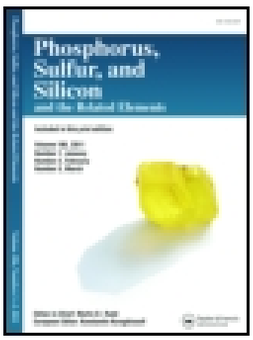

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Wittig reactions of non-stabilized phosphonium ylides bearing a phosphaheteratriptycene skeleton containing group 14 and 15 elements with benzaldehyde

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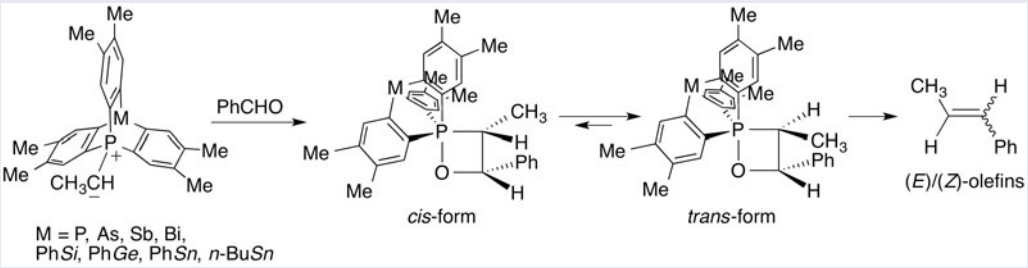
ABSTRACT

Wittig reactions of non-stabilized phosphonium ylides bearing a phosphaheteratriptycene skeleton containing Group 14 and 15 elements (Ph*Si*, Ph*Ge*, Ph*Sn*, *n*-Bu*Sn*, P, As, Sb, and Bi) at another bridgehead position with benzaldehyde provided (*Z*)-olefins as a major product in the cases of period 3 elements (Ph*Si*, P) and (*E*)-olefins as a major product in the cases of below period 4 elements (Ph*Ge*, Ph*Sn*, *n*-Bu*Sn*, As, Sb, and Bi). These results are attributed to stereochemical drift of the intermediates come from the heteroatom effect at another bridgehead position of the phosphaheteratriptycene skeleton.

GRAPHICAL ABSTRACT



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Wittig reaction; non-stabilized phosphonium ylide; phosphaheteratriptycene; 1,2-oxaphosphetane; heteroatom effect

Results and discussion

Alkyl groups on the phosphorus atom of non-stabilized phosphonium ylides affect stereochemical drift, leading to (*E*)-selective olefin formation as reported in the Wittig reaction of stabilized phosphonium ylide with carbonyl compounds.[1,2] We have previously revealed the origin of stereochemical drift of the intermediates in (*E*)-selective Wittig reactions of a non-stabilized phosphonium ylide bearing a phosphastibatriptycene skeleton, which contains Sb at another bridgehead position with benzaldehydes based on the observation of the isomerization from *cis*-1,2-oxaphosphetanes to *trans*-forms by VT-$^{31}P\{^1H\}$ NMR spectroscopy.[3–5] Herein, we wish to report on Wittig reactions of non-stabilized phosphonium ylides **1** bearing a phosphaheteratriptycene skeleton containing Group 14 and 15 elements (Si, Ge, Sn, P, As, Bi) at another bridgehead position with benzaldehyde (PhCHO) in order to clarify the effect of elements involved in the tridentate ligands on the phosphorus atom of the ylides.

Wittig reactions of non-stabilized phosphonium ylides **1** bearing a phosphaheteratriptycene skeleton, which were generated by the deprotonation of the corresponding ethylphosphonium iodides with TMS_2NNa, with PhCHO were conducted at −90 °C in THF and the reaction mixtures were allowed to warm to 25 °C for over 3 hours (Scheme 1). Wittig reactions provided (*Z*)-olefins as major product in the cases of period 3 elements (Ph*Si*, P in entries 1 and 5 of Table 1) and (*E*)-olefins as a major product in the cases of below period 4 elements (Ph*Ge*, Ph*Sn*, *n*-Bu*Sn*, As, Sb, and Bi in entries 2–4 and 6–8 of Table 1). The selectivity of the olefin formation under the reaction condition was attributed to the heteroatom effect at another bridgehead position of a phosphaheteratriptycene skeleton on stereochemical drift by the isomerization from *cis*-1,2-oxaphosphetanes **2a** to *trans*-forms **2b** in Scheme 1.

The isomerization of 1,2-oxaphosphetanes bearing a phosphaheteratriptycene skeleton containing Group 15 elements was observed at 0 °C for P, −20 °C for As, −40 °C for Sb,[3,4] and −60 °C for Bi by VT-$^{31}P\{^1H\}$ NMR spectroscopy, the temperature of which became lower as a raw number increases (Table 1, entries 1–4). It was comparable with the

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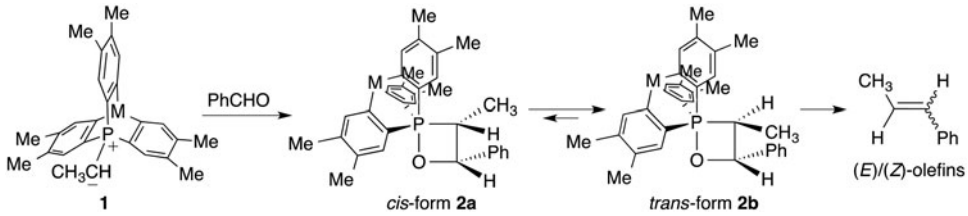

Scheme 1. Wittig reactions of non-stabilized phosphonium ylides **1** bearing a phosphaheteratriptycene skeleton (M = P, As, Sb, Ph*Si*, Ph*Ge*, Ph*Sn*, *n*-Bu*Sn*) with PhCHO.

Table 1. Yields and (*E*)/(*Z*) ratios of olefins produced in the Wittig reaction.

Entry	M	Electronegativity[6]	Isomerization temperature (°C)[a]	Yield (%)	(*E*)/(*Z*) ratio
1	P	2.19	0	15	49/51
2	As	2.18	−20	32	65/35
3	Sb[3,4]	2.05	−40	87	87/13
4	Bi	2.02	−60	43	74/26
5	Ph*Si*	1.90	−20	39	38/62
6	Ph*Ge*	2.01	−50	72	83/17
7	Ph*Sn*	1.96	−50	34	79/21
8	*n*-Bu*Sn*	1.96	−60	45	74/26

[a]Observed by VT-$^{31}P\{^1H\}$ NMR spectroscopy.

tendency of electronegativity[6], affecting M–C polarization of a phosphaheteratriptycene skeleton. On the other hand, Group 14 elements substituted by the phenyl group at another bridgehead position did not show the similar electric effect based on the electronegativity[6], judging from the isomerization, which was observed at −20 °C for Ph*Si*, −50 °C for Ph*Ge*, and −50 °C for Ph*Sn* (Table 1, entries 5–7). For the Wittig reaction bearing a phosphastannatriptycene skeleton, the substituent effect of phenyl and *n*-butyl groups (−50 °C for Ph*Sn* and −60 °C for *n*-Bu*Sn* (Table 1, entries 7,8)) on the isomerization temperature was observed and an equilibrium between *cis*-1,2-oxaphosphetane and an unidentified species was detected by VT-$^{31}P\{^1H\}$ NMR spectroscopy. The investigation is in progress.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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