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Observation of intermediates in Wittig reactions of non-stabilized phosphonium ylides bearing a phosphaheteratriptycene skeleton containing Group 15 elements with benzaldehyde

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ABSTRACT

The heteroatom effect of Group 15 elements (P, As, Sb and Bi) has been investigated on stereochemical drift in the Wittig reactions of non-stabilized phosphonium ylides bearing a phosphaheteratriptycene skeleton with benzaldehyde. 1,2-Oxaphosphetanes were observed as intermediates and the isomerization from cis-form to trans-form, the origin of stereochemical drift, was detected between -90 °C and 25 °C by VT-³¹P{¹H} NMR spectroscopy. The isomerization was found to start at lower temperatures as the raw number of heavier period elements. Cross experiments showed that the isomerization occurred through equilibrium between 1,2-oxaphosphetanes and phosphonium ylides-benzaldehyde.

GRAPHICAL ABSTRACT



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Introduction

Non-stabilized triphenylphosphonium ylides are well-known to be reacted with benzaldehydes to give (Z)-olefins as a major product in the Wittig reaction.^[1] On the other hand, the reaction of non-stabilized tri(n-butyl)phosphonium ylides with benzaldehydes was reported to give (E)-olefins as a major product.^[2] The selectivity of (E)- and (Z)-olefins is considered to the substituent groups on the phosphorus atom of the ylides, which affect the stereochemical drift of the intermediates. We have recently reported (E)-selective Wittig reactions of non-stabilized phosphonium ylides bearing a phosphastibatriptycene skeleton with benzaldehydes.^[3-5] The results showed that the tridentate ligand in the 1,2-oxaphosphetanes bearing the phosphastibatriptycene skeleton has the similar substituent effects with n-butyl groups on the phosphorus atom of 1,2-oxaphosphetanes. Herein, we will report about the heteroatom effect of Group 15 elements in a phosphaheteratriptycene skeleton on the isomerization from cis-1,2-oxaphosphetanes to trans-forms in Wittig reactions of non-stabilized phosphonium ylides with benzaldehyde.

Results and discussion

Synthesis of ethylphosphonium iodides bearing a phosphaheteratriptycene skeleton

Ethylphosphonium iodides 1, 2 and 4 bearing a phosphaheteratriptycene skeleton containing Group 15 elements (P, As and Bi) were synthesized by the similar method of phosphastibatriptycene derivative 3 (M = Sb).^[3-5] The reaction of tris(2-bromo-4,5-dimethylphenyl)phosphine with t-BuLi followed by the addition of a THF solution of MCl_3 (M = P, As and Bi) afforded diphosphatriptycene 5, phosphaarsatriptycene 6 and phosphabismatriptycene 8 in 7%, 6% and 10% yields as reported for phosphastibatriptycene 7 (Scheme 1). Phosphaheteratriptycenes 5, 6 and 8 reacted with ethyl iodide in CHCl₃ at 70 °C to afford ethylphosphonium iodides 1, 2 and 4 in 75%, 93% and 80% yields, respectively. Phosphorus-31 signals of each ethylphosphonium iodide were observed at lower field than those of phosphaheteratriptycenes. Proton signals of CH₃CH₂ group showed reasonable P-H coupling and the integral ratio. The NMR spectra indicated successful ethylation at the phosphorus atom.



Scheme 1. Synthetic route of ethylphosphonium iodides bearing a phosphaheteratriptycene skeleton.



Scheme 2. Wittig reactions of non-stabilized phosphonium ylides with benzaldehyde.



Scheme 3. Observation of isomerization between cis- and trans-1,2-oxaphosphetanes.

Wittig reactions of non-stabilized phosphonium ylides with benzaldehyde

Non-stabilized phosphonium ylides **9–12** were generated in a J-Young NMR tube by the reactions of ethylphosphonium iodides **1–4** with TMS₂NNa in THF at 0 °C for 10 min (**Scheme 2**). In the ³¹P NMR spectra, phosphorus-31 signals of **9–12** were observed at significant upper field than those of **1–4**. Wittig reactions of **9–12** with benzaldehyde gave (*E*)- and (*Z*)-olefins in 15%, 32%, 87% and 42% yields together with phosphine oxides **13–16**, respectively. The ratio of (*E*)- and (*Z*)-olefins was almost 1:1 in the case of diphosphatriptycene derivative and (*E*)-olefin was obtained as a major product in the cases of phosphaarsatriptycene, phosphastibatriptycene and phosphabismatriptycene derivatives (**Scheme 2**).

Observation of intermediates by Variable Temperature (VT)-³¹P{¹H} NMR spectroscopy

The trialkylphosphonium ylide systems showed the isomerization between *cis*- and *trans*-1,2-oxaphosphetanes, which is considered as the origin of stereochemical drift.^[2] Similarly, the isomerization was observed at -40 °C in the case of phosphastibatriptycene derivative and its mechanism was revealed to be not a pathway through Schlosser type intermediate^[6] but that via equilibrium between 1,2-oxaphosphetanes and a phosphonium ylide-benzaldehydes, which was revealed by exchange reaction of benzaldehyde units in 1,2-oxaphosphetanes.^[3-5] In order to investigate heteroatom effects at the other bridgehead position of a phosphaheteratriptycene in the equilibrium, Wittig reactions of non-stabilized phosphonium ylides 9-12 with benzaldehyde were conducted at -90 °C and intermediates were observed at temperatures between -90°C and 25°C by VT-³¹P{¹H} NMR spectroscopy. The isomerization from cis-1,2-oxaphosphetanes to trans-forms was detected at 0 °C for 17, -20 °C for 18, -40 °C for 19 or -60 °C for 20 (Scheme 3, Figure 1). The results showed that the isomerization occurred at lower temperature as the raw number of heavier period elements increases. The selectivity of (E)and (Z)-olefins depended on the isomerization, the origin of stereochemical drift, based on the heteroatom effect in the equilibrium between 1,2-oxaphosphetanes and phosphonium ylides-benzaldehyde. The equilibrium was attributed to electronegativity, 2.19 for P, 2.18 for As, 2.05 for Sb and 2.02 for Bi.^[7]



Figure 1. VT-³¹P{¹H} NMR spectra of isomerization between *cis*- and *trans*-1,2-oxaphosphetanes.



Scheme 4. Mechanism of the Wittig reactions of non-stabilized phosphonium ylides 9-12 bearing a phosphaheteratriptycene skeleton with benzaldehyde.

Mechanism of the Wittig reactions depending on isomerization of intermediates

Wittig reactions of non-stabilized phosphonium ylides **9–12** bearing a phosphaheteratriptycene skeleton containing Group 15 elements with benzaldehyde gave (*E*)- and (*Z*)-olefins as final products in the ratios, which depended on a phosphaheteratriptycene skeleton, together with phosphine oxides **13–16**. The stereospecific olefin formation was considered to proceed via the isomerization from *cis*-1,2-oxaphosphetanes to *trans*-forms because *cis*-1,2-oxaphosphetanes to *trans*-forms because *cis*-1,2-oxaphosphetanes **17a–20a** were observed as a kinetic product at the first stage by VT-³¹P{¹H} NMR spectroscopy and *trans*-forms **17b–20b** were detected at different temperatures depending on a phosphaheteratriptycene skeleton containing Group 15 elements. The isomerization is regarded as the origin of stereochemical drift, which was reported for the first time in

the (E)-selective Wittig reaction of a non-stabilized tri(nbutyl)phosphonium ylide with benzaldehyde.^[2] The isomerization has also been revealed to proceed via an equilibrium of 1,2-oxaphosphetanes and phosphonium ylides-benzaldehyde based on the reported exchange reaction of benzaldehydes in the deprotonation of β -hydroxyalkyl phosphonium salt with TMS₂NNa.^[3,4] A tridentate ligand in this system is constructed by three aryl groups, so that the reactivities of 1,2-oxaphosphetanes bearing a phosphaheteratriptycene containing Group 15 elements should be similar to those of 1,2oxaphosphetanes formed from non-stabilized triphenylphosphonium ylides^[1] rather than those of non-stabilized tributylphosphonium ylides.^[2] However, the result was reverse. Therefore, heteroatom at the other bridgehead position of a phosphaheteratriptycene skeleton affects the equilibrium rather than thermodynamic stability of 1,2-oxaphosphetanes. The isomerization from cis-1,2-oxaphosphetanes to transforms occurred more easily, as the raw number of heavier elements increases. The reason was why the heteroatom effect derived from electronegativity^[7] induced polarization of M–C bonds to stable non-stabilized phosphonium ylides bearing a phosphaheteratriptycene skeleton containing Group 15 elements, from which the equilibrium inclined to the right hand.

Conclusions

The heteroatom effect of Group 15 elements in a phosphaheteratriptycene skeleton on the equilibrium between 1,2oxaphosphetanes and phosphonium ylides-benzaldehyde in the isomerization from cis-1,2-oxaphosphetanes to transforms has been investigated in Wittig reactions of non-stabilized phosphonium ylides 9-12 with benzaldehyde. The heteroatom at the other bridgehead position of a phosphaheteratriptycene skeleton affected the isomerization temperature to start observing trans-forms, which became lower as the raw number of heavier elements increases, showing the selectivity of (E)- and (Z)-olefins under the same reaction condition. However, we could not reveal whether the equilibrium occurred via a betaine intermediate or the direct retro [2+2] cycloaddition-reconstruction. The investigation on the reaction mechanism is in progress.

Disclosure statement

No potential conflict of interest was reported by the authors.

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