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A FACILE PREPARATION OF 2-ARYLETHENEPHOSPHONATES

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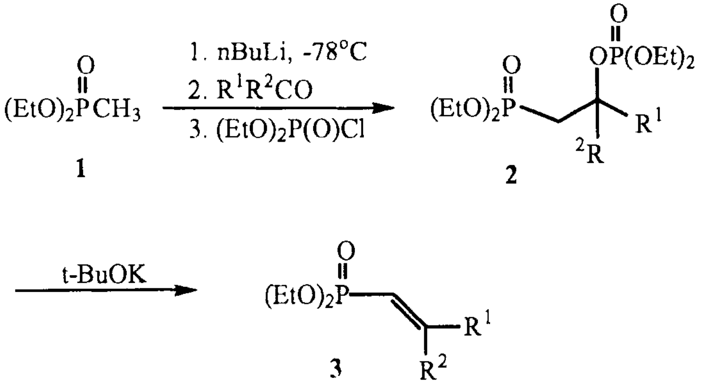
Abstract : *Vinylphosphonates 3 could be prepared with E-selectivity by the condensation of diethyl methylphosphonate 1 with a series of carbonyl compounds using diethyl chlorophosphate.*

Vinylphophonates[1] have been utilized in a variety of ways, e.g., Diels-Alder reaction,[2] Michael additions,[3,4] hydroboration/oxidation,[5] reduction,[6,7] and ene reaction[8]. And vinylphosphonats are versatile intermediates for the synthesis of some hetero- and carbocyclic compounds.[9-12] For the preparation of the 1-alkenephosphonates, only a few reports are found in the literature.[13-15] Especially for the preparation of 2-arylethenephosphonates, only few synthetic methods are known. One of these methods is the nickel - catalyzed Arbuzov reaction.[14]

But this method requires transition - metal salt and a high temperature. And palladium - catalyzed phosphonylation[16] requires α-haloolefins as starting material and some of these are not easily available. Koizumi *et al.*[17] reported a synthetic method for 2-arylethenephosphonates, but it apparently suffers the limitation that functional groups which are vulnerable to the organolithium reagent may not be present.

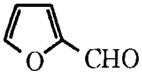
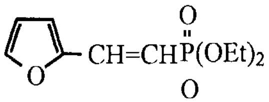
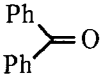
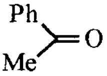
In the preceding paper, we reported synthesis of acetylenic sulfones via enol phosphate.[18] As an extention of this work, we investigated that this reaction could be applied to stereoselective synthesis of vinylphosphonates (**Scheme**).



Scheme

Reaction of α-lithio methylphosphonate with carbonyl compounds in THF followed by addition of diethyl chlorophosphate gave the phosphate derivatives **2**. The phosphates **2** were converted into the elimination product, vinylphosphonates **3**, by treatment with t-BuOK in THF. The procedure is simple with moderate overall yield (**Table**).[19]

Table. Synthesis of Vinylphosphonates

Entry	R^1R^2CO	Product[a,b]	Yield(%)[c]
3a	PhCHO	$\mathrm{PhCH{=}CH\overset{\overset{O}{\|}}{P}(OEt)_2}$	83%
3b	$\mathrm{m\text{-}NO_2C_6H_4CHO}$	$\mathrm{m\text{-}NO_2C_6H_4CH{=}CH\overset{\overset{O}{\|}}{P}(OEt)_2}$	80%
3c	$\mathrm{p\text{-}ClC_6H_4CHO}$	$\mathrm{p\text{-}ClC_6H_4CH{=}CH\overset{\overset{O}{\|}}{P}(OEt)_2}$	86%
3d	$\mathrm{p\text{-}CH_3OC_6H_4CHO}$	$\mathrm{p\text{-}CH_3OC_6H_4CH{=}CH\overset{\overset{O}{\|}}{P}(OEt)_2}$	87%
3e			80%
3f		$\mathrm{(Ph)_2C{=}CH\overset{\overset{O}{\|}}{P}(OEt)_2}$	81%
3g		$\mathrm{Ph(Me)C{=}CH\overset{\overset{O}{\|}}{P}(OEt)_2}$	79%

[a] All the compounds were fully characterized (^{1}H-NMR, ^{13}C-NMR and MS). Only one stereoisomer of each **3a-e** was obtained, and they are represented as having E configuration as J_{HH} across the double bond is ca. 16Hz. The E configuration is expected from analogous chemistry. [b] **3 g** has the E configuration deduced from NOE technique. [c] Isolated yield.

In summary, the present method is facile and proceeds in one pot, avoiding the necessity of isolation of the intermediate phosphate derivatives **2**, and the starting material are easily available.

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19. **Typical Procedure** : To a stirred solution of **1**(1mmol) in 5mL of dry THF was added *n*-BuLi (1.1mmol, 1.6M in hexane) at -78°C under nitrogen atmosphere. After being stirred for 1h at -78°C, diethyl chlorophosphate (1.1mmol) was added and allowed to stand at room temperature for 3h. Then

the mixture was cooled to -78°C. A solution of *t* -BuOK(1.2mmol) in 5mL THF was added to the reaction mixture followed by stirring for 10min. Normal work-up was performed. The desired vinylphosphonate was isolated by column chromatography on silica gel using 1:1 hexane/EtOAc as eluent.

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