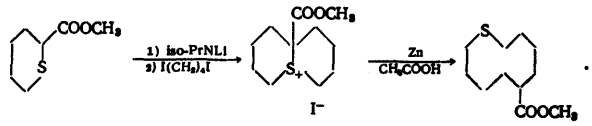


On heating to 260–270 °C in chloroform or methylene chloride, each isomer is converted into a 3:2 equilibrium mixture of the *cis*- and *trans*-isomers, formed as a result of pyramidal inversion at the sulphur atom. Heating at a lower temperature (110 °C) gives rise to a mixture in which the *trans*-isomer predominates (up to 70%).[96]

Sulphonium ylides have been obtained from *cis*- and *trans*-1-thioniabicyclo[4.4.0]decanes and their interconversion by pyramidal inversion at the sulphur atom has been investigated. It has been shown that the ylide structure in which the electron pairs of the carbanion and the heteroatom are orthogonal has the lowest energy.[97-99]



Although a more detailed consideration of these interesting compounds is not feasible within the framework of the present review, one should note that Eastman's salts and ylides based on them are important intermediates in the synthesis of macrocyclic compounds with a ring size which is not attainable by direct cyclisation, for example, of thiacyclodecane derivatives:[97]



The ylides of 1-thioniabicyclo[4.4.0]decanes are alkylated stereoselectively, which leads to the possibility of introducing new chiral centres at this stage.[97]

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