Configurationally and Conformationally Homogeneous Cyclic $N$-Aryl Sulfimides. II.

$^{13}$C- and $^1$H NMR Spectra

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The configuration and (in case of mobile ring systems) the preferred conformation in a series of thiane- and of cis- and trans-1-thiadecalin-1-$N$-4-chlorophenyl imides were assigned by means of $^{13}$C- and $^1$H nmr spectroscopy. $^1$H nmr criteria known to be valid for determination of the stereochemistry of cyclic sulfoxides may be applied (with limitations) to cyclic $N$-aryl sulfimides, if both isomers ($S$--N bond equatorial and axial, respectively) are known. The assignments are easier, and unambiguous for single isomers, by comparison of $^{13}$C nmr chemical shifts of ring carbon atoms of sulfimides and sulfides. The influence of equatorially and axially oriented sulfimide groups on the chemical shifts of neighbouring protons, and on the carbon atoms of the heterocyclic rings are discussed in detail.

Konfigurativ und konformationell einheitliche cyclische $N$-Aryl-sulfimide. II.

$^{13}$C- und $^1$H-NMR-Spektroskopie

Die Konfiguration und (bei beweglichen Ringssystemen) die bevorzugte Konformation einer Reihe von Thiän- und von cis- und trans-1-Thiadekalin-1-$N$-4-chlorophenylimiden wurde durch $^{13}$C- und $^1$H-NMR-Spektroskopie bestimmt. Bekannte $^1$H-NMR-Kriterien zur Festlegung der Stereochemie cyclischer Sulfoxide sind (mit Einschränkungen) auch bei cyclischen $N$-Arylsulfimiden anwendbar, wenn beide Isomere ($S$--N-Bindung äquatorial bzw. axial) bekannt sind. Leichter, und auch bei Vorliegen von nur einem Isomeren eindeutig, gelingt die Zuordnung durch Vergleich der $^{13}$C-NMR-Verschiebungen der Ringkohlenstoffatome von Sulfimid en und Sulfiden. Die Einflüsse äquatorial oder axial orientierter Sulfimidgruppen auf die chemischen Verschiebungen benachbarter Wasserstoffe und der Kohlenstoffe des Heteroringes werden diskutiert.
Introduction

In order to get information about the stereospecificity of rearrangements of \( N \)-aryl sulfimides (1d)\(^1\), a series of configurationally and conformationally homogeneous cyclic \( N \)-aryl sulfimides were prepared. Synthetic procedures and considerations about the reaction mechanism are reported in a preceding paper\(^2\). To assign the configurations on sulfur we examined the \(^{13}\)C- and \(^1\)H nmr spectra of these compounds.

\(^1\)H nmr spectroscopy has been shown to be a useful technique to define the configuration of the sulfoxide bond in cyclic sulfoxides (2); the observed effects of the sulfoxide group on the \(^1\)H chemical shifts and coupling constants depending on the steric orientation of the \( S\)—O bond have recently been summarized\(^3\),\(^4\). \(^{13}\)C nmr spectroscopy has been used in a number of investigations to determine the stereochemistry of cyclic sulfoxides\(^5\)–\(^10\). Analogous investigations on sulfimides are few, with the exception of studies, by Lambert et al.\(^11\), of the conformational behaviour of cyclic \( N \)-arylsulfonyl- and \( N \)-acylsulfimides (1a, 1c).

From the available data the double bond character of the \( S\)—X bond in 1d (\( X = N \); 45–58 %\(^12\)) has to be placed between that of N-tosyl sulfimides 1a (\( X = N \); 45 %\(^13\)) and that of dimethyl sulfoxide (\( X = O \); 65.5 %\(^12\)). Hence one may conclude that the introduction of an \( N \)-aryl imide moiety will have effects comparable to 1a and 2 on the protons of a thiane ring, especially on the protons bound to carbon atoms next to sulfur (\( \alpha \)-hydrogens), anisotropy effects of the phenyl ring in a preferentially transoid orientation hopefully being negligible.

\(^{13}\)C nmr spectra of cyclic sulfimides proved far more useful than proton spectra for identification of configurational and conformational isomers, the chemical shifts being very sensitive to steric factors, and the spectra being easier to interpret. The reasonable expectation that the shift effects caused by equatorial and axial \( N \)-aryl imide groups should be similar to the ones observed for other six-membered cyclic systems, especially the thiane-1-oxides, was confirmed. A communication reporting some of the results described in the sequel has been published\(^14\).

The formulas of the compounds investigated are collected in Schemes 1 (thiane-), 2 (trans-1-thiadeclin-) and 3 (cis-1-thiadeclin-1-N-4-chlorophenyl-imides). Most of the compounds investigated proved to be largely or completely conformationally homogeneous, due to the presence of biasing substituents (in the thiane-1-imide series), the rigidity of the ring system (in the trans-1-thiadeclin-1-imides series) or severe \( \text{syn} \)-axial interactions in one of the conformers (in the cis-1-thiadeclin-1-imide series). For the rest of compounds which represent conformationally mobile systems (3, 4, and 25\(^\beta\)) the \( N \)-aryl imide...