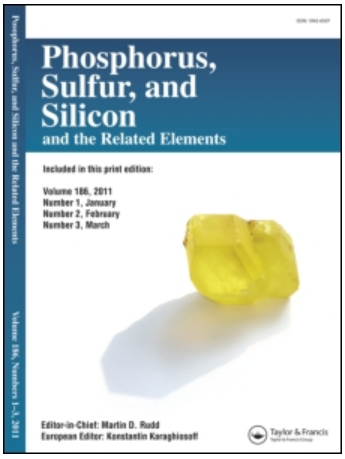

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Preparation and Kinetic Study of Antiapicophilicity Pseudorotamers of Substituted Spirophosphoranes with Martin Ligand

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Anti-apicophilic pseudorotamers bearing a Martin ligand with equatorial-*O* and apical-*C*, that is*O-cis* isomer, were prepared selectively. Kinetic study of BPR of *O-cis* isomer to *O-trans* isomer is discussed.

Keywords: Anti-apicophilic pseudorotamers; oxidation; dianion of monocyclic P-H (apical) phosphoranes; Berry pseudorotation; kinetics

INTRODUCTION

According to the fundamental idea to freeze the usually very rapid Berry pseudorotation of pentacoordinate phosphoranes, we prepared spirophosphoranes with two Martin ligands and succeeded in the separation of diastereomers bearing an isomenthyloxycarbonylmethyl group. Based on the result, we extended our research and prepared optically pure P-H (equatorial) spirophosphorane bearing asymmetry only at phosphorus. The alkylation of the P-H bond in the presence of base (DBU) proceeded with retention of configuration and we tried a couple of reactions using racemic P-H phosphorane[1].

When two equiv of alkyllithiums were added to the P-H phosphorane at low temperature in THF, monocyclic P-H (apical) phosphoranes **1** were obtained in good yield. We were surprised to find that *O-cis* isomers that have a Martin ligand with equatorial-*O* and apical-*C* were obtained as major products accompanied by the

corresponding *O-trans* isomer when **1** were heated in THF in the presence of pyridine[2]. In order to obtain *O-cis* isomers selectively in high yields, several attempts were carried out.

PREPARATION OF *O*-CIS ISOMERS

The dianions **4-a** [δP (Et_2O) = -33.5], **4-b** [δP (Et_2O) = -23.1] and **4-c** [δP (Et_2O) = -10.1] were generated in situ by the reaction of **1-a** [δP ($CDCl_3$-51.9], **1-b** [δP ($CDCl_3$) = -33.4] and **1-c** [δP ($CDCl_3$) = -14.7, -43.0] with 2 equivalents of *n*-BuLi in Et_2O at -78 °C, respectively.

The treatment of **4** at room temperature for 10 min with oxidizing reagents such as 30% H_2O_2, *m*CPBA or I_2 led to the predominant or almost exclusive formation of *O-cis* spirophosphorane **2**. In the case of **4-c** (R = *t*-Bu), treatment with 30% H_2O_2 resulted in recovery of the starting material **1-c**. By the oxidative cyclization with I_2, *O-cis* isomer **2** could be isolated in high yield (**2-a**; 56%, **2-b**; 86%, **2-c**; 99%) after TLC separation (SiO_2: hexane:CH_2Cl_2 = 2:1) and recrystallization (hexane or acetonitrile). Surprisingly, when Br_2 was used, **2a** and **2b** gave *O-trans* isomers exclusively, while *O-cis* isomer **2-c** (R = *t*-Bu) was formed quantitatively under the same conditions.

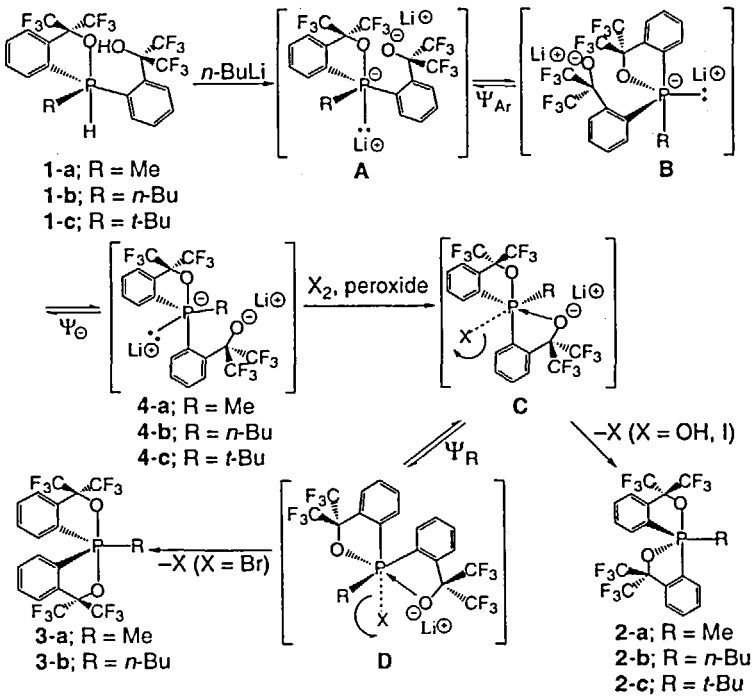
TABLE The Ratio of *O-cis* **2** and *O-trans* **3** Isomers by Oxidation of Dianions **4**

Oxidizing Agent	2-a : 3-a	2-b : 3-b	2-c : 3-c
30% H_2O_2	93 : 7	88 : 12	—
mCPBA	92 : 8	> 99 : < 1	88 : 12
I_2	88 : 12	94 : 6	> 99 : < 1
Br_2	< 1 : > 99	< 1 : > 99	> 99 : < 1

The oxidative cyclization can be rationalized as shown in Scheme 1. Initially generated dianion **A** bearing an apical lone pair of electrons isomerizes to a more stable dianion **4** bearing an equatorial lone pair and an apical oxygen through two BPR processes with the pivot group of Ar and the lone pair, respectively that is Ψ_{Ar} and Ψ-. The equatorial lone pair is oxidized with the formation of P-X bond (X = OH, I, Br) to generate **C**. Then, **C** undergoes cyclization to *O-cis* spirophosphorane **2** by an S_Ni type

nucleophilic attack of the oxyanion anti to the P-C bond of the ring through an octahedral transition state. On the other hand, **D** generated by a one step BPR (Ψ_R) of **C** gives *O-trans* spirophosphorane **3** by an S_Ni type nucleophilic attack of the oxyanion anti to the P-O bond through an octahedral transition state. *O-cis* isomer **2** was formed predominantly from **C** when the leaving group was the hydroxide and the iodide. In the case of the bromide, pseudorotation (Ψ_R) of **C** takes place before the cyclization to give *O-trans* isomers **3a** and **3b**, however, **2c**(R=*t*-Bu) was not obtained because pseudorotation ($\Psi_{t\text{-Bu}}$) should be very slow due to steric hindrance compared with bromide anion extrusion.

Diastereomeric **1-d** (R=*t*-Bu) that have one methyl group instead of a trifluoromethyl group were also oxidized to the corresponding *O-cis* isomers with iodine.



SCHEME I

KINETIC STUDY OF PSEUDOROTATION

When a solution of **2-b** in toluene-d_8 was cooled to 193 K, four separate CF_3 groups were observed cleary by ^{19}F NMR. At 293 K, they showed two kinds of CF_3 groups due to coalescence at 235 K. Analysis of temperature dependent ^{19}F NMR gave kinetic factors as $\Delta H^{\ddagger} = 10.0 \pm 0.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -3.4 \pm 0.4$ eu for one step BPR between **2b*R*P** and **2b*S*P**. Then, **2b** was heated in toluene-d_8 to isomerize to **3b** by BPR and the kinetic factors were obtained as $\Delta H^{\ddagger} = 21.8 \pm 0.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = -9.0 \pm 1.2$ eu. Kinetic factors for isomerization from **3b*R*P** to **3b*S*P** were obtained as $\Delta H^{\ddagger} = 33.8 \pm 2.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -8.7 \pm 4.5$ eu by using separated diastereomers with one methyl group. The energy diagram is shown in Figure 1.

By using diastereomers (R = *t*-Bu, ***exo*** and ***endo*** indicates the relative stereochemistry of the methyl group), we could discriminate the two possibilities of isomerization from *41* to *21* and *14* to *12* for the first time and isomerization between *41* and *14* could not be observed. This process will be also presented.

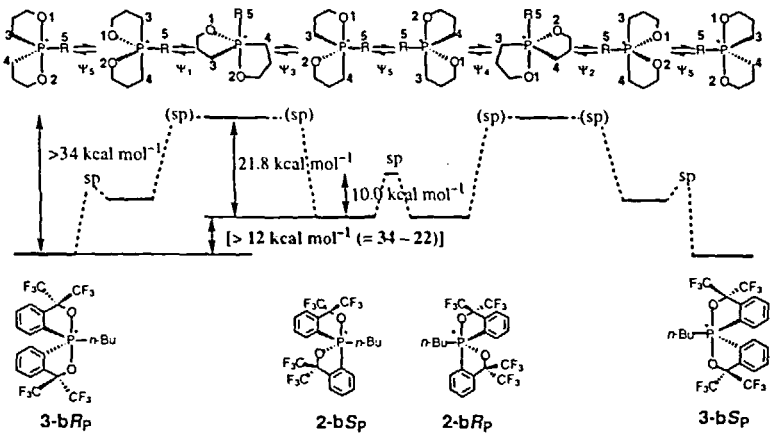


FIGURE 1

References

[1] S. Kojima, K. Kajiyama and K. -y. Akiba, *Bull. Chem. Soc. Jpn.* **68**, 1785 (1995).
[2] S. Kojima, K. Kajiyama. M. Nakamoto and K. -y. Akiba, *J. Am. Chem. Soc.* **118**, 12866 (1997).