

Mechanistic Study of the Wittig Reaction of Non-stabilized Phosphonium Ylides Containing Phosphaheteratriptycenes with PhCHO

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In order to reveal the mechanism of the Wittig reaction of non-stabilized phosphonium ylides containing phosphaheteratriptycenes with Group 13, 14, and 15 elements (PhB⁻, PhSi, PhGe, PhSn, *n*-BuSn, P, As, Sb, Bi) with PhCHO, (1) the ratios of the olefins were estimated by ¹H NMR spectroscopy, (2) ³¹P{¹H} NMR spectra were observed at -90 °C to 25 °C and (3) DFT calculation was performed to investigate stability of the intermediates and P–O bond energies of 1,2-oxaphosphetanes.[1,2,3] We wish to show the results as follows and a possible mechanism of the Wittig reaction in the presentation.

(1) Ratios of (*E*)- and (*Z*)-olefins

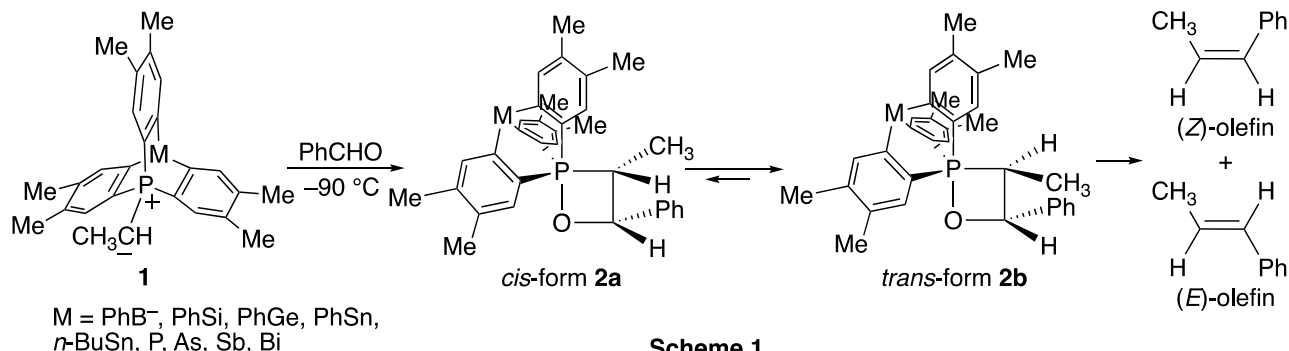
The Wittig reactions of non-stabilized phosphonium ylides **1** containing a phosphaheteratriptycenes with Group 14 and 15 elements (PhSi, PhGe, PhSn, *n*-BuSn, P, As, Sb, Bi) at another bridgehead position with PhCHO provided (*Z*)-olefin as a major product in the cases of period 3 elements (PhSi, P) and (*E*)-olefin as a major product in the cases of below period 4 elements (PhGe, PhSn, *n*-BuSn, As, Sb, Bi) (**Scheme 1**). On the other hand, the reaction of non-stabilized phosphonium ylide containing phosphaboratatriptycene with Group 13 element (PhB⁻) with PhCHO gave not olefins but β-hydroxyalkylphosphonium salt.

(2) Stereochemical drift due to the isomerization between *cis*- and *trans*-1,2-oxaphosphetanes

VT-³¹P{¹H} NMR spectroscopy between -90 °C and 25 °C showed the isomerization of *cis*- and *trans*-1,2-oxaphosphetanes **2** as intermediates. The isomerization between the intermediates **2a** and **2b**, which was considered as the origin of stereochemical drift, was observed at lower temperatures, as the row number of heavier period elements increases and it occurred at lower temperatures in the systems of Group 14 elements than in those of Group 15 elements

(3) Stability and P–O bond energy of 1,2-oxaphosphetanes

DFT calculations were performed to evaluate statistic energy and P–O bond energy of 1,2-oxaphosphetanes, indicating that *trans*-forms were ca. 2 kcal/mol more stable than *cis*-forms and the P–O bond energies of 1,2-oxaphosphetanes became weaker due to the longer P–O bond lengths as row number of elements increases.



References

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- [2] Y. Uchiyama, S. Kuniya, R. Watanabe, T. Ohtsuki, *Phosphorus, Sulfur, and Silicon and the Related Elements*, **2019**, 194, 281-294.
- [3] Y. Uchiyama, S. Kuniya, R. Watanabe, T. Ohtsuki, *Heteroat. Chem.*, **2018**, 29, e21473, 1-17.