The Phospha-Bora-Wittig Reaction

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ABSTRACT: Here, we report the phospha-bora-Wittig reaction for the direct preparation of phosphaalkenes from aldehydes, ketones, esters, or amides. The transient phosphaborene Mes*P=B-NR_2 reacts with carbonyl compounds to form 1,2,3-phosphaboraoxetanes, analogues of oxaphosphetane intermediates in the classical Wittig reaction. 1,2,3-phosphaboraoxetanes undergo thermal or Lewis acid/base-promoted cycloreversion, yielding phosphaalkenes. Experimental and density functional theory studies reveal far-reaching similarities between classical and phospha-bora-Wittig reactions.

Phosphaalkenes are closely related to alkenes.[1] The similar electronegativity of carbon and phosphorus makes C=P π bonds structurally and chemically similar to alkenes, albeit with narrower HOMO-LUMO gaps as a result of the weaker 2p-3p π bond.[1] Because the replacement of C=C with C=P units alters frontier orbital energies without significantly polarizing the π-system, phosphaalkenes are attractive 'building blocks' for main-group π-conjugated molecules and materials.[2] Their advance from laboratory curiosity to chemical workhorse has also seen phosphaalkenes used as ligands for transition-metal catalyzed transformations,[3,4] and incorporated into inorganic polymers.[5,6]

The first preparations of phosphaalkenes exploited 1,3-silyl migration[7] or elimination chemistry,[8–10] necessitating preformed P–C σ bonds.[11] Synthetically, it is more convenient to install "RP=" functionality in one step at a late stage. The direct synthesis of phosphaalkenes from carbonyl compounds, akin to the Wittig reaction, is therefore particularly attractive due to the availability and synthetic access to suitable carbonyl precursors. The first phospha-Wittig reagent, reported by Mathey in 1988,[12,13] enables just such a conversion (**I**, Figure 1a).

Several 'phospha-Wittig'[2,14] reagents are now available. These compounds can be viewed as phosphinidenes coordinated by a Lewis base and/or to a Lewis acid. Organometallic terminal phosphinidene complexes (e.g. Cp_2Zr=PMes*(PMe_3), **II**) can be used to prepare phosphaalkenes from aldehydes or ketones.[15,16] Phosphoranylidenephosphines (ArP=PMe_3 ↔ ArP^--P^+Me_3)[17,18] (**III**) perhaps bear the closest resemblance to classical Wittig reagents (R_2C=PPh_3 ↔ R_2C^-–P^+Ph_3), given the closely-related resonance forms, and the common phosphine-oxide by-product.

Despite the similarities between the Wittig and 'phospha-Wittig' reaction, the latter is less well-developed and understood. Few mechanistic studies have been made.[19,20] Furthermore, the reported 'phospha-Wittig' reagents can be unstable or challenging to prepare. Phosphinidene transfer reactions are generally limited to aldehydes or activated carbonyl compounds. A widely-applicable method of preparing phosphaalkenes directly from a range of carbonyl compounds remains desirable.

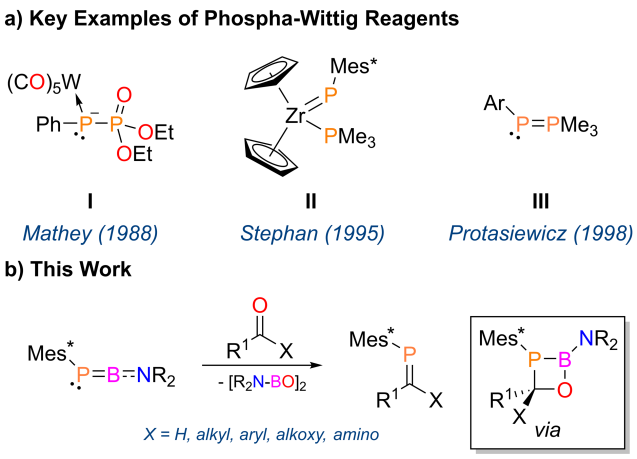

Figure 1. a) Selected phospha-Wittig reagents; b) the phospha-bora-Wittig reaction reported here.

We have recently demonstrated that transient phosphaborenes [Mes*P=BNR_2] (Mes* = 2,4,6-tri-*tert*-butylphenyl; NR_2 = 2,2,6,6-tetramethylpiperidine) can be accessed in solution and subsequently trapped by unsaturated compounds including phenylacetylene to give the corresponding formal [2+2] cycloaddition product.[21] In 1986, Nöth reported that transient methyleneboranes [R_2C=BNR'$_2$] undergo a Wittig-type reaction with ketones to give the corresponding alkene.[22] Considering the isoelectronic relationship between CR_2 and PR, and the reported reactivity of phosphinoboranes $R_2PBR'_2$ with C=O bonds,[23–25] we suspected that that phosphaborenes might be used to prepare phosphaalkenes.

Here, we report the development of the 'phospha-bora-Wittig' reaction (Figure 1b). Using the stabilizing Mes* substituent at P, we demonstrate the synthesis of known and novel phosphaalkenes directly from a wide range of carbonyl compounds including ketones, aldehydes, esters and amides. We show that the reaction proceeds by a stepwise cycloaddition/cycloreversion mechanism, analogous to that considered operative in the classical Wittig reaction.[26]

We initially investigated the reaction of diphosphadiboretane **1** with benzophenone. Heating **1** with two equivalents of benzophenone in C_6D_6 at 80 °C resulted in consumption of all

starting materials and the emergence of new resonances at δ 15.4 and 38.6 in the ^{31}P and ^{11}B NMR spectra respectively. X-ray diffraction experiments on crystalline product confirmed the identity of the formal [2+2] cycloaddition product as **2a** (Figure 2). **2a** is analogous to the oxazaboretidines obtained from the reaction of iminoboranes with ketones and aldehydes.[27] No evidence of the [4+2] cycloaddition product of **1** and benzophenone was observed, in contrast to the behavior of diazodiboretanes ([RBNR]$_2$).[28]

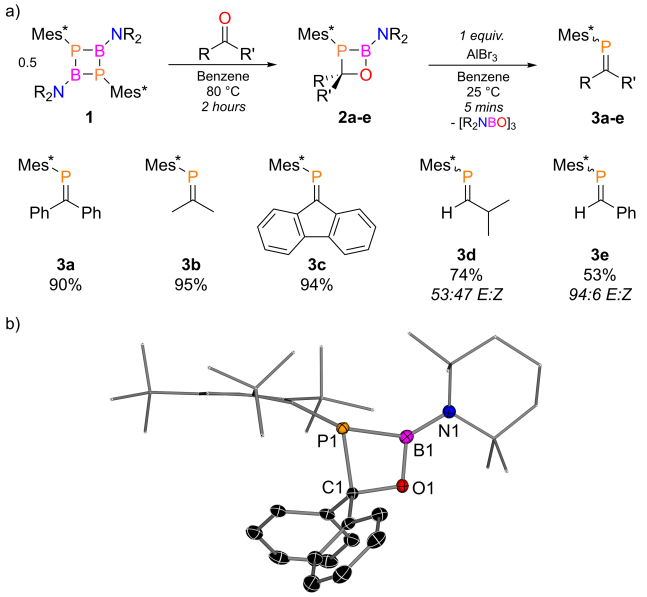

Figure 2. a) Preparation of 1,2,3-phosphaboraoxetanes **2a-e** and their subsequent conversion into phosphaalkenes **3a-e**. (Mes* = 2,4,6-tri-*tert*-butylphenyl; NR_2 = 2,2,6,6-tetramethylpiperidino). b) Structure of **2a**; thermal ellipsoids at 50% probability and hydrogen atoms omitted.

Diphosphadiboretane **1** also reacts cleanly with acetone, forming the dimethyl 1,2,3-phosphaboraoxetane, **2b**. In contrast (to P=B), N≡B bonds react with the enol tautomer of acetone by 1,2 addition.[29] 9-fluorenone, isobutyraldehyde, or benzaldehyde also react with **1**, forming **2c-2e**. Aldehyde-derived **2d**/**2e** have stereogenic P and C centers in their central PBCO ring. Only one of the expected two pairs of diastereomers of **2d**/**2e** was observed spectroscopically; either **2d** and **2e** are formed stereospecifically, or inversion at phosphorus is facile. **2a-e** were characterized by NMR spectroscopy and single-crystal X-ray diffraction (see SI).

1,2,3-phosphaboraoxetanes **2a-e** are reminiscent of the four-membered oxetane intermediates in the classical Wittig reaction.[26] We thus considered that their conversion into phosphaalkenes may be possible. Elimination of the O=BNR_2 fragment and its subsequent oligomerization would provide a thermodynamic incentive through B–O bond formation. The likelihood of such an elimination appears increased upon examination of the structures of **2a-e**. For example, the structure of **2a** (Figure 1b) reveals a planar, strained, central PBCO ring. The internal angles at C1 (92.07(8)º) and B1 (94.10(9)º) are particularly narrow. The NR_2 substituent at B1 is oriented to allow B=N π-bonding, leading to the short B1–N1 distance (1.410(2) Å).

We did not observe thermal elimination of phosphaalkenes from the 1,2,3-phosphaboraoxetanes **2a-e**, even at elevated temperatures. However, addition of $AlBr_3$ (1 equivalent) immediately converted **2a-e** into their corresponding phosphaalkenes **3a-e**. The major initial boron-containing by-product resonates at δ 20.0 in the ^{11}B NMR spectrum. Subsequent addition of pyridine (to sequester $AlBr_3$) led to the replacement of this signal with one at δ 22.3, which we assign to $[R_2NBO]_3$.[22] Al(III) halides promote the intramolecular decomposition of Mes*-substituted phosphaalkenes.[30] We did not observe such reactivity except with super-stoichiometric (to **2a-e**) quantities of $AlBr_3$. A preference for $AlBr_3$ complexation of $[R_2NBO]_3$ (consistent with the ^{11}B NMR signal at δ 20.0) over coordination to phosphaalkenes is thus likely. Conversion of **2a-e** to phosphaalkenes could also be achieved with sub-stoichiometric quantities of $AlBr_3$, or *N*-heterocyclic carbene (see SI).

Phosphaalkenes **3a-e** are conveniently prepared in one pot from **1** and the corresponding ketone or aldehyde. After formation of the 1,2,3-phosphaboraoxetanes **2a-e** (80 °C, 2 hours), $AlBr_3$ addition affords known and novel phosphaalkenes **3a-e** in good purity and yield (Figure 2a, 53-95%). Fluorenylidene phosphaalkenes (e.g. **3c**) are promising components for organic materials based on their optoelectronic and redox properties.[31–35]

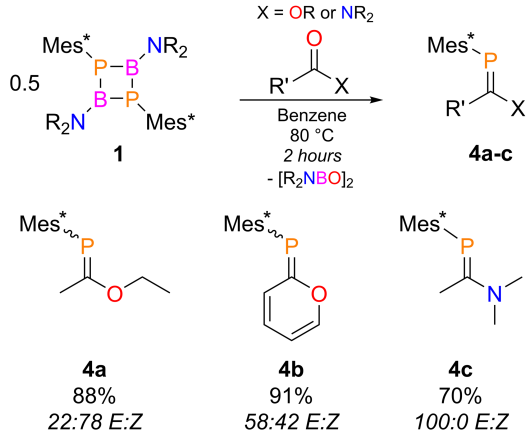

Figure 3. Synthesis of phosphaalkenes **4a-c** directly from esters and amides. (Mes* = 2,4,6-tri-*tert*-butylphenyl; NR_2 = 2,2,6,6-tetramethylpiperidino).

When diphosphadiboretane **1** was reacted with esters in place of ketones/aldehydes, direct conversion to the 2-alkoxy-phosphaalkene products occurred (Figure 3). For example, the reaction of **1** and ethyl acetate led to the new phosphaalkene **4a** as a mixture (22:78) of *E* and *Z* isomers, identified by signals in the ^{31}P{^{1}H} NMR spectrum at δ 120.1 and 104.4. ^{11}B NMR spectroscopy revealed the formation of $[R_2NBO]_2$,[36] indicated by a resonance at δ 28.1, which we confirmed crystallographically. Monitoring the reaction of **1** and ethyl acetate by NMR spectroscopy revealed that it proceeds through a transient 1,2,3- phosphaboraoxetane intermediate: signals at δ –115.7 (^{31}P{^{1}H}) and δ 39.0 (^{11}B) are consistent with those for **2a-e** (Figure S1). We extended the reaction of esters with **1** to α-pyrone to afford the exocyclic phosphaalkene **4b** as a mixture (58:42) of *E* and *Z* isomers. We also prepared the known 2-aminophosphalkene **4c**[37] from **1** and *N,N*-dimethylacetamide. Phosphaalkenes **4a-c** were easily isolated in high purity and yield (70-91%).

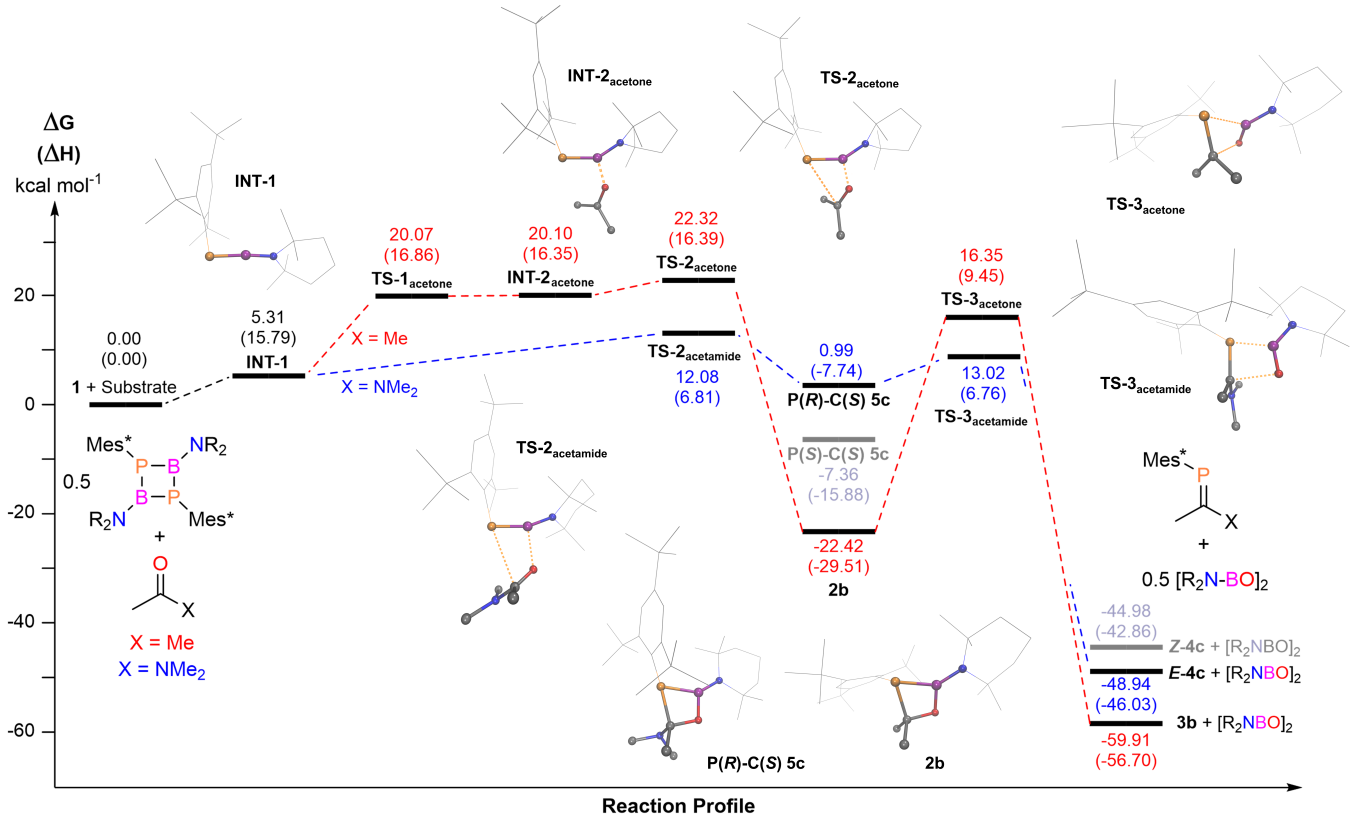

Figure 4. Computed reaction profiles for the reactions of **1** with acetone and acetamide (M06-2X/def2svp), ΔG^{298} (ΔH) in kcal mol^{-1}.

We used density functional theory calculations (M06-2X/def2svp)[38] to probe the mechanism of the reaction of **1** with carbonyl compounds. The first step in the reaction pathway (Figure 4) is the dissociation of **1** into the monomeric phosphaborene **INT-1**.[21] Phosphaborenes have orthogonal P=B and B=N π systems and can exhibit both nucleophilic (at P) and electrophilic (at B) reactivity.[21] For the initial interaction with acetone, we thus considered i) formation of a betaine-like intermediate[26] by attack of P at the carbonyl carbon, and ii) interaction of the carbonyl oxygen atom with boron. We could not locate a betaine-type structures as minima. Instead, phosphaborene **INT-1** and acetone react via **TS1$_{acetone}$** (+20.07 kcal mol^{-1}) to form acetone adduct **INT-2$_{acetone}$**, (+20.10 kcal mol^{-1}).

Coordination of acetone to boron in **INT-2$_{acetone}$** increases electrophilicity at the carbonyl carbon (C–O distance: 1.24 Å vs acetone, 1.20 Å). As a result, intramolecular attack of the phosphorus center at the carbonyl carbon occurs via the very early transition state **TS-2$_{acetone}$** (+22.32 kcal mol^{-1}), closing the 4-membered ring. The resulting isolable phosphaoxaboretane **2b** is substantially stable relative to its precursors (–22.42 kcal mol^{-1}).

Phosphaborene **INT-1** and acetamide follow an alternative pathway. Attempts to optimize acetamide counterparts of adduct **INT-2$_{acetone}$** minimized only to **INT-1** and acetamide. **INT-1** and acetamide instead react by cycloaddition through **TS-2$_{acetamide}$** (+12.08 kcal mol^{-1}) to form the phosphaoxaboretane P(*R*)-C(*S*)-**5c** (–7.36 kcal mol^{-1}). The amino-phosphaboraoxetane **5c** can exist as two pairs of diastereomers due to stereogenic P and C centers in the 4-membered ring. P(*R*)-C(*S*)-**5c** is less stable than its diastereomer P(*S*)-C(*S*)-**5c** relative to 0.5 **1** + acetamide (+0.99 vs –7.36 vs kcal mol^{-1}. We could not locate transition states leading to P(*S*)-C(*S*)-**5c** from **INT-1** + acetamide; inspection of **TS-2$_{acetamide}$** reveals that inversion of either P or C centers would generate an unfavorable 1,2 steric interaction between Mes* and NMe$_2$ groups. Experimental insight into the stereochemistry of the intermediates **5c** is limited by the ready interconversion of *E* and *Z*-phosphaalkenes.[39,40]

Close inspection of the geometry of **TS-2$_{acetone}$** and **TS-2$_{acetamide}$** reveals that they adopt markedly different structures (Table S8). **TS-2$_{acetone}$** is highly puckered (P–B–O–C torsion = 48.8º) with a much more fully formed B–O than P–C bond (B–O distance 1.561 vs **2a** 1.386 Å [–13%]; P–C 3.015 vs 1.921 Å [–57%]). In contrast, in **TS-2$_{acetamide}$** the developing P–C and B–O bonds form synchronously (B–O: 2.055 vs 1.393 Å [–48 %]; P–C: 2.947 vs 1.974 Å [–49%]). The developing PBCO ring is much flatter (P–B–O–C torsion = –24.2º).

Why is **TS-2$_{acetamide}$** substantially lower in energy than **TS-2$_{acetone}$**? We ascribe this to two factors: i) the synchronous formation of P–C and B–O bonds in **TS-2$_{acetamide}$** proceeds with a lesser decrease in B-N π-bonding as the P=B=N angle is distorted from away from linear in **TS-2** (160º vs 129º); ii) The more planar P–B–C–O ring in **TS-2$_{acetamide}$** enables the formation of C–H···O hydrogen bonds between the amide oxygen and the methyl groups of the tetramethylpiperidine substituent at boron. The C–H···O distances, angles, and C=O···H angles in **TS-2$_{acetamide}$** (2.2–2.3 Å, 125-130º, and 135–145º, Table S10) are ideal for interactions of this kind, whereas those in the puckered **TS-2$_{acetone}$** are not (Table S9).[41] Such interactions can amount to as much as 4 kcal mol^{-1} with optimum geometry.[42]

The second barrier, for the cycloreversion of phosphaboraoxetanes **2b**/**5c** to phosphaalkenes and transient [R$_2$NBO] is much higher for **2b** than it is for **5c** (+38.77 vs +13.02 kcal mol^{-1}). The high energy of **TS-3$_{acetone}$** (+16.35 kcal mol^{-1}) is consistent

with the observed thermal stability of **2b,** which requires the addition of $AlBr_3$ to promote cycloreversion.

Examination of the structures of **TS-3** reveal their asynchronous character: in both cases, compared to precursors **2a**/**5c**, substantial C–O bond elongation (+51%, +55%) is observed with only minimal P–B elongation (+14, +4 %, Table S11). This behavior strongly suggests that the lower energy of **TS-3$_{acetamide}$** vs **TS-3$_{acetone}$** can be attributed in part to stabilization of the developing positive charge at the carbon center by its NMe_2 substituent. Alkoxy substituents can be expected to fulfil the same π-donor role, which explains the differing fates in reactions of **1** with amides/esters and ketones/aldehydes. Similarly, we propose that $AlBr_3$ coordination to **2a-e** lowers the energy of **TS-3$_{acetone}$** by polarizing the C–O (and thus the forming C–P) bonds.

Our studies reveal deep and far-reaching mechanistic similarities between the reactions of **1** and carbonyl compounds and the Wittig reaction. We thus propose the term 'phospha-bora-Wittig' to describe phosphaalkene-forming reactions of phosphaborenes with carbonyl compounds. In the Wittig reaction, the nature of transition states for cycloaddition between ylide (Ph_3P=CHR) and carbonyl compound are subtly influenced by factors including 1,2 and 1,3 steric interactions, dipole/dipole interactions, and C=O···H hydrogen bonds.[26,43] 1,2 interactions play a role in the formation of **5c**, though the importance of 1,3 interactions is negated by the two-coordinate nature of the P/B centers. CH hydrogen bonding in **TS-3** is also observed. We also note the similarity to borata-Wittig reactions of borata-alkenes, $[R_2C{=}BR_2]^-$, with carbonyl compounds.[22,44–48]

The classical Wittig reaction is limited in scope for esters/amides, generally requiring careful substrate modification to counteract the effect of the OR and NR_2 substituents.[49] This limitation is absent in the reactions of **1** with esters or amides. We ascribe this to the greater electrophilicity of the boron in $RP{=}B{=}NR_2$ compared to the phosphorus center in phosphorus ylides, $R_3P{=}CR_2$. On this basis, and considering the close relationship between CR_2 and :PR, we wish to propose here that reagents of the type $R_2C{=}BNR_2$[22] may prove practical and general bora-Wittig reagents for the formation of alkenes from simple amides and esters.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

Synthetic procedures, NMR spectra, and computational details (PDF)

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Author Contributions

AMB conceived the study and co-wrote the manuscript. AMB and EFR carried out experimental work. GSN performed crystallography. MJC designed and coordinated the research programme, performed DFT studies, and co-wrote the manuscript. All authors have given approval to the final version of the manuscript.

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(50) Deposition Numbers 1913519 (for $[R_2NBO]_2$), 2088200 (**2a**), 2088201 (**2b**), 2088202 (**2c**), 2088203 (**2d**) and 2088204 (**2e**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe: Access structures service www.ccdc.cam.ac.uk/structures.