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Theoretical DFT study of 1,3,2-dioxa-phosphoranes formation by oxidative addition of methanol on monocyclic phospholanes

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Abstract

Oxidative addition of aliphatic alcohols on monocyclic phospholanes leads to the formation of monocyclic phosphoranes, exhibiting a P–H bond, which are in equilibrium with the starting materials. Theoretical DFT study has allowed us to precise the geometrical characteristics, thermodynamic and kinetic parameters, vibrational normal mode wave numbers and atomic charge distribution of intervening molecules and the transition state. According to Hammond postulate, this transition state is described as react-like type one. The analysis of the pathway obtained by the IRC method indicates that phosphoranes formation follows a two-step mechanism in which a pseudo-phosphonium ion intervenes as a reaction intermediate.

Keywords: Oxidative addition on phospholanes; Phosphoranes with P–H bond; Phosphonium ion; Transition state; biphily; IRC

1. Introduction

An increasing number of phosphoranes, which are pentacoordinated phosphorus compounds with P–H bond, have been described within recent years. This interest is a consequence of their role as intermediary reagent in several important chemical or biological reactions [1–26]. In particular, the intervention of monocyclic phosphoranes with P–H bond constitutes the starting step in alcoholysis reaction of intracyclic [23] or extracyclic [7] P–N bonds. Several reagents exhibiting labile hydrogen as amines, alcohols and phenols react with phospholanes leading to phosphoranes in equilibrium with the starting materials [14,22] (Scheme 1). Rarely, phosphoranes have been isolated [3,16,18,21,25].

Despite the increasing detection of such compounds, the kinetics and the mechanism of the phosphorane formation have retained little attention [27–34]. A previous kinetic study of phosphoranes formation by oxidative addition of alcohols on monocyclic phospholanes [35] was performed in our laboratory. It concerned the 2,4,4,5,5 pentamethyl 1,3,2-dioxaphospholane and 2-phenyl-4,4,5,5 tetramethyl 1,3,2-dioxaphospholane.

In all experimental requirements, the reactions follow second order kinetics; first order with respect to both phospholane and alcohol. At the same temperature, the quotient of rate constants, obtained for methanol and its homologue methanol-D, k_H/k_D is of 4.3 in cyclohexane. This isotopic effect confirms the important kinetic role of mobile hydrogen. A reaction mechanism was proposed based on the hypothesis that phosphorus lone pair attack on hydrogen atom of the hydroxyl group is the determining step. A probable formation of pseudo-phosphonium ion as a reaction intermediate has been suggested [22].

We report in this paper the theoretical study of the reaction that takes place between methanol and the1,3,2-dioxaphospholanes **1a** and **1b**, 2-substituded by $R=CH_3$ and $R=C_6H_5$ respectively (Scheme 1). It is an oxidative addition which leads to the formation of the 1,3,2-dioxaphosphoranes **2a** and **2b**. DFT theoretical calculations were carried out in order to precise the structure and the energetic characteristics of reagents, transition states and products. The aim of the pathway determination by means of the IRC method should lead to a better understanding of the reaction mechanism.

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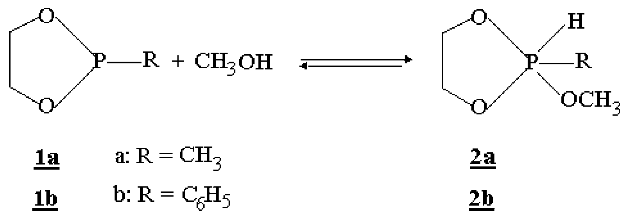

Scheme 1. Representation of the oxidative addition of methanol on phospholanes **1a** and **1b**.

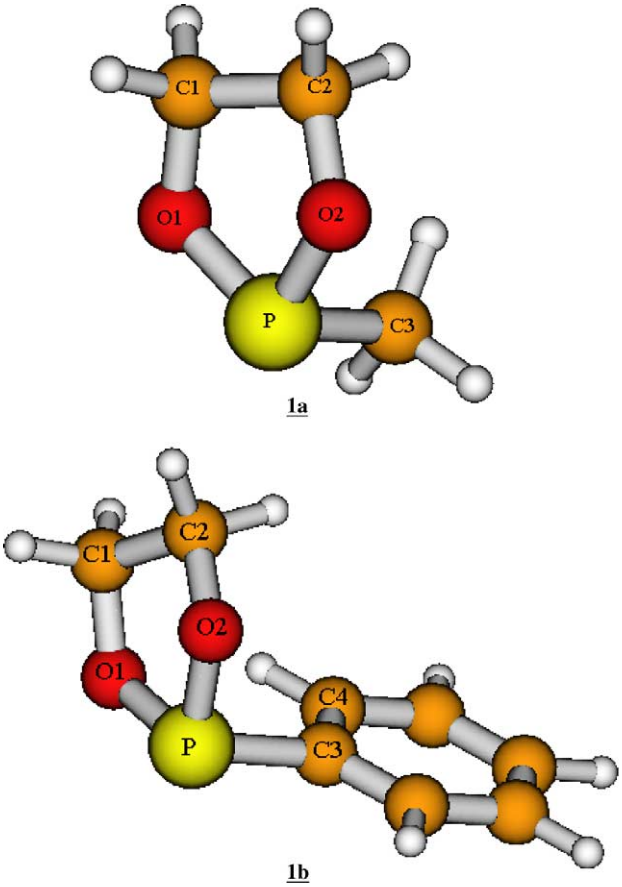

Fig. 1. Geometry of the phospholanes **1a** and **1b**.

In this work, we will indicate the values reporting to the “**na** series” compounds ($n = 1$–4) and we will place their homologues of the “**nb** series” between parenthesis.

2. Computational details

DFT calculations were supported by the GAUSSIAN 98 algorithm [36], including the pseudo-potential suggested by Durand and Barthelat [37]. For C and O atoms, the valence electrons were described through [4s4p/3s3p] GTO basis sets [38]. We added polarisation functions to these basis sets with the exponents 0.80 and 0.85 for C and O, respectively. Beck3lyp functional have been used in DFT calculations. NBO analysis has also been carried out in order to have more accurate information about electronic density distribution in the studied entities.

3. Results and discussion

*3.1. Structural study of reagents **1** and products **2***

The monocyclic phosphoranes have rarely been isolated [5,35] because of the perpetuation of the equilibrium between them and the starting phospholanes. The structures of intervening compounds were only assumed accordingly to spectroscopic analysis. So, the first aim of this work is to calculate the geometry parameters in order to compensate the lack of experimental structure data. The theoretical IR spectra that are shown in a following part of this paper may be helpful in the confirmation of structural attributions.

Figs. 1 and 2 depict the obtained geometry for the phospholanes **1a**, **1b** and the phosphoranes **2a**, **2b**. Selected geometrical parameters are gathered in Annexe 1. As expected, structural determination of the phosphoranes **2a** and **2b** (Fig. 2) reveals a trigonal-bipyramid geometry in which hydrogen and 2-R ligand are in equatorial positions but the methoxy **–O3–CH$_3$** is in axial one as it is attested by the angle O2PO3 of 172.13° (169.99°).

Comparison between the structures of the studied compounds doesn’t show any signifying influence of the phenyl presence on phosphoryl ring. In both compounds **1a** and **1b**, P–O and P–C bond lengths are roughly 170 pm and 186.5 pm respectively. The intra-ring O1PO2 and the extra-ring O1PC3 bond angles are nearly 92.8° and 99.5° respectively. Those angles are characteristic of phosphorus sp [3] hybridization.

The five-membred dioxaphosphoryl ring is not planar and takes in **1a** and **1b** a twisting disposition in which the two P–O bonds form an angle of roughly 18° (19°). One of those bonds is positioned over and the other under the averaged plane formed by the carbons C1, C2 and phosphorus. The two groups CH$_2$ of the dioxaphosphoryl ring avoid an eclipsed disposition and prefer the one in which two corresponding CH bonds have an angle of 30°.

The phenyl ring makes with the averaged plane aforementioned an angle of 100°. It is interesting to note that the P–O1 bond is exactly in the phenyl plane as it is attested by the dihedral angle O1-P-C3-C4 of roughly 180.0°, assuming that one π oxygen lone pair is conjugated with the phenyl. This conjugation affects weakly the geometry around the phosphorus atom by decreasing the PO1 bond length in phenyl substituted compounds relatively to PO2.