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A Convenient Synthesis of β -Keto Phosphonates from Diethylphosphonoacetic Acid

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β -Keto phosphonates are valuable intermediates for organic synthesis, especially for the preparation of α,β -unsaturated carbonyl compounds by the Horner-Wadsworth-Emmons condensation.¹ Commonly, β -keto phosphonates are prepared by the Arbuzov reaction and acylation of alkylphosphonate anions. The Arbuzov reaction of trialkyl phosphite and α -halogeno ketones leads to β -keto phosphonates. The latter method is restricted to highly reactive α -halogeno ketones or α -halogeno ketones containing a carbonyl protecting group, because of the nucleophilicity of phosphites and competition from the Perkow reaction to give enol phosphates.² The most commonly used method for preparing β -keto phosphonates is acylation of alkylphosphonate anions with carboxylic acid esters,³ carboxylic acid chlorides,⁴ *N*-methoxy-*N*-methylcarboxamides,⁵ or nitriles followed by hydrolysis.⁶ Recently, β -keto phosphonates were also obtained by either base-induced isomerization of enol phosphates or reaction of ketone enolates with dialkylphosphorochloridite followed by aerial oxidation.⁷ Other miscellaneous methods include acylation of 1-(trimethylsilyl)vinylphosphonates,⁸ hydrolysis of vinylogous phosphoramides,⁹ reaction of 2-(diethoxyphosphinyl)carboxylic acid chlorides with organometallic reagents,¹⁰ the use of (diethoxyphosphoryl)acetonitriles oxides,¹¹ *via* allene oxide,¹² nucleophilic addition of allenic phosphonate with diethylamine and subsequent hydrolysis,¹³ Pd(0)-catalyzed rearrangement of the 2,3-epoxyalkyl phosphonates,¹⁴ reaction of phosphite with epoxysulfones,¹⁵ chloroepoxide,¹⁶ or α -nitro epoxides,¹⁷ oxidation of β -hydroxyalkylphosphonates,¹⁸ reaction of silyl enol ethers with phosphite using hypervalent iodine compound,¹⁹ alkylation of β -keto phosphonates,²⁰ acylation of triethyl phosphonoacetate,²¹ and reaction of nitroalkenes with phosphite.²²

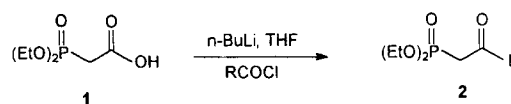
Herein we wish to report a convenient synthesis of β -keto phosphonates **2** from diethylphosphonoacetic acid **1**. Under anhydrous conditions diethylphosphonoacetic acid was treated with 2.2 equiv. of *n*-butyllithium in THF at -78°C . The resulting diethyl phosphonoacetate dianion underwent a facile reaction with carboxylic acid chlorides. On aqueous workup β -keto phosphonates **2** were isolated in good yields. Noteworthy was that both aromatic and aliphatic carboxylic acid chlorides were compatible with this

Table 1. Preparation of β -keto phosphonates **2** from diethylphosphonoacetic acid **1**

Entry	R	Product	Yield ^a
1	Ph	2a	88
2	<i>p</i> -C ₆ H ₄ CH ₃	2b	87
3	<i>p</i> -C ₆ H ₄ Cl	2c	81
4	<i>m</i> -C ₆ H ₄ Br	2d	78
5	<i>trans</i> -CH=CHPh	2e	90
6	C ₂ H ₅	2f	73
7	<i>n</i> -C ₅ H ₁₁	2g	78
8	cyclo-C ₆ H ₁₁	2h	74
9	CH(OAc)CH ₃	2i	65

^a Isolated yields are based on diethylphosphonoacetic acid.

methodology and both gave high yields.



The aromatic carboxylic acid chlorides containing electron rich and electron deficient substituents reacted with equal efficiency (entry 1-4). In the aliphatic carboxylic acid chlorides series, primary and secondary acid chlorides gave good yields (entry 5-9). Compared with general synthetic route for the preparation of β -keto phosphonates by the acylation of alkylphosphonate,³⁻⁶ the present procedure is inexpensive and convenient.

In conclusion, we have developed a new convenient procedure for the preparation of β -keto phosphonates based on the acylation of diethyl phosphonoacetate dianion with carboxylic acid chlorides in THF.

Experimental Section

All reactions were carried out under nitrogen atmosphere. ^1H and ^{13}C NMR were measured at 200 and 50 MHz, respectively, in CDCl₃ with TMS as internal standard. Mass spectra were recorded on HP 5985A or Jeol HX100/HX110.

Diethylphosphonoacetic acid²³ and all carboxylic acid chlorides were obtained from commercial suppliers and were used without further purification. THF was distilled from sodium benzophenone ketyl. Column chromatography was performed on Merck silica gel 60 (230-400 mesh).

The general experimental procedure. To stirred solution of diethyl phosphonoacetic acid (0.392 g, 2.0 mmol) in THF (5 mL) was added n-butyllithium (4.4 mmol) at -78 °C. After stirring 0.5 h carboxylic acid chloride (2.4 mmol) was added dropwise and the solution was allowed to warm at room temperature for 4 h. The reaction was quenched by adding saturated NH₄Cl solution and extracted with ethyl ether. The organic layer was dried over MgSO₄ and concentrated. The residual oil was purified by silica gel column chromatography using ethyl acetate as an eluent.

Diethyl 2-phenyl-2-oxoethylphosphonate (2a). IR (neat) 2980, 1675 (C=O), 1260 (P=O), 1060, 1025 (P-O), 970 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 1.28 (t, 6H, J=7.0 Hz), 3.65 (d, 2H, J=22.7), 4.07-4.22 (dq, 4H), 7.44-7.65 (m, 3H), 7.99-8.04 (m, 2H); ¹³C NMR (CDCl₃, 50 MHz) δ 16.21 (d, J=6.05), 38.51 (d, J=129.1), 62.63 (d, J=6.38), 128.58, 129.03, 133.61, 136.60, 191.93 (d, J=5.52); MS (m/z) 256 (M⁺, 0.7%), 151 (5.4), 105 (100); HRMS: calcd for C₁₂H₁₇O₄P 256.0864, found 256.0868.

Diethyl 2-(p-tolyl)-2-oxoethylphosphonate (2b). IR (neat) 2930, 1670 (C=O), 1260 (P=O), 1029, 970 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 1.28 (t, 6H, J=7.1 Hz), 2.42 (s, 3H), 3.61 (d, 2H, J=22.7), 4.06-4.21 (m, 4H), 7.24-7.30 (m, 2H), 7.80-7.94 (m, 2H); ¹³C NMR (CDCl₃, 50 MHz) δ 16.38, 21.86, 38.62 (d, J=129.0), 62.73, 129.41; MS (m/z) 270 (M⁺, 2.1%), 119 (100); HRMS: calcd for C₁₃H₁₉O₄P 270.1021, found 270.1033.

Diethyl 2-(p-chlorophenyl)-2-oxoethylphosphonate (2c). IR (neat) 2990, 1675 (C=O), 1255 (P=O), 1129, 970 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 1.29 (t, 6H, J=6.0 Hz), 3.61 (d, 2H, J=22.8), 4.06-4.22 (m, 4H), 7.40-7.48 (m, 2H), 7.90-7.99 (m, 2H); ¹³C NMR (CDCl₃, 50 MHz) δ 16.30 (d, J=5.75), 38.71 (d, J=128.6), 62.80 (d, J=6.15), 128.98, 130.58, 190.73; MS (m/z) 292 (M+2, 1.2%), 290 (M⁺, 0.7), 180 (7.1), 154 (19.5), 139 (100).

Diethyl 2-(m-bromophenyl)-2-oxoethylphosphonate (2d). IR (neat) 2990, 1679 (C=O), 1255 (P=O), 1025, 970 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 1.30 (t, 6H, J=7.0 Hz), 3.65 (d, 2H, J=22.8), 4.01-4.26 (m, 4H), 7.30-8.18 (m, 4H); ¹³C NMR (CDCl₃, 50 MHz) δ 16.00 (d, J=6.15), 38.37 (d, J=128.9), 62.63 (d, J=6.35), 127.47, 130.00, 131.72, 136.22, 190.38 (d, J=6.55); MS (m/z) 336 (M+2, 1.5), 334 (M⁺, 1.6%), 224 (6.5), 183 (100).

Diethyl (4-phenyl-2-oxobut-3-en-1-yl)phosphonate (2e). IR (neat) 3005, 2990, 1650 (C=O), 1255 (P=O), 970 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 1.34 (t, 6H, J=7.1 Hz), 3.33 (d, 2H, J=22.7), 4.09-4.25 (m, 4H), 6.90 (d, 1H, J=16.1), 7.30-7.70 (m, 6H); ¹³C NMR (CDCl₃, 50 MHz) δ 16.27, 41.08 (d, J=127.1), 62.57, 125.74, 128.59, 128.98, 130.88, 144.75.

Diethyl 2-oxobutylphosphonate (2f). IR (neat) 2990, 1710 (C=O), 1255 (P=O), 1036, 970 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 1.07 (t, 3H, J=7.23), 1.34 (t, 6H, J=7.0 Hz), 2.65 (q, 2H, J=7.3), 3.08 (d, 2H, J=22.8), 4.07-4.23 (m, 4H); ¹³C NMR (CDCl₃, 50 MHz) δ 7.54, 16.27, 37.35, 42.12 (d, 126.7), 62.50; MS (m/z) 208 (M⁺, 10.3%), 180

(11.5), 179 (100), 151 (52.5).

Diethyl 2-oxoheptylphosphonate (2g). IR (neat) 2990, 1710 (C=O), 1254 (P=O), 1035, 970 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 4.08-4.19 (dq, 4H), 3.09 (d, 2H, J=22.8), 2.63 (t, 2H, J=7.2), 1.62-1.23 (m, 12H), 0.89 (t, 3H, J=6.5); ¹³C NMR (CDCl₃, 50 MHz) δ 202.16 (d, J=5.8), 62.51, 43.98, 42.24 (d, J=122.1), 31.05, 23.04, 22.33, 16.28, 13.80; MS (m/z) 250 (M⁺, 1.4%), 221, 179 (100), 151; HRMS: calcd for C₁₁H₂₃O₄P 250.1334, found 250.1341.

Diethyl 2-cyclohexyl-2-oxoethylphosphonate (2h). IR (neat) 2990, 1715 (C=O), 1255 (P=O), 1030, 970 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 4.04-4.27 (dq, 4H), 3.12 (d, 2H, J=22.4), 2.52-2.70 (m, 1H), 1.60-1.98 (m, 8H); ¹³C NMR (CDCl₃, 50 MHz) δ 205.07 (d, J=5.8), 62.29, 51.19, 40.05 (d, J=128.1), 28.01, 25.54, 16.14; MS (m/z) 262 (M⁺, 0.5), 179, 151.

Diethyl 3-acetoxy-2-oxoheptylphosphonate (2i). IR (neat) 2990, 1720 (C=O), 1250 (P=O), 1025, 970 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 5.16 (q, 1H, J=7.1), 4.00-4.23 (m, 4H), 3.14 (dq, 2H, J=14.2, 27.4), 2.08 (s, 3H), 1.37 (d, 3H, J=6.8), 1.15-1.31 (m, 6H); ¹³C NMR (CDCl₃, 50 MHz) δ 199.38 (d, J=6.15), 75.05, 62.63, 38.12 (d, J=130.1), 20.57, 16.19, 16.07; MS (m/z) 267 (M⁺+1), 266, 238, 194, 179, 153, 152, 137, 125, 109; HRMS: calcd for C₁₀H₁₉O₆P (M⁺+1) 267.0998, found 267.0991.

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The Effects of One- and Multi-Particle Basis on ${}^2A_1' \rightarrow {}^2A_2''$ Transition of Al_3

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The diversity of electronic structures of metal clusters has been subjected by many experimental and theoretical studies. As one of the simplest member of clusters, aluminum trimer also has several low-lying electronic states, and many experimental works¹⁻⁷ have been devoted to characterize these states. In order to make further understandings on these states, reliable theoretical results are required for energetic properties and vibrational properties. In spite of more than fifteen theoretical works treated Al_3 system, only some of them⁸⁻¹³ are interested on the characterization of the excited states. Though the identity of the ground states, $2A_1'$ in D_{3h} structure, established by ESR and photoelectron experiments^{5,7} are supported by an *ab initio* study,⁸ there are some disagreements between previous theoretical results on the properties of these states, *i.e.*, the geometries, vibrational properties, the correct order of states, and energetic splittings between them. One of the main reason of these discrepancies stems from the fact that the effect of one- and multi-particle basis size is not explored completely. In con-

strating to Al_2 , where several extensive studies with basis containing f-functions are reported,^{14,15} no comparable theoretical study is reported yet for Al_3 .

According to previous theoretical studies and experimental results, the adiabatic energetic splittings between these low-lying states are expected to be only a few tenths of eV. The harmonic frequencies range from 150 cm^{-1} to 350 cm^{-1} . In order for a theoretical result to be informative and predictive enough for these closely spacing states, proper choice of one-particle basis set and adequate treatment of electron correlations are indispensable. The main purpose of this work is to report the effects of f-type basis function, the effects of core-correlation, and the effects of triple excitations in electron correlations on the ${}^2A_1' \rightarrow {}^2A_2''$ vibronic transition of Al_3 , for which reliable experimental results are reported recently.^{6,7}

The potential energy surface of these states are very flat and the electron correlations are treated by the coupled-cluster correlation methods which are highly efficient and size