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A Convenient Synthesis of β -Keto Phosphonates from Nitroalkenes

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β -Keto phosphonates are commonly employed as synthetic reagents for the synthesis of α,β -unsaturated carbonyl compounds by the Wadsworth-Horner-Emmons condensation.¹ Although a number of syntheses have been developed with

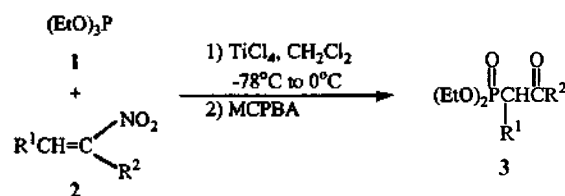
Table 1. Preparation of β -Keto Phosphonates 3

No.	R ¹	R ²	Isolated Yield (%) ^a
3a	C ₆ H ₅	Me	92
3b	C ₆ H ₅	Et	78
3c	<i>p</i> -OMe, C ₆ H ₄	Me	93
3d	<i>p</i> -OMe, C ₆ H ₄	Et	81
3e	<i>p</i> -Cl, C ₆ H ₄	Me	84
3f	<i>p</i> -Cl, C ₆ H ₄	Et	72
3g	H	C ₆ H ₅	85

^aBased on nitroalkenes.

the goal of providing a route to β -keto phosphonates, they have limitations in terms of the reaction conditions employed, competition from other reactions, and the preparation of starting materials. The commonly used methods for preparing β -keto phosphonates are the Arbuzov reaction² and the acylation of alkylphosphonate anions.³ Both methods suffer from individual restrictions and have a common limitation in their reliance upon nucleophilic phosphorus reagents. Syntheses involving acylation of 1-(trimethylsilyl)vinylphosphonate anions⁴ and hydrolysis of vinylogous phosphoramidates⁵ suffer from the limited availability of starting materials. Recently, Wiemer⁶ reported the preparation of β -keto phosphonates through C-P bond formation by the reaction of ketone enolates with dialkylphosphorochloridite, followed by aerial oxidation.

In the course of our studies on the addition to nitroalkenes, we recently reported a synthesis of 1-aryl-1-cyanomethylphosphonates,⁷ α -aryl ketones,⁸ and 1-aryl-2-oxoalkylphosphonates.⁹ We now report a facile synthesis of β -keto phosphonates 3 from readily available nitroalkenes. In the presence of titanium(IV) chloride, addition of triethyl phosphite 1 to nitroalkenes 2 affords α -phosphoryl nitronates^{7,9} which, on treatment with MCPBA, are smoothly converted into phosphonates 3.



Present procedure can guarantee excellent yields of β -keto phosphonates 3 which are summarized in Table 1. The identity of the phosphonates 3 was confirmed by IR, ¹H-NMR, and mass spectroscopy. In a previous paper,⁹ we have reported the preparation of 1-aryl-2-oxoalkylphosphonates from nitroalkenes and diethyl phosphite under basic condition. Compared with our previous approach,⁹ this procedure has some advantages in yields and reaction time.

The general experimental procedure is as follows: To a stirred solution of nitroalkene 2 (1 mmol) in methylene chloride (8 ml) was added dropwise TiCl₄ (0.11 ml, 1 mmol) at -78°C. After being stirred at -78°C for 10 min, triethyl phosphite 1 (0.19 ml, 1.1 mmol) was added dropwise and the reaction mixture was stirred at -78°C for 30 min. After being warmed to 0°C, MCPBA (0.414 g, 1.2 mmol, 50%

purity) in methylene chloride (5 ml) was added to the reaction mixture. The resulting solution was left for 1 h to reach room temperature. It was washed with 1 M Na₂SO₃, saturated aqueous NaHCO₃, and water and then dried (MgSO₄) and evaporated to leave a crude oil. This was purified by flash chromatography on silica gel (diethyl ether).

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