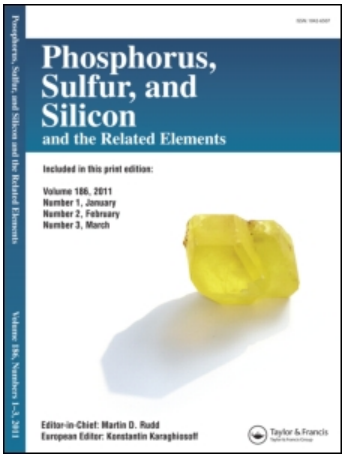

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EFFECT OF σ^*_{P-O} ORBITAL ON STRUCTURE, STEREOMUTATION, AND REACTIVITY OF *C*-APICAL *O*-EQUATORIAL SPIROPHOSPHORANES

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Effect of σ^*_{P-O} orbital of C-apical O-equatorial (O-cis) spirophosphorane was investigated both experimentally and theoretically. O-cis phosphoranes revealed to be much more electrophilic on the phosphorus atom than O-trans isomers by experimental studies. Theoretically, the energy of the σ^*_{P-O} orbital of O-cis phosphorane was calculated to be lower than that of the σ^*_{P-C} orbital of O-trans phosphorane by 18.7 kcal/mol, and the result supports the enhanced electrophilicity of O-cis spirophosphoranes compared with O-trans isomer.

Keywords: Hypervalent; σ^*_{P-O} orbital; phosphorus; reactivity; reversed apicophilicity

INTRODUCTION

We have reported on the synthesis, structure, and stereomutation of *C*-apical *O*-equatorial (*O-cis*) spirophosphorane **1a** and its stable stereoisomer of *O*-apical *C*-equatorial (*O-trans*) spirophosphorane **2a**.[1] The phosphorane **1a** was the first example exhibiting reversed apicophilicity, which could be converted to its stable pseudorotamer **2a**. *O-cis* phosphorane **1** has one of the two P—O bonds on the equatorial plane and therefore has a σ^*_{P-O} orbital on the same plane. On the other

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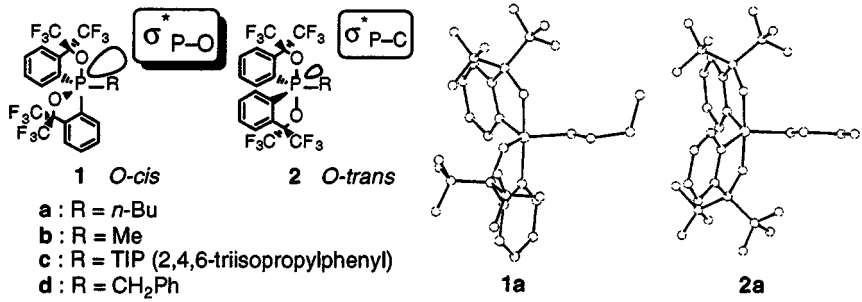


FIGURE 1

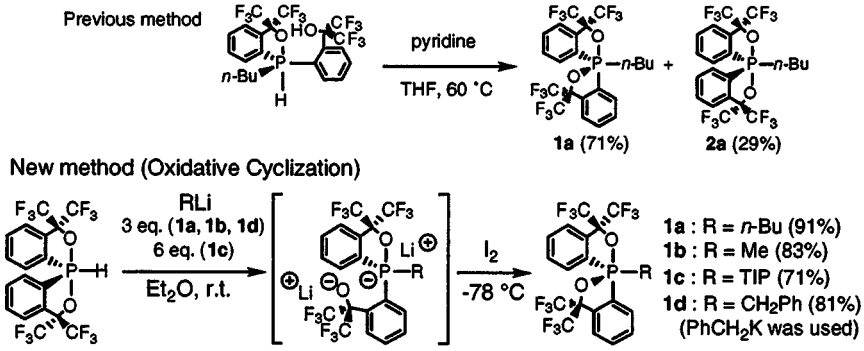
hand, *O-trans* phosphorane **2** has the corresponding P—C bond on the equatorial plane; hence σ^*_{P-C}, too (Figure 1). Since the energy level of σ^*_{P-O} should be significantly lower than that of σ^*_{P-C}, there should be an apparent effect of σ^*_{P-O} to show the difference between **1** and **2** in reactivity such as nucleophilicity and stability of α-carbanions. Now we describe the effects of σ^*_{P-O} orbital of **1** from both an experimental and theoretical viewpoint.

RESULTS AND DISCUSSION

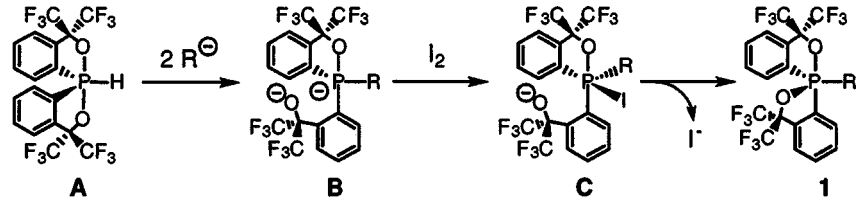
Synthesis of *O-cis* Spirophosphoranes by Oxidative Cyclization of the Dianion

As reported in 1996, we succeeded to isolate *O-cis* spirophosphorane **1a** by thermal cyclization of P—H(apical) monocyclic phosphorane.[1] However this method is not suitable for synthesis of *O-cis* phosphoranes because the thermal conditions accerelate stereomutation to the corresponding *O-trans* isomer. Indeed, **1a** was obtained in 71% yield and **2a** in 29% yield by this thermal method. To improve this problem, a milder oxidative cyclization method was developed in our laboratory[2] (Scheme 1). The new protocol provided **1a** and **1b** exclusively at low temperatures in high yields, and aryl derivative **1c** could also be synthesized for the first time.

The possible reaction mechanism is shown in Scheme 2. The reaction of P—H (equatorial) phosphorane **A** with more than 2 equivalents of RLi provides the dianion **B**, where one equivalent of RLi works as a base and the other as a nucleophile. In the resulting dianion **B**, the lone pair electrons on phosphorus occupy an equatorial position because of its extreme electron-donicity. In this situation, oxidant I_2 reacts with the



SCHEME 1

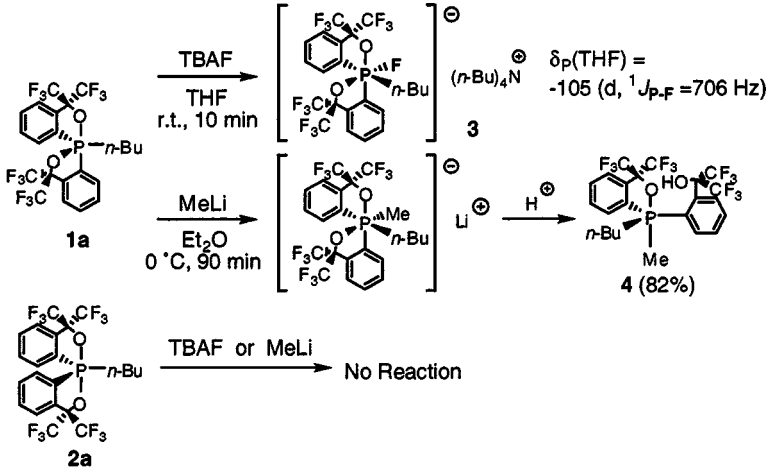


SCHEME 2

dianion **B** to produce P–I (equatorial) phosphorane **C**, and the remaining alkoxide anion rapidly cyclizes with simultanious elimination of I^- to form *O-cis* spirophosphorane **1** exclusively.

Enhanced Electrophilicity of *O-cis* Phosphorane 1: Effect of σ^*_{P-O} Orbital in the Equatorial Plane

Reactions of *O-cis* **1a** and *O-trans* **2a** with nucleophiles were examined. Using TBAF (tetrabutylammonium fluoride; $[n\text{-Bu}]_4N^+F^-$) as a nucleophile, the reaction of **1a** readily afforded a hexacoordinate phosphate bearing a P–F bond **3** ($^1J_{P-F} = 706$ Hz) while **2a** did not react at all. Configuration of the phosphate **3** could not be determined because of rapid decomposition by trace amounts of H_2O. However, we have already characterized the corresponding hexacoordinate fluoroantimonate with two Martin ligands by X-ray analysis;[3] therefore, the fluorine atom in phosphate **3** is also likely to be located anti to the oxygen due to the trans influence as the fluoroantimonate. In the case of the reaction with MeLi, **1a** reacted under mild conditions to afford a monocyclic phosphorane **4** after aqueous work up but **2a** did not (Scheme 3).



SCHEME 3

Stabilization of Lone Pair Electrons Adjacent to the Phosphorus of *O-cis* 1: Effect of σ^*_{P-O} Orbital in the Equatorial Plane

Deprotonation of *O-cis* **1d** with KHMDS (potassium hexamethyldisilazide; $(Me_3Si)_2N^-K^+$) occurred in THF at 0°C during 30 min and gave α-deuterated product (40% yield) after quenching the mixture with D_2O. However, *O-trans* **2d** could not be deprotonated under the same conditions. Moreover, the benzyl anion of **1d** was much more stable thermally than the neutral molecule of **1d**. In THF, *O-cis* **1d** was totally converted to *O-trans* **2d** at 60°C during 5 h. Under the same conditions, the benzyl anion of **1d** remained almost unchanged, which shows the significant stability of the *O-cis* benzyl anion compared to the corresponding neutral molecule.

Theoretical Study on σ^* Orbitals of *O-cis* and *O-trans* Phosphoranes in the Equatorial Plane

In order to evaluate a difference in energy between the σ^*_{P-O} orbital of *O-cis* phosphorane and that of *O-trans* isomer, theoretical calculations for **1b** and **2b** were carried out (B3LYP/6-31G(d)). As shown in Figure 2, the energy of σ^*_{P-O} of **1b** (LUMO+4) is lower than that of σ^*_{P-C} of **2b** (LUMO+5) by 18.7 kcal/mol. Other LUMOs below σ^*_{P-X} (X = O or C) were distributed on the aromatic rings of the Martin ligands. Therefore, the responsible orbitals toward nucleophilicity and stabilization of α-carbanion should be the σ^*_{P-X} orbitals. As a result, the large

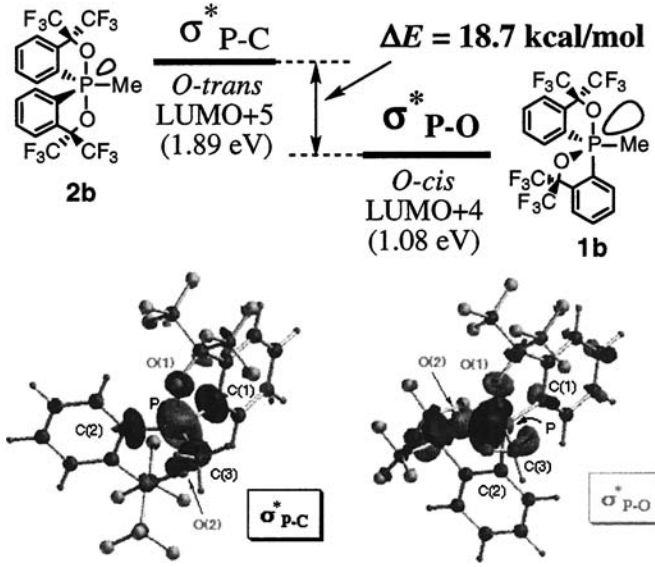


FIGURE 2

difference in energy between σ^*_{P-O} and σ^*_{P-C} orbital provided theoretical evidence for the enhanced reactivity of *O-cis* spirophosphorane **1** compared with *O-trans* isomer **2**, as shown in Scheme 3.

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