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A Convenient Synthesis of β-Keto Phosphonates from Nitroalkenes

Dae Young Kim*, Joo Yang Mang, Jae Wook Lee†,
and Dong Young Oh†

Department of Chemistry, Soonchunhyang University,
Onyang P.O.Box 97, Chungnam 336-600
†Department of Chemistry, Advanced Institute
of Science and Technology, Taejon 305-701

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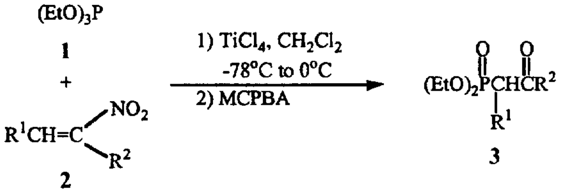
β-Keto phosphonates are commonly employed as synthetic reagents for the synthesis of α,β-unsaturated carbonyl compounds by the Wadsworth-Horner-Emmons condensation.[1] Although a number of syntheses have been developed with the goal of providing a route to β-keto phosphonates, they have limitations in terms of the reaction conditions empolyed, competition from other reactions, and the preparation of starting materials. The commonly used methods for preparing β-keto phosphonates are the Arbuzov reaction[2] and the acylation of alkylphosphonate anions.[3] Both methods suffer from individual restrictions and have a common limitation in their reliance upon nucleophilic phosphours reagents. Syntheses involving acylation of 1-(trimethylsilyl)vinylphosphonate anions[4] and hydrolysis of vinylogous phosphoramidates[5] suffer from the limited availability of starting materials. Recently, Wiemer[6] reported the preparation of β-keto phosphonates through C-P bond formation by the reaction of ketone enolates with dialkylphosphorochloridite, followed by aerial oxidation.

Table 1. Preparation of β-Keto Phosphonates **3**

No.	R^1	R^2	Isolated Yield (%)[a]
3a	C_6H_5	Me	92
3b	C_6H_5	Et	78
3c	*p*-OMe, C_6H_4	Me	93
3d	*p*-OMe, C_6H_4	Et	81
3e	*p*-Cl, C_6H_4	Me	84
3f	*p*-Cl, C_6H_4	Et	72
3g	H	C_6H_5	85

[a] Based on nitroalkenes.

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-arly-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, ^{1}H-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 m*l*) was added dropwise $TiCl_4$ (0.11 m*l*, 1 mmol) at −78℃. After being stirred at −78℃ for 10 min, triethyl phosphite **1** (0.19 m*l*, 1.1 mmol) was added dropwise and the reaction mixture was stirred at −78℃ for 30 min. After being warmed to 0℃, 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 Na_2SO_3, saturated aqueous $NaHCO_3$, and water and then dried ($MgSO_4$) and evaporated to leave a crude oil. This was purified by flash chromatography on silica gel (diethyl ether).

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