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Configurationally and Conformationally Homogeneous Cyclic *N*-Aryl Sulfimides. I.

Synthesis and Mechanism of Formation

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Reactions of thianes and *cis*- and *trans*-1-thiadecalins with 4-chloroaniline and *N*-chlorsuccinimide or *tert*-butylhypochlorite gave configurationally homogeneous cyclic *N*-4-chlorophenyl sulfimides. With appropriately substituted sulfides conformationally homogeneous thiane- and cis-1-thiadecalin-1-imides were obtained. Formation of sulfimides with axially oriented S—N bond is strongly disfavoured. Reactions with conformationally rigid ring systems yielded only sulfimides with equatorial S—N bond; two isomeric sulfimides, both with equatorial S—N bond, were obtained with the mobile *cis*-1-thiadecalin. Sulfimides with axial S—N bond were prepared from conformationally rigid sulfoxides with equatorial S—O bond. It is assumed that formation of sulfimides with rigid ring systems proceeds via *N*-chloroanilines, while reactions of conformationally mobile systems with *N*-chlorosuccinimide may also occur via intermediate succinimidyl sulfonium ions.

Konfigurativ und konformationell einheitliche cyclische N-Aryl-sulfimide. I. Synthese und Bildungsmechanismus

Durch Umsetzung von Thianen und von *cis*- und *trans*-1-Thiadekalinen mit 4-Chloranilin und *N*-Chlorsuccinimid oder *tert*-Butylhypochlorit wurden konfigurativ einheitliche cyclische *N*-4-Chlorphenylsulfimide dargestellt. Bei geeigneter Substitution am Heteroring wurden konformativ einheitliche Thian- und *cis*-1-Thiadekalin-1-imide erhalten. Die Bildung von Sulfimiden mit axial orientierter S—N-Bindung ist stark benachteiligt. Konformativ starre Ringsysteme führen praktisch ausschließlich zu den Sulfimiden mit äquatorialer S—N-Bindung; aus dem konformativ beweglichen *cis*-1-Thiadekalin werden bei der Umsetzung mit *tert*-Butylhypochlorit zwei isomere Sulfimide, beide mit äquatorialer S—N-Bindung, erhalten. Sulfimide mit axialer S—N-Bindung wurden aus konformativ starren Sulfoxiden mit äquatorialer S—O-Bindung erhalten. Es wird angenommen, daß die Sulfimidbildung bei konformativ starren Ringsystemen weitgehend über *N*-Chloraniline, bei Umsetzung von beweglichen Ringsystemen mit *N*-Chlorsuccinimid auch über Succinimidylsulfoniumionen verläuft.

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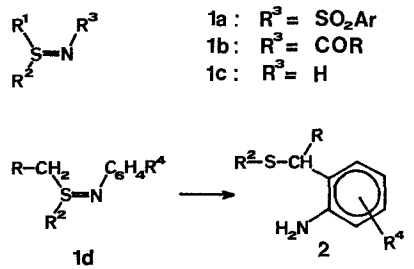
Introduction

Sulfimides (**1**) (Scheme 1), the isoelectronic nitrogen analogues of sulfoxides, show a pronounced dependence of their physical and chemical properties on the nature of the substituent on nitrogen (R^3), in addition to the smaller effects observed upon structural changes of the substituents on sulfur. The chemical properties of *N*-arylsulfonyl imides (**1 a**; $R^3 = SO_2$—Aryl) have been extensively investigated and the nature of the S—N bond of **1 a** and of *N*-acyl sulfimides (**1 b**; R^3 = Acyl) has been discussed during the last ten years[1,2]. Sulfimides bearing hydrogen on nitrogen (**1 c**; $R^3 = H$) have also recently become available[3,4].

In 1968 we reported, for the first time, a synthesis of *N*-aryl sulfimides[5] (**1 d**; R^3 = Aryl) and we have since been interested in that class of compounds[6] (which is readily available through improved syntheses[7,8]). Recently the S—N bond length of a sulfimide **1 d** ($R^3 = p$-NO_2—C_6H_4) and S—N bond moments of a number of *N*-aryl sulfimides have been determined by X-ray analysis and by dipole moment measurements by *Eliel et al.*, and the ionic character of the S—N bond has been estimated[9]. An interesting reaction of *N*-aryl sulfimides **1 d** with α-hydrogens is their smooth rearrangement to *o*-alkyl-thioalkyl substituted anilines (Scheme **1**, **2**), a process which has been investigated by us[6b,c,f], and which more recently has been used by *Gassmann et al.*[10] for the preparation of heterocycles, especially indoles. Of interest, also, is the rearrangement of *N*-aryl imides of 1,3-dithiane to yield dithioacetals of *o*-aminobenzaldehydes[11,12]; this reaction in part prompted the present investigation.

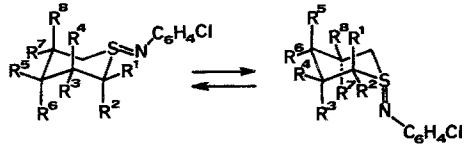
Scheme 1



Attempts to get information about the stereospecifity of rearrangements of *N*-aryl imides with optically active compounds **1 d** did not lead to satisfactory results[6f]; so, as an alternative, we tried to answer the questions using cyclic derivatives. For these investigations we needed conformationally homogeneous diastereomeric cyclic sulfimides **1 d** with

R^1 and R^2 part of a six-membered ring, and with a well defined configuration of the sulfimide function. As in cyclohexanes it is possible to define the steric position of substituents on thianes or thiane derivatives by nmr-techniques, if ring inversion (which otherwise takes place with a rather low enthalpy of activation[13]: 9–10 kcal/mol) is prohibited. This can be achieved either by freezing inversion of the two chair forms (Scheme 2, **e** and **a**) and thus allowing observation (nmr spectroscopy) of both forms in an equilibrated mixture, or by introduction of "biasing" or "holding" groups in suitable positions of the ring. These groups shift the conformational equilibrium very much to the side of one of the two possible forms and make the observed averaged spectrum virtually identical to the spectrum of the preferred conformer. Finally, ring inversion can be completely excluded in suitably condensed or bridged ring systems, e.g. *trans*-1-thiadecalin (**18**).

Scheme 2



e **a**

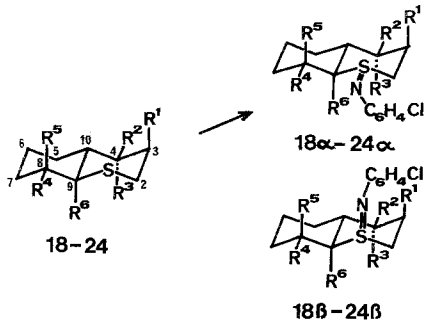
All R's = H, unless noted

3 all R's = H
4 $R^5 = R^6 = CH_3$
5 $R^5 = CH_3$
6 $R^6 = CH_3$
7 $R^5 = tert\text{-}C_4H_9$
8 $R^6 = tert\text{-}C_4H_9$
9 $R^3 = R^7 = CH_3$
10 $R^4 = R^8 = CH_3$
11 $R^3 = R^8 = CH_3$
12 $R^1 = R^2 = R^5 = CH_3$
13 $R^1 = R^2 = R^6 = CH_3$
14 $R^1 = R^5 = R^6 = CH_3$
15 $R^2 = R^5 = R^6 = CH_3$
16 $R^3 = R^4 = R^7 = CH_3$
17 $R^3 = R^4 = R^8 = CH_3$

The synthesis of the following cyclic sulfimides will be reported in this paper (configurational assignments are based on ^{13}C- and ^1H nmr spectra, which are discussed in a separate paper[14]):

Thiane-1-N-aryl imides (Scheme 2). The thiane rings of compounds **3** and **4** bear no biasing substituents; the *N*-aryl imide function on sulfur leads to a preference of conformation *e* with S—N equatorial[15,16]. The rest of the compounds in Scheme 2 proved to be largely (**6**) or completely

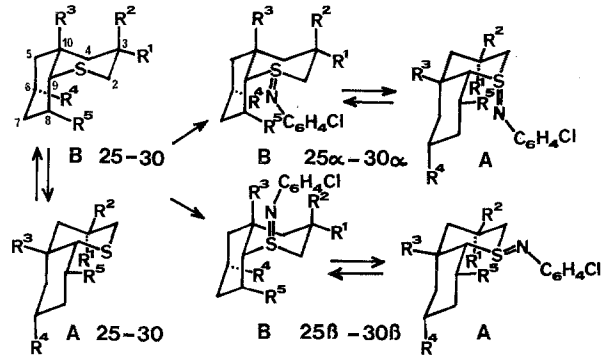
Scheme 3



All R's = H, unless noted

18	all R's = H	**22**	$R^4 = CH_3$ (8α-CH_3)
19	$R^1 = CH_3$ (3β-CH_3)	**23**	$R^5 = CH_3$ (8β-CH_3)
20	$R^2 = CH_3$ (4β-CH_3)	**24**	$R^6 = CH_3$ (9-CH_3)
21	$R^3 = CH_3$ (4α-CH_3)		

Scheme 4



All R's = H, unless noted

25	all R's = H	**28**	$R^4 = CH_3$ (6α-CH_3)
26	$R^1 = CH_3$ (3α-CH_3)	**29**	$R^5 = CH_3$ (8α-CH_3)
27	$R^2 = CH^3$ (3β-CH_3)	**30**	$R^3 = CH_3$ (10-CH_3)

(**5**, **7**, **8**, **9**, **10**, **11**, **12**, **14**, **16**) conformationally homogeneous; in most cases the inability of the ring to invert was already inherent to the parent thiane. Compounds **13**, **15**, and **17** have not been isolated so far.

trans-1-Thiadecalin-1-N-aryl imides (Scheme 3). Ring inversion in the *trans*-1-thiadecalin series is prohibited by the fusion of the thiane

and cyclohexane rings, and the sulfimide functionality is therefore fixed in either equatorial (**18**α-**24**α) or axial (**18**β-**24**β) orientation. (For nomenclature see footnote a, Table 1.) Only one sulfimide with axial S—N bond (**18**β) has been isolated so far (see discussion).

cis-1-Thiadecalin-1-N-aryl imides (Scheme 4). *cis*-1-Thiadecalin (**25**) is a conformationally mobile ring system which at room temperature inverts rapidly between conformations **A** and **B**[17b]. Sulfimide synthesis starting with *cis*-1-thiadecalins therefore can lead to two isomeric sulfimides (**25**α-**30**α, **25**β-**30**β) which are again subject to ring inversion: α**A** ⇄ α**B** and β**A** ⇄ β**B**, respectively. Conformations α**A** are largely prohibited by two CH_2/N *syn*-axial interactions (N with C-5 and C-7; see Scheme 4). Additionally, suitable biasing groups can shift the conformational equilibria to the side of one conformer (see discussion).

Apart from the compounds listed above we have investigated 1-*N*-aryl imides of 1,3-dithianes; these results will be reported elsewhere. Part of the experiments described in the sequel have been published as a short communication[18].

Discussion

In the majority of cases synthesis of the sulfimides was achieved by reaction of the corresponding sulfides and anilines in dichloromethane at —60 °C with a slight excess of either *N*-chlorosuccinimide (NCS) or *tert*-butylhypochlorite (*tert*-BuOCl)[19] in a procedure described by us[7]. 4-Chloroaniline was used to prepare the sulfimides investigated in this paper, because nearly all sulfimides derived from this amine were crystalline compounds at room temperature, and the symmetrical AA'BB'-pattern of the aromatic hydrogens in the ^{1}H-nmr spectra facilitated detection of isomeric sulfimides in the crude product mixtures. No attempts were made to isolate the intermediate azasulfonium salts, which were converted into the free sulfimides by treatment with base. The sulfimides prepared are listed in Table 1.

In contrast to the oxidation of cyclic sulfides to sulfoxides, where both isomers in almost pure form as well as mixtures of almost any composition can be synthesized by suitable choice of oxidants and reaction conditions[20], formation of sulfimides from *p*-chloroaniline* with axial orientation of the S—N bond is apparently strongly inhibited,

* It must be emphasized that the results described here are pertinent only for 4-chloroaniline. Different substituents on aniline may lead to product mixtures with different composition; an experiment with 4-methylthiane, 4-nitroaniline and *tert*-BuOCl gave **5** and **6** (with —NO_2 instead or —Cl) in nearly equal amounts. Further investigations regarding the influence of substituents on aniline are under way.

Table 1. *Preparation of cyclic N-p-chlorophenyl-sulfimides*

Compound[a]	Yield[b], %	mp[c], °C	Elemental analysis	
			Calcd.	Found
3	79 (A)	146-150	C 58.01, H 6.20	C 58.17, H 6.36
4	60 (B)	120-121	C 61.04, H 7.09	C 61.10, H 7.07
5	73 (B)	149-153	C 59.61, H 6.67	C 59.68, H 6.84
6	11 (C)	77-79	C 59.61, H 6.67	C 59.19, H 6.70
7	58 (A), 82 (B)	205-209	C 63.47, H 7.81	C 63.38, H 7.93
8	10 (C)	122-124.5	C 63.47, H 7.81	C 63.66, H 7.56
9	52 (A), 78 (B)	134-136	C 61.04, H 7.09	C 60.87, H 7.09
10	8 (C)	130-133	C 61.04, H 7.09	C 61.08, H 7.07
11	58 (A)	92-95	C 61.04, H 7.09	C 60.44, H 7.10
12	30 (A)	92-96	C 62.32, H 7.47	C 62.15, H 7.45
14	55 (A)	95-99	C 62.32, H 7.47 S 11.88	C 61.99, H 7.28, S 12.12
16	93 (A)	oil	—	—
18α	58 (A), 74 (B)	129-131	C 63.92, H 7.15, N 4.97	C 64.09, H 7.16, N 4.98
18β	10 (C)	108-110	C 63.92, H 7.15	C 64.08, H 7.01
19α	77 (A)	114-119	C 64.95, H 7.49	C 65.15, H 7.58
20α	67 (A)	163-165	C 64.95, H 7.49	C 64.96, H 7.52
21α	43 (A), 51 (B)	117-120	C 64.95, H 7.49	C 64.76, H 7.43
22α	55 (A) 61 (B)	104-108	C 64.95, H 7.49	C 65.08, H 7.46
23α	79 (A)	165-169	C 64.95, H 7.49, N 4.73	C 65.22, H 7.39, N 4.75
24α	62 (B)	96-99	C 64.95, H 7.49, N 4.73	C 65.39, H 7.53, N 4.71
25α	19 (B)[d]	114-115	C 63.92, H 7.15	C 63.75, H 7.13
25β	38 (A)	161-167	C 63.92, H 7.15	C 64.10, H 7.23
26α	51 (A)	169-172	C 64.95, H 7.49	C 64.90, H 7.42
27β	60 (A)	96-98	C 64.95, H 7.49	C 65.15, H 7.44
28β	81 (A)	160-162	C 64.95, H 7.49	C 64.81, H 7.67
29β	24 (A)	152-155	C 64.95, H 7.49, N 4.73	C 65.04, H 7.53, N 4.66
30β	80 (A)	154-156	C 64.95, H 7.49, N 4.73	C 65.32, H 7.39, N 4.68

[a] "β": substituent is on the same side of the ring as the hydrogen (or substituent) on C-10 of 1-thiadecalins: "α": on the side opposite to this hydrogen (substituent).

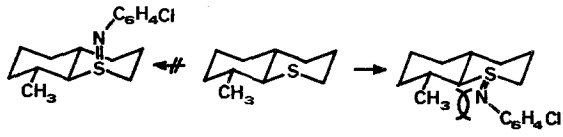
[b] Yields of once recrystallized materials; (method used for preparation; A: sulfide—NCS, B: sulfide—*tert*-BuOCl, C: sulfoxide—P_2O_5).

[c] Highest mp observed; some sulfimides decompose at the mp; products recrystallized from ether, ether—*n*-hexane or chloroform—ether.

[d] Besides 42% **25**β.

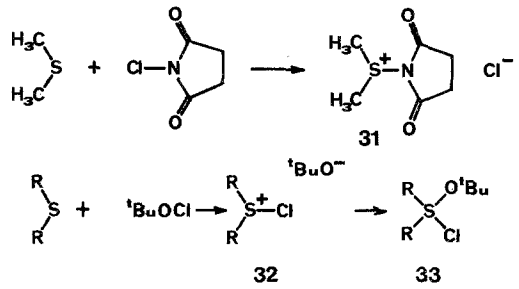
and the products with equatorial S—N are formed preferentially, regardless of the method (reagents NCS or *tert*-BuOCl). Presence of traces of the "axial" sulfimides could sometimes be suspected by thin layer chromatography of the crude product mixtures, but the compounds could not be isolated or identified by nmr. An exception in that respect are the reactions with 1,3-dithianes[18]. An attempt to force the formation of the axial S—N bond in the *trans*-1-thiadecalin series through introduction of an (equatorial) 8α-methyl group (in compound **22**), which places the (equatorial) 1α-*N*-aryl substituent in a relatively strained position* (see Scheme 5) was unsuccessful: only 1α-imide **22**α was formed in good yield (compare Table 1).

Scheme 5



22β **22** **22α**

Scheme 6



The details of the mechanism of sulfimide formation are still unknown. In the reaction of dimethyl sulfide with NCS, *Vilsmaier* and *Sprügel*[21] obtained a crystalline compounds **31**, a succinimidylsulfonium chloride (or, possibly, a sulfurane with tetracovalent sulfur). The same authors report[22] that the succinimidyl group in **31** can be replaced, presumably with inversion on sulfur, by nucleophiles (e.g. anilines) with formation of azasulfonium salts.

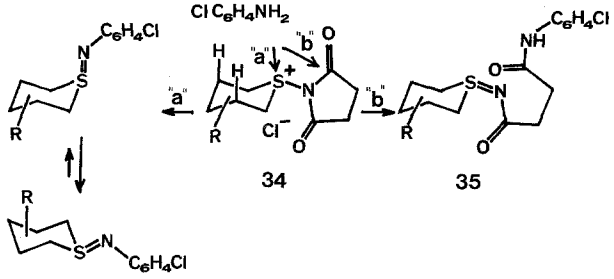
* The effect is similar to a 1,3-*syn*-axial interaction and is subsequently termed so.

When sulfides react with *tert*-BuOCl, chlorosulfonium ions **32** are supposedly[23,24] formed in a fast reaction. These are rapidly further converted to sulfurane intermediates **33,** which, according to *Swern*[24], are no longer able to react with anilines or amides to yield azasulfonium salts. If aniline is present in the reaction mixture from the beginning, as is the case in our synthetic procedure, sulfimides are obtained in excellent yields after deprotonation of the intermediates with base.

Reactions with N-Chlorosuccinimide (Method A)

Intermediates **34** (analogous to **31**), although not isolated, are obviously formed in reactions of cyclic sulfides with NCS. An indication is the isolation of byproducts **35**, which were found in varying amounts (up to 30%).

Scheme 7



The ring-opened products **35** must have identical configuration on sulfur as their precursors **34**, since there is no reason to expect ring opening to be connected with inversion on sulfur. Compounds **35** from conformationally rigid ring systems were always found to have equatorial orientation of the S—N bond. This implies that the succinimidyl group in conformationally rigid intermediates **34** is largely equatorial. Nucleophilic attack of aniline on the positively charged sulfur in **34** (Scheme 7, path "a") is apparently hindered, probably by steric interaction with the axial protons at C-3 and C-5, or at C-3, C-10 and C-8 in the *trans*-1-thiadecalin series. Attack on a carbonyl carbon (Scheme 7, path "b") is less hindered, leading to ring opening and to products **35**. This type of attack ("b") can, however, be prevented in more severely sterically hindered cases, for instance by an axial methyl group at C-3 or C-8 in *trans*-1-thiadecalin (compounds **19, 23**), and no products **35** are detected in these cases.

Intermediates **34** with axial S—N-orientation might be intermediates in the formation of sulfimides with equatorial S—N bond. While these "S—N-axial **34**" cannot be excluded, their existence appears highly unlikely for the following reasons. 1,3-*syn*-axial interactions with the axial hydrogens on C-3 and C-5 are responsible for a high conformational preference of the equatorial form in thiane-1-*N*-arylimides[15,16]; corresponding *syn*-axial interactions (and with hydrogens at C-3, C-10 and C-8 in the *trans*-1-thiadecalin series) must be the reason why no "axial" sulfimides are formed with conformationally rigid thianes. Similar *syn*-axial interactions should oppose the formation of "S—N-axial **34**"; their formation, in substantial extent, would seem impossible in the syntheses with 3β-CH_3-*trans*-1-thiadecalin (**19**) and 8β-CH_3-*trans*-1-thiadecalin (**23**), where a methyl group instead of a proton is *syn*-axial to an axial substituent on sulfur; nevertheless sulfimide synthesis in both cases leads smoothly and with excellent yields to the 1α-sulfimides (**19**α, **23**α).

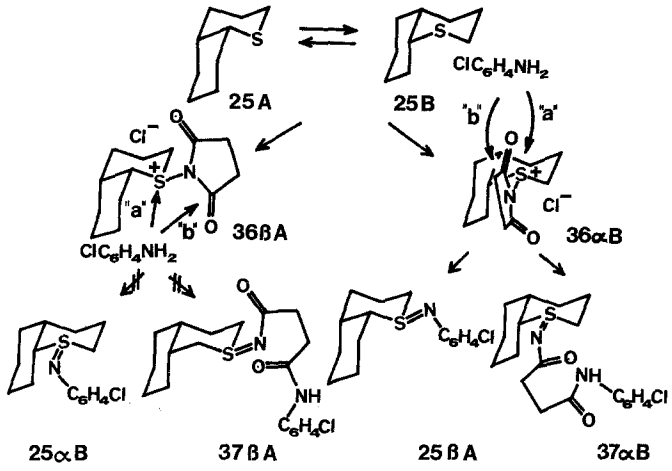
Since there is no reason to suppose that replacement of an equatorial succinimidyl group on sulfur takes place with retention of configuration, and since formation of "S—N axial **34**" is also unlikely, one has to look for mechanisms other than substitution on intermediates **34** to explain the exclusive formation of "equatorial" sulfimides in conformationally biased ring systems. However, this does not exclude the effectiveness of such a mechanism in conformationally mobile systems. An example is the reaction of *cis*-1-thiadecalin (**25**). At the temperature of synthesis **25** exists in a ratio of 58:42 of the two conformers **25 A** and **25 B**[17b] (Scheme 8). Two isomeric intermediates **34** can be formed, both of which should exist preferentially in the form with equatorial S—N bond, **36**β **A** and **36**α **B** (Scheme 8; only preferred conformations are shown).

In fact, reaction of **25** with anilines and NCS gave only one sulfimide, **25**β (largely in conformation **A**[15]), and one ringopened product with α-configuration on sulfur and conformation **B**, **37**α. This suggests the conclusion that replacement of the succinimidyl group in **36**α **B** by aniline, with inversion on sulfur, leads to sulfimide **25**β **A** and that **37**α **B** is formed from the same intermediate in a side reaction. The axial attack on sulfur in **36**α is probably facilitated by the ability of the compound to invert in the transition state already.

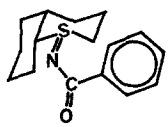
Two explanations come to mind, why formation of **25**α via **36**β does not occur. Either, **36**β is formed together with **36**α but an attack of aniline on sulfur is ruled out by sterical hindrance of the methylene groups of the cyclohexane ring (C-5, C-7); or **36**β is not formed at all. This latter assumption might not seem plausible; it becomes more likely, however, by the surprising finding that reaction of **25** with *N*-bromobenzamide gave only one benzoyl imide, **38**α[25], with α-

configuration. No simple explanation for the predominance of α-products in the reaction of **25** with *N*-haloamides is at hand. One might suggest an energetic disadvantage of the **36** β-isomer through steric interactions of an axially oriented chlorine with the hydrogens on C-5 and C-7, either in an ion pair **36** β **A**, or in a corresponding sulfurane.

Scheme 8



Furthermore, reactions of conformationally mobile *cis*-1-thiadecalins seem to be rather sensitive towards small changes in steric requirements: while **25** gave the products described above (**25** β and **38** α, respectively) upon reaction with aniline/NCS or *N*-bromobenzamide, reaction of 10-CH_3-*cis*-1-thiadecalin (Scheme 4, **30**) in both cases gave products with β-



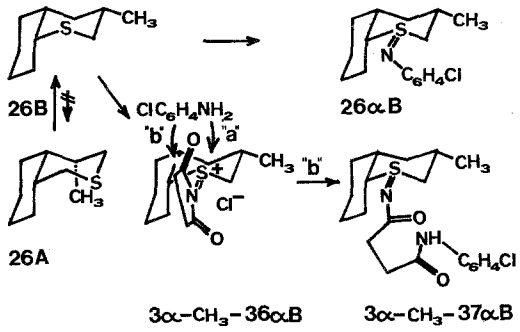
38 α

configuration and conformation A (**30** β and 10-CH_3-*cis*-1-thiadecalin-1β-*N*-benzoyl imide, respectively), although sulfide **30** exists largely (67 % at −70 °C) in conformation **B**[17b].

The situation is different if the starting *cis*-1-thiadecalin is fixed in conformation **B** by suitable substitution[17b]: in case of 3α-CH_3-*cis*-1-

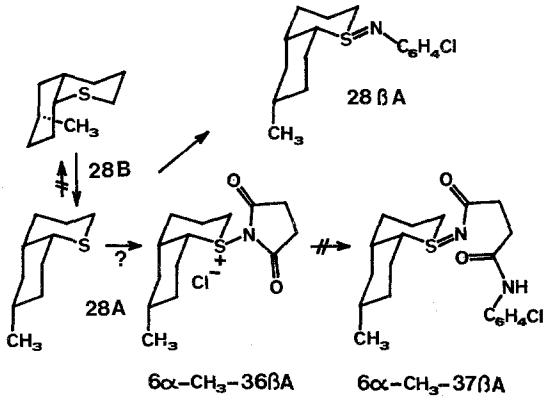
thiadecalin (Scheme 9, **26**) only α-imide **26** α **B** is isolated, in good yield. It is significant that the yield of succinimidyl ringopened product with α-configuration (3α-CH_3-**37** α **B**) is quite high.

Scheme 9



These results are in agreement with the observations made with other conformationally rigid systems; the formation of **26** α can hardly be explained with a substitution at sulfur. Axial attack on an intermediate 3α-CH_3-**36** α **B** (Scheme 9, "a") would lead to a sulfimide **26** β **B** with axial S—N (compare Scheme 4); ring inversion to conformation A is prohibited by the *syn*-axial interaction between CH_3 and C-5; hence, this attack is energetically less favourable than the competing attack ("b") on the carbonyl carbon, and 3α-CH_3-**36** α **B** gives ringopened product 3α-CH_3-**37** α **B**, while **26** α **B** must have been formed in some different process.

Scheme 10

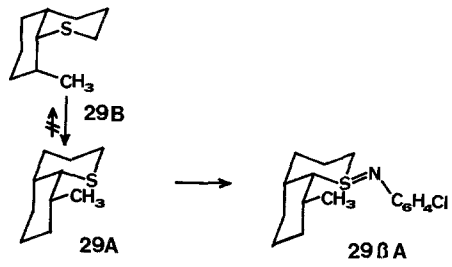


Starting with a *cis*-1-thiadecalin fixed in conformation **A**, for instance **28** (Scheme 10; ring inversion is prohibited by the *syn*-axial interaction between CH_3 and C-4[17b]), one obtains sulfimide **28** β **A** in good yield.

Once more a substitution on an intermediate 6α-CH_3- **36** β **A** is hard to imagine. As in case of 3β-CH_3-*trans*-1-thiadecalin (**19**) and 8β-CH_3-*trans*-1-thiadecalin (**23**) (*vide supra*) no ring-opened succinimidyl product 6α-CH_3-**37** is isolated: both attacks on sulfur and on carbonyl carbon are badly sterically hindered.

Reaction of 8α-CH_3-*cis*-1-thiadecalin (**29**), locked in conformation **A** (Scheme 11; *syn*-axial interactions between CH_3 and C-2, C-4 in conformer **29 B**[17b]) gives only poor yields of sulfimide **29** β: while a *syn*-axial methyl group was not sufficient to prevent formation of **22** α in case of the analogously substituted 8α-CH_3-*trans*-1-thiadecalin (see Scheme 5), both orientations of the S—N bond in this instance are badly constrained.

Scheme 11



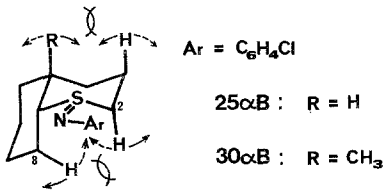
Reactions With tert-Butyl Hypochlorite (Method B)

Generally reactions with tert-butyl hypochlorite lead to similar results as the ones with NCS described above: if conformationally homogeneous starting sulfides are used, nearly exclusive formation of sulfimides with equatorial S—N bond takes place (notice footnote* on p. 613).

A noticeable exception is the reaction with the conformationally mobile *cis*-1-thiadecalin **25**. Here both sulfimides **25** α and **25** β (Schemes 4, 8) are obtained in a ratio of ~ 1:2, in contrast to the results with NCS. 10-CH_3-*cis*-1-thiadecalin (**30**) once more yields only sulfimide **30** β. A reason for the preference for configuration β of the sulfimides derived from **30** (and, hence, for conformation **A** because of an additional CH_3/N *syn*-axial interaction in **B**) may be that the thiane ring becomes more

puckered upon formation of the sulfimide, leading to a closer approach of H_a-8 and H_a-2 in *cis*-1-thiadecalin-α-sulfimides, which finds relief in bending apart C-2 and C-8. This in turn forces together the axial substituents on C-3 and C-10, two protons in case of **25** α but a proton and a methyl group in case of **30** α. The methyl substituent at C-10 thus prevents minimization of strain caused by the approach of C-2 and C-8 and makes **30** α energetically unfavourable.

Scheme 12



Two mechanistic possibilities can be envisaged for the reaction with *tert*-BuOCl: either a chlorosulfonium intermediate **32** is intercepted by aniline prior to its reaction to a sulfurane **33** (which according to *Swern* no longer reacts with aniline[24]), or the reaction proceeds via intermediate *N*-chloroanilines.

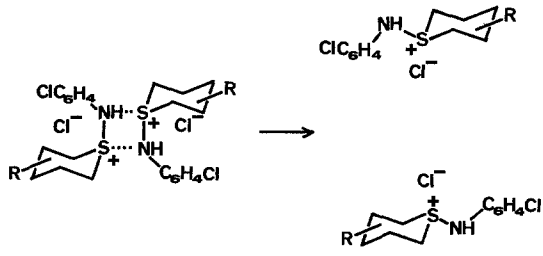
If the first assumption is correct, conformationally homogeneous sulfides must either react stereoselectively to intermediates **32** (with equatorial S—Cl) which then react stereospecifically with retention of configuration on sulfur with anilines; or, an axial S—Cl bond must be formed stereoselectively and opened with inversion. Both suggestions are unsatisfactory, especially if considered in connection with the analogous results with NCS.

A largely irreversible reaction of sulfide with an intermediate *N*-chloroaniline to sulfimides with a large preference of the S—N equatorial configuration, on the other hand, seems entirely plausible. Independent of the (rapidly established) reversible equilibrium between sulfide, NCS and intermediate **34**, which leads to ringopened products **35**, the formation of *N*-chloroaniline may also take place in reactions with NCS discussed earlier. The question why reaction of **25** with *N*-chloroaniline should mostly give a product with β-configuration (**25** β) while the only product formed with *N*-bromobenzamide has α-configuration (**38** α) remains unanswered.

One other important point must be considered: independent of the mechanism of original S—N bond formation we cannot rule out pyramidal inversion, or fast exchange together with inversion, taking place after reaction to the azasulfonium salts. Only few data of $\Delta G^{\ddagger}$ for

pyramidal inversion of sulfur in sulfimides and azasulfonium salts have been reported: ~ 29 kcal/mol for *N*-tosyl sulfimides (**1a**), ~ 34 kcal/mol for *N*-acyl sulfimides (**1b**), and ~ 26 and ~ 29 kcal/mol, respectively, for *N*-tosyl and *N*-acyl azasulfonium salts[26]; no data for *N*-aryl sulfimides are available as yet. It must remain open for the moment if the barrier of inversion in case of *N*-aryl azasulfonium salts is lowered so much that inversion can play a significant role. However, it seems hard to find a satisfactory explanation why a mixture of **25** α and **25** β is not formed with aniline/NCS (but is formed with aniline/*tert*-BuOCl) from **25** if the barrier of inversion were that low. As to the possibility of exchange with inversion, exchange experiments between preformed azasulfonium salts and added aniline under standard reaction conditions did not show noticeable exchange, but do not rule out such an exchange nor one between dimerically associated azasulfonium ions (Scheme 13). Finally, there exists the possibility of isomerization to the energetically most favourable isomer through pseudorotation of intermediate sulfuranes.

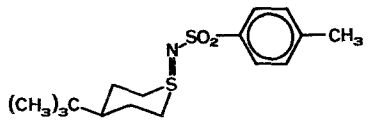
Scheme 13



By way of a summary we believe that a number of mechanisms of formation of *N*-aryl sulfimides are operative, with their relative importance varying, depending on the structure of the starting sulfide. In case of reaction with NCS rapid formation of a succinimidyl sulfonium salt **34,** followed by replacement of the succinimidyl moiety with inversion on sulfur seems possible only in the case of conformationally mobile sulfides. In rigid systems a reaction with intermediate *N*-chloroaniline removes the sulfides from the rapidly established equilibrium between NCS, sulfide and intermediate **34.** Reactions with *tert*-BuOCl presumably proceed via *N*-chloroanilines. In addition, isomerization processes following S—N bond formation and leading to the thermodynamically most stable product must be considered.

Sulfimides With Axial S—N *Bond via Thiane Oxides (Method C)*

Inversion of configuration on sulfur in reactions of sulfoxides with arylsulfonyl amides to give *N*-arylsulfonyl imides **1 a** is well known[27]. *Johnson*[28] obtained *cis*-4-*tert*-butylthiane-1-*N*-tosyl imide (**39**), with reversed configuration on sulfur, from *trans*-4-*tert*-butyl-thiane oxide and *p*-toluene sulfonamide in rather poor yield; the product isomerized to the *trans*-isomer when stored at room temperature for two days.



39

Starting with a cyclic sulfoxide with an equatorial sulfoxide function (*trans*-4-methyl- and *trans*-4-*tert*-butyl-thiane oxide, *cis*-3-*cis*-5-dimethyl-thiane-1-*r*-oxide and *trans*-1-thiadecalin-1 α-oxide) and using a modified procedure originally described[6a] for the synthesis of *S,S*-dimethyl sulfimides **1 d** we were able to isolate the corresponding sulfimides with inverted configuration at sulfur (i.e. axial S—N bond: **6, 8, 10,** and **18**) in moderate yields together with varying amounts of the isomeric sulfimides with equatorial S—N bonds. The yields of sulfimides with inverted or retained configuration on sulfur depend strongly on the conditions employed: an increase of the amount of P_2O_5, or the use of other electrophilic activating agents such as SO_3[8] favoured formation of the "equatorial" sulfimide, and prolonged reaction periods led to reduced yields of "axial" sulfimides, presumably through equilibration either of the activated sulfoxide or of the azasulfonium salt.

Reactions of sulfoxides with P_2O_5 are supposed to give rise, reversibly, to reactive sulfonium intermediates[6a,8] which are attacked by nucleophiles such as amines. The equilibrium in this reaction is assumed to be far on the side of the starting materials. In case of reactions of cyclic sulfoxides with equatorial S—O bond, axial attack of aniline on the sulfur of the sulfonium intermediate is again hindered, and formation of "axial" sulfimides is thus kinetically disfavoured; at the same time aniline is consumed by reaction with P_2O_5.

In contrast to the reported facile isomerization of **39**[28], all *N*-aryl sulfimides with axial S—N bond proved entirely stable at ambient temperatures.

Acknowledgement

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Elemental analyses were carried out by Dr. *J. Zak* (Institute of Physical Chemistry, University of Vienna).

Experimental

Thin layer chromatography was carried out on precoated plastic sheets (SIF, Riedel-de Haen, or Polygram Alox N/UV_{254}, Macherey-Nagel), with $CHCl_3$ as solvent. Column chromatography was effected using glass columns of 40–60 cm length, 2.5–4 cm o.d. (adsorbent "Aluminiumoxid 90", Merck, activity II–III), or of 10 cm length (adsorbent "Kieselgel 60", Merck, 70–230 mesh ASTM), with $CHCl_3$ as solvent. Melting points were determined on a *Kofler* micro-hotstage and are uncorrected. The yields reported are not optimized.

Spectral data (^1H- and ^{13}C-nmr spectra) are reported in a separate paper[14].

Starting materials. Sulfides were prepared according to the literature (thiane[20,29], 4-methylthiane[20,29], 4-*tert*-butylthiane[20], 4,4-dimethylthiane[30], *cis*- and *trans*-3,5-dimethylthiane[30], 3,3,5-trimethylthiane[30]) or by procedures developed in this laboratory (2,2,4-trimethylthiane and 2,4,4-trimethylthiane: see below; *trans*- and *cis*-1-thiadecalins: [17a] and the literature cited there).

4-Chloroaniline was purified by distillation before use. *N*-Chlorosuccinimide[31] and *tert*-butyl hypochlorite[32] (stored in the dark at −25 °C) were prepared by known procedures. Solvents were "Merck" grade; CH_2Cl_2 and $CHCl_3$ for the synthesis of sulfimides were dried over P_2O_5 and distilled.

2,2,4-Trimethylthiane (**40**) (Scheme 14)

3,5-Dimethylhex-1-ene-5-thiol (**41**). To a suspension of 63.4 g magnesium turnings in 1,000 ml anhydrous ether a solution of 89 g 3-chlorobutene-1 was added over a period of 8 h. The resulting mixture was heated to reflux for an additional 30 min., and a solution of 29 g isobutylene sulfide[33] in 100 ml anhydrous ether was added gradually. After the addition was complete the mixture was heated to reflux over night, cooled and hydrolyzed with an aqueous solution of NH_4Cl. The ether phase was separated, the aqueous layer was repeatedly extracted with ether, the ether phases were combined, washed with 10% solution of $NaHCO_3$ and dried over Na_2SO_4. The solvent was distilled off to give 38.4 g **41**, which was used for the synthesis of **40** without further purification.

2,2,4-Trimethylthiane (**40**). A solution of 36 g **41** and 4 g azobis-isobutyronitrile in 200 ml benzene was heated to reflux for 24 h. The solvent was distilled off on a small *Vigreux* column at atmospheric pressure, and the residue was distilled at 63–64 °C/19 Torr; yield 14.6 g **40** (30% from isobutylene sulfide).

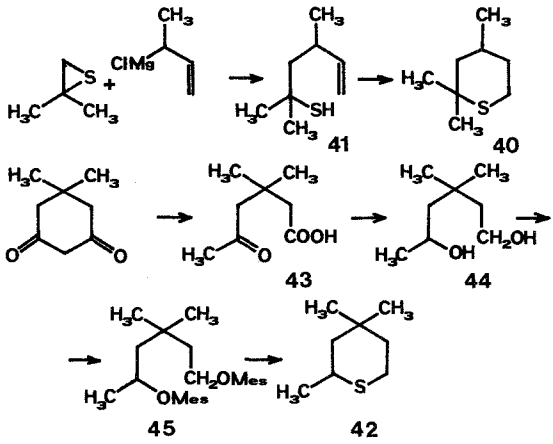
For ^{13}C- and ^1H-nmr data see [30].

$C_8H_{16}S$ (144.3). Calc. C 66.66, H 11.18. Found C 66.73, H 11.30.

2,4,4-Trimethylthiane (**42**) (Scheme 14)

3,3-Dimethyl-5-oxo-hexanoic acid (**43**). Dimedone[34] (14.7 g) and 166 g NaOH were dissolved in 150 ml water, and the mixture was heated to reflux for 24 h and then poured on 1500 ml ice-water. The mixture was made acidic with HCl and then extracted with ether. The ether extracts were dried over Na_2SO_4, the solvent was distilled off and the residue was distilled in a *Kugelrohr* distillation unit (air bath 150 °C, 12 Torr; bp [35] 150 °C, 12 Torr), yield 10.8 g **43** (65 %).

Scheme 14



2,5-Dihydroxy-3,3-dimethylhexane (**44**). A solution of 10.8 g **43** in anhydrous ether was slowly added to a suspension of 4 g $LiAlH_4$ in anhydrous ether, and the mixture was heated to reflux for 12 h. After hydrolyzing carefully with water and acidification with H_2SO_4 the phases were separated, the aqueous phase was repeatedly extracted with ether, the ether phases were combined and dried over Na_2SO_4 and the solvent was distilled off. The residue was distilled on a *Kugelrohr* unit (air bath 140 °C, 12 Torr): yield 9,3 g (94 %) **44**, pure by gas chromatography.

2,5-Bismethylsulfonyloxy-3,3-dimethylhexane (**45**). To a solution of 9.3 g **44** in 170 ml anhydrous pyridine 20 ml methanesulfonyl chloride were added at 0 °C. After addition was complete the solution was left in a refrigerator for 100 h and then poured on a mixture of ice, water and HCl. The product was extracted with CH_2Cl_2, the organic layer was dried over Na_2SO_4 and the solvent was distilled off. The residual oil was used for the next step without further purification (yield of raw material 17.7 g).

2,4,4-Trimethylthiane (**42**). A solution of 16.5 g of the crude **45** in the minimum amount of *DMF* was added to a solution of 13.1 g $Na_2S \cdot 9\,H_2O$ (1.5 mol-equivalents) in 200 ml 50 % aqueous ethanol. The mixture was heated and worked up following[30], to yield 5.6 g of a mixture of **42** and of a second,

unidentified compound (presumably 2-ethyl-3,3-dimethylthiolane) in a ratio of 78:22 (determined by GC; yield of **42** ≃ 55%). The mixture could be separated by preparative GC (column: 4 m long, 0.375-in o.d., aluminum; phase: 20% Carbowax 20 M, 10% KOH on Chromosorb A, 60/80 mesh; 120 °C) to give pure **42**.

For ^{13}C- and ^{1}H-nmr data see [30].

$C_8H_{16}S$ (144.3). Calcd. C 66.66, H 11.18. Found C 66.86, H 11.37.

Procedures for the Synthesis of N-Aryl Sulfimides

Sulfide—NCS (Method A): According to [7].

Sulfide—*tert*-BuOCl (Method B): According to [7].

In both procedures the reaction mixture was kept in a freezer at −20 °C over night when addition of NCS- or *tert*-BuOCl-solution was complete. The solvent was distilled at atmospheric pressure with the exception of the synthesis of sulfimides which were or were supposed to be sensitive to elevated temperatures (**6**, **8**, **10**, **12**, **18**β, **24**α, **25**α, and **29**β); in these cases reduced pressure and bath temperatures < 40 °C were used.

Purification procedures depended on the composition of the mixture of products. If the thin layer chromatogram of the crude mixture indicated a yield of sulfimide > 50% (in most cases of method B) the residue after distillation of the CH_2Cl_2 was recrystallized from ether, from ether/*n*-hexane, or in case of sulfimides of low solubility (**7**, **23**α, **25**β, **27**β-**30**β) from $CHCl_3$/ether (with cooling to −20 °C). Yields of products could be improved by column chromatography (Al_2O_3, $CHCl_3$) of the mother liquors.

In case of mixtures of sulfimides (lower retention time product listed first) (**5** and **6**, **7** and **8**, **9** and **10**, **18**α and **18**β, **25**β and **25**α), for separation of sulfimides (**3**, **9**, **11**, **12**, **14**, **18**α, **20**α, **21**α, **24**α, **25**β, **26**α) from succinimide ring-opened products if Method A was used, and to isolate sulfimides from strongly colored reaction mixtures (**22**α, **24**α, **29**β) it was necessary to separate the products by column chromatography prior to crystallization. Ring-opened products **35** generally had much lower *Rf*-values on TLC, and higher retention on column chromatography. Yields in Table 1 are for products once recrystallized. Isolation via the picrates[6c,7] is a further possibility to isolate pure sulfimides but does not offer additional advantages for the compounds reported in this paper.

Sulfoxide—P_2O_5 (Method C): The procedure reported in [6a] was used in a modified manner for the synthesis of **6**, **8**, **10**, and **18**β:

cis-4-Methylthiane-1-N-p-chlorophenyl-imide (**6**). In 75 ml anhydrous $CHCl_3$ containing 1% $(C_2H_5)_3N$ 10.8 g P_2O_5 were suspended and a solution of 5 g of a mixture of ~ 75% *trans*-4-methylthiane-1-oxide, ~ 15% *cis*-4-methyl-thiane-1-oxide and ~ 10% 4-methylthiane-1,1-dioxide (prepared from 4-methylthiane with O_3[20]) in 35 ml $CHCl_3$ containing 1% $(C_2H_5)_3N$ was added over 10 minutes with stirring. After the addition of the sulfoxide mixture was complete, a solution of 4.8 g 4-chloroaniline in 50 ml $CHCl_3$ + 4 ml $(C_2H_5)_3N$ was gradually added over 50 minutes. The mixture was stirred at ambient temperature for 4 h, and was then poured with stirring into 100 ml 5% aqueous NaOH solution containing some ice. The chloroform layer was separated, the aqueous phase was extracted with $CHCl_3$, the chloroform extracts were combined and dried over Na_2SO_4 and the solvent was distilled at reduced pressure. The residual

mixture was separated by column chromatography (Al_2O_3, $CHCl_3$); yield 1.02 g (11.1 %) **6** and 0.75 g (8.2 %) **5**.

Other sulfimides with axial S—N bond were prepared in a manner analogous to **6**:

8: 2.3 g P_2O_5, 1.0 g of a mixture of ~ 90 % *trans*-4-tert-butylthiane-1-oxide and ~ 10 % *cis*-4-tert-butylthiane-1-oxide (from 4-tert-butylthiane and O_3[20]; crude product mixture partially separated by column chromatography on Al_2O_3; solvent $CHCl_3$ distilled from P_2O_5) and 1.7 g 4-chloroaniline (reaction period: 3 hours) yielded 0.17 g (9.9 %, after recrystallization 6.5 %) **8** besides small amounts of **7**.

10: 5.3 g P_2O_5, 2.58 g of a mixture of ~ 75 % *cis*-3-*cis*-5-dimethylthiane-1-*r*-oxide and ~ 25 % *trans*-3-*trans*-5-dimethylthiane-1-*r*-oxide (from *cis*-3,5-dimethylthiane and O_3 according to [20]) and 2.3 g 4-chloroaniline (reaction period: 5 hours) yielded 0.44 g (9.6 %, after recrystallization 6.2 %) **10** and 0.96 g (21 %) **9**.

18β: 4.3 g P_2O_5, 2.5 g of a mixture of ~ 90 % *trans*-1-thiadecalin-1α-oxide and ~ 10 % *trans*-1-thiadecalin-1β-oxide (from *trans*-1-thiadecalin and O_3 according to [20]; 1α-oxide partially separated from 1β-oxide and 1,1-dioxide by column chromatography on Al_2O_3) and 3.2 g 4-chloroaniline (reaction period: 3.5 hours) yielded 0.42 g (10.3 %, after recrystallization 8.7 %) **18**β besides small amounts of **18**α.

Ring-Opened Products **35**

Succinimidyl ring-opened products (**35**), formed as side products in Method A, were found in case of the following syntheses of sulfimides, and were isolated by column chromatography (parenthesized: yields of products **35**): **3** (27 %), **9** (7 %), **11** (16 %), **12** (3 %), **14** (25 %), **7** (traces), **18**α (9 %), **20**α (13.5 %), **21**α (15 %), **24**α (17 %), **25**β (15.5 %), **26**α (29.5 %). Products **35** were identified by ^{1}H-nmr spectra of the crude materials; only a limited number has been characterized in more detail (see below; for a discussion of the nmr data see [14]):

Thiane-1-N-propionyl[3'-(N-chlorophenyl)-carboxamido]imide (**35**, R = H).

Mp 153—154 °C ($CHCl_3$/*n*-hexane).

MS (in parentheses: % of base peak): M^+ 326 (3 %, $C_{15}H_{19}ClN_2O_2S$), 209 (15), 200 (100), 181 (3), 154 (5), 153 (5), 144 (21), 127 (18), 101 (46), 55 (40).

trans-1-Thiadecalin-1α-N-propionyl[3'-(N-4-chlorophenyl)-carboxamido]-imide (ring opened product **35** from *trans*-1-thiadecalin, **18**).

Mp 158—161 °C ($CHCl_3$/*n*-hexane).

MS: M^+ 380 (1), 254 (30), 209 (89), 181 (21), 154 (49), 153 (48), 127 (96), 55 (100).

$C_{19}H_{25}ClN_2O_2S$ (380.9). Calcd. C 59.91, H 6.62, N 7.35.
Found C 59.73, H 6.55, N 7.37.

cis-1-Thiadecalin-1α-N-propionyl[3'-(N-4-chlorophenyl)-carboxamido]imide (**37**α **B**).

Mp 169—172.5 °C ($CHCl_3$/ether).

MS: M^+ 380 (< 1), 254 (5), 209 (64), 181 (9), 154 (21), 153 (26), 127 (70), 55 (100).

$C_{19}H_{25}ClN_2O_2S$ (380.9). Calcd. C 59.91, H 6.62, N 7.35.
Found C 59.43, H 6.53, N 7.26.

3α-Methyl-cis-1-thiadecalin-1α-N-propionyl[3'-(N-4-chlorophenyl)-carboxamido]imide (3α-CH_3-**37** α **B**).

Mp 88—91 °C ($CHCl_3$/ether).

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