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# Facile Synthesis of 1-Alkynylphosphonates

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# Facile Synthesis of 1-Alkynylphosphonates

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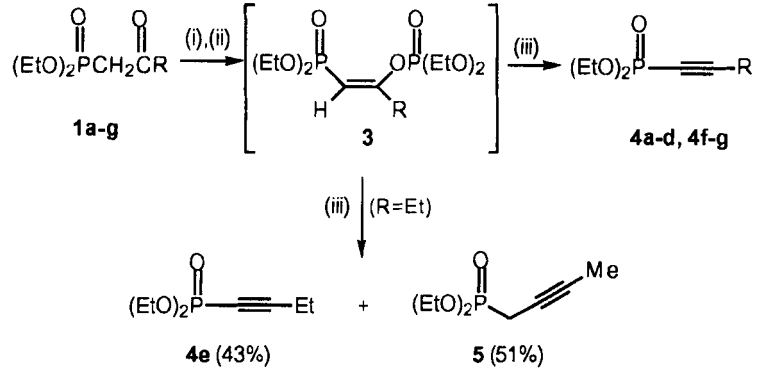
***Abstract*** *: 1-Alkynylphosphonates **4** are prepared by the in situ β-elimination of enol phosphates **3**, which are readily generated by the reaction of sodium enolate of 2-oxophosphonate with diethyl chlorophosphate.*

1-Alkynylphosphonates **4** have been used to synthesize a wide variety of unsaturated and saturated functional derivatives of organophosphorus compounds.[1] A literature survey on the preparation of 1-alkynylphosphonates **4** showed that some of the methods reported involve the preparation of explosive alkynyl bromides,[2] while other methods are either limited scope or give low overall yields.[3] Most widely used method of them involves the reaction of alkynylmagnesium

bromide with diethyl chlorophosphate.[4] Recently, we reported preparation of 2-arylethenephosphonates by β-elimination of phosphates.[5] As an extension of this work, we investigated that this reaction could be applied to synthesis of 1-alkynylphosphonates **4a-h** using 2-oxophosphonates **1a-h** which could be readily prepared by commonly used methods.[6](**Scheme**)

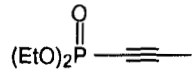
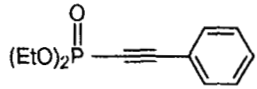
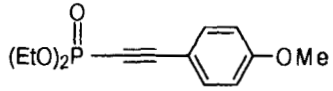
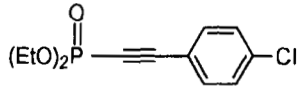
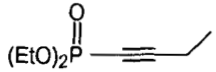
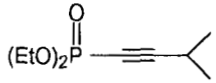
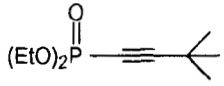
**Scheme**




*Reagents* : (i) NaH, THF, r.t. (ii) $(EtO)_2P(O)Cl$ **2**, r.t. (iii) t-BuOK, -78°C

Reaction of 2-oxophosphonates **1** (1mmol) with NaH(1.1mmol) in dry THF followed by addition of diethyl chlorophosphates **2** (1.1mmol) gave the enol phosphates **3**. To prepare 1-alkynyl phosphonates **4** in one pot reaction, we carried out the β-elimination reaction of enol phosphates **3** by *t*-BuOK(1.5mmol) at -78 °C, without isolation of **3**. Reaction mixtures should be quenched at -78 °C and worked up. The reaction proceeded satisfactorily with 2-oxophosphonates **1a-d** containing a methyl and an aryl substituents. The conversion of 2-

**Table.** Preparation of 1-Alkynylphosphonates **4a-g**

| Entry | product | yield[a], % |
|---|---|---|
| 1 | **4a**  | 90% |
| 2 | **4b**  | 91% |
| 3 | **4c**  | 88% |
| 4 | **4d**  | 95% |
| 5 | **4e**  | 43% |
| 6 | **4f**  | 72% |
| 7 | **4g**  | 77% |

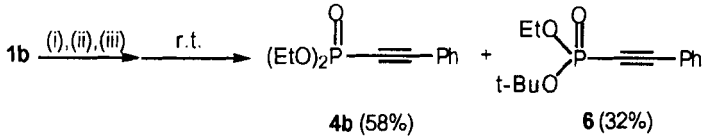
[a] Isolated yield

oxophosphonates **1e-g** with a moderately sized alkyl group to acetylenic phosphonates **4e-g** was also successful to some extent (**Table**).

In case of **1e** (R=Et), the reaction underwent prototrophic isomerization[7] to give a mixture of **4e**(43%) and propagylic phosphonate **5** (51%).

In our experiments, though enol phosphate was not isolated, only one isomer of enol phosphate was detected by TLC. We could presume that this isomer was (Z)-enol phosphate as the consequence of an internally chelated enolate.[8]

Interestingly, when the reaction temperature of step (iii) was allowed to room temperature after elimination at -78°C, the unexpected subsequent transesterification of **4b** was observed. Hence *t*-butylethyl alkynylphosphonate **6** was obtained as side-product along with the expected diethyl alkynylphosphonate **4b** due to the subsequent transesterification by excess *t*-BuOK. However, in cases of alkynylphosphonates with aliphatic substituents (**4a**, **4e-g**), we could obtain none of the transesterified products but the complicated mixtures. This unexpected transesterification and its application to organic synthesis are under study.




In summary, the present method is facile and proceeds in one pot, avoiding the necessity of isolation of the intermediate phosphate derivatives, and the starting materials are easily available.

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