Tetrahedron Letters No.31, pp. 3511-3514, 1968. Pergamon Press. Printed in Great Britain.

SYNTHESIS AND NMR SPECTRA OF STEREOISOMERIC 1,3,5-TRICHLOROCYCLOHEXANES

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(Received in UK 30 April 1968; accepted for publication 8 May 1968)

In studies of conformational equilibria by NMR, the knowledge of the values of the vicinal coupling constants (J_T, J_G) in the individual conformers is usually required. The general procedure (1) of simultaneous adjustment of energy and coupling parameters has recently been criticized (2) and, where possible, the use of coupling parameters derived from conformationally rigid model compounds is to be preferred. As part of a systemmatic study of the conformational structure of polyvinyl chloride model compounds (3,4), the cis- (I) and trans-1,3,5-trichlorocyclohexanes (II), considered as cyclic trimers, have been synthesized and their NMR parameters determined.

By direct chloration of cyclohexane, P. Sabatier and A. Mailhe (5) claimed to have prepared a crystalline trichlorocyclohexane (m.p. 66°) with an assumed 1,3,5-structure. Based on detailed studies by R. Riemschneider (6), their work has been shown to be incorrect.

We have investigated the synthesis of compounds I and II from the corresponding 1,3,5-cyclohexanetriols (prepared according to (7), but with hydrogenation of floroglucine at 30 at.) or from the p-tosylesters of these triols. The tri-p-toluenesulfoester of cis-1,3,5-cyclohexanetriol was prepared according to (7), and the derivative of the trans-form in an analogous way. In the latter, tosylation of hydroxyl groups is incomplete, the product is amorphous, sticky, and all attempts of its crystallization have been unsuccessful; for further reactions it has been used in this unpurified form.

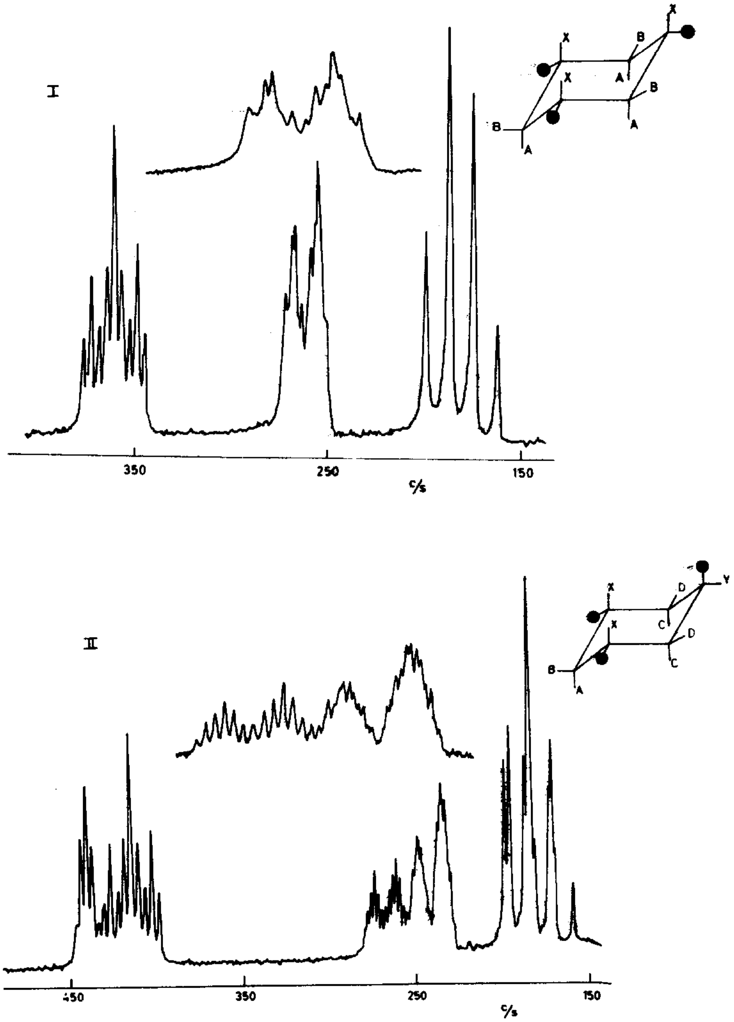
The cyclohexanetriols have been converted to the respective trichloroderivatives by the action of thionylchloride under various conditions and in different media (dimethylformamide, pyridine, large excess of thionyl chloride and their combinations). Tosyloxygroups have been exchanged for chlorine by reaction of the tri-p-toluenesulfoesters with LiCl in dimethylsulfoxide at 60° for different times. In all cases substitution is accompanied by large scale elimination reducing strongly the yield of the main product. Best results concerning yield and simplicity of procedure have been obtained by reaction of the triols with a large excess of thionyl chloride serving simultaneously as solvent, with pyridine as catalyst: 3 moles of $SOCl_2$, 0.03 moles of pyridine and 0.2 moles of a pure stereoisomer of 1,3,5-cyclohexanetriol (or mixture of both stereoisomers) have been mixed at -30°, the mixture slowly heated and refluxed for 5 hours. Excess $SOCl_2$ was distilled off and the reaction products extracted by dichloromethane. By vacuum rectification a lower boiling fraction (35-40 % of theory referred to the triol) - identified as 3,5-dichlorocyclohexene (positive reaction with $AgNO_3$, with AgOH yields 5-chloro-2-cyclohexenol giving a negative $AgNO_3$ test, forms benzene with KOH and 4-chlorocyclohexene by Pd/C hydrogenation with a calculated amount of hydrogen)- and a higher boiling fraction (10-15 % of theory) which is an essentially pure stereoisomer of 1,3,5-trichlorocyclohexane corresponding to the configuration of the original triol, have been obtained. The stereoisomeric trichlorocyclohexanes have been separated by adsorption chromatography on silicagel 60-120 μ, activated by heating to 120°. In elution with hexane, II exhibits a shorter elution time. Separation of the isomers has been followed by gas chromatography or by thin layer chromatography using Silica Gel G acc. to Stahl (Merck).

Physical Constants of the Products

For gas chromatographic analysis, The Argon Chromatograph Pye has been used: effective column length 120 cm, diameter 0.5 cm, filled with 10 % Apiezon L on Chromosorb W (80-10 mesh), argon flow 10 ml/16 min. The working temperature of the column is given in brackets following the relative retention times t_r. All the given structures have been controlled by NMR and IR spectra.

I: b.p.$_{10}$ 100-102°; crystals m.p. 61-62°; t_r: 18.3 min (150°). Anal. calc. for $C_6H_9Cl_3$: C, 38.43; H, 4.84; Cl, 56.73. Found: C, 38.64; H, 4.86; Cl, 56.62. II: b.p.$_{10}$ 96-98°; crystals m.p. 21.2°; n_D^{25}: 1.5102; t_r: 15.3 min (150°). 3,5-dichlorocyclohexene: b.p.$_{10}$ 69-71°; n_D^{20}: 1.5125; t_r: 17.1 min (110°). Anal. calc. for $C_6H_8Cl_2$: C, 47.71; H, 5.34; Cl, 46.95. Found: C, 47.69; H, 5.38; Cl, 47.31. Note: In subsequent gas chromatographic analysis on a 50 m capillary column (Fractometer 116 E, Perkin-Elmer) incomplete separation into 2 peaks with an approx. ratio 1:4 has been observed, indicating the presence of a mixture of stereoisomers. 3,5-Dichlorocyclohexanol: Isolated from the mixture after the reaction of the incompletely tosylated trans-1,3,5-cyclohexanetriol with LiCl in DMSO. Crystals m.p. 75-76°, t_r: 23.3 min (150°). Anal. calc. for $C_6H_{10}Cl_2O$: C, 42.63; H, 5.96; Cl, 41.95. Found: C, 42.43; H, 5.95; Cl, 42.12. 5-Chloro-2-cyclohexenol: Colourless viscous liquid, b.p.$_1$ 54.5°; n_D^{20}: 1.5094; t_r: 12.2 min (125°). Anal. calc. for C_6H_9ClO: C, 54.35; H, 6.84;Cl, 26.74. Found: C, 54.25; H, 6.86; Cl, 26.71. 4-Chlorocyclohexene: Colourless liquid b.p.$_{720}$ 141°; n_D^{20}: 1.4821 (lit. (8) n_D^{20}: 1.4822); t_r: 14.1 min (75°). Anal. calc. for C_6H_9Cl: C, 61.81; H, 7.78; Cl, 30.41. Found: C, 62.08; H, 8.02; Cl, 30.37.

The steric purity and conformational structure of I and II is proved by their IR and NMR (Fig.1) spectra. The IR spectrum of I exhibits in the region of the C-Cl stretching vibrations only one very strong band at 728 cm^{-1}, indicating the presence of only equatorial Cl atoms (9). In isomer II, the two strong C-Cl stretching bands at 730 and 652 cm^{-1} and their intensity ratio are characteristic of two equatorial and one axial chlorine atom. The temperature independence of IR spectra indicates that the triequatorial form of I and the diequatorial form of II are the only conformers present.



$\nu_A = 1.81$ $J_{AB} = -12.4$
$\nu_B = 2.60$ $J_{AX} = 12.7$
$\nu_X = 3.60$ $J_{BX} = 4.3$

$\nu_A = 1.84$ $J_{AB} = -12.8$
$\nu_B = 2.74$ $J_{AX} = 12.75$
$\nu_X = 4.18$ $J_{BX} = 4.3$
$\nu_C = 1.91$ $J_{BD} = -2.2$
$\nu_D = 2.45$ $J_{CD} = -14.5$
$\nu_Y = 4.43$ $J_{CX} = 12.3$
$J_{CY} = 3.3$
$J_{DX} = 4.2$
$J_{DY} = 3.6$
$J_{DD} = -2.4$

Fig. 1

NMR Spectra of I and II, 0,5 M in CCl$_4$ with HMDS, at 100 Mc/s (VarianHA 100)

In absence of long range couplings between the X protons, NMR spectra of I and II can be analyzed in terms of the effective frequency method (10) as a superposition of four (I) and six (II) six-spin systems, involving only the methylene protons. The whole spectrum of II and the A and X bands of I are satisfactorily reproduced by this calculation, assuming the presence of only one type of long range interaction (J_{BB}, J_{DD}, J_{BD}). In I, other types of long range interactions should probably also be considered in order to reproduce the shape of the B band, but the resulting vicinal coupling constants are not expected to be much affected by them. The NMR parameters obtained are summarized in Fig.1. The following types of vicinal couplings have been found in these models:

J_T: $J_{aa} = 12.75$; $J_{aa}^{t} = 12.3$ J_G: $J_{ae} = 4.3$; $J_{ae}^{t} = 3.3$; $J_{ee} = 3.6$

(J^t refers to couplings with a Cl atom in trans position with respect to one of the coupling protons.) The discussion of these values in connection with the structure of other vinyl polymer model compounds will be published elsewhere.

We wish to thank Miss M. Burešová for technical assistance, Miss V. Mikotová and Mrs. E. Plachetková for the gas chromatographic analyses. The elementary analyses were performed in the analytical department (Dr. J. Petránek, head).

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