1993, *648*, 101.
10. Pretsch, E.; Seibl, J.; Simon, W.; Clerc, T. *Tables of Spectral Data for Structure Determination of Organic Compouds ^{13}C-NMR ^{1}H NMR IR MS UV/VIS*, Translated by Biemann, K.: Springer-Verlag: Berlin, Germany, 1989; p H160.

A Convenient Synthesis of β-Keto Phosphonates from Diethylphosphonoacetic Acid

Dae Young Kim

Department of Chemistry, Soonchunhyang University, Onyang P. O. Box 97, Chungnam 336-600, Korea
Received November 15, 1996

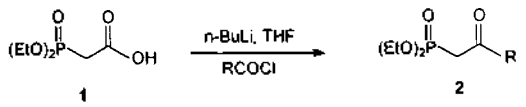
β-Keto phosphonates are valuable intermediates for organic synthesis, especially for the preparation of α,β-unsaturated carbonyl compounds by the Horner-Wadsworth-Emmons condensation.[1] Commonly, β-keto phosphonates are prepared by the Arbuzov reaction and acylation of alkylphosphonate anions. The Arbuzov reaction of trialkyl phosphite and a-halogeno ketones leads to β-keto phosphonates. The latter method is restricted to highly reactive α-halogeno ketones or a-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 a-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 methodology and both gave high yields.

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

Entry	R	Product	Yield[a]
1	Ph	**2a**	88
2	*p*-$C_6H_4CH_3$	**2b**	87
3	*p*-C_6H_4Cl	**2c**	81
4	*m*-C_6H_4Br	**2d**	78
5	*trans*-CH=CHPh	**2e**	90
6	C_2H_5	**2f**	73
7	*n*-C_5H_{11}	**2g**	78
8	cyclo-C_6H_{11}	**2h**	74
9	$CH(OAc)CH_3$	**2i**	65

[a] Isolated yields are based on diethylphosponoacetic acid.



1 2

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. ^{1}H and ^{13}C NMR were measured at 200 and 50 MHz, respectively, in $CDCl_3$ with TMS as internal standard. Mass spectra were recorded on HP 5985A or Jeol HX100/HX110.

Diethylphosphonoacetic acid[23] 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 NH_4Cl solution and extracted with ethyl ether. The organic layer was dried over $MgSO_4$ 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 ($CDCl_3$, 200 MHz) δ 1.28 (t, 6H, *J*= 7.0Hz), 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); ^{13}C NMR ($CDCl_3$, 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 $C_{12}H_{17}O_4P$ 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 ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 $C_{13}H_{19}O_4P$ 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 ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 ($CDCl_3$, 200 MHz) δ 1.34(t, 6H, *J*=7.1Hz), 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); ^{13}C NMR ($CDCl_3$, 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-oxobutylphosphoante (2f). IR (neat) 2990, 1710 (C=O), 1255 (P=O), 1036, 970 cm^{-1}; ^1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 50 MHz) d 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 $C_{11}H_{23}O_4P$ 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 ($CDCl_3$, 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): ^{13}C NMR ($CDCl_3$, 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 ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 $C_{10}H_{19}O_6P(M^+$+1) 267.0998, found 267.0991.

References

1. For general reviews, see: (a) Maryanoff, B. E.; Beitz, A. B. *Chem. Rev.* **1989**, *89*, 863. (b) Wadsworth, W. S. Jr. *Org. React. (N. Y.)*, **1977**, *25*, 73. (c) Walker, B. J. *Organophosphorus Reagents in Organic Synthesis*, Cadogan, J. I. G. Ed. Academic Press: New York, 1974, pp 155-206. (d) Kelly, S. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Schreiber, S. L., Eds.; Pergamon Press: Oxford, 1991; Vol. 1, Chapter 3. 1, pp 755-782.
2. (a) Lichtenthaler, F. W. *Chem. Rev.* **1961**, *61*, 607. (b) Honda, M.; Katsuki, T.; Yamaguchi, M. *Tetrahedron Lett.* **1984**, *25*, 3857. (c) Crobel, B.; Medinger, L.; Haelters, J. P.; Sturtz, G. *Synthesis* **1985**, 1048. (d) Kitamura, M.; Tokunaga, M.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 2931.
3. (a) Corey, E. J.; Kwiatkowski, G. T. *J. Am. Chem. Soc.* **1966**, *88*, 5654. (b) Coutrout, P.; Savignac, P.; Mathay, F. *Synthesis* **1978**, *36*. (c) Aboujaoude, E. E.; Colligan, N.; Savignac, P. *J. Organomet. Chem.* **1984**, *264*, 9. (d) Rudisill, D. E.; Whitten, J. P. *Synthesis* **1994**, 851. (e) Narkunam, K.; Nagarajan, M. *J. Org. Chem.* **1994**, *59*, 6386. (f) Mikolajczyk, M.; Mikine, M. *J. Org. Chem.* **1994**, *59*, 6760.
4. (a) Clark, R. D.; Kozar, L. G.; Heathcock, C. H. *Synthesis* **1975**, 635. (b) Grieco, P. A.; Pogonowski, C. S. *J. Am. Chem. Soc.* **1973**, *95*, 3071. (c) Mathey, F.; Savignac, P. *Synthesis* **1976**, 766. (d) Savignac, P.; Mathey, F. *Tetrahedron Lett.* **1976**, 2829. (e) Mathey, F.; Savignac, P. *Tetrahedron* **1978**, 649. (f) Aboujaoude, E.; Colligan, N.; Teulade, M. P.; Savignac, P. *Phosphorus and Sulfur* **1985**, *25*, 57.
5. Theisen, P. D.; Heathcock, C. H. *J. Org. Chem.* **1988**, *53*, 2374.

6. (a) Lee, K.; Oh, D. Y. *Bull. Korean Chem. Soc.* **1989,** *10*, 613. (b) Lee, K.; Oh, D. Y. *Synth. Commun.* **1991,** *21*, 279.
7. (a) Lee, K.;Wiemer, D. F. *J. Org. Chem.* **1991,** *56*, 5556. (b) Calogeropoulou, T.; Hammond, G.B.; Wiemer, D. F. *J. Org. Chem.* **1987,** *52*, 4185. (c) An, Y. Z.; Wiemer, D. F. *J. Org. Chem.* **1992,** *57*, 317. (d) An, Y. Z.; An, J. G.; Wiemer, D. F. *J. Org. Chem.* **1994,** *59*, 8197.
8. Hong, S.; Chang, K.; Ku, B.; Oh, D. Y. *Tetrahedron Lett.* **1989,** *30*, 3307.
9. Boeckman, R. K. Jr.; Walters, M. A.; Koyano, H. *Tetrahedron Lett.* **1989,** *30*, 4787.
10. Coutrot, P.; Ghribi, A. *Synthesis* **1986**, 661.
11. (a) Tsuga, O.; Kanemasa, S.; Suga, H,; Nakagawa, N. *Chem. Lett.* **1986,** *60*, 2463. (b) Tsuga, O.; Kanemasa, S.; Suga, H,; Nakagawa, N. *Bull. Chem. Soc. Jpn.* **1987,** *60*, 2463. (c) Kanemasa, S.; Nakagawa, N.; Suga, H.; Tsuge, O. *Bull. Chem. Soc. Jpn.* **1989,** *69*, 171.
12. Kabat, M. M. *Tetrahedron Lett.* **1993,** *34*, 8543.
13. Altenbach, H. J.; Dorff, R. *Tetrahedron Lett.* **1981,** *22*, 5175.
14. Ohler, E. ; Kang, H, S,; Zbiral, E. *Synthesis* **1988,** *623*.
15. Koh, Y. J.; Oh, D. Y. *Tetrahedron Lett.* **1993,** *34*, 2147.
16. Gasteiger, T.; Herzig, C. *Tetrahedron Lett.* **1980,** *21*, 2687. Herzig, C.; Gasteiger, T. *Chem. Ber.* **1982,** *115*, 601.
17. Kim, D. Y.; Kong, M. S. *J. Chem. Soc., Perkin Trans. 1* **1994**, 3359.
18. (a) Nicolaou, K. C.; Seitz, S. P.; Pavia, M. R.; Petasis, N. A. *J. Org. Chem.* **1979,** *44*, 4011. (b) Nicolaou, K. C.;Pavia, M. R.; Seitz, S. P. *J. Am. Chem. Soc.* **1981,** *103*, 1224. (c) Lim, M.; Marquez, V. E. *Tetrahedron Lett.* **1983,** *24*, 4051. (d) Mikolajczyk, M.; Balczewski, P. *Synthesis* **1984**, 691.
19. Kim, D. Y.; Mang, J. Y.; Oh, D. Y. *Synth. Commun.* **1994,** *24*, 629.
20. (a) Ruder, S. M.; Kulkarni, V. R. *Synthesis* **1993**, 945. (b) Ruder, S. M.; Kulkarni, V. R. *J. Chem. Soc. Chem. Commun.* **1994**, 2119.
21. (a) Kim, D. Y.; Kong, M. S.; Rhie, D. Y. *Synth. Commun.* **1995,** *25*, 2865. (b) Kim. D. Y.; Kong, M. S.; Kim, T. H. *Synth. Commun.* **1996,** *26*, 2487. (c) Corbel, B.; Hostis-Kervella, I. L.; Haelters, J. P. *Synth. Commun.* **1996,** *26*, 2561.
22. (a) Kim, D. Y.; Lee, K.; Oh, D. Y. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2451. (b) Kim, D. Y.; Mang, J. Y.; Lee, J. W.; Oh, D. Y. *Bull. Korean Chem. Soc.* **1993,** *14*, 526.
23. Diethylphosphonoacetic acid can be prepared by Arbuzov reaction or by the hydrolysis of triethyl phosphonoacetate. For example, see: (a) Coutrot, P.; Snoussi, M. Savignac, P. *Synthesis* **1978**, 133. (b) Lombardo, L.; Taylor, R. J. K. *Synthesis* **1978**, 131. (c) Katusumura, S.; Isoe, S. *Chem. Lett.* **1982**, 1689. (d) Lombard, L.; Taylor, R. J. K. *Synth. Commun.* **1978,** *8*, 463.

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

Kyoung-Koo Baeck

Department of Chemistry, Kangnung University, Kangnung 210-702, Korea
Received November 29, 1996

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 works[1-7] 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 them[8-13] 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 constrating 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 treatement of electron correlations are indispensible. 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