

## A New Synthesis of 1-Aryl-2-oxoalkylphosphonates from Nitroalkenes and Diethyl Phosphite

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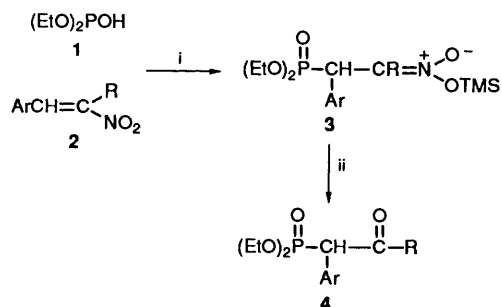
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Addition of diethyl phosphite to nitroalkenes affords  $\alpha$ -phosphoryl nitronates which, on treatment with *m*-chloroperbenzoic acid, are converted into 1-aryl-2-oxoalkylphosphonates.

$\beta$ -Keto phosphonates are useful intermediates for the synthesis of  $\alpha,\beta$ -unsaturated carbonyl compounds by the Wadsworth–Horner–Emmons condensation.<sup>1</sup> Although a number of syntheses have been developed with the goal of providing a route to this class of compounds, they have limitations in terms of the reaction conditions employed, competition from other reactions, and the preparation of starting materials. Commonly,  $\beta$ -keto phosphonates are prepared by the Arbuzov reaction of trialkyl phosphites and  $\alpha$ -halogeno ketones.<sup>2</sup> The latter method is restricted to highly reactive  $\alpha$ -halogeno ketones, because of the poor nucleophilicity of phosphites and competition from the Perkow reaction to give enol phosphates. The acylation of alkylphosphonate anions<sup>3</sup> suffers from the problem of low reactivities resulting from proton exchange between the  $\beta$ -keto phosphonates generated and 1-lithioalkylphosphonates, the  $\alpha$ -protons of the former being more acidic than those of the starting alkylphosphonates. Syntheses involving acylation of 1-(trimethylsilyl)vinylphosphonate anions<sup>4</sup> and hydrolysis of vinylogous phosphoramides<sup>5</sup> suffer from the limited availability of starting materials. Recently, Wiemer<sup>6</sup> reported the preparation of  $\beta$ -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 of nitroalkenes, we recently reported a synthesis of 1-aryl-1-cyanomethylphosphonates<sup>7</sup> and  $\alpha$ -aryl ketones.<sup>8</sup> Here, we report a new and facile synthesis of 1-aryl-2-oxoalkylphosphonates **4** from readily available nitroalkenes. In the presence of DBU and chlorotrimethylsilane addition of diethyl phosphite **1** to nitroalkenes **2** affords  $\alpha$ -phosphoryl nitronates **3**<sup>7</sup> which, on



Scheme 1 i, DBU, TMSCl, CH<sub>2</sub>Cl<sub>2</sub>; ii, MCPBA

treatment with *m*-chloroperbenzoic acid,<sup>9</sup> are smoothly converted into phosphonates **4**. By this procedure, 1-aryl-2-oxoalkylphosphonates **4** were prepared in good yields. The results are summarized in Table 1. The Nef reaction step was crucial for obtaining the desired carbonyl compounds. We found that treatment of an HCl solution instead of *m*-chloroperbenzoic acid to  $\alpha$ -phosphoryl nitronates **3** affords  $\beta$ -keto phosphonates **4** in poor yields. The identity of the

Table 1 Preparation of 1-aryl-2-oxoalkylphosphonates **4**

No.	Ar	R	Yield (%) <sup>a</sup>
<b>4a</b>	Ph	Me	85
<b>4b</b>	Ph	Et	87
<b>4c</b>	C <sub>6</sub> H <sub>4</sub> OMe- <i>p</i>	Me	81
<b>4d</b>	C <sub>6</sub> H <sub>4</sub> OMe- <i>p</i>	Et	84
<b>4e</b>	C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i>	Me	71
<b>4f</b>	C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i>	Et	65

<sup>a</sup> Isolated yield.

phosphonates **4** was confirmed by <sup>1</sup>H NMR and IR spectroscopy and elemental analysis. The advantages of this synthetic route are high yields of product and the ease of preparation of nitroalkenes as starting materials.

### Experimental

Methylene dichloride was refluxed over P<sub>2</sub>O<sub>5</sub> under nitrogen and distilled prior to use. The nitroalkenes **2** were prepared as reported previously.<sup>10</sup>

**General Experimental Procedure: 1-Aryl-2-oxoalkylphosphonates 4.**—To a stirred solution of diethyl phosphite **1** (0.166 g, 1.2 mmol) and the nitroalkene **2** (1.0 mmol) in methylene dichloride (5 cm<sup>3</sup>) was added dropwise DBU (0.198 g, 1.3 mmol) at 0 °C. After 20 min, chlorotrimethylsilane (0.19 cm<sup>3</sup>, 1.5 mmol) was added dropwise to the reaction mixture. The mixture was stirred at room temperature for 1 h after which a solution of MCPBA (0.259 g, 1.5 mmol) in methylene dichloride (5 cm<sup>3</sup>) was added dropwise to it at 0 °C. The resulting solution was left for 1 h to reach room temperature. It was then washed with aqueous Na<sub>2</sub>SO<sub>3</sub> (1 mol dm<sup>-3</sup>; 20 cm<sup>3</sup>), HCl (1 mol dm<sup>-3</sup>; 20 cm<sup>3</sup>), saturated aqueous NaHCO<sub>3</sub> (20 cm<sup>3</sup>) and water (20 cm<sup>3</sup>) and then dried (MgSO<sub>4</sub>) and evaporated to leave a crude oil. This was purified by flash chromatography on silica gel (ether). Compound **4a** *R*<sub>f</sub> 0.57;  $\nu_{\text{max}}$ /cm<sup>-1</sup> 3460 (enol OH), 2958, 2910, 1569, 1255 (P=O) and 1050–1022 (P–O);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>, 80 MHz) 0.92–1.50 (6 H, m), 2.44 (3 H, s), 3.8–4.6 (5 H, m) and 7.23–7.70 (5 H, m) (Found: C, 57.2; H, 7.2. C<sub>13</sub>H<sub>19</sub>O<sub>4</sub>P requires C, 57.8; H, 7.09%).

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