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STEREOSPECIFIC [2,3]-SIGMATROPIC REARRANGEMENTS OF CYCLIC N-ARYL SULFIMIDES

Peter K. Claus*, Werner Rieder and Friedrich W. Vierhapper
Organisch-Chemisches Institut der Universität Wien
A-1090 Wien, Austria

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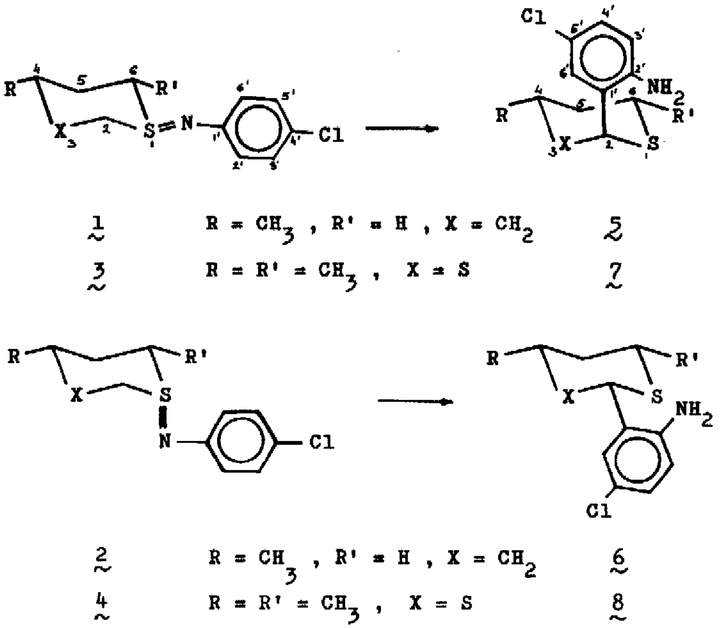
The rearrangement of N-aryl sulfimides to o-alkyl-thioalkyl anilines has been suggested to proceed as a [2,3]-sigmatropic rearrangement of intermediate azasulfonium ylids[1,2]. Though processes of this type are of widespread occurence[3], only few investigations concerning their stereochemistry have been reported, indicating high stereospecifity in rearrangements of allyl sulfonium ylids[4], allyl sulfoxide-sulfenate[5] and Wittig rearrangements[6]. We now wish to present stereochemical evidence for the concertedness of rearrangements of N-aryl sulfimides.

Substrates used in this investigation[7] were 4-methyl-thiane-1-(N-aryl) imides **1** and **2** and cis-4,6-dimethyl-1,3-dithiane-1-(N-aryl) imides **3** and **4**. **1** was obtained in 80% yield by reaction of 4-methyl-thiane with N-chlorosuccinimide (NCS) and 4-chloroaniline by a procedure recently reported[8]. No cis-isomer **2** could be detected in the reaction mixture. **2** could be prepared in 11% yield together with 8% **1** by reaction of trans-4-methyl-thiane-1-oxide[9] with P_2O_5 and 4-chloroaniline (applying a modified procedure reported earlier[10] for synthesis of S,S-dimethyl sulfimides), isolation and purification of **1** and **2** via their picrates[2] and separation of the recovered sulfimides by column chromatography (Al_2O_3, $CHCl_3$). Reaction of cis-4,6-dimethyl-1,3-dithiane[11] with NCS and 4-chloroaniline gave a mixture of **3** and **4** in a ratio of ~10 : 1 (total yield 70%), which could be separated with difficulty by fractional crystallization from ethyl ether to give the pure isomers.

Configurational assignments were made by ^{13}C-NMR and ^{1}H-NMR spectroscopy (Table I). In the ^{13}C-NMR spectra of **2** (which exists with predominantly axial sulfimide functionality[12]) and **4**[13], C-atoms 2, 6 and 5 (and 3 in case of **2**) resonate at considerably higher field as compared with the corresponding trans-compounds **1** and **3**, because of the smaller β-effect ($\beta_a < \beta_e$) and the γ-gauche effect of the axial nitrogen[12,14]. Confirmation comes from the ^{1}H-NMR spectra : $\Delta\delta_{ae}$(H-2) is smaller for **2** and **4**[15], and the axial proton(s) at C-5 (and C-3) in **2** and **4** are 0.4 to 0.7 ppm downfield compared to **1** and **3**, as expected from data reported on corresponding sulfoxides[16].

Pure sulfimides **1** - **4** could be rearranged in the manner indicated in Scheme I, to yield rearranged products containing less than 5% of the configurational isomers according to ^{1}H- and ^{13}C-NMR spectra. 1 - 4 differed greatly in respect of ease of their rearrangement : 1 and 2 were heated in triethanolamine for 1 hour at 120 - 140°; 3 in benzene-triethylamine (1:1) for 10 hours at 80°. In contrast, the cis-isomer 4 rearranged rapidly at very mild conditions even in absence of base (f.i. on short heating in ether, or on attempted column chromatography on Al_2O_3).



1 $R = CH_3$, $R' = H$, $X = CH_2$ 5

3 $R = R' = CH_3$, $X = S$ 7

2 $R = CH_3$, $R' = H$, $X = CH_2$ 6

4 $R = R' = CH_3$, $X = S$ 8

Scheme I

Rearranged products were isolated and purified by column chromatography (silicagel, $CHCl_3$). Other products obtained were 4-chloroaniline (scission of S-N bond) and some products unidentified, presumably formed by S-C bond scission. Yields of rearranged products were 40 to 60%.

Configurational assignments for products 5 - 8 are based on NMR data (Table I). 6 and 8 are conformationally homogeneous, with equatorial aryl substituent; 5 exists, at room temperature, predominantly in the conformation with equatorial aryl and axial methyl group; in contrast, the aryl group in 7 is entirely in the axial position[13]. This is borne out by the shieldings of the ring carbon atoms α, β and γ to the axial substituents in 5 and 7 compared to 6 and 8, by the shift difference of axial and equatorial CH_3-groups in 5 and 6 and by the close similarity of the shift values of 7 and 8 to the reported spectra[17] of the 2-phenyl-4,6-cis-dimethyl-1,3-dithianes. The aromatic o-protons of rearranged products with axial aryl group (7)[7] are persistently shifted downfield by 0.2 to 0.3 ppm compared with the shifts of H-6' of equatorially oriented aryl groups.

Further confirmation comes from the chemical shifts and coupling constants of the protons included in Table I.

Table I. Pertinent ^{1}H- and ^{13}C-NMR Shift Data[a] of Cyclic Sulfimides **1** - **4** and Rearranged Products **5** - **8**

Compound[b]	^{1}H					^{13}C					
	H-2$_e$	H-2$_a$	$\Delta\delta_{ae}$[c]	H-3,5$_a$	H-3,5$_e$	C-2	C-3	C-4	C-5	C-6	CH$_3$
1 (149-153)	3.16	2.68	+0.48	1.5[d]	2.01	48.05	31.90	30.92	31.90	48.05	21.44
2 (77-79)	2.87	2.66	+0.21	2.18	1.68	42.09	25.22	29.90	25.22	42.09	21.29
3 (103-109)	3.87	3.83[e]	+0.04	2.03	2.39	48.40	---	38.46	45.93	58.47	20.21[f] 17.49[g]
4 (99-102)	3.72	3.90[h]	-0.18	2.44	1.61	47.55	---	38.11	32.75	51.23	21.27[f] 18.15[g]
	H-2[i]		H-6'[i]	CH$_3$[i]							
5 (not cr.)	4.05(d,10 of d,3)		7.17(d,3)	1.03(d,7)		35.38	37.27	27.47	32.25	24.58	17.64
6 (not cr.)	3.83(d,11 of d,3)		7.13(d,3)	0.99(d,6)		42.62	40.62	33.53	35.37	30.50	23.14
7 (106-107)	4.98(s)		7.54(d,3)	1.23$_5$(d,7)		42.87	---	35.56	43.20	35.56	21.83
8 (113-115)	5.22(s)		7.32(d,3)	1.29(d,7)		49.47	---	41.08	43.37	41.08	21.46

[a] In ppm; solvent CDCl$_3$ + 5% Me$_4$Si. Spectra were recorded on a Varian XL-100, 100 MHz ^{1}H-spectra in the CW mode; the ^{13}C-spectra in the FT-mode at 25.16 MHz. Only relevant data are included. [b] In parentheses : mp, °C. All new compounds gave satisfactory elemental analysis. For numbering of atoms see Scheme I. [c] $\delta_{H-2e} - \delta_{H-2a}$; the negative sign in case of **4** was proven by recording the spectrum of **4**-2-d$_e$, prepared from r-2-deuterio-cis-4, cis-6-1,3-dithiane[11a]. [d] Superimposed multipletts. [e] In **3**-2-d$_e$: 3.82; H-2$_e$=D. [f] CH$_3$-4. [g] CH$_3$-6. [h] In **4**-2-d$_e$: 3.90; H-2$_e$=D. [i] In parentheses : multiplicity, and coupling constants in Hz.

In summary, rearrangement of cyclic N-aryl sulfimides could be shown to proceed with a stereospecifity of ≥95% suprafacially with respect to the sulfoniumylid fragment, regardless of relative acidities of α-hydrogens and stabilities of rearranged products, thus confirming the assumption of a concerted mechanism. Similar stereospecifity, observed in rearrangement of conformationally rigid systems as trans-1-thiadecalin-1-(N-aryl) imides[7] will be reported in a full paper.

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