

Synthesis and stereochemistry of 4-*tert*-butyl-4-oxo-3,5,8-trioxa (3,5-dioxa-8-thia)-4-phosphabicyclo [5.1.0]octanes and related acetals

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Abstract

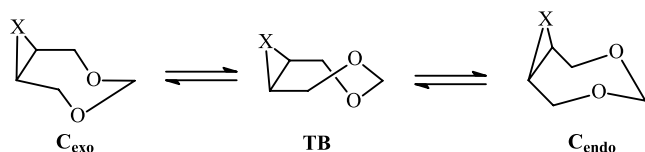
X-ray, ¹H NMR and IR spectroscopy methods have been applied to a series of heterobicyclo[5.1.0]octanes. Endo epoxide and exo thiirane based on 2-*tert*-butyl-2-oxo-1,3,2-dioxaphosphepine exhibit chair form in a crystal state. Strong predominance of the chair conformation takes place in solution also as for similar bicyclic acetals produced from 2-*tert*-butyl-1,3-dioxacyclohept-5-ene. 3,5-Dioxa-8-thiabicyclo[5.1.0] octane bearing no a bulky substituent was found to exist as a mixture of stereoisomers in solution.

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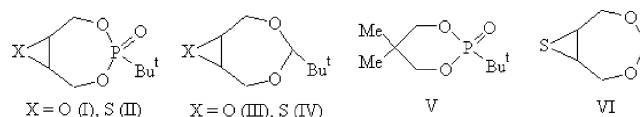
Keywords: Heterobicyclo[5.1.0]octanes with oxygen; Sulfur; Phosphorus atoms; Synthesis; X-ray crystallography; IR; ¹H NMR spectroscopy

1. Introduction

The common feature of 3,5-dioxabicyclo[5.1.0]octanes are that they are prone to coexist in both C_{endo} and C_{exo} conformations with a twist-boat form in addition. For example, the cyclopropane containing acetal (X = CH₂) was found to populate the chair conformations in which a three-membered ring occupies endo and exo positions [1]. When X = CCl₂ or CBr₂ a conformational equilibrium is strongly shifted to exo chair forms to avoid repulsive Cl(Br) ⋯ O contacts [2]. Finally, epoxide (X = O) exhibits ternary conformational equilibrium with C_{exo} form to be the least stable [3].



This paper is devoted to the synthesis and stereochemical examination of new bicyclic molecules (I) and (II) including thiirane fragment (X = S) or (and) phosphorus atom being built-in instead of C⁴. For comparative purposes our attention has also been focused on the parent acetals (III) and (IV) encompassing the same alkyl group.



The presence of a bulky substituent adjacent to phosphorus (carbon) atoms permits to reduce a number of possible conformers and allows to rule out the chair form with axial alkyl group [4]. Six-membered phosphonate (V) have been prepared as a model of anancomeric chair form. Acetal (VI) with thiirane fragment, by contrast, as a potential conformationally heterogeneous object. The compounds

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