This article was downloaded by: [University of Windsor] On: 13 November 2014, At: 03:46 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



# Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/gpss20

## Synthesis, Isolation, and Skeletal Inversion of 5,10-Dihydrophosphanthrenes

Yosuke Uchiyama<sup>a</sup> & Yasuhiro Mazaki<sup>a</sup>

<sup>a</sup> Department of Chemistry, School of Science , Kitasato University , Sagamihara , Kanagawa , Japan Published online: 25 Apr 2011.

To cite this article: Yosuke Uchiyama & Yasuhiro Mazaki (2011) Synthesis, Isolation, and Skeletal Inversion of 5,10-Dihydrophosphanthrenes, Phosphorus, Sulfur, and Silicon and the Related Elements, 186:4, 822-825, DOI: <u>10.1080/10426507.2010.515957</u>

To link to this article: <u>http://dx.doi.org/10.1080/10426507.2010.515957</u>

### PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <a href="http://www.tandfonline.com/page/terms-and-conditions">http://www.tandfonline.com/page/terms-and-conditions</a>



Phosphorus, Sulfur, and Silicon, 186:822–825, 2011 Copyright © Taylor & Francis Group, LLC ISSN: 1042-6507 print / 1563-5325 online DOI: 10.1080/10426507.2010.515957

#### SYNTHESIS, ISOLATION, AND SKELETAL INVERSION OF 5,10-DIHYDROPHOSPHANTHRENES

#### Yosuke Uchiyama and Yasuhiro Mazaki

Department of Chemistry, School of Science, Kitasato University, Sagamihara, Kanagawa, Japan

**Abstract** Two stereoisomers, the trans form **1a** and the cis form **1b**, of 2,3,7,8-tetramethyl-5,10-diphenyl-5,10-dihydrophosphanthrene dioxide (**1**) were formed by spontaneous oxidation in air of the corresponding 5,10-dihydrophosphanthrenes **2** and were separated by recrystallization. Both **1a** and **1b** were characterized by X-ray crystallographic analysis, which revealed configurations at the phosphorus and conformations of the central tricyclic system. The <sup>31</sup>P NMR of the reaction mixture showed at first two signals at -15.3 and -15.1 ppm, which shifted to 9.11 and 10.3 ppm after purification of the reaction mixture under aerobic conditions by oxidation of phosphorus atoms. The reaction of **1b** with HSiCl<sub>3</sub> in toluene-d<sub>8</sub> at 100 °C gave no change, whereas **1a** reacted with HSiCl<sub>3</sub> to give reduced compounds **2a** and **2b** under the same conditions. The trans–cis isomerization of **2** occurred via vertex inversion at phosphorus atom. VT-NMR, X-ray analysis, and density functional theory (DFT) calculation showed that the conformational exchange of the cis form **1b** proceeded via skeletal inversion of the tricyclic ring.

Keywords Isomerization; skeletal inversion; stereochemistry; VT-NMR; X-ray crystallographic analysis

#### INTRODUCTION

Conformational and configurational exchanges are important and fundamental phenomena in a molecular control system.<sup>1</sup> 5,10-Disubstituted-5,10-dihydroheteroanthrenes with group 15 elements have been expected to be one of the interconversion systems allowing both of the configurational and conformational exchanges. 5,10-Dihydrophosphanthrene and 5,10-dihydroarsanthrene were reported, but the structure and reactivity to electrophiles of only configurational isomers, a *trans* form and a *cis* form, are known. As for the conformational isomers of these compounds, an *exo\_cis* and an *endo\_cis* form, the isolation and property studies remain to be investigated.<sup>2</sup> We will report here the synthesis and isolation of two stereoisomers, the *trans* form **1a** and the *cis* form **1b**, of

Received 24 July 2010; accepted 12 August 2010.

This study was partially supported by a Grant-in-Aid for Encouragement of Young Scientists (B) to Y. U. (No. 16750041 and No. 18750037) from the Ministry of Education, Culture, Sports, Science and Technology of Japan and a Kitasato University Research Grant for Young Researchers.

Address correspondence to Yosuke Uchiyama, Department of Chemistry, School of Science, Kitasato University, 1-15-1 Kitasato, Minami-ku, Sagamihara, Kanagawa 252-0373, Japan. E-mail: yosuke@kitasato-u.ac.jp



Figure 1 Molecular structure of the trans form 1a and the endo\_cis form 1b' drawn with 50% probability.

5,10-dihydrophosphanthrene dioxide 1 and will describe the equilibrium of the *trans-cis* and the *endo\_cis-exo\_cis* isomerizations.

#### **RESULTS AND DISCUSSION**

Bis(2-bromo-4,5-dimethylphenyl)phenylphosphine (**3**) was obtained by the reaction of 4,5-dibromo-*o*-xylene with *n*-BuLi followed by the addition of PhPCl<sub>2</sub>. The reaction of diarylphenylphosphine **3** with 4 equiv. of *t*-BuLi followed by the addition of PhPCl<sub>2</sub> afforded the dioxide **1** in 58% yield (Scheme 1).<sup>3</sup> The crude material reproducibly contained two stereoisomers **1a** and **1b** in the ratio of 1:1, which was estimated by the <sup>1</sup>H NMR spectroscopy. In the <sup>31</sup>P NMR of the reaction mixture, the signals were at first observed at -15.3 and -15.1 ppm. After workup under aerobic conditions, the signals were shifted to 9.11 and 10.3 ppm. The results show that compound **2** formed at first was spontaneously oxidized in air to afford the dioxide **1**. Recrystallization of the stereoisomeric mixture of **1a** and **1b** from CH<sub>3</sub>CN gave the *cis* form **1b** ( $\delta_P$  10.3). Then the solvent of the filtrate was evaporated and the residue recrystallized from benzene to afford the *trans* form **1a** ( $\delta_P$ 9.11). The structures were determined by X-ray crystallographic analysis (Figure 1).



Scheme 1

The *trans* form **1a** has a planar structure because of the steric repulsion between the substituents at 5,10-positions and the central tricyclic ring. In the *cis* form **1b**, the central six-membered ring adopts a boat conformation with the two phenyl groups in the pseudoaxial positions, referred to as the *endo\_cis* form **1b**', which is expected to be in equilibrium with the *exo\_cis* form **1b**'' in solution.

#### Y. UCHIYAMA AND Y. MAZAKI

The reaction of **1a** with HSiCl<sub>3</sub> at 100°C for 2 h gave products that have two <sup>31</sup>P signals at -15.7 and -16.6 ppm in toluene- $d_8$ . The results indicate that **1a** was reduced to give 5,10-dihydrophosphanthrene **2a**, and the *trans-cis* isomerization occurred *via* vertex inversion at the phosphorus to provide a mixture of **2a** and **2b** (Scheme 2). On the other hand, the reduction of the *cis* form **1b** did not proceed at all under the same condition as **1a**, because of large steric repulsion between phenyl groups at 5,10-positions.



In the <sup>1</sup>H and <sup>31</sup>P NMR spectra, it was difficult to detect the equilibrium between **1b**' and **1b**'' even at -105 °C, though the signals of the methyl groups at 2,3,7,8-positions and the phosphorus signals were observed as somewhat broad signals. The conformational exchange proceeded quickly in a CD<sub>2</sub>Cl<sub>2</sub> solution due to the low energy barrier suggested by density functional theory (DFT) calculations [B3LYP/6–31(d)] (Scheme 3).



The transition state of the *endo\_cis–exo\_cis* isomerization of the dioxide without methyl groups was obtained by the synchronous transit-guided quasi-newton (STQN) method. The conformational isomerization proceeds *via* skeletal inversion, and the transition state is less stable than the ground states by 3.1 and 0.10 kcal/mol, in agreement with the experimental results by the VT-NMR as well as the conformational behavior of the 9,10-dihydroanthracene derivatives.<sup>1,4</sup>

#### CONCLUSION

We report the synthesis, isolation, and skeletal inversion of 5,10-dihydrophosphan threne dioxides **1**. The structures of the *trans* and the *cis* forms were revealed by X-ray crystallographic analysis. The *trans–cis* and the *endo\_cis–exo\_cis* isomerizations were expected to proceed *via* vertex inversion at the phosphorus and skeletal inversion of the tricyclic system based on experimental and calculated results, respectively.<sup>5,6</sup> The skeletal inversion would be new interconversion mode in a molecular control system and 5,10-dihydrophosphanthrene skeletons have the possibilities of multifunctional abilities.

#### 5,10-DIHYDROPHOSPHANTHRENES

#### REFERENCES

- Eliel, E. L.; Wilen, S. H. Stereochemistry of Organic Compounds; John Wiley & Sons: New York, 1993.
- (a) Davis, M.; Mann, F. G. Chem. Ind. 1962, 1539–1540; (b) Davis, M.; Mann, F. G. J. Chem. Soc. 1964, 3770–3785; (c) Akutsu, H.; Ogasawara, M.; Saburi, M.; Kozawa, K.; Uchida, T. Bull. Chem. Soc. Jpn. 1996, 69, 1223–1226.
- (a) Uchiyama, Y.; Yamamoto, G. Chem. Lett. 2005, 34, 966–967; (b) Uchiyama, Y.; Sugimoto, J.; Shibata, M.; Yamamoto, G.; Mazaki, Y. Bull. Chem. Soc. Jpn. 2009, 82, 819–828.
- 4. Zieger, H. E.; Schaeffer, D. J.; Padronaggio, R. M. Tetrahedron Lett. 1969, 10, 5027-5030.
- 5. The energies of vertex inversion of 5,10-diphenyl-5,10-dihydrophosphanthrene were 28.6 and 28.9 kcal/mol of the *endo\_cis-trans* and the *exo\_cis-trans* isomerizations, which were obtained by DFT calculation [B3LYP/6–31G(d)] of the transition state using the STQN method.
- The inversion energies of PH<sub>3</sub> were reported to be 35.0 (6a) and 34.7 (6b) kcal/mol, respectively.
  (a) Dixon, D. A.; Arduengo, III, A. J. J. Am. Chem. Soc. 1987, 109, 338–341; (b) Moc, J.; Morokuma, K. Inorg. Chem. 1994, 33, 551–560.