



## The phosphorus-Claisen condensation

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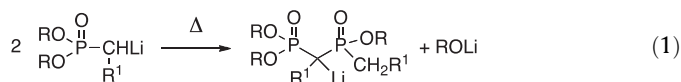
### ABSTRACT

1,1-Bisphosphorus compounds are easily synthesized through the phosphorus-Claisen (phospha-Claisen) condensation between a phosphorus-stabilized anion and a phosphorus electrophile. The preliminary scope of this reaction is investigated in terms of employable phosphorus reagents. Valuable intermediates are conveniently prepared in a single step. Overall, the method is competitive with multistep procedures which require the preparation of PCI intermediates derived from the P(OR) reagents we instead employ directly, and it delivers complex organophosphorus compounds in moderate to good isolated yields. An example of the intramolecular version of the reaction, the phospha-Dieckmann condensation, is also reported.

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Because of our laboratory's continued efforts in the preparation of 1,1-bisphosphorus compounds,<sup>1</sup> we became interested in investigating the condensation between a phosphonate-stabilized anion and a phosphonate electrophile, a process analogous to the Claisen ester condensation. Because phosphorus compounds provide much more structural variety than their carboxylic ester counterparts, we decided to explore this reaction, and its generalized version: the phosphorus-Claisen condensation (heretofore referred to as 'phospha-Claisen').

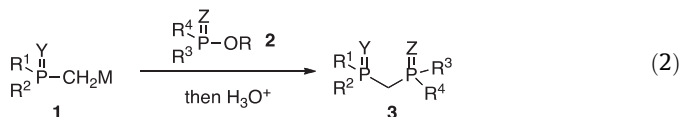
Examination of the literature revealed surprisingly few examples of this reaction, always limited to the self-condensation of a phosphonate diester anion. In pioneering research nearly thirty years ago, Savignac and co-workers studied the thermal stability of various phosphonate diester  $\alpha$ -anions  $(RO)_2P(O)CHLiR^1$  and reported on their generally undesirable self-condensation (Eq. 1).<sup>2</sup> As in the classic Claisen condensation, the driving force is the formation of a stabilized anion with lower basicity. Further, realizing the potential of this type of intermediate, Savignac and co-workers also described some synthetic application through the Wadsworth-Horner-Emmons (WHE) olefination.<sup>2</sup>



However, very little work has appeared concerning the use of the autocondensation products, except in the simplest case  $(RO)_2P(O)CH_2P(O)(OR)CH_3$ . For example, McClard<sup>3</sup> reported the alkylation of  $(RO)_2P(O)CHMP(O)(OR)CH_3$ , and the corresponding

dianion  $(RO)_2P(O)CHMP(O)(OR)CH_2M$ .<sup>4</sup> On the other hand, the condensation between a phosphonate anion and a P-Cl electrophile has been used more commonly to prepare various 1,1-bisphosphorus compounds.<sup>1b-d,5</sup> Of course, this approach necessitates a reactive electrophile, which is either commercially/readily available  $R_2P(Y)Cl$  ( $Y = \text{lone pair, O, BH}_3$ , etc.), or requires prior synthesis of a chlorophosphonate  $R^1P(O)(OR)Cl$  from the corresponding phosphonate diester. Alternatively, another approach has been the Arbuzov or Michaelis-Becker reactions between  $P(O)CH_2X$  and  $P(OR)_3$ , or  $MOP(O)(OR)_2$ , respectively.<sup>1a,6</sup>

Thus, it occurred to us that the general phospha-Claisen condensation between a nucleophile **1** and an electrophile **2** would be a convenient and powerful tool for the synthesis of methylene-1,1-bisphosphorus compounds **3** (Eq. 2), with enormous versatility in terms of substitution pattern and functional groups. Preliminary studies of the feasibility of the reaction are presented below.



Because the condensation product is a stabilized anion and alcohol, nucleophile **1** either needs to be used in excess, or the base to generate it must be present in at least two molar equivalents (Eq. 1). Based on this requirement and on Savignac's autocondensation studies, the first nucleophile we selected was  $(i\text{-PrO})_2P(O)CH_2Li$  **1a**. This compound is generated easily from the deprotonation of the corresponding phosphonate with  $n\text{-BuLi}$  at low temperature.

Table 1 shows the results obtained for the condensation between **1a** and a range of phosphorus electrophiles **2**. Various

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