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CONFIGURATIONALLY AND CONFORMATIONALLY HOMOGENEOUS CYCLIC N-ARYL SULFIMIDES—III[1]

STEREOCHEMISTRY OF REARRANGEMENT

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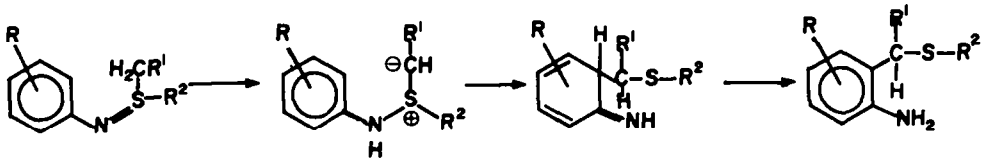
Abstract—Configurationally and conformationally homogeneous thiane- and *trans*- and *cis*-1-thiadecalin-1-N-*p*-chlorophenyl imides were rearranged to the corresponding 2-(2'-amino-5'-chlorophenyl)-sulfides and the configurations of the products were assigned by ^{1}H-NMR spectroscopy. If sterically unhindered, rearrangements proceeded with a high degree (>95%) of stereospecifity: sulfimides with equatorial S–N-bond gave rearranged products with axial, sulfimides with axial S–N-bond gave rearranged products with equatorial aryl substituent. The proposed concerted mechanism via a cyclic transition state is supported by these results.

The rearrangement of N-aryl-S,S-dialkylsulfimides (1) generally yields *o*-alkyl-thioalkylanilines (4) in good yields.[2] If a β-carbon of one of the S-alkyl substituents in 1 bears hydrogen, elimination of the alkyl substituent as an alkene may occur as a side reaction and the yields of 4 are diminished.[3,4]

of sulfonium ylids.[7] It has been shown that a doubly suprafacial overlap of orbitals of the two rearrangement fragments occurs in the transition state of [2,3]-sigmatropic rearrangements.[8]

Earlier attempts to investigate the stereospecifity of the rearrangement reactions using chiral sulfimides 1



1 2 3 4

Scheme 1.

Earlier results[2-4] indicated that following the formation of azasulfonium ylids 2 rearrangement to 4 takes place via cyclohexadiene imines 3 in a concerted [2,3]-sigmatropic way. *o*-Substituted anilines were formed exclusively.[2] When rearrangements were allowed to proceed in the presence of reactive anilines or phenols, no crossover was observed.[2,5] Starting with 2,6-dimethyl substituted sulfimides (1: R = 2,6-di-CH_3) intermediates 3 were isolated. Removal of an α-hydrogen was identified as the rate determining step by a primary kinetic isotope effect ($k_H/k_D \approx 3$).[6] The rate of rearrangement was shown to be considerably larger than the rate of reprotonation by the low exchange with the protons of the solvent in the rearrangement of α-perdeuterated sulfimides in ethanol.[6] Introduction of electron withdrawing substituents at the aromatic nucleus changes the equilibria of protonation at the nitrogen atom and reduces the rate of rearrangement.[6]

Sigmatropic rearrangements usually proceed with a high degree of stereospecifity, regardless if a heteroatom is part of the 5- or 6-membered transition state, provided no isomerisation takes place via different mechanisms. A high transference of asymmetry from sulfur to a carbon atom has been observed in the concerted rearrangement

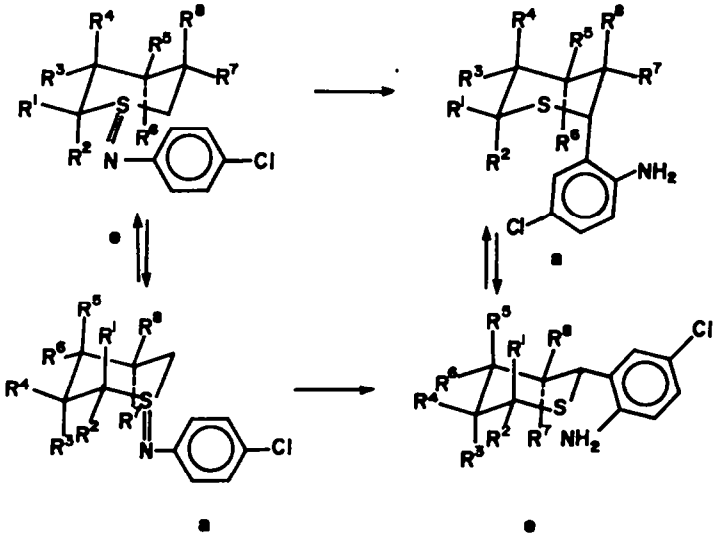
were unsuccessful.[3] Optically active sulfimides with known configuration at sulfur and of known optical purity were not available. When optically active sulfimides were prepared, the resulting cyclohexadiene imines 3 were indeed optically active, but the configuration at C-2 and the optical purity were once more unknown.

In an alternate approach we tried to obtain information using diastereomeric cyclic sulfimides. The configuration of these compounds was readily established by NMR-techniques. The rearrangement reactions of the sulfimides so prepared[1a] and identified[1b] will be discussed in the sequel.

Starting sulfimides

Thiane-1-N-p-*chlorophenyl imides* (Scheme 2). Sulfimides 5 and 6 of this series bear no biasing substituents suitable for referencing; the results of these rearrangements are included for sake of completeness. The substituents on the thiane ring are biasing 8 (largely),[9] 10 and 12 (completely) towards conformation a and 7, 9, 11, 13, 14 and 15 completely towards conformation e.

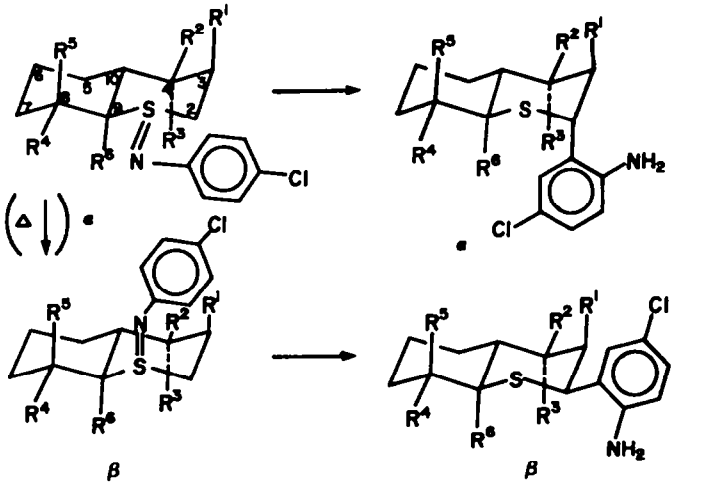
trans - 1 - *Thiadecalin* - 1 - N - p - *chlorophenyl imides*



all R's = H unless indicated

5	all R's = H	5U
6	$R^6 = R^9 = CH_3$	6U
7	$R^5 = CH_3$	7U
8	$R^9 = CH_3$	8U
9	$R^5 = C(CH_3)_3$	9U
10	$R^9 = C(CH_3)_3$	10U
11	$R^3 = R^7 = CH_3$	11U
12	$R^4 = R^9 = CH_3$	12U
13	$R^3 = R^9 = CH_3$	13U-1
13	$R^4 = R^7 = CH_3$	13U-2
14	$R^1 = R^2 = R^6 = CH_3$	
15	$R^1 = R^5 = R^6 = CH_3$	15U

Scheme 2.



all R's = H unless indicated

16α	all R's = H	16Uα, 16Uβ
16β	all R's = H	16Uβ
17α	$R^1 = CH_3(3\beta\text{-}CH_3)$	17Uα, (17Uβ)*
18α	$R^2 = CH_3(4\beta\text{-}CH_3)$	18Uα, (18Uβ)*
19α	$R^3 = CH_3(4\alpha\text{-}CH_3)$	19Uα, 19Uβ
20α	$R^4 = CH_3(8\alpha\text{-}CH_3)$	20Uα, (20Uβ)*
21α	$R^5 = CH_3(8\beta\text{-}CH_3)$	21Uα, (21Uβ)*
22α	$R^6 = CH_3(9\text{-}CH_3)$	

*Product was formed in minor amount only and was not isolated.

Scheme 3.

(Scheme 3). Both starting sulfimides† and rearranged products† are conformationally homogeneous since the *trans* fusion of thiane and cyclohexane rings prevents inversion.

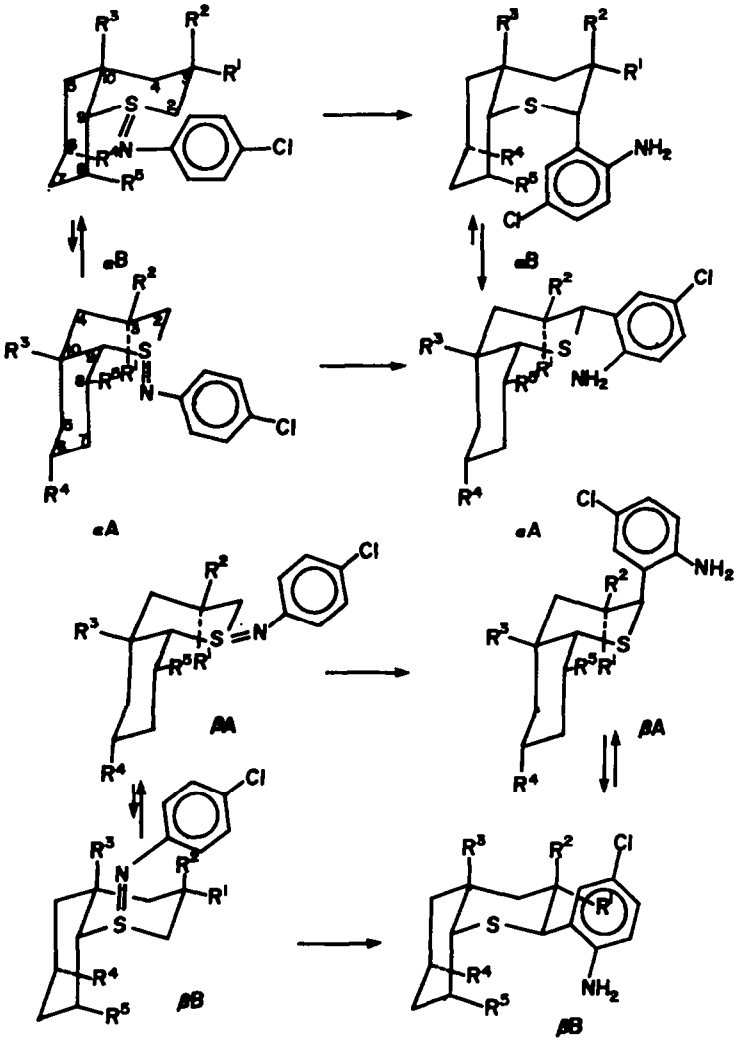
cis-1-*Thiadecalin*-1-N-p-*chlorophenyl imides* (Scheme 4). Rearrangements of both α- and β-imides† were investigated. The *cis*-1-thiadecalin-1α-imides are conformationally homogeneous (conformation B) even without additional holding groups since inversion to conformation A is badly hindered (*syn*-axial interactions between N and C-5, C-7). Conformationally homogeneous *cis*-1-thiadecalin-1β-imides could be obtained[1] from suitably methyl-substituted *cis*-1-thiadecalins.[10] The parent (23β), at $-69°$, is very largely in conformation A.[9]

The preparation and the rearrangement reactions of 1,3-dithiane-1-N-*p*-chlorophenyl imides will be discussed elsewhere.[11] The results of the rearrangements of 7 and 8 have been reported in a preliminary communication.[12]

†Nomenclature: "β" means "the substituent (16–28: the 1-N-aryl imide group; 16U–28U: the 2-aryl group) is on the same ringside as the substituent (or hydrogen) at C-10"; "α" means "the substituent is on the opposite ringside". For numbering see Schemes 3 and 4.

DISCUSSION

The rearrangement of thiane- and 1-thiadecalin-1-N-aryl imides takes place much less easily than that of open-chained sulfimides, especially of S-Me substituted compounds; this is in contrast to results obtained with 1,3-dithiane-1-N-aryl imides.[11] As a consequence, fairly drastic reaction conditions had to be used: heating in



all R's = H unless indicated

23α	all R's = H	23Uα
23β	all R's = H	23Uβ
24α	R' = CH_3(3α-CH_3)	
	R' = CH_3(3α-CH_3)	24Uβ
25β	R' = CH_3(3β-CH_3)	25Uβ
26β	R' = CH_3(10-CH_3)	26Uβ
27β	R' = CH_3(6α-CH_3)	27Uβ
28β	R' = CH_3(8α-CH_3)	28Uβ

Scheme 4.

triethanolamine at 100–200°. The yields of rearranged products are only moderate, and in some instances quite low (see Table 1), because side reactions (elimination, or cleavage of the S–N-bond by substitution on sulfur) become important at these temperatures.

The results are already indicated in Schemes 2–4. In most cases only a single rearranged product could be detected by gc or tlc; rearrangements thus proceed with a stereospecifity of >95%. Investigations of the configuration of the rearranged products revealed that the steric relation (*cis* or *trans*) of the 2-aryl group to the substituent used as a reference is identical with the relation of the 1-imide group to this substituent in the starting sulfimide; in the thiadecalin series this means that 1α-imides yield 2α-aryl-1-thiadecalins, and 1β-imides yield 2β-aryl-1-thiadecalins.

Exceptions were mainly found in the rigid *trans*-1-thiadecalin-1α-imide series, and in case of 3α-methyl-*cis*-1-thiadecalin-1α-imide (24α), where the rearrangement is very constrained. In case of the *trans*-1-thiadecalin-1α-imides (i.e. equatorial S–N; see Scheme 3) only moderate yields were obtained, with the 2α-aryl compound the major product and with <5% 2β-aryl isomer if the reaction temperature was ~100° (with very prolonged reaction times), but up to 25% β-isomer at 200° (percentages are relative to the total yield of 2-aryl-1-thiadecalin). The cyclic transition states for the formation of 2α-aryl-*trans*-1-thiadecalins from 1α-imides are doubtlessly difficult to attain because of the rigidity of the system, and are more strained by the steric interactions with H-4a and H-9 which cannot bend away for the same reason. Thus the barrier for the rearrangement 1α-imide→2α-aryl product is raised in comparison to the more flexible thiane system. We believe that formation of the 2β-aryl products does not take place directly from the 1α-imide in a non-[2,3]-sigmatropic way, but rather that an inversion of the 1α- to the 1β-imide occurs, the barrier to inversion being now

Table 1. Products of rearrangements of cyclic sulfimides

Starting Sulfimide [a,b]		Product [a,c]				Yield [d]	Mp [e]
5		5U				65	64 - 65.5
6		6U				42	101 - 103
7		7U				44	(160/0.1)
8		8U				46	(160/0.1)
9		9U				57	69 - 71
10		10U				27	114 - 116.5
11		11U				12	77 - 78.5
12		12U				30	(140/10^{-3})
13		13U-1	(50),	13U-2	(50)	23	(140/10^{-3})
15		15U				23	110 - 113
16α	(100)	16Uα	(95),	16Uβ	(5)	17	89 - 91
	(160)		(83)		(17)	25	
	(200)		(75)		(25)	22	
16β		16Uβ				57	97.5 - 99.5
17α		17Uα	(>95),	17Uβ	(<5)	55	70 - 72
	(200)		(88)		(12)	71	
18α	(100)	18Uα	(>97),	18Uβ	(<3)	25	88 - 90
			(94)		(6)	35	
	(200)		(82)		(18)	40	
19α		19Uα	(60)			25	82 - 83.5
		19Uβ	(40)				124 - 125
20α	(105)	20Uα	(89),	20Uβ	(11)	43	89 - 90.5
			(90)		(10)	[f]	
	(200)		(86)		(14)	57	
21α	(105)	21Uα	(>95),	21Uβ	(<5)	27	90 - 92
	(170)		(>95)		(<5)	55	
23α		23Uα	(~35),	23Uβ	(~65)	12	123.5 - 125 [g]
23β		23Uβ				60	122 - 123.5
24α		24Uβ				21	126 - 127.5
25β		25Uβ				16	146 - 147.5
26β		26Uβ				27	139 - 140
27β		27Uβ				40	76 - 78.5
28β		28Uβ				32	78 - 80

[a] For formulas see Schemes 2–4. [b] In parentheses: reaction temperature in °C. Reaction temperature 150° unless indicated. [c] If two products were formed, the ratio as determined by GC is indicated in parentheses. [d] Rearranged products, % theory. [e] Of recrystallized major product. If products did not crystallize, air bath temperature (°) and pressure (Torr) of Kugelrohr-distillation are reported in parentheses. [f] Not determined. [g] M.p. of 23Uα.

comparable to the barrier of rearrangement. This is followed by the more facile rearrangement of the 1β-imide to the 2β-aryl product.

Evidence for this hypothesis is found in the rearrangements of *trans*-1-thiadecalin-1α-imides with axial methyl groups γ to the imide group (3β-Me-, **17α**; 8β-Me-, **21α**). There is no reason to expect that these Me groups will hinder a rearrangement of the 1α-imide to a 2β-aryl product; on the other hand, they are likely to obstruct the pyramidal inversion to a 1β-imide (or the corresponding ylid), and there is indeed very little 2β-aryl product formed from **17α** and **21α**, even at high reaction temperatures.

An 8α-Me group (in **20α**) does not increase the amount of 2β-product formed upon rearrangement. This is readily explained by the increased rate of rearrangement brought about by the sterical strain of the interaction between 8α-CH_3 and imide nitrogen (equivalent to a 1,3-*syn*-axial interaction), rather than an increase in inversion to give 2β-aryl product via an intermediate 1β-imide.

The rearrangement of the 4α-CH_3-*trans*-1-thiadecalin-1α-imide (**19α**) also requires mention. Both the 2α-(**19Uα**) and the 2β- (**19Uβ**) aryl products are formed, in a ratio of 3:2. Here the product of *cis*-rearrangement is formed only in comparatively slight excess, again very likely for reasons of strain, since the ^{1}H NMR data (*vide infra*) indicate that **19Uα** no longer occupies a double chair conformation, but has the thiane ring in a boat or twist form to minimize the considerable interactions between 4-Me- and 2-aryl substituents.

Only the expected rearranged product (**15U**) was isolated in the rearrangement of the similarly substituted *trans*-2,4,4-trimethylthiane-1*r*-N-*p*-chlorophenyl imide (**15**), although the *syn*-axial interactions in **15U** (CH_3-2/CH_3-4 in **15Ue**, aryl-2/CH_3-4 in **15Ua**) are partly avoided by the escape of the compound into a twist form; the barrier for rearrangement must once more be lower in the more flexible thiane derivative compared to the rigid *trans*-1-thiadecalin system, and inversion to the alternate sulfimide does not occur.

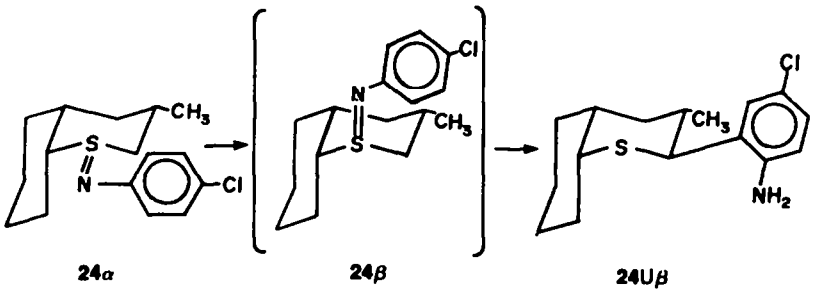
No rearrangements to geminally C-2 substituted products takes place even if consistent with a [2,3]-sigmatropic mechanism: no 2-aryl-2,4,4-trimethyl-thiane, and no 9-aryl-*trans*-1-thiadecalins could be detected in the product mixtures of **15** and the appropriate *trans*-1-thiadecalin-1α-imides, respectively. Axial or equatorial substitution on C-3, on the other hand, apparently has no influence upon the ease of rearrangement: both **13U-1** and **13U-2** were found, in equal amounts, upon rearrangement of **13**.

cis-1-Thiadecalin is a conformationally mobile ring system with both conformations A and B approximately equally populated ($\Delta G° = 0.59$ kJ/mol[10b]). The products obtained in moderate yields upon rearrangement of the sulfimides derived from it (**23α**, **23β**) are conformationally biased by the aryl group at C-2. While the rearrangement of *cis*-1-thiadecalin-1β-imide (**23β**) gives only one product, **23Uβ**, in respectable 60% yield, both **23Uα** and **23Uβ** are obtained in a ratio of ~1:1 upon rearrangement of **23α** (in triethanolamine, in extremely poor yield; see Table 1). Apart from the severe *syn*-axial interactions between aryl group and CH_2-8 (see Scheme 4) which necessarily arises in a transition state to the 2α-aryl product, the poor overall yields may be caused by the formation of unstable sulfenamide, a side reaction for which *cis*-1-thiadecalin-1α-imides are favourably arranged (axial CH_2-group β to the imide group; see below for **14** and **22α**). In case of very mild reaction conditions (rearrangement in benzene with n-butyllithium at +5°[13]) this elimination can be avoided, and only **23Uα** is formed in 75% yield. The conformation of the *cis*-1-thiadecalin skeleton (A or B) upon rearrangement changes to the more stable, aryl-equatorial one: **23α**B→ **23Uα**A; **23β**A→**23Uβ**B, respectively.

Sulfimides derived from Me substituted *cis*-1-thiadecalins are biased towards conformations A or B either because the parent sulfides are already conformationally homogeneous[10b,1] (**24α**, **27β**, **28β**) or because additional interactions arise in one conformation by the introduction of the 1-imide group[1] (**25β**, **26β**). In the first instance the products of rearrangement can also be expected to be conformationally homogeneous; this is the case for **27Uβ**A and **28Uβ**A (axial 2-aryl substituent). Compound **24Uα**, the predicted product of the rearrangement of **24α**, would be highly strained in both possible conformations and is not formed. The only product which could be isolated in low yield was **24Uβ**, in conformation B with an equatorial 2-aryl group. Of all compounds investigated this is the only case where the product not consistent with a [2,3]-sigmatropic rearrangement of the starting sulfimide is exclusively formed; again, isomerisation to an intermediate 3α-methyl-*cis*-1-thiadecalin-1β-imide (**24β**) and rearrangement of this compound in a [2,3]-sigmatropic way seems likely (Scheme 5).

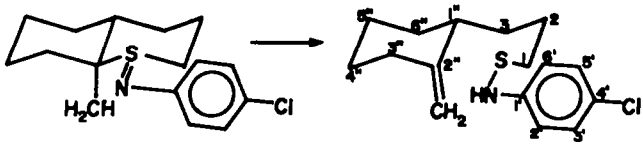
Sulfimide **25β** (derived from 3β-CH_3-*cis*-1-thiadecalin, the isomer of the parent sulfide of **24α**) rearranges in the expected way to give **25Uβ**; product and starting sulfimide are in different conformations since the axial 2-aryl substituent in **25Uβ**A is more hindered (2 *syn*-axial H's) than the axial methyl group in **25Uβ**B (1 *syn*-axial H, 1 *syn*-axial electron pair).

No rearranged products (**14U** or **22U**, respectively)



24α **24β** **24Uβ**

Scheme 5.



22α 30

Scheme 6.

were obtained upon reaction of 14 and 22α in triethanolamine. Major products were unstable compounds, which, from their ^{13}C and ^{1}H NMR spectra, were identified as sulfenamides (e.g. 30 from 22α; Scheme 6). In both cases as well as in *cis*-1-thiadecalin-1α-imides a Me (or methylene) group is positioned axially, β to the imide group. This structural arrangement is favourable for an intramolecular proton transfer, and elimination, to form a sulfenamide.[3,4] Because of their low stability, identification of these products was only possible in case of sulfimides 14 and 22α.

Summarizing the results, rearrangement of cyclic sulfimides proceeds with formation of the C-2-aryl bond *cis* to the original position of the 1-imide substituent, i.e. suprafacially at the S-ylid fragment. In case of conformationally homogeneous cyclic sulfimides this results in the formation of products with equatorial 2-aryl substituents starting with sulfimides with axial 1-imide groups, and of axially 2-aryl substituted products starting with sulfimides with equatorial 1-imide groups. These results meet exactly the expectations based on the assumption of a concerted reaction mechanism which thus is strongly supported. For the "axial" sulfimides the result appears trivial, since they might be expected to rearrange into the sterically less hindered 2-equatorial position even in a non-concerted reaction. This is not so for the "equatorial" sulfimides; the fact that they also rearrange in a *cis*-manner to give the sterically more constrained 2-axially substituted products is a convincing proof for the concertedness of the process.

The high stereospecifity observed is obviously due to the strict requirements for conservation of orbital symmetry in a concerted process. An alternative explanation might be a large difference in acidity of the hydrogens at C-2 of the starting sulfimides. While this explanation cannot be ruled out completely, it is highly improbable: in case of "equatorial" sulfimides H-2a would have to be more acidic by a factor of at least 20; and investigations on cyclic sulfoxides have shown that the stereochemistry of electrophilic reactions at α-sulfinyl carbanion centers is not necessarily dependent on the orientation of the proton removed and is strongly influenced by solvent, type of reaction and by various other factors.[14]

The high degree of stereospecifity also confirms that configurational isomerization by pyramidal inversion of sulfimides or intermediate azasulfonium structures generally does not occur, with the exception of the *trans*-1-thiadecalin-1α-imides, at very drastic reaction conditions, discussed above. The enthalpy of activation, ΔG^{+}, for pyramidal inversion at the asymmetric center of N-aryl-sulfimides and N-arylazasulfonium salts is as yet unknown, but the data for N-tosyl- and N-acyl compounds (120–150 kJ/mol for sulfimides, 100–125 kJ/mol for azasulfonium salts)[15] may be used as an approximation. Since barriers are lower in sulfonium ylids,[15] the value for azasulfonium ylids should also be smaller (< 100 kJ/mol); thus the barrier for the rearrangement process has to be even lower than this last value, which is consistent with an expected barrier for a concerted process.

Configurational assignments and conformational equilibria

The determination of configurations of the rearranged products was generally achieved by ^{1}H NMR spectroscopy, in a few instances aided or confirmed by ^{13}C NMR. Assignment was facilitated by the fact that most compounds were conformationally homogeneous; even ring systems without biasing substituents were represented by only one conformation because of the high equatorial preference of the 2-aryl group.

The following criteria were used:

(1) Coupling constants of H-2. The signal of the proton at C-2 is well separated from the other protons because of its benzylic character. If C-3 bears two protons an equatorial H-2 displays two small (*gauche*, 2–5 Hz) couplings, and an axial H-2 displays a large (*anti*, 8–12 Hz) and a small (*gauche*) coupling.

(2) Chemical shift of H-6'. The signal of the proton ortho to C-2 of the thiane, and to chlorine, on the aromatic ring is upfield in isomers with equatorial aryl group (7.10–7.18 ppm) compared to the aryl-axial isomers (7.28–7.40 ppm). The two shift regions are sufficiently separated and narrow enough to allow structural assignments even if only one of the possible configurational isomers is available.

(3) ^{13}C NMR allowed unambiguous assignments in questionable cases: large upfield shifts of ring carbons γ_a to (axial) aryl substituents, as well as palpable reductions of α- and β-effects in these isomers.

The ^{1}H and ^{13}C NMR data are collected in Tables 2 and 3. Characteristic features of the various products are discussed below.

2-(*2'-Amino-5'-chlorophenyl*)-*thianes* (see Scheme 2)

The parent, compound 5U, is predominantly in conformation e at room temperature: the signal of H-2a (3.78 ppm) is in the narrow chemical shift range observed for H-2a of conformationally homogeneous *cis*-4-methyl- (8U) and *cis*-4-*t*-butyl- (10U) derivatives, with a large J_{anti} and a small J_{gauche}. In the ^{13}C-spectrum the signal of C-4 is barely shifted compared to thiane[16] (no γ_a effect).

H-2a is shifted downfield to 3.99 ppm by the steric compression of the axial Me-group at C-4 in 6U. The same effect is seen at H-2a (4.05 ppm; $J_a + J_g = 13$ Hz) of 7U, which consequently exists predominantly in the conformation with axial 4-Me and equatorial 2-aryl group. Confirmation for this preference comes from the chemical shift of H-6' (7.17 ppm) and from the ^{13}C-spectrum: the ring carbon atoms γ to the Me substituent, C-2 and C-6, are shifted upfield by −7.05 and −5.98 ppm, respectively; the Me signal (17.64 ppm) is very close to the signal of the analogously orientated 4-Me of 2-$CH_{3eq.}$-4-$CH_{3ax.}$-thiane[16] (17.09 ppm); the α- and β-effects are

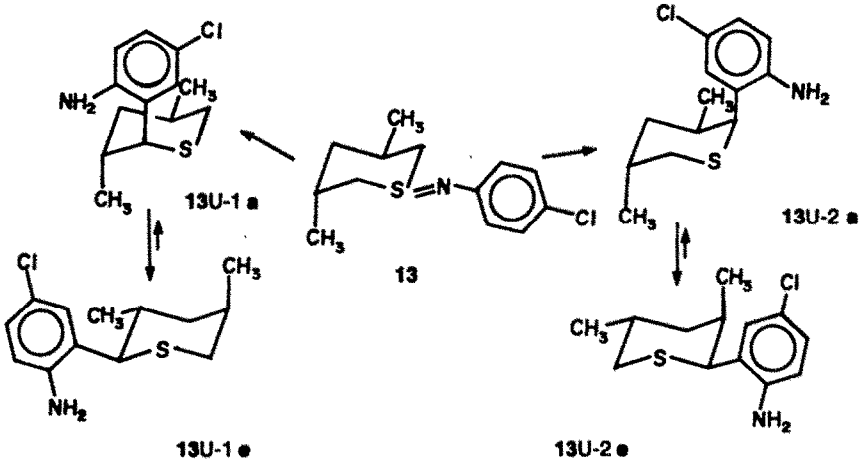
also in agreement. Although the form with axial 2-Me group predominates in *trans*-2,4-dimethylthiane (75% at −95°C)[16], the above result is not surprising considering the much greater energy difference of axial/equatorial aryl (12.6 kJ/mol) than Me (7.1 kJ/mol) in phenyl- or methylcyclohexanes,[17a] especially when the axial phenyl ring may be forced partly into the energetically less favourable "parallel" form [17b] by the 2'-amino group.

The additional *gauche* Me group in 12U shifts H-2a upfield to 3.44 ppm (J_{anti} = 11 Hz). A similar effect allows assignment of H-2a in one of the two rearrangement products of 13 (Scheme 7), 13U-1, while in the other (13U-2) H-2a is shifted downfield to 4.02 ppm (J_{gauche} = 2.5 Hz) by the *anti* Me group. Both compounds exist in conformations e (Scheme 7) because steric effects are minimized that way: a large ΔG° of the axial aryl plus the ΔG° of the axial CH_3 in a is opposed by only the relatively small (5.9 kJ/mol[16]) ΔG° of the axial CH_3 in e in both isomers. The absence of the appreciable *gauche* 2-aryl/3-Me interaction (see below for 17Uα) in 13U-1 a is not enough to produce a palpable contribution of this conformer.

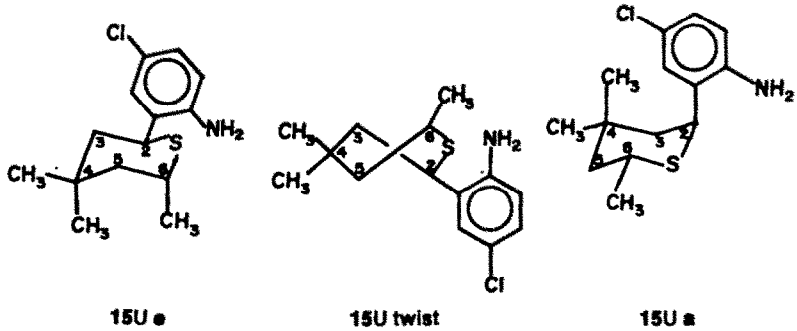
Equatorial protons at C-2 appear at lower field than axial ones: H-2e in 9U resonates at 4.02 ppm (J: 5, 4.5 Hz). In 11U H-2e is again shifted upfield (3.75 ppm) by the *gauche* Me group (see above for 12U and 13U-1).

Both chair conformations of 15U are severely strained, with 15U a the less favourable form. The ^{1}H NMR spectrum indicates that the compound escapes partly into a twist form: H-2, the benzylic proton, appears at 4.16 ppm as a doublet of doublets (*J*: 11.5, 3 Hz), consistent with both 15U e and 15U twist; H-6, on the methyl-substituted C-6, shows two couplings of 7 and 4.5 Hz (apart from the 7 Hz coupling to the Me protons), intermediate to the two *gauche* couplings it encounters in 15U e, and the large *anti* and small *gauche* coupling of 15U twist. The signal of the aromatic H-6'-proton occurs at 7.22 ppm, also intermediate to the typical phenyl-equatorial or - axial shifts.

Only four (7U, 9U, 13U-1 and 15U) of the eleven 2-(2'-amino-5'-chlorophenyl)-thianes investigated might have been expected to show appreciable contributions of a second conformation; in the others the differences in free energy between the preferred and other conformers are obviously too large for these alternate forms to contribute. Only in case of 15U a twist form does really occur in considerable amounts, while 7U is >90% in conformation e and 9U >90% in conformation a. The conformational free energy of a 4-Me group on thiane has been determined[16] as 7.5 kJ/mol, identical to methylcyclohexane; the corresponding value for the 4-t-Bu group is supposedly close the one calculated[18] for t-butylcyclohexane (22.6 kJ/mol). The latter is higher than the energy difference calculated by a force field method[19] for the chair/boat-twist equilibrium (16.9 kJ/mol), and while some of the values obtained by this method[19] have been shown to differ from the experimental results,[10,16] the order of magnitude may still be correct, since a substantial contribution of twist conformer has been reported for *trans*-3,5-di-*t*-butylthiane.[20] The difference



Scheme 7.



Scheme 8.

Table 2. ^{1}H NMR chemical shifts[a] and coupling constants[b]

Compd	H-2[c]	H-6'	H-4'	H-3'	NH_2	CH_3[d]	Others[e]
5U	3.78 (d, 8.5 of d, 5)	7.12	6.98	6.52	4.07	---	2.45 - 3.0 (H-6; m); 2.2 - 1.25
6U	3.99 (d, 10 of d, 4)	7.08	6.96	6.50	4.08	1.02, 0.96	3.03 (H-6a; d, 13.5 of d, 11 of d, 5); 2.44 (H-6e; d, 13.5 of t, 3.5); 2.0 - 1.4
7U	4.05 (d, 13 of d, 3)	7.17	6.98	6.52	4.10	1.03 (7)	3.01 (H-6a; d, 13.5 of d, 10 of d, 4); 2.55 - 1.6
8U	3.83 (d, 11 of d, 3)	7.13	6.98	6.55	4.03	1.00 (6)	2.55 - 3.05 (H-6; m); 2.15 - 1.2
9U	4.02 (d, 5 of d, 4.5)	7.35	7.00	6.55	3.87	0.89	2.8 - 1.4
10U	3.78 (d, 10.5 of d, 2.5)	7.12	7.01	6.54	4.05	0.87	2.77 (H-6; m); 2.4 - 0.85
11U	3.73 (d, 4.8)	7.28	6.96	6.57	3.75	1.09 (6)[f] 1.03 (7)[g]	2.7 - 0.8
12U	3.44 (d, 11)	7.10	6.98	6.54	3.91	0.96 (6)[f] 0.86 (6.5)[g]	0.90 (H-5a; m); 2.7 - 1.6
13U-1[h]	3.43 (d, 10.5)	7.09	6.96	6.52	3.78	1.03 (7)[g] 0.92 (6)[f]	3.3 - 1.4
13U-2[h]	4.07 (d, 2.5)	7.09	6.96	6.52	3.78	1.25 (7)[f] 0.74 (6)[g]	3.3 - 1.4
15U	4.16 (d, 11.5 of d, 3)	7.22	7.04	6.61	4.10	1.42 (7.2), 1.08, 1.03	3.22 (H-6e; d, 7 of qu, 7.2 of d, 4.5) 2.2 - 1.5
16Uα	3.94 (d, 4.5 of d, 4)	7.38	7.03	6.59	3.95	---	2.7 - 2.1 (3 H); 1.85 - 1.0 (11 H)
16Uβ	3.90 (d, 8 of d, 6)	7.14	7.00	6.58	3.95	---	2.66 (H-9; m); 2.3 - 0.9
17Uα	3.59 (d, 4)	7.40	7.05	6.60	3.94	1.25 (7)	2.75 - 2.3 (2 H); 1.9 - 1.0 (12 H)
18Uα	3.98 (d, 5 of d, 3)	7.36	7.05	6.62	4.00	1.00 (6.5)	2.85 - 1.0
19Uα	4.15 (d, 12 of d, 2.5)	7.28	6.98	6.54	4.05	0.88 (6)	2.94 (H-9; t, 11 of d, 4); 2.4 - 1.1
20Uα	3.96 (d, 4.5 of d, 4.5)	7.31	6.99	6.55	4.00	0.92 (5)	2.8 - 0.9
21Uα	3.94 (d, 4.5 of d, 4.5)	7.39	6.98	6.54	4.00	1.04 (7)	2.78 (H-9; d, 10.5 of d, 4.5); 2.6 - 1.2
23Uα	3.86 (d, 10 of d, 2)	7.13	6.98	6.55	4.12	---	3.49 (H-9; 1/2-width 8); 2.5 - 0.9
23Uβ	3.98 (d, 8 of d, 6)	7.18	7.04	6.60	4.10	---	2.78 (H-9; d, 12 of t, 3.5); 2.35 - 1.2
24Uβ	3.68 (d, 11)	7.12	6.97	6.56	3.98	0.85 (6.5)	2.75 (H-9; d, 12 of t, 4); 2.5 - 1.15

25UB	4.28 (d, 2.7)	7.18	6.98	6.57	3.92	1.07 (7)	2.80 (H-9; d, 12 of t, 4); 2.5 - 1.2
26UB	4.00 (d, 11.5 of d, 2)	7.16	7.02	6.58	4.10	1.30	2.6 - 1.15
27UB	3.89 (d, 4 of d, 4)	7.31	6.97	6.53	3.90	0.97[i]	3.20 (H-9; 1/2-width 10); 2.3 - 1.2
28UB	3.90 (d, 4.5 of d, 4.5)	7.31	7.00	6.55	4.00	0.96 (6.5)	3.24 (H-9; 1/2-width 8); 2.5 - 1.0

[a] In ppm, from Me_4Si. Values are centers of signals in the spectra. [b] In parentheses; apparent couplings measured on the spectra, in Hz. [c] Benzylic proton; for numbering of other protons see Schemes in Text. [d] Doublets if a coupling constant is added, or else singlets. [e] Spectral ranges without further explanation are the broad envelopes of the thiane or thiadecalin protons. [f] CH_3-3. [g] CH_3-5. [h] Recorded as a mixture of isomers. [i] Broad singlet, 1/2-width 6 Hz.

Table 3. Pertinent ^{13}C shifts and shift differences[a] of rearranged products

Compd	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	CH_3
5U	42.43	32.10	(27.04)	(26.91)	30.56	---	---	---	---	---
	+13.37	+4.34	+0.59	-0.85	+1.50					
7U[b]	35.38	37.27	27.47	32.25	24.58	---	---	---	---	17.64
	+6.58	+1.26	-4.84	-3.76	-4.22					-5.37
	-7.05	+5.17	+0.43	+5.34	-5.98					
8U[c]	42.62	40.62	33.53	35.37	30.50	---	---	---	---	23.14
	+13.82	+4.61	+1.22	-0.64	+1.70					+0.13
	+0.19	+8.52	+6.49	+8.46	-0.06					
16Uα	(43.56)	(29.75)	(30.00)	34.16	(26.27)	(26.52)	32.38	38.60	(43.27)	---
	+13.52	+1.52	-4.40	-0.40	-0.07	-0.24	-0.20	-8.41	-1.00	
16UB	(43.71)	(32.19)	(34.97)	(34.09)	(26.20)	(26.57)	(32.54)	48.35	(43.52)	---
	+13.67	+3.96	+0.57	-0.47	-0.14	-0.19	-0.04	+1.34	-0.75	

[a] In ppm, from Me_4Si. Signals occurring in too close a range for unambiguous assignment are parenthesized. Second line of figures: $\delta_{2\text{-erythiane}} - \delta_{\text{thiane}}$ (see Ref. 16 and 10b. [b] Third line of figures: $\delta_{7U} - \delta_{5U}$. [c] Third line of figures: $\delta_{8U} - \delta_{5U}$.

in conformational free energy between axial and equatorial 2-(2'-amino-5'-chloro)phenyl in thiane should consequently be about 13 kJ/mol.

2-(2'-Amino-5'-chlorophenyl)-trans-1-thiadecalins (Scheme 3)

The chemical shifts of the H-2 signals of the products of rearrangement of *trans*-1-thiadecalin-1-N-aryl imides fall in the narrow range of 3.9–4.0 ppm, regardless to their axial or equatorial position, if the signals are not shifted by Me substituents at C-3 (17Uα) or C-4 (19Uα, 19Uβ). However, the position of H-2 can be determined unambiguously from its coupling (H-2e: $J_s + J_s = 8$–9 Hz; H-2a: $J_a + J_s = 13$ Hz) and from the shift of H-6' (phenyl axial: 7.3–7.4 ppm; phenyl equatorial: 7.1–7.2 ppm). Additional evidence comes once more from the ^{13}C NMR spectra: the influence of an equatorial 2-aryl group on the bridgehead carbon C-9 is only small, and downfield shifting (+1.34 ppm in 16Uβ compared to *trans*-1-thiadecalin[10c]); the effect of an axial 2-aryl is very large, and upfield shifting (16Uα: −8.41 ppm). The same effects, but smaller, are observed on C-4 (+0.57 and −4.40 ppm, respectively). Differences between β_a- and β_e- (on C-3) and α_a- and α_e-effects (on C-2), on the other hand, are surprisingly small and insignificant (Table 3).

While the couplings of H-2e are consistent with an axial 2-aryl on a thiane ring in a chair conformation in 16Uα–18Uα, 20Uα and 21Uα, in case of 19Uα (2α-aryl-4α-methyl-*trans*-1-thiadecalin) the couplings deviate significantly. Model considerations show that the strain engendered by the aryl/Me *syn*-axial interaction is relieved, and the couplings observed (J: 9.5, 3.7 Hz) are explained, if the thiane ring occupies at least partly a boat conformation. Compound 17Uα, with an axial 3-methyl ($\Delta G^\circ \sim 5.9$ kJ/mol[10c]) and an axial 2-aryl ($\Delta G^\circ \sim$ 13 kJ/mol) might also be expected to show a palpable contribution of a conformation with the thiane ring in a boat- or twist form. The fact that none is observed indicates that the resulting 2-aryl/3-Me *gauche* interaction must be fairly substantial ($\geq$6.3 kJ/mol) to compensate for the gain in free energy if both aryl and Me groups were to become equatorial.

2-(2'-Amino-5'-chlorophenyl)-cis-1-thiadecalins (Scheme 4)

Differentiation between the configurations α and β is primarily an assignment of conformations A and B. For this the chemical shift and the coupling behaviour of proton H-9 (on C-9) is an important indicator. In conformers B (e.g. 23Uβ) this signal occurs at 2.75–2.80 ppm, with a half width of more than 20 Hz, because of the large *anti*-coupling (~12 Hz) to H-8a. In conformers A (e.g. 23Uα), H-9 is shifted downfield by comparison to ~3.45 ppm; it is again coupled to H-10, H-8a and H-8e, all of which are now *gauche* positioned; the signal appears as a singlet with a half width of 7–9 Hz. The equatorial or axial position of the phenyl ring is once more apparent from the chemical shift of H-6' (7.13–7.18 vs 7.31 ppm) and from the coupling pattern of H-2 (H-2a: $J_a + J_s = 12$–14 Hz; H-2e: $J_s + J_s = 8$–9 Hz). By these criteria the products derived from the parent *cis*-1-thiadecalin are found to be totally in the conformations with equatorial aryl ring (23UαA and 23UβB), as expected.

It has already been mentioned that formation of 24Uα, the [2,3]-sigmatropic product of 24α, is difficult to imagine for reasons of strain, and indeed, there is no conformation of 24Uα that would explain the observed couplings of H-9 (2.75 ppm; d, 12 of d, 4 Hz) and of H-2 (J: 11 Hz). Thus both *a priori* model considerations and the interpretation of the ^1H NMR spectrum lead to the same result, that 24Uβ is formed exclusively (presumably via isomerisation, see above).

The sulfimide derived from the second 3-methyl-*cis*-1-thiadecalin, 25β, yields the expected product 25Uβ. The rearrangement is accompanied by inversion of the thiadecalin system. In the starting sulfimide the 1-imide and the 3-Me group are in the favourable equatorial position (conformation A). In the rearranged product the 3-Me group is axial, the 2-aryl substituent is equatorial (H-6': 7.18 ppm) and the ring system is in conformation B (H-9): 2.80 ppm; d, 12 of t, 4 Hz). If the *gauche* interactions of 3-Me/2-aryl in the two conformations are considered approximately equal, the ΔG°s of axial 3-Me and of conformation B (0.59 kJ/mol[10b]) together are not sufficient to compensate for the preference of the 2-aryl group for the equatorial position. A similar situation obtains upon rearrangement of 26β; 26Uβ has the 2-aryl group in the equatorial position in conformation B; the Me group in this case is placed into the slightly more favourable position axial to the thiane ring (ΔG° = 1.2 kJ/mol[10b]). Both 27Uβ and 28Uβ, finally, are in conformation A with the 2-aryl substituent axial: as in the case of 9U and 11U the alternate forms are excluded because of severe *syn*-axial Me/methylene interactions.

EXPERIMENTAL

Tlc was performed on aluminum foil plates covered with silicagel (SIF, Riedel-de-Haen) with $CHCl_3$ as solvent. Glass columns (40–60 cm length, 2.5–4 cm o.d.) with Kieselgel 60, 70–230 mesh (Merck) and $CHCl_3$ distilled from P_2O_5 were used for column chromatography. Gas chromatography was carried out on a Varian Aerograph Series 1400 equipped with a flame ionization detector, on a 2 m long, 0.125 in. o.d. stainless steel column packed with 20% Dexsil on Chromosorb W, 80–100 mesh. Column temp. 250°, carrier gas N_2.

The compounds prepared are listed in Table 1. Total distillations were carried out in a Kugelrohr apparatus in bulb tubes with ground glass joints; b.ps reported are air bath temps. M.ps were measured on a Kofler micro hotstage. All compounds gave satisfactory elemental analysis, determined by Dr. J. Zak, Institute of Physical Chemistry, University of Vienna.

60-MHz NMR spectra were measured on a Varian EM 360 spectrometer with ^1H internal lock facility. 100 MHz ^1H NMR spectra were recorded on a Varian XL-100 pulsed Fourier transform NMR spectrometer, in the C.W. mode, in 5 mm o.d. tubes; ^{13}C NMR spectra were recorded in the pulsed mode at 25.16 MHz, in 12 mm o.d. tubes. Solvent was $CDCl_3$, with 2–5% Me_4Si added as internal reference.

Starting sulfimides were prepared as previously reported.[1] Commercial triethanolamine was distilled at reduced pressure before use.

Rearrangements. Sulfimide (1 g) was dissolved in 8–10 ml triethanolamine in a 25 ml round bottom flask. The mixture was protected from moisture and heated for 1 (at 200°) to 16 (at 100°) hr. in a silicon oil bath while stirring magnetically. The mixture was brought to room temp. and dissolved in 50 ml CH_2Cl_2, the solution was washed twice with 50 ml H_2O and dried over Na_2SO_4. The solvent was distilled off, and the residual mixture was separated by column chromatography. Following a fraction of low retention not further investigated rearranged product was obtained, followed by *p*-chloroaniline. In some instances isomers were separated by a second chromatography of the fraction containing the rearranged products (e.g. 16Uα and 16Uβ; 19Uα and 19Uβ).

No 2-(2'-amino-5'-chlorophenyl)-thianes were isolated in case of the rearrangements of 14 and 22α; low retention fractions of

the column chromatography were identified as the sulfenamides **30** and **31**. The compounds also formed if solutions of **14** or **22α** in $CDCl_3$ were kept at room temp. for a few days. but could not be isolated in pure form.

3 - (2" - Methylene - cyclohexyl) - N - (*p* - chlorophenyl) - propane - sulfenamide (**30**; from **21α**; for numbering see Scheme 6).

^{13}C ($CDCl_3$; ppm from Me_4Si; doubtful assignments parenthesized); C-2", 152.4$_7$; C-1', 146.4$_6$; C-3',5', 128.9$_9$; C-2',6', 115.9$_1$; C-4' (not seen); $=CH_2$, 105.8$_8$; C-1", 42.8$_9$; C-3", 38.3$_8$; C-1, 34.5$_5$; C-6", (33.8$_4$); C-3, (31.1$_1$); C-2, (28.7$_7$); C-5", (25.5$_4$); C-4", (24.0$_6$).

^1H ($CDCl_3$; ppm from Me_4Si): 7.3–6.9 (4 H; arom. AA'BB'); 5.4 (1 H; NH); 4.6 (d, 5 Hz; $=CH_2$); 3.2–0.8 (15 H).

3,5-Dimethyl-N-(*p*-chlorophenyl)-hexene(5)-sulfenamide (**31**; from **14**).

^{13}C: C-1', 146.2$_4$; C-5, 144.2$_6$; C-3',5', 129.0$_2$; C-2',6', 115.8$_8$; C-4', (not seen); C-4, 45.6$_8$; C-2, 35.8$_7$; C-1, 34.3$_5$; C-3, 29.9$_8$; CH_3(5), (22.2$_1$); CH_3(3), (19.3$_9$).

^1H: 7.2–6.9 (4 H; arom. AA'BB'); 5.3 ppm (1 H; NH); 4.6$_5$ (d, 5 Hz; $=CH_2$); 2.6 (d, 8 of d, 6; 2 H; H-1); 2.2–1.1 (5 H); 1.6$_7$ (s, 3 H; CH_3(5)); 0.8$_1$ (d, 7 Hz; 3 H; CH_3(3)).

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