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

SYNTHESIS, CONFIGURATION AND STEREOCHEMISTRY OF THE REARRANGEMENT OF 1,3-DI-THIANE-1-N-*p*-CHLOROPHENYLIMIDES†

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Abstract—1,3-Dithiane-1-N-*p*-chlorophenylimides (**1**, **4–9**) were prepared and their configuration and conformation was determined by ^1H and ^{13}C NMR. The compounds were rearranged to the corresponding 2-(2'-amino-5'-chlorophenyl)-1,3-dithianes (**1U**, **4U–9U**). The rearrangement reactions took place with ≥95% stereospecifity. The mechanism of the reaction was investigated with the aid of analogs specifically deuterated at C-2.

1,3-Dithiane has been of interest to numerous research groups ever since Corey and Seebach reported[2] the high synthetic utility of the carbanion derived from this compound. In particular, stereochemical questions as to the conformational behavior, the influence of substituents on the ring geometry, the stereoselectivity of reactions at C-2, and ^1H and ^{13}C NMR-spectra as probes to these questions have been extensively investigated.[3–9]

In connection with our work on N-aryl sulfimides we became interested in sulfimides derived from cyclic systems.[1,10b] A report on a [2,3]-sigmatropic rearrangement of allyl sulfonium ylids of 1,3-dithiane to give β, γ-unsaturated aldehydes (e.g. γ-cyclocitral)[11] led us to investigate the synthesis and rearrangement reaction of 1,3-dithiane-1-N-arylimides.[12] At the same time Gassman reported[13] the synthesis of *o*-aminobenzaldehydes using this reaction.

In addition to the synthetic possibilities the mechanistic and stereochemical aspects of the rearrangement reaction were of interest to us. The results of experiments carried out to obtain information on these questions are described in the sequel; they are related to our recent work on the synthesis and rearrangement reactions of configurationally and conformationally homogeneous thiane- and *cis*- and *trans*-1-thiadecalin-1-imides.[1,10b] A result presented in this paper has been reported in a short communication.[14]

†Dedicated to Prof. Dr. O. E. Polansky, Max-Planck-Institut für Kohlenforschung, Mühlheim/Ruhr, on the occasion of his 60th birthday.

Discussion of results

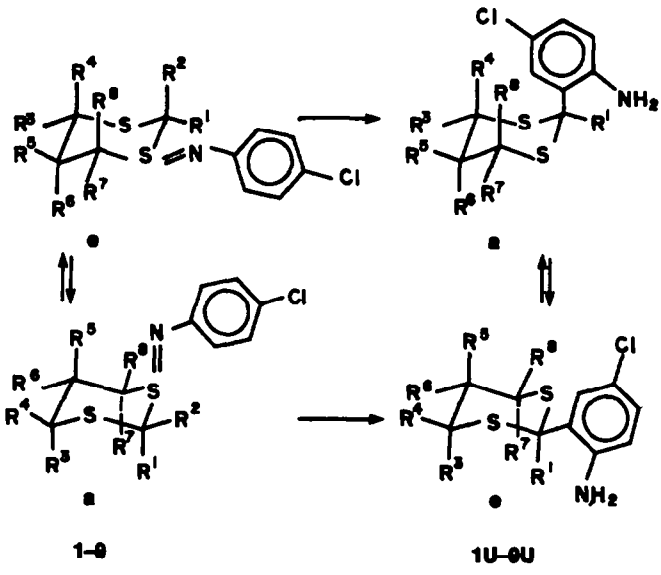
Synthesis of 1,3-dithiane-1-N-arylimides. In order to investigate the stereochemistry of the rearrangement reaction we needed anancomeric, diastereomeric sulfimides. 1,3-Dithiane-1-oxides have been reported in numerous publications;[4,5,8] 1,3-dithiane-1-imides in contrast are hardly known: recently we reported the synthesis of a few 1,3-dithiane-1-N-arylimides,[15] and a number of 1,3-dithiane-1-N-tosylimides have been prepared, some of them substituted at C-5 of the dithiane ring.[7]

The procedure to obtain N-aryl sulfimides[15] by the reaction of the sulfide and aniline with t-butyl hypochlorite or N-chlorosuccinimide at −20° to −70° can be used for the synthesis of 1,3-dithiane-1-N-arylimides (with the exception of anilines bearing strongly electron withdrawing substituents). Yields of 55–90% sulfimide are obtained (Table 1). The compounds prepared are summarised in Scheme 1.

Table 1. Synthesis of 1,3-dithiane-1-N-*p*-chlorophenylimides

Compound [a]	Yield, % [b]	Mp, °C	Elemental Analysis Calc'd	Found
Parent, **1** [c]	c	c	c	c
trans-2-Methyl- , **2**	35 [d], 30 [e]	114 – 124 (d)	C 50.85 H 5.43	C 50.74 H 5.31
trans-2-Methyl- , **3**	67 [d], 42 [e]	103 – 105.5	C 58.62 H 6.71	C 58.52 H 6.67
cis-4-cis-6-Dimethyl- , **4**	65 [e]	103 – 109 [g]	C 50.95[g] H 6.06[g]	C 51.07 H 6.12
trans-4-trans-6-Dimethyl- , **5**	9 [e]	100 – 105.5 [h]		
trans-5-Methyl- , **6**	48 [e]	138 – 140.5	C 50.85 H 5.43	C 50.82 H 5.48
cis-5-Methyl- , **7**	23 [e]	120 – 122.5	C 50.85 H 5.43	C 50.81 H 5.49
trans-5-tert.-Butyl- , **8** [i]	34 [e]	105 – 109	C 55.70 H 6.68	C 56.00 H 6.73
cis-5-tert.-Butyl- , **9** [h,i]				

[a] 1,3-Dithiane-1-*r*-N-*p*-chlorophenylimide, unless indicated. [b] Of repeatedly recrystallized product. [c] See Ref. 15. [d] As picrate. [e] After recrystalization (ether-*n*-hexane). [f] 1-*r*-N-phenylimide. [g] Compound crystallized with 0.5 equivalents water, which could not be separated completely without decomposition of the sulfimide. [h] Because of very facile rearrangement no elemental analysis was performed. [i] Mixture of isomers **8** and **9** is formed in essentially quantitative yield; ratio **8**:**9** = 70:30 (by NMR), Yield of mixture of picrates 70%.



all R's = H unless indicated
parenthesized compounds not isolated

1	all R's = H	1U
1-d_2	$R^1 = R^2 = D$	
2	$R^7 = CH_3$	
(3)	$R^8 = CH_3$	
4	$R^8 = R^7 = CH_3$	4U
4-d_1	$R^1 = D$; $R^8 = R^7 = CH_3$	4U-d_1
4-d_1	$R^2 = D$; $R^8 = R^7 = CH_3$	
4-d_2	$R^1 = R^2 = D$; $R^8 = R^7 = CH_3$	
5	$R^4 = R^8 = CH_3$	5U
5-d_1	$R^8 = D$; $R^4 = R^8 = CH_3$	
5-d_1	$R^1 = D$; $R^4 = R^8 = CH_3$	5U-d_1
6	$R^6 = CH_3$	6U
7	$R^6 = CH_3$	7U
8	$R^6 = C(CH_3)_3$	8U
8-d_1	$R^1 = D$; $R^6 = C(CH_3)_3$	8U-d_1
(9)	$R^6 = C(CH_3)_3$	9U
(9-d_1)	$R^2 = D$; $R^6 = C(CH_3)_3$	
	$R^1 = D$; $R^6 = C(CH_3)_3$	9U-d_1

Scheme 1.

Reaction of anancomeric thianes and 1-thiadecalins resulted in the practically exclusive formation of sulfimides with equatorial S–N bond.[10b] In contrast, mixtures of configurational isomers 4 and 5, and 8 and 9 are formed from *cis*-4,6-dimethyl-1,3-dithiane and 5-t-butyl-1,3-dithiane. This may be due to the absence of one steric interaction with a *syn*-axial hydrogen in position 3 of the dithiane ring in the transition state leading to the S–N-axial sulfimide. The proportion of "axial" sulfimide is highest in case of 5-methyl-1,3-dithiane, which at room temperature exists to about 82% in the conformation with the equatorial Me group;[6c] the conformationally inhomogeneous *trans*-1-imide 7, formed in 23% yield, prefers the conformation with equatorial imide and axial Me group (~70% at −80°[16]).

The yields, and isomeric compositions, which are obtained with t-butyl hypochlorite and N-chlorosuccinimide are about equal. A comparison is problematic because of the high reactivities of 5, 7 and 9, and the difficulties in their separation from 4, 6 and 8.

Separation of isomeric sulfimides could be achieved only by fractional crystallization from ether-n-hexane at low temperature. Other methods, as fractional crystallization of the picrates and subsequent recovery of the sulfimides,[17] or column chromatography on aluminum oxide, gave only the stable S–N-equatorial isomers 4 or 8, and the rearrangement products of 5 or 9, 5U or 9U. The tendency to rearrange decreases in the series 9 > 5 > 7, with 7 largely in the conformation with equatorial S–N.[16] It was possible to obtain 5 and 7 in crystalline form from the mother liquors, after separation of most 4 and 6. The very soluble and instable 9 could not be isolated, but the extent of its formation could be estimated from the ^{1}H NMR spectra (two overlapping AB-systems for H-2_{ax}) and the ^{13}C NMR spectra of the crude sulfimide mixture and of the mixture of picrates, and also from the amounts of the rearranged product 9U, which does not form from the configurational isomer 8.

Only the *trans*-isomer 2 could be isolated from the reaction of 2-methyl-1,3-dithiane, the compound being considerably less stable thermally than other anancomeric 1,3-dithiane-1-imides with equatorial S–N.

Table 2. Rearrangements of 1,3-dithiane-1-N-*p*-chlorophenylimides

Compound[a]	Method[b]	Yield, %[c]	Mp, °C[d]	Elemental Analysis Calc'd	Found
Parent , 4U	A	68	e	C 48.87 H 4.92	C 48.98 H 5.03
trans-4-trans-6-Dimethyl- , 4U	A	72	106 - 107.5	C 52.63 H 5.89 S 23.42	C 52.98 H 6.00 S 23.55
cis-4-cis-6-Dimethyl- , 5U	B	60	113.5 - 115	C 52.63 H 5.89 S 23.42	C 52.97 H 6.00 S 23.82
cis-5-Methyl- , 6U	A	75	88 - 89	C 50.85 H 5.43	C 51.09 H 5.34
trans-5-Methyl- , 7U	B	64	104 - 106	C 50.85 H 5.43	C 50.78 H 5.33
cis-5-tert.-Butyl- , 8U	A	71	113 - 115	C 55.70 H 6.68 S 21.24	C 55.63 H 6.80 S 21.36
trans-5-tert.-Butyl- , 9U	f	22 f	176.5 - 178	C 55.70 H 6.68	C 55.99 H 6.65

[a] 2-*r*-(2'-Amino-5'-chlorophenyl)-1,3-dithiane. See Scheme 1. [b] See Experimental. [c] After isolation by column chromatography. [d] After crystallisation from *n*-hexane. [e] Not crystalline at room temperature. [f] Rearrangement during column chromatography of mixture of sulfimides 8 and 9 after synthesis (see Text).

Thermal decomposition very likely occurs via an intramolecular proton transfer from the 2-Me carbon to the imide nitrogen, followed by elimination. Results in the thiane- and 1-thiadecalin series[1] indicate that this reaction might be still more facile for the *cis*-isomer 3. It proved impossible to rearrange 2 without thermal decomposition.

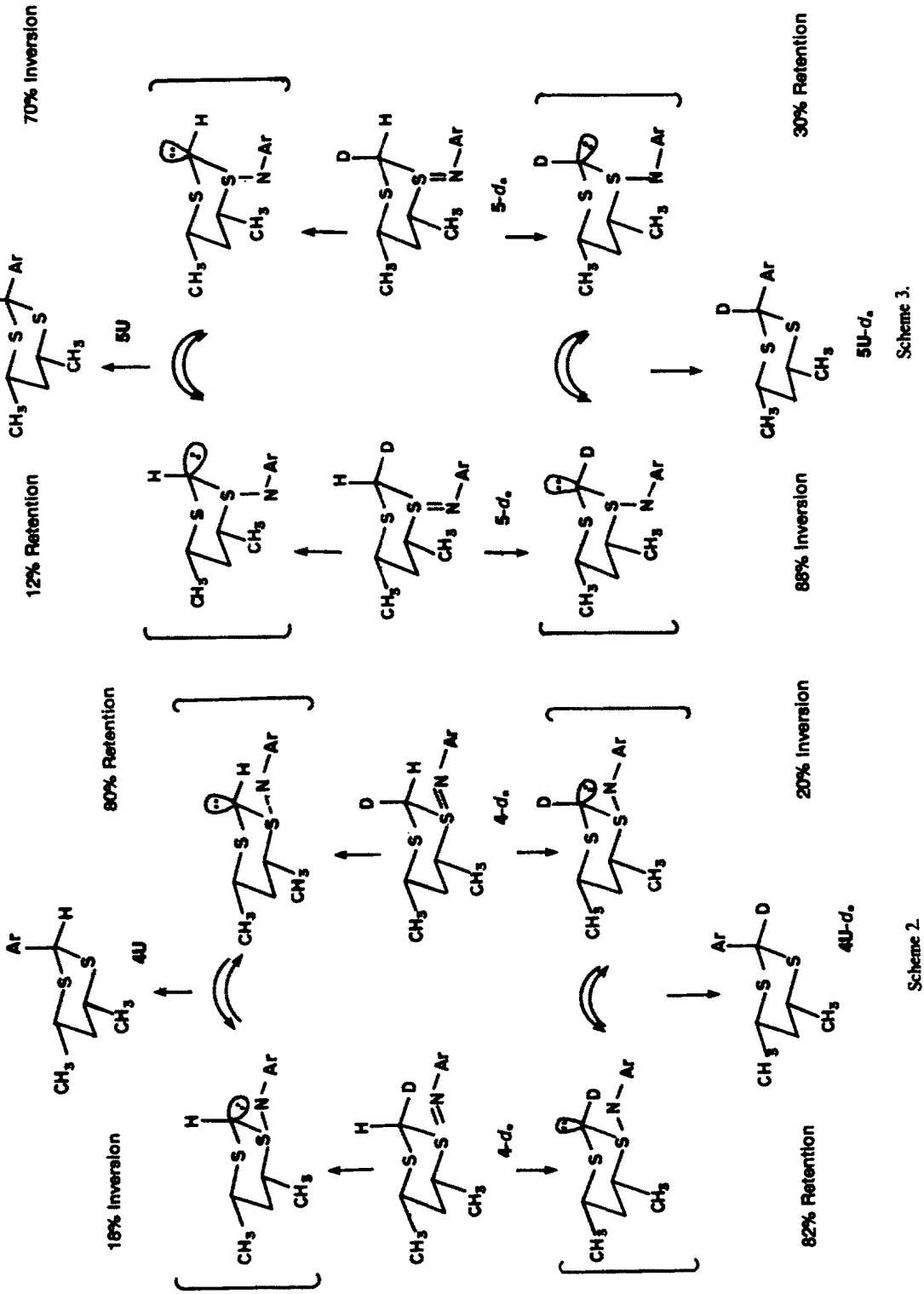
Rearrangement reactions

Base-catalysed rearrangement of 1,3-dithiane-1-N-arylimides to cyclic mercaptals of *o*-aminobenzaldehydes (Scheme 1) takes place at much milder conditions than the rearrangement of thiane- and 1-thiadecalin-1-N-arylimides,[1] probably because of the greater acidity of the protons at C-2. Yields of the crude rearranged products, after heating in benzene-triethylamine at 80°, followed by column chromatography, are around 75% (Table 2). 1,3-Dithiane-imides with axial S–N-functionality show a considerably higher tendency for rearrangement than their S–N-equatorial isomers. The 5-Me derivative 7, largely in conformation 7e,[16] is stable when heated in anhydrous ether, but rearranges without addition of base when heated in moist ether, while conformationally homogeneous equatorial 1,3-dithiane-imides are reasonably stable at these conditions. The anancomeric axial sulfimides 5 and 9 rearrange so easily that their isolation is problematic (see above); rearrangement takes place even at temperatures below 0° in unpolar solvents.

The results of the rearrangement experiments are consistent with the ones obtained in the thiane series.[1] The reaction is highly stereospecific (at least 95%), leading to the compound with the 2-aryl-group *cis* to the position of the original S-imide substituent. The extent of stereospecifity could be derived from NMR and gas chromatographic analysis of the rearrangement mixture and of the mother liquors after separation of the main reaction product. It can be considered as a lower limit, since the configurational purity of the starting sulfimides could not be guaranteed above 95% in every instance.

Eliel *et al*[34] have reported a higher kinetic acidity for H-2_e in the lithiation of anancomeric 1,3-dithianes, and that formation of the pyramidal carbanion with equatorial lone pair (i.e. equatorial lithium) is thermodynamically strongly preferred. Quantum mechanical calculations[18] predict an equatorial preference of electron pairs in carbanions flanked by two S atoms. The high reactivity of 1,3-dithiane-1-imides with axial N-aryl group, in terms of a pyramidal carbanion centre, might have its cause in a preferentially equatorial deprotonation of C-2 and formation of the "equatorial" carbanion suitable for a concerted rearrangement. To find an answer we investigated the rearrangement of sulfimides 4 (Scheme 2), 5 (Scheme 3), 8 and 9, specifically deuterated at C-2. For instance, abstraction of an axial proton or an equatorial deuterium, respectively, from *trans* - 2 - deuterio - *trans* - 4 - *trans* - 6 - dimethyl - 1,3 - dithiane - 1 - N - *p* - chlorophenylimide (4-d_e) results in the formation of an intermediate ylid or carbanion with equatorial deuterium or axial proton. The former yields 4U-d_e with retained configuration at C-2, whereas an inversion of configuration has to take place in the latter to allow formation of the rearranged product with axial aryl ring. Similar considerations apply to the other 2-*d*-sulfimides. Experimentally the contributions of the respective pathways outlined in Schemes 2 and 3 could be derived from the ^{1}H NMR and mass spectra of the rearranged products.

The results are summarised in Table 3. They indicate



Scheme 2.

Scheme 3.

Table 3. Rearrangements of 2-deuterio Compounds

Starting [a] Material	MS data [b]	Products d_0, % [c]		d_1, % [c]		
4-d_e	274 (37), 273 (8)	18 ± 2	4U	82 ± 2	4U-d_e	82 % Retention
4-d_a	274 (14.5), 273 (36)	80 ± 4	4U	20 ± 4	4U-d_e	80 % Retention
5-d_e	274 (35), 273 (4.5)	12 ± 2	5U	88 ± 2	5U-d_a	88 % Inversion
5-d_a	274 (18), 273 (36)	74 ± 4	5U	26 ± 4	5U-d_a	74 % Inversion
8-d_e	302 (48), 301 (10)	18 ± 2	8U	82 ± 2	8U-d_e	82 % Retention
9-d_e	302 (50), 301 (12)	20 ± 2	9U	80 ± 2	9U-d_e	80 % Inversion

[a] For formulas see Scheme 1. Isotopic purity ≥ 95%. [b] $m/e = M + 1$, M. In parentheses: intensity in % of base peak intensity. Base peak: 171 (d_0) or 172 (d_1). [c] Good agreement of product ratios as determined by evaluation of mass spectra and by integration of proton spectra was usually observed.

that for both the axial and equatorial orientation of the N-arylimide group in the starting sulfimide the axial hydrogen or deuterium at C-2 is replaced preferentially by the 2'-aminoaryl group, in a ratio of about 4 : 1 over H-2_e. Rearrangement of imides **4** and **8** (equatorial S–N) takes place largely with retention of configuration at C-2. Imides **5** and **9** (axial S–N) rearrange with inversion of configuration at C-2; the equatorial proton or deuterium in the sulfimide is found in the axial position in the rearranged product.

While the orientation of the 2-aryl substituent in the rearranged product depends on the stereoelectronic requirements of the transition state, one may assume that the relative acidities of the hydrogens at C-2 (H-2_a and H-2_e) are the deciding factor for their abstraction. If this assumption is valid (which is not necessarily so; see below), then the results indicate that H-2_a is considerably more acidic for both steric orientations of the S–N bond. For the imides with axial S–N bond this is in agreement with exchange experiments on sulfoxides[19] at equilibrium conditions (greater acidity of the proton *gauche* to the lone pair and *anti* to the oxygen at the adjacent sulfur atom). For the imides **4** and **8**, however, the preferentially abstracted H-2_a is positioned *anti* to the lone pair and *gauche* to the imide group, a configuration which gave slowest exchange in the corresponding sulfoxides.†

No information is available on the geometry of intermediate α-sulfinimidyl carbanions, or of the anionic centers of intermediate azasulfonium ylids. Even for α-sulfinyl carbanions this question has not yet been fully answered. Pyramidal geometry has been suggested for ions not stabilised additionally by resonance with suitable substituents.[20] On the other hand, planar geometry has recently been found by ^1H and ^{13}C NMR spectroscopy for α-lithiated thiane-1-oxides.[21] But these geometries of metallated derivatives in nonpolar solution can not be simply transferred to carbanions formed at equilibrium conditions in polar media. A planar anionic center in an azasulfonium ylid is stereoelectronically suitable for a concerted rearrangement with suprafacial overlap, regardless which of the two protons is split off. In case of formation of a planar carbanion synchronous to the deprotonation the results thus imply an actually higher kinetic acidity of H-2_a in both "equatorial" and "axial" imides. However, if the geometry is pyramidal, then an initial *trans*-position of electron pair and imide nitrogen necessitates pyramidal inversion prior to rearrangement. In analogy to results obtained on sulfoxides,[19]† a higher acidity might be expected for H-2_e in the "equatorial" imides **4** and **8** (*gauche* to the lone pair and imide nitrogen on sulfur), but sigmatropic rearrangement with suprafacial overlap could only take place after inversion of the resulting carbanionic center to the less stable configuration with axial lone pair. If this inversion is energetically unfavorable, then the rearrangement may still proceed via reprotonation, abstraction of H-2_a and irreversible rearrangement, even if H-2_e is less acidic than H-2_a. For the rearrangement of sulfimides **5** and **9** an interpretation of the observations in terms of an intermediate pyramidal carbanionic center would imply preferred abstraction of the kinetically more acidic H-2_a, followed by inversion to the carbanion with equatorial lone pair which allows the formation of a cyclic transition state. Our results do not allow any conclusions as to the configuration of the intermediate carbanionic center.

Another point to be considered is the question if deprotonation at C-2 is the rate determining step, similarily to the earlier investigated[17] rearrangements of S,S-dimethylsulfimides, for which considerable isotope effects were found. The isotope effects observed for the 1,3-dithiane-1-N-arylimides are quite small: on the assumption that the effects are identical for both orientations at C-2[3c] (necessary for the lack of other information), one obtains an isotope effect of 1.1 ± 0.2 for the rearrangement of **4**, and of 1.8 ± 0.3 for **5**. Ambiguities due to exchange of protons from the *ortho*-position of the aromatic ring could be excluded by rearrangement experiments with 4-d_2, which gave only 4U-d_e and no 4U. An explanation for the negligibly small isotope effect in case of **4** must be somewhat conjectural: in this case the actual rearrangement step might be rate determining, because of the strain the cyclic transition state must experience when the product with axial aryl group is formed; the small isotope effect could be due to the preceding fast equilibration. Rearrangement of **5**, on the other hand, is facilitated by the *syn*-axial interaction of the nitrogen atom and H-5_a in the sulfimide; together with the high acidity of H-2_a this may be the reason for the ease of the reaction.

†It must be emphasised that this comparison is only justified within limitations depending on the nature of the proton transfer from the α-carbon to the imide nitrogen.

Table 4. ^{13}C chemical shifts [a] of 1,3-dithiane-1-N-*p*-chlorophenylimides

Comp.	C-2	C-4	C-5	C-6	C-1'	C-2',6'	C-3',5'	C-4'	Others
1	48.9$_7$	28.1$_1$	28.7$_5$	49.3$_2$	153.1$_0$	119.1$_2$	128.7$_6$	121.7$_1$	---
1-2-d_2	b	28.0$_3$	28.7$_5$	49.2$_7$	153.1$_1$	119.1$_3$	128.7$_7$	121.7$_1$	---
1 c,d	48.2$_5$	28.0$_5$	29.4$_7$	48.2$_5$	153.4$_3$	118.4$_2$	129.0$_6$	120.6$_6$	---
2	61.5$_8$	30.0$_4$	30.0$_4$	50.6$_6$	155.8$_0$	118.2$_8$	128.9$_7$	117.3$_9$	CH_3 16.2$_4$
4	48.4$_0$	38.4$_6$	45.9$_3$	58.4$_7$	154.4$_1$	119.2$_7$	128.7$_7$	121.6$_4$	CH_3(4) 20.2$_1$ CH_3(6) 17.4$_9$
5	47.5$_5$	38.1$_1$	32.7$_5$	51.2$_3$	b	120.8$_8$	128.5$_3$	b	CH_3(4) 21.2$_7$ CH_3(6) 18.1$_5$
6 c	48.3$_8$	35.1$_7$	36.9$_6$	56.4$_8$	154.4	119.5$_7$	129.0$_2$	121.4	CH_3 22.29
7 c	48.4$_5$	34.9$_3$	30.1$_2$	54.4$_8$	154.7$_1$	119.6$_6$	129.0$_0$	121.3$_0$	CH_3 19.1$_4$
7e e,f	49.1$_3$	34.4$_1$	32.9$_4$	55 g	153.9$_9$	118.5$_5$	128.9$_8$	120.5$_2$	CH_3 17.5$_3$
7a e,f	42.7$_0$	34.0$_7$	21.3$_9$	47.4$_5$	153.9$_9$	119.1$_2$	128.9$_8$	120.5$_2$	CH_3 22.5$_9$
8	48.6$_4$	29.7$_1$	51.2$_2$	51.8$_2$	153.0$_3$	119.0$_9$	128.8$_8$	121.9$_7$	CH_3 27.0$_3$ C(CH_3)$_3$ 34.5$_3$
8 e	48.3$_0$	29.5$_1$	50.9$_2$	51.4$_2$	153.0$_4$	118.9$_4$	128.7$_3$	121.4$_8$	CH_3 26.9$_0$ C(CH_3)$_3$ 34.3$_3$
9 e	43.9$_2$	28.7$_0$	34.9$_3$	44.7$_5$	153.7$_3$	119.8$_9$	128.5$_4$	121.2$_2$	CH_3 26.9$_0$ C(CH_3)$_3$ 33.4$_3$

[a] In ppm from Me_4Si. Solvent $CDCl_3$, at +29°C, unless indicated. [b] Not seen. [c] Solvent 80% CH_2Cl_2 + 20% acetone-d_6. [d] At −95°C. [e] Mixture of configurational isomers. For composition see Table 1. [f] At −80°C. [g] Overlaid by signal of CH_2Cl_2.

Configurational analysis

^{13}C NMR spectra. Analysis of ^{13}C shift data has turned out to be the method of choice for the determination of cyclic sulfoxides (see Ref. 4*f* and the lit cited) and sulfimides.[10b,7] Comparison of the shifts of corresponding C atoms of S–X substituted compounds and of the parent sulfides, especially of the α-carbons (less deshielded for the isomer with axial S–X; $\beta_A < \beta_e$) and β-carbons (more shielded for S–X axial; $\gamma_a > \gamma_e$) allowed unambiguous structural assignment even if only one isomer was available. A comparison between the sulfoxides and N-arylimides in the thiane series showed a generally slightly smaller deshielding influence of the N-arylimide group on the α-carbons as compared to the oxygen. The shift differences between α-carbons of configurational isomers ($\delta_e - \delta_a$) and the chemical shifts of the β-carbon atoms were very similar to the corresponding sulfoxides.[10b]

The extensive tabulation of shift data of 1,3-dithianes[3e] allows a similar investigation of 1,3-dithiane-1-imides. The ^{13}C NMR spectra of a number of 1,3-dithiane-1-oxides have recently been reported.[4f]

^{13}C Chemical shifts of the 1,3-dithiane-1-N-arylimides are collected in Table 4, and the shift differences to the parent dithianes in Table 5. Assignment of the signals to the various carbon atoms was based partly on the signal multiplicities in the off-resonance decoupled spectra. More important was a comparison with calculated shift values, starting with the spectra of the 1,3-dithianes[3e] and using as a first approximation parameters derived in the thiane- and 1-thiadecalin-1-imide series.[10b] For compound 1, in which C-4 and C-5, and C-2 and C-6 have very similar chemical shifts, assignment was accomplished by comparison with the spectrum of the 2,2-dideuterio analog (1-d_2), where the signal due to C-2 was no longer observed (split into a quintet and loss of NOE) and C-4 and C-6 were shifted slightly upfield.

Carbon atoms adjacent to an equatorially N-aryl substituted sulfur atom are deshielded, C-2 by ~17 ppm and C-6 by 19–20 ppm, if the sulfimide group is not otherwise

Table 5. Effects [a] of imide substitution [b] on the ^{13}C chemical shifts of 1,3-dithianes

Comp.	C-2	C-4	C-5	C-6	Others
1	+17.0$_2$	−1.7$_5$	+2.1$_6$	+19.4$_6$	---
2 c	+19.4$_3$	−0.8$_8$	+4.5$_3$	+19.7$_4$	CH_3 −4.8$_8$
4	+15.0$_6$	−0.7$_5$	+1.3$_8$	+19.2$_6$	CH_3(4) −1.6$_9$ CH_3(6) −4.4$_1$
5	+14.2$_1$	−1.1$_0$	−11.8$_2$	+12.0$_2$	CH_3(4) −0.6$_3$ CH_3(6) −3.7$_5$
6 d	+16.8	−1.7	+4.8	+19.6	CH_3 +0.1 f
7e d,e	+17.1	−1.8	+8.2	+18.8	CH_3 +1.3 f
7a d,e	+11.2	−2.8	−10.8	+10.6	CH_3 +0.4 f
8	+17.3$_9$	−1.3$_1$	+3.9$_7$	+20.8$_0$	CH_3 +0.0$_2$ C(CH_3)$_3$ +0.5$_6$
9	+12.6$_7$	−2.3$_2$	−12.3$_2$	+13.7$_3$	CH_3 −0.1$_1$ C(CH_3)$_3$ −0.5$_4$

[a] $\delta_{3\text{-sulfimide}} - \delta_{3\text{-sulfide}}$, in ppm. A plus-sign indicates that the signal in the sulfimide appears at lower field. Temperature +29°C, solvent $CDCl_3$, unless indicated. Data for 1,3-dithianes from Ref. 3*e*. [b] 1-N-*p*-chlorophenylimides. [c] Spectrum of 2-methyl-1,3-dithiane recorded at room temperature; the compound exists to 96% in the CH_3-equ. conformation. [6c] [d] Sulfimide in CH_2Cl_2 + acetone-d_6; sulfide data calculated from shift parameters[3e] for conformations with equatorial or axial methyl group. [e] Sulfimide at −80°C. [f] Methyl shifts of sulfides taken from spectra of *trans*-or *cis*-2-tert.-butyl-5-methyl-1,3-dithianes.[3e]

sterically constrained. These values are quite similar to the results obtained with thiane-1-N-arylimides. The influence on C-2 is smaller than on C-6, analogous to but less pronounced than in 1,3-dithiane-1-oxides.[4f] The *gauche* 6-Me group in **4** causes an additional steric effect ($\beta_e\gamma_e$), which reduces the overall shift effect on C-2 to +15 ppm.

The shift effects observed at the only anancomeric 1,3-dithiane-1-N-arylimide with axial S–N bond isolated in pure form, **5**, are misleading because of the effect of the *gauche* 6-Me group ($\beta_a\gamma_e$; increase of the shift effect on C-2 to overall +14.2 ppm). Compound **7**, *trans*-5-methyl-1,3-dithiane-1-N-*p*-chlorophenylimide, is conformationally heterogeneous, but the two conformations **7e** (equatorial S–N) and **7a** (axial S–N) can be observed upon freezing the ring inversion at −80°.[16] The shifts of **9** could be obtained from its mixture with **8**. The deshielding influence on C-2 and C-6 in **7a** and **9** is considerably smaller than in the equatorial sulfimides (C-2: +11.5 to +12.7 ppm; C-6: +10.9 to +13.7 ppm), again in agreement with observations in the thiane-imide series.

The most significant shift differences between configurational isomers are observed at C-5 (γ-effects). An equatorial S–N bond causes a downfield shift of +3 to +5 ppm (**1e**, **6**, **8**); additional steric constraint in **4** ($\beta_e\gamma_e$) causes a reduction (+1.4 ppm). The exceptional situation in **7e** is discussed below. Axial imide groups are strongly shielding (**5**: −11.8, **7a**: −11, **9**: −12.3 ppm). We note that the effect caused by the axial S–N is analogous to the results in the thiane series, whereas in equatorial thiane imides the N-arylimide group acts slightly shielding, in contrast to the equatorial dithiane-1-imides. As a consequence the shift difference ($\delta_e - \delta_a$) between the corresponding carbon atoms in configurationally isomeric 1,3-dithiane-imides is much larger (>13 ppm) than in the thiane- and 1-thiadecalin-1-imides (5–8 ppm).[10b] The behaviour of the dithiane-1-imides is very similar to the corresponding oxides.[4f]

Recently an exceptionally large deshielding for C-3 in 3,3-dimethylthiane-1-N-*p*-tosylimide and for C-5 in 5,5-dimethyl-1,3-dithiane-1-N-*p*-tosylimide (both S–N-equatorially substituted) has been reported.[7b] The authors explained this by an electronic 1,3-interaction: a hyperconjugative interaction of the C(2)–C(3)-bond with the formally positively charged sulfur atom of the sulfimide group leading to palpable contributions of canonical forms with a tertiary carbonium ion at C-3 or C-5, respectively. We see a similarly large deshielding for C-5 in **7e**, but not in **6**.† The effect can thus be observed also on tertiary C atoms (Ref. 7*b* compared only quarternary and secondary carbons), but only if the Me substituent is in an axial position. We also observe a considerable influence on the chemical shift of the axial Me group upon introduction of the imide functionality (in **7e**: +1.3 ppm), but not on the equatorial Me in either **6** (equatorial S–N) or **7a** (axial S–N). It seems interesting that similar, if smaller, shift effects are observed upon N-methylation of *trans*-decahydroquinolines[23] for analogously oriented C atoms, axially, but not equatorially Me substituted. The sum of these observations indicates that the theory presented by DeMember *et al.*[7b] is not sufficient as an explanation.

The shift effects on C-4 (δ-effects) are slightly shielding, independent of the orientation of the sulfimide bond. Finally, the chemical shifts of the aromatic carbons are nearly unaffected by the axial or equatorial orientation of the S–N bond (except possibly C-1'), once more similar to the thiane-1-imides.[10b] A noticeable exception in this respect is compound **2**, where the 2-Me group causes palpable shift effects on C-1' and C-4'.

The configurational assignments of the rearranged products **4U**–**9U** were based mainly on ^{1}H NMR spectroscopic investigations (see below); ^{13}C NMR spectra were recorded for **1U**, **4U**, **5U**, **6U** and **7U** (Table 7). Apart from additional shielding caused by the 2'-amino group, the chemical shifts are very similar to 2-phenyl-1,3-dithianes reported by Eliel *et al.*[3e] Substitution by an axial phenyl ring leads to a much smaller deshielding of C-2 (in **4U** +9.53 ppm; compared to **5U** +16.13 ppm) and to a considerable shielding of C-4, 6 (aryl axial −3.6 ppm; aryl equatorial +1.3 to +2.2 ppm). The configuration and preferred conformation of **6U** and **7U** can also be established by comparison of the shift values of the 5-Me groups (**6U**: 16.2 ppm; **7U**: 22.35 ppm) with the Me signals of the 2-*t*-butyl-5-methyl-1,3-dithianes[3e] (*cis*: 16.37 ppm; *trans*: 22.20 ppm). Isomer **7U** exists exclusively, isomer **6U** largely in the conformation with equatorial 2-aryl ring, the conformational free energy of the 2-aryl group being much larger than the ΔG° of the 5-Me group.

^{1}H NMR spectra. A number of criteria have been established to differentiate between configurational isomers of thiane-1-oxides and thiane-1-N-arylsulfonylimides, and these criteria have been shown[4a] to apply also to 1,3-dithiane-1-oxides. Briefly, α-protons of isomers or conformers with equatorial S–X-bond show (a) larger geminal shift difference, (b) smaller geminal coupling and (c) the center of the AB-quartet at lower field. The validity of these criteria could be demonstrated for thiane- and 1-thiadecalin-1-N-arylimides,[10b] although substituent effects, additional coupling and overlap of signals create problems, and unambiguous interpretation of the 100 MHz-spectra is occasionally difficult. In the 1,3-dithiane series the signals due to the protons at C-2 are well separated, which facilitates the determination of the configuration and conformation of the compounds. The ^{1}H NMR data of the dithiane-imides are collected in Table 6.

The observation of a long range (J^5) coupling with H-4$_e$, 6$_e$ (≤2.5 Hz) allows easy identification of the signals due to H-2$_e$ in the AB-quartet at 3.93–3.98 ppm in equatorial sulfimides. The signals due to H-2$_a$, uncoupled except to H-2$_e$, appear at 3.37–3.60 ppm. The chemical shift difference ($\Delta\delta = \delta$H-2$_e$ − δH-2$_a$) is 0.36 to 0.59 ppm; J_{gem} is ~12.5 Hz. The comparison with axially S–N substituted compounds is problematic, since **7** is conformationally heterogeneous and **5** (as **4**) shows an atypical behaviour because of the methyl group *gauche* to the imide nitrogen. **9** could not be isolated in pure form, but the signals for H-2$_e$ and H-2$_a$ can be seen in the mixture with **8**, and assigned by comparison with the deuterated isomer **9**-d_e. The axial sulfimide group causes a reversal of the chemical shifts; H-2$_a$ appears at 3.84 ppm and H-2$_e$ at 3.59 ppm. The chemical shift difference thus becomes negative ($\Delta\delta = -0.25$ ppm); the geminal coupling constant is 13.6 ppm, larger than in the S–N equatorial compounds. The first two of the criteria mentioned above thus seem to be valid; the position of the center of the AB-system apparently is insignificant. The *gauche* Me group in **4** causes a slight upfield shift for H-2$_e$, and a considerable downfield shift for H-2$_a$; $\Delta\delta$ becomes

†Similar observations apply for sulfimides **11**, **16** and **19α** in Ref. 10*b*, and for thianium salts with axial β-Me groups.[22]

Table 6. ^{1}H NMR chemical shifts of 1,3-dithiane-1-N-arylimides[a]

Comp.	H-2_e	H-2_a	J_{gem}	$\Delta\delta$	Others [b]
1	3.93	3.53	12.6	+0.40	7.12 - 6.66 (arom., 4H); 3.5 - 1.9 (m, 6H)
2	-	3.62 (q, 7)	-	-	7.15 - 6.7 (arom., 4H); 3.5 - 2.0 (m, 6H); 1.53 (d, 7; 3H)
4	3.86	3.82	13.5	+0.04	7.1 - 6.75 (arom., 4H); 3.03 (m, 2H; H-4,6_a); 2.39 (d, 15 of t, 2.5; H-5_e); 2.03 (d, 15 of t, 2.5; H-5_a); 1.36 (d, 7; CH_3-6); 1.26 (d, 7; CH_3-4)
4-d_e	-	3.82	-	-	as in 4
4-d_a	3.84	-	-	-	as in 4
5	3.72	3.90	14	-0.18	7.1 - 6.8 (arom., 4H); 2.88 (m, 2H; H-4,6_a); 2.44 (d, 14 of t, 11; H-5_a); 1.61 (d, 14 of t, 2.5; H-5_e); 1.29 (d, 7; CH_3-6); 1.20 (d, 6.5; CH_3-4)
5-d_e	-	3.90	-	-	as in 5
6	3.93	3.37	12.5	+0.56	7.15 - 6.65 (arom., 4H); 3.18 (d, 10.5; H-6_e); 2.8 - 2.0 (m, 4H); 1.08 (d, 5.5; CH_3)
7	3.87	3.46	13	+0.41	7.15 - 6.75 (arom., 4H); 3.1 - 2.7 (m, 4H); 2.35 (d, 14 of d, 5; H-4_e); 1.32 (d, 6.5; CH_3)
8	3.95	3.45	12.6	+0.52	7.15 - 6.75 (arom., 4H); 3.39 (d, 12.3 of m; H-6_e); 2.78 (d, of d, 12; H-6_a); 2.72 (d, 13; H-4_e); 2.43 (d, 13 of d, 10.5; H-4_a); 2.11 (t, 11 of t, 2.5; H-5_a); 0.96 (s, 9H;$(CH_3)_3$)
9 [c]	3.59	3.84	13.6	-0.25	0.92 (s, 9H;$(CH_3)_3$); other signals overlaid by 8

[a] In ppm from Me_4Si; solvent $CDCl_3$. Shifts of H-2_e and H-2_a are calculated; the rest are centers of signals in the spectra. In parentheses: sign multiplicities and coupling constants (in Hz). [b] Only clearly recognizable couplings are reported. The aromatic protons show an AA'BB' pattern. [c] From a mixture of 8 and 9; for composition see Table 1.

Table 7. ^1H and ^{13}C NMR data of rearranged products 1U and 4U–9U[a]

Comp.	^1H				^{13}C			
	H-2	H-6'	1,3-Dithiane	Others[b]	C-2[c]	C-4,6[c]	C-5[c]	Others[d]
1U	5.18	7.27	2.8 – 3.1 (m, 4H) 1.6 – 2.3 (m, 2H)	6.54, 7.02; 4.06 (NH_2);	47.74 (+15.8)	31.81 (+1.95)	25.08 (-1.51)	143.00, 128.94, 128.18, 124.47, 123.22, 118.02
4U	4.98	7.54	2.9 – 3.25 (m, H-4, 6); 2.12 (d, 14 of t, 3; H-5$_e$); 1.42 (d, 14 of t, 11; H-5$_a$)	6.57, 7.03; 4.11 (NH_2); 1.24 (d, 7)	42.87 (+9.53)	35.56 (-3.65)	43.20 (-1.37)	142.79, 128.57, 128.05, 127.87, 123.20, 118.47; 21.45 (CH_3)
5U	5.18	7.30	2.7 – 3.3 (m, H-4, 6$_a$); 2.12 (d, 14 of t; 2.5; H-5$_e$); 1.3 (H-5$_a$; overlaid)	6.59, 7.04; 4.07 (NH_2); 1.26 (d, 7)	49.47 (+16.13)	41.08 (+1.87)	43.37 (-1.20)	129.07, 128.45, 118.15; 21.45 (CH_3)
6U	5.07	7.32	3.31 (d, 14 of d, 3; H-4,6$_a$); 2.65 (d, 14 of d, 4; H-4,6$_e$); 2.13 (m, H-5$_e$)	6.56, 7.04; 4.07 (NH_2); 1.33 (d, 6)	47.98 (+16.94)	37.99 (+1.31)	23.31 (-1.14)	143.03, 128.92, 128.37, 124.89, 123.39, 118.07; 16.20 (CH_3)
7U	5.07	7.25	2.62 (m, 4H); 1.99 (m, H-5$_a$)	6.46, 6.95; 4.10 (NH_2); 0.94 (d, 6)	47.51 (+16.30)	38.75 (+2.16)	31.07 (-1.28)	143.13, 129.03, 128.26, 123.82, 123.41, 118.05; 22.35 (CH_3)
8U	4.94	7.55	2.82 (m, 4H); 1.77 (m, H-5$_a$)	6.54, 7.04; 4.08 (NH_2); 0.91 (s, 9H)			[e]	
9U	5.12	7.21	2.5 – 3.1 (m, 4H); 1.76 (m, H-5$_a$)	6.48, 6.96; 4.10 (NH_2); 0.92 (s, 9H)			[e]	

[a]Shift values in ppm from Me_4Si; solvent $CDCl_3$. [b]H-data: parenthesized values are signal multiplicities and coupling constants (in Hz). Only clearly recognizable couplings are reported. [c]First two figures: H-3', H-4'. [d]Parenthesized: shift difference to parent 1,3-dithiane.[3a] [e]Shift values > 100 ppm: aromatic carbon atoms. [e]Not recorded.

therefore very small. The spectrum of 5-d_e proves that H-2$_a$ in **5** (as in **9**) appears at lower field than H-2$_e$; $\Delta\delta$ is again negative and the criterion of the geminal shift difference holds for this pair of configurational isomers.

The ^{1}H NMR data of the rearranged products are collected in Table 7. The configurational assignments were mainly based on the following two criteria:

(1) Axial hydrogens at C-2 of a 2-substituted 1,3-dithiane normally appear at lower field than the equatorial hydrogens in the isomeric compounds.[3a] In case of the 2-aryl-1,3-dithianes the signals of H-2$_e$ in **4U** and **8U** appeared at 4.94 ppm, and the signals of H-2$_a$ in **1U**, **5U**, **6U**, **7U** and **9U** at 5.07–5.18 ppm. The isomeric 2-(2'-amino-5'-chlorophenyl)-5-methyl-1,3-dithianes **6U** and **7U** show identical chemical shifts for H-2 (5.07 ppm), but very different values for the Me groups (**6U**: 1.33 ppm; **7U**: 0.94 ppm). Both compounds exist in the conformation with equatorial 2-phenyl substituent (see above for the ^{13}C-spectra). Since the influence of substituents on both the dithiane- and the aryl ring[24] may have a noticeable influence on the chemical shift of H-2, the shift-difference-of-H-2 criterion is only unambiguous if both configurational isomers are available for comparison.

(2) The signal of H-6' in the 2'-aminoaryl substituent appears at lower field in 2-aryl axially substituted isomers (**4U**: 7.54; **8U**: 7.75 ppm) than in the equatorially substituted compounds (**1U**, **5U–7U**, **9U**: 7.21–7.32 ppm), similar to rearrangement products derived from thiane- and 1-thiadecalin-1-N-arylimides.[1]

EXPERIMENTAL

Tlc was performed on aluminum foil plates covered with silicagel (SIF, Riedel-de Haen) or plastic sheets covered with aluminum oxide (Merck, 60F 254 neutral, type E). Glass columns (40–60 cm length, 2.5 to 4 cm o.d.) with aluminum oxide (90; 70–230 mesh ASTM, Merck) for mixtures of rearrangements were used for column chromatography; the solvent $CHCl_3$ was distilled from P_2O_5 before use. Melting points were determined on a Kofler micro-hot stage. Elemental analyses were carried out by Dr. J. Zak, Institute of Physical Chemistry, University of Vienna.

60 MHz Proton NMR spectra were recorded on a Varian EM 360 spectrometer with ^{1}H internal lock facility. 100 MHz Proton NMR spectra were measured on a Varian XL-100 NMR spectrometer, in the C.W. mode in 5 mm o.d. tubes. ^{13}C spectra were recorded in the pulsed mode at 25.16 MHz, in 12 mm o.d. tubes. Solvent was $CDCl_3$ (or, in a few instances, CH_2Cl_2 with 20% CD_3COCD_3 added as lock substance), with 2–5% Me_4Si added as internal reference. Mass spectra were recorded on a Varian MAT CH7 spectrometer (ionisation: 70 eV).

Starting materials. 1,3-Dithiane was obtained commercially and was used without purification. 2-Methyl-1,3-dithiane, *cis*-4,6-dimethyl-1,3-dithiane and 5-t-butyl-1,3-dithiane were prepared as described in the literature.[3a,c,25] 5-Methyl-1,3-dithiane was prepared by known procecures:[3a,c,6b,25] diethyl methyl malonate was reduced to 2-methyl-propane-1,3-diol, the ditosylate was reacted with $Na_2S.9H_2O$ and sulfur to give 4-methyl-1,2-dithiolane, which was cleaved reductively with LAH to give 2-methyl-propane-1,3-dithiol. Cyclisation with dimethoxy-methane and $BF_3.(C_2H_5)_2O$ gave 5-methyl-1,3-dithiane.

4-Chloroaniline was distilled at reduced pressure prior to use. N-Chlorosuccinimide[26] and t-butylhypochlorite[27] were prepared according to the literature. $CHCl_3$ and CH_2Cl_2 were distilled from P_2O_5 prior to use.

r-2-Deuterio-*cis*-4-*cis*-6-dimethyl-1,3-dithiane and 2,2-dideuterio-*cis*-4,6-dimethyl-1,3-dithiane were prepared as previously reported.[3c] *r*-2-Deuterio-*trans*-4-*trans*-6-dimethyl-1,3-dithiane was synthesised by a slightly modified procedure.[3c,28] 2.2 g 2,2-dideuterio-*cis*-4,6-dimethyl-1,3-dithiane were dissolved in 10 ml anhyd. THF and 20 ml TMEDA and the soln was cooled to −30°. BuLi soln (9 ml; 15% in hexane) was slowly added and the mixture was stirred at +5° for 2.5 hr, cooled once more to −30° and hydrolysed by gradually adding 5 ml 6 N HCl. The mixture was brought to room temp., diluted with water and extracted with petroleum ether. The organic layer was washed with dil. HCl and with NACl aqu. and dried over Na_2SO_4. The solvent was distilled off and the residue was distilled in a Kugelrohr distillation unit. The product was pure by gas chromatography. Degree of deuteration: 98% d_1 by mass spectrum.

r-2-Deuterio-*trans*-5-t-butyl-1,3-dithiane was prepared analogously to *r*-2-deuterio-*cis*-4-*cis*-6-dimethyl-1,3-dithiane;[3c] only 91% deuteration could be attained by one sequence of lithiation and quenching with D_2O–DCl. 2,2-Dideuterio-1,3-dithiane and 5-t-butyl-2,2-dideuterio-1,3-dithiane were prepared via lithiation and exchange with DMSO-d_6,analogously to 2,2-dideuterio-*cis*-4,6-dimethyl-1,3-dithiane.[3c] A selective back-exchange of the equatorial deuterium at C-2 in the latter by the procedure reported above for the 4,6-dimethyl compound proved unsuccessful; more vigorous reaction conditions led to an unselective reprotonation.

1,3-Dithiane-1-N-arylimides

General procedure. Equimolar amounts (generally 10 mMol) 1,3-dithiane and aniline were dissolved in anhyd. CH_2Cl_2 (50 ml) and cooled to −60°. To the stirred soln an equimolar amount of t-butyl-hypochlorite or N-chlorosuccinimide (dissolved in anhyd. CH_2Cl_2) was slowly added; moisture was excluded by tubes filled with $CaCl_2$. After addition was complete (30 min) the mixture was stirred at −60° for 1 hr and then kept at −20° for 10–15 hr. After extraction with 5% NaOHaqu. (50 ml) the organic layer was dried over Na_2SO_4, the solvent was distilled off at reduced pressure at low temp., the residue was dissolved in the little anhyd. ether and crystallised at −20°, if necessary after addition of small amounts of n-hexane. Yields of the various sulfimides prepared are collected in Table 1.

Separation of isomeric 1,3-dithiane-1-imides. Separation of isomers **4** and **5**, and of **6** and **7** was achieved by recrystallisation from anhyd. ether, the imides with equatorial S–N-bond (**4**, **6**) being less soluble. In case of the separation of **4** and **5**, anhyd., peroxide-free solvent had to be used and the temps above 0° were avoided as much as possible. Progress of separation was followed by recording the ^{1}H NMR spectrum of each fraction. The equatorial isomers **4**, **6** and **8** could be obtained in pure form by column chromatography of the mixture of products on Al_2O_3 with $CHCl_3$; the axial isomers were rearranged during this procedure.

Rearrangement of 1,3-dithiane-1-N-arylimides

Method A (rearrangement of **1**, **4**, **6** and **8**). A soln of the sulfimide in anhyd. benzene-triethylamine (1:1; 25–50 ml per g sulfimide) was heated to 75–80° (bath temp.) for 10–15 hr; the condenser was protected with a tube filled with $CaCl_2$. The solvent was distilled off at reduced pressure, and the residual mixture of products was separated by column chromatography (silicagel, $CHCl_3$). The rearranged products were recrystallised if solid.

Method B (rearrangement of **5** and **7**). A soln of the sulfimide in peroxide-free, moist ether (25 ml per g sulfimide) was heated to reflux for 30 min. Isolation and purification of the products as described for Method A. Yields of the rearranged products are reported in Table 2.

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