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Preliminary communication

Analytically significant steric effects on ^{29}Si NMR chemical shifts as observed in trimethylsilylated steroids *

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Abstract

^{29}Si NMR chemical shifts were measured in four trimethylsilylated stereoisomers of 3ξ-hydroxy-5ξ-cholestane. The chemical shifts obtained in dilute deuteriochloroform solutions fall into two distinct ranges one around δ 13.2, indicative of axial position of the trimethylsiloxy group on the cyclohexane ring, and the other around δ 14.9 ppm.

In one of the first reports on application of ^{29}Si NMR spectroscopy to structure determination we reported [1] three different ^{29}Si chemical shifts for three trimethylsilylated stereoisomers of 3ξ-hydroxy-5ξ-cholestane. The different chemical shift values indicate the sensitivity of the silicon shielding to steric effects but the values were difficult to rationalize into structural terms. Without such rationalization the sterically induced chemical shifts would be of little practical use for structure determination.

In the intervening years the measuring techniques have been considerably improved; not only have spectrometer magnetic fields and signal-to-noise ratios been increased but also general polarization transfer schemes (INEPT [2] and DEPT [3]) have been introduced. Now, these techniques allow the practical application of ^{29}Si

* Dedicated to Professor C. Eaborn on the occasion of his 65th birthday

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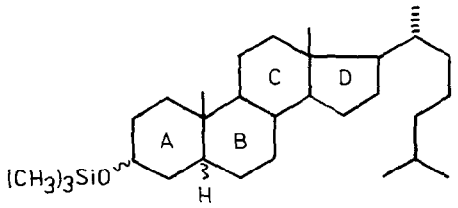
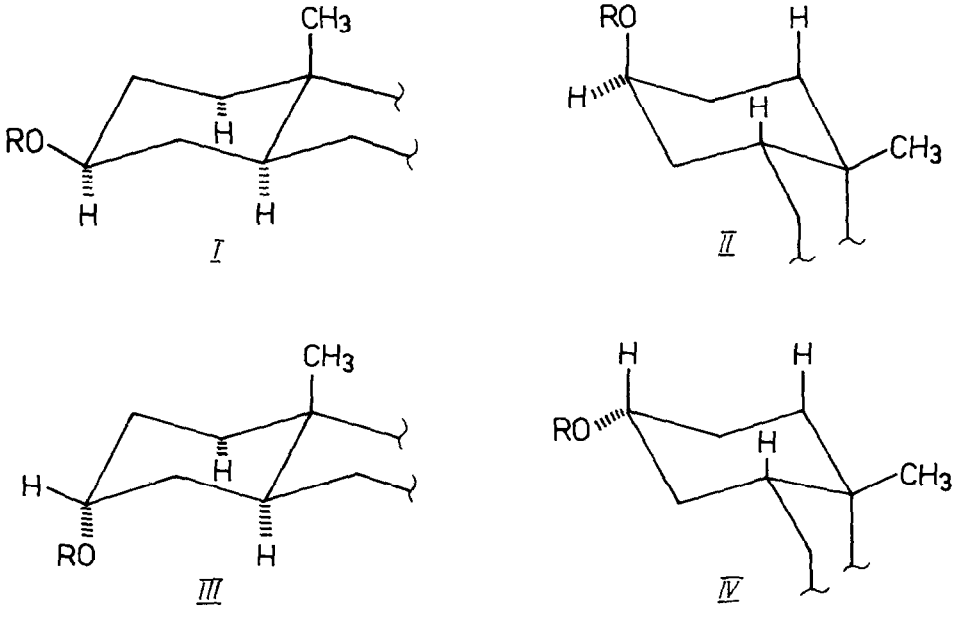


Scheme 1. 3β-trimethylsilyloxy-5α-cholestane (I) (δ 15.26 ppm),
3β-trimethylsilyloxy-5β-cholestane (II) (δ 13.23 ppm),
3α-trimethylsilyloxy-5α-cholestane (III) (δ 13.25 ppm),
3α-trimethylsilyloxy-5β-cholestane (IV) (δ 15.04 ppm).

NMR spectroscopy to the study of polyfunctional organic compounds; small samples of trimethylsilylated compounds can be routinely measured [4] as dilute solutions in suitable solvents without it being too time consuming.

Repeated measurements of each of the four 3ξ-trimethylsilyloxy-5ξ-cholestanes I to IV in dilute deuteriochloroform solutions yielded the chemical shifts given in Scheme 1.

The chemical shifts fall into two distinct ranges, one around δ 13.2 and the other around δ 14.9 ppm. Inspection of the molecular models offers straightforward rationalization of the two chemical shift ranges (see partial perspective formulae of compounds I to IV, in Scheme 2, only ring A of the steroid is indicated): oxygen atoms of the trimethylsilyloxy groups in compounds II and III are in essentially



R = $Si(CH_3)_3$

Scheme 2.

identical steric arrangements, the most prominent feature being the diaxial interactions with hydrogen atoms in positions 1 and 5. Oxygen atoms of the compounds I and IV are exposed to lesser intramolecular interactions, once again both identical. One can thus conclude that the low chemical shift found (δ 13.2 ppm) in compounds II and III is due to the axial position of the trimethylsilyloxy group, and the 2 ppm upfield shift is associated with the steric interactions involved.

Measurements of larger series of 3ξ-trimethylsiloxy-5ξ-cholestane derivatives [5] confirm that the given difference in chemical shifts is maintained providing that other substituents are at least three bonds away from the C(3) carbon atom.

The described steric effect exceeds by two orders of magnitude the experimental error of the chemical shift measurement and, hence, the effect can be used for structure determination of hydroxy steroids. We hope that future work will help to elucidate the mechanism by which the silicon chemical shifts are influenced by the steric effects that are so important in organosilicon compounds.

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