

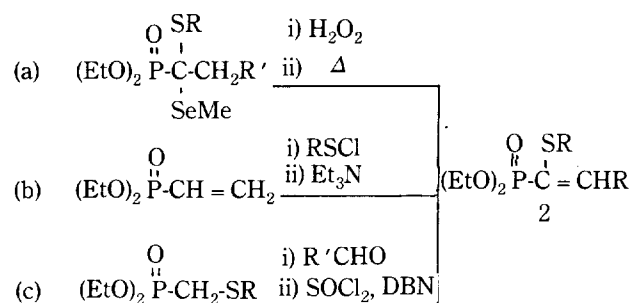
The Synthesis of Vinylphosphonates by Eliminative Deoxygenation of Sulfoxides

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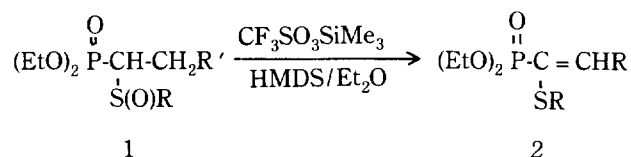
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Vinylphosphonates which are substituted with electron withdrawing group on the α -carbon atom have used synthetically as versatile reagents for the preparations of heterocyclic or carbocyclic rings by the Michael addition and subsequent intramolecular Wittig-Horner reaction.¹ α -Sulfur-substituted vinylphosphonates (2) have been prepared by the following methods; (a) addition of elemental selenium to phosphonate carbanions followed by alkylation and oxidative elimination of the organoselenium moiety,^{1a} (b) addition of methane sulfonyl chloride to diethyl vinylphosphonate and subsequent dehydrochlorination,^{1b} and (c) treatment of methylthio-methanephosphonate with aldehyde.^{1c}



trimethylsilyl triflate in ice bath. The reaction mixture was stirred at room temperature for about 2-3h., quenched by cold 2N H₂SO₄ and extracted with ether. The organic layer was washed with dilute sodium hydrogen carbonate, dried and evaporated. The crude product was chromatographed on silica gel. The structural assignment of 2a was made on the basis of authentic spectral data.^{1a}



Table

	R	R'	Yield (%)
2a	CH ₃	H	75
2b	CH ₃	CH ₃	75
2c	CH ₃	CH=CH ₂	85
2d	CH ₃	C ₆ H ₅	85
2e	C ₆ H ₅	H	75
2f	C ₆ H ₅	CH ₃	75
2g	4-CH ₃ C ₆ H ₄	H	70
2h	4-ClC ₆ H ₄	H	70

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We wish to describe the method of mild and general procedure to provide a new way to α -sulfur-substituted vinylphosphonates (2) from α -sulfinyl phosphonates (1) by the eliminative deoxygenation. Miller and coworker have recently reported the preparation of vinyl sulfides from sulfoxides using the silylating reagent in the presence of amine bases.² We also explored the use of trimethylsilyl triflate as the silylating reagent in the presence of weak base hexamethyl-disilazane to result in vinylphosphonates. Using this procedure, a variety of vinylphosphonates (2) were prepared in good yields as shown in Table. All of 2b, 2c, 2d, and 2f resulted in E/Z isomeric mixture. While this was clear from the vinyl region in the ¹H nmr spectra, E/Z ratio was not determined. α -Sulfinyl phosphonates (1) as starting agent were prepared by the oxidation of α -sulfenyl phosphonates with the acetone-water solution of sodium metaperiodate³.

The typical experimental procedure is as follows; To a stirred solution of the α -sulfinyl phosphonate (2 mmol) and the HMDS (5 mmol) in dry ether (10 ml) was added