Synthesis and Stereochemistry of Some New 1,3-Dioxane Derivatives of 1,4-Diacetylbenzene

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Summary. The synthesis and stereochemistry of new 1,3-dioxane derivatives of 1,4-diacetylbenzene are reported. The anacomic structure of these compounds, the axial orientation of the aryl group for both 1,3-dioxane rings, and the cis and trans isomerism of some of these compounds is discussed considering data of conformational analysis, NMR investigations, and single crystal X-ray diffractometry.

Keywords. 1,3-Dioxanes; Conformation analysis; NMR; cis-trans-Isomers; X-Ray.

Introduction

Investigations of the stereochemistry of 1,3-dioxane derivatives bearing aryl groups at position 2 of the heterocycle revealed interesting structural aspects. The A values (free conformational enthalpy [1]) of aryl groups located in the acetal part of the 1,3-dioxane ring are high (e.g. \( A_{Ph} = 13.04 \text{kJ/mol} \) [2, 3]). The 2-aryl-1,3-dioxanes are anacomic compounds with the characteristic conformational equilibrium between I and II shifted toward I with the aryl group in the equatorial position (Scheme 1 [4–8]). The conformational equilibrium of 2,2-disubstituted-1,3-dioxanes (III, IV; e.g. 2-phenyl-2-methyl-1,3-dioxanes, Scheme 1) is shifted toward the conformer exhibiting the aryl group in the axial position [2, 9, 10]. The axial preference of the phenyl group is predicted from the higher A value of the methyl group at position 2 \( (A_{Me} = 16.63 \text{kJ/mol} \) [2]) with respect to the A value of the phenyl group \( (A_{Ph} = 13.04 \text{kJ/mol} \) [2]) at the same position. Thermodynamic measurements of 2-methyl-2-phenyl-1,3-dioxanes showed a considerably higher preference of the methyl group for the equatorial position \( (\Delta G_{III-IV}^{0} = 10.11 \text{kJ/mol} \) [2]) than that calculated from the A-values of methyl and phenyl groups \( (\Delta A = A_{Me} - A_{Ph} = 3.63 \text{kJ/mol}) \).

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Studies on the rotameric behaviour of the aryl groups revealed a weak preference of the equatorial phenyl group for the bisectonal orientation (I_a) [11–13] and a high preference of the axial phenyl group for the orthogonal orientation (IV_b, Scheme 2 [9, 10, 14–18]). This is consistent with the ¹H NMR shifts [9].

For some 2-aryl-2,5,5-trimethyl-1,3-dioxanes, the chemical shifts for the signals belonging to the equatorial methyl groups at C₅ are close to 0 ppm or even exhibit negative values [10]. The axial protons at positions 4 and 6 are located in the deshielding area of the orthogonal aryl groups, whereas the equatorial protons at these positions are in the shielding area. The differences between the chemical shifts of the equatorial and axial protons of these positions are considerably lower.