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A New Synthesis of Vinyl Phosphonates from α-Phenyl β-Oxo Phosphonates and Dialkyl Phosphite

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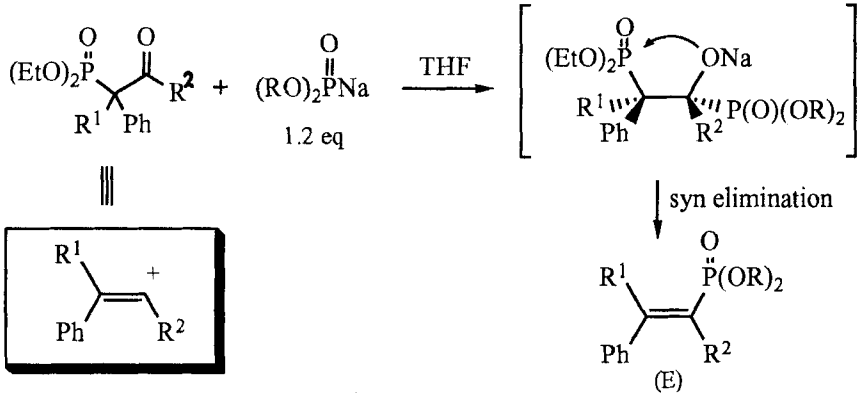
Abstract ; Reaction of 1-phenyl 2-oxo phosphonates with dialkyl phosphite sodium salt gave (E) vinyl phosphonates in good yield.

Recently, the synthesis and use of vinyl phosphonates has become important in organic synthesis, because of synthetic utilities[1] and fungicidal and fungistatic activities.[2] Therefore, the numerous synthetic routes to vinyl phosphonates have been reported.[1] These methods can be divided in two groups; (a) olefin formation via elimination reaction or Wittig (Wadsworth-Emmons-Horner) procedure,[3] (b) the direct formation of vinylic carbon to phosphorus bonds.[4] Among a variety of synthetic methods of vinyl phosphonate, the use of dialkyl phosphite as nucleophile is limited

to the transition metal-catalyzed coupling reactions which require vinyl halides as starting material and some of these are not easily available.

In the preceding paper,[5] we reported the synthesis of β-keto phosphonates from aryl epoxy sulfones and diethyl phosphite, and unexpected formation of *trans*-styryl phosphonate in the case of the reaction of 2-phenyl-1-(phenylsulfonyl)-1,2-epoxyethane. Thus we supposed that initially formed 1-formyl benzyl phosphonate reacted with additional sodium diethyl phosphite. Here, we report the new synthesis of vinyl phosphonates from the reaction of dialkyl phosphite anion with various α-phenyl-β-oxo phosphonates which function as vinyl cation equivalent.(scheme 1)



Scheme 1

1-Formyl benzyl phosphonates could be synthesized from both the formylation of lithiated benzyl phosphonate with ethyl formate and Lewis acid catalyzed rearrangement of epoxy phosphonates.[6] Typical procedure is as follows: To a suspension of sodium hydride (80 % dispersion in mineral oil, 45 mg, 1.5 mmol) in 5 ml of THF, diethyl phosphite (0.15 ml, 1.2 mmol) was added dropwise at room temperature under nitrogen.

Table I. Synthesis of Vinyl Phosphonates from α-Phenyl β-Oxophosphonates

Entry	R	R^1	R^2	condition	Yield (%)[a]
1	Me	H	H	r.t. / 3 hr	90
2	Et	H	H	r.t. / 3 hr	94
3	i-Pr	H	H	r.t. / 3 hr	87
4	n-Bu	H	H	r.t. / 3 hr	85
5	Et	Me	H	r.t. / 3 hr	82
6	Et	Et	H	r.t. / 3 hr	87
7	Et	H	Me	reflux / 1 day	25
8	Et	H	Et	reflux / 1 day	20
9	Et	Me	Me	reflux / 1 day	52

[a]Isolated yield based on α-phenyl β-oxo phosphonates

After 10 min, diethyl 1-formyl benzyl phosphonate (256 mg, 1.0 mmol) in 5 ml of THF was added and stirred for 30 min at r. t. (entry 1). After quenching with aq. NH_4Cl and work up with methylene chloride, the combined organic layer was dried, evaporated and purified by column chromatography to give pure (E) diethyl 2-phenyl ethene phosphonate in 94 % yield.[7] It could be assumed that diethyl phosphite anion attacked on carbonyl carbon of formyl phosphonates to give unstable intermediate which perform *syn*-elimination of diethyl phosphoryl and sodium alkoxide due to the existence of α-electron stabilizing group, Ph, to afford thermodynamically stable (E) vinyl phosphonates without any (Z) isomer.

The reaction of α-formyl phosphonates shows good results in mild condition (entry 1-6), but α-acetyl phosphonates needed more drastic condition to give corresponding vinyl phosphonates with moderate yield (entry 7-9). So, 1-Phenyl 2-oxo phosphonates will be the useful synthetic equivalent of *trans* styryl cations in organic synthesis.

References and Notes

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7. Spectra of Diethyl 2-phenylethenephosphonate (Entry 1) ; ^{1}H NMR ($CDCl_3$) : d 1.30 (t, J=7.0 Hz, 6H), 4.07 (dq, 4H, J=7.0 Hz), 6.20 (t, 1H, J=17.6Hz), 7.31-7.52 (m, 6H); ^{13}C NMR : 16.4 (d, J=4 Hz), 61.8 (d, J=4 Hz), 114.0 (d, J=127 Hz), 127.6, 128.8, 130.0, 134.9 (d, J=5 Hz), 148.7 (d, J=4 Hz); IR : 161, 1240, 1163, 1020, 950.

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