The Free Internet Journal for Organic Chemistry

Paper

Archive for Organic Chemistry

Arkivoc **2020**, part iv, 0-0

to be inserted by editorial office

Highly efficient and extremely simple protocol for the oxidation α-hydroxyphosphonates to α-ketophosphonates using Dess-Martin periodinane

Ravindra V. Kupwade,[a] Satish D. Mitragotri, [b]* Makarand A. Kulkarni,[c] Uday V. Desai[d] and Prakash P. Wadagaonkar.[e]

[a]Department of Chemistry, Smt. Kasturbai Walchand College, Sangli 416410, India
[b]Department of Chemistry, Walchand College of Arts and Science, Solapur 413 006, India
[c]Instrumentation center, P.A.H.Solapur University, Solapur 413 255, India
[d]Department of Chemistry, Shivaji University, Kolhapur 416 004, India
[e]Polymer Science and Engineering Division, National Chemical Laboratory, Pune-411 008, India
Email: sdmitragotri@rediffmail.com

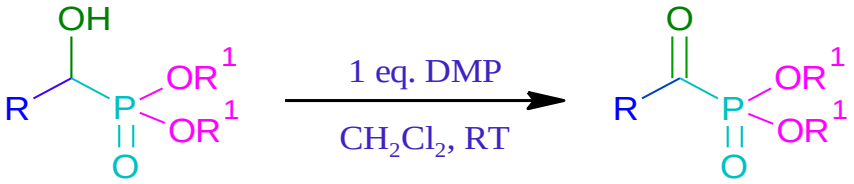
Dedicated to all medical and paramedical staff around the world, fighting with CORONA bravely

Received mm-dd-yyyy **Accepted** mm-dd-yyyy **Published on line** mm-dd-yyyy

Dates to be inserted by editorial office

Abstract

Dess-Martin periodinane has been demonstrated for the first time to be an efficient reagent in metal – free oxidation of α-hydroxyphosphonates to α-ketophosphonates under ambient conditions. Acquiescent reaction conditions and a simple isolation procedure are the noteworthy features of the developed protocol.



Keywords: α-Hydroxyphosphonates, α-ketophosphonates, Dess-Martin periodinane, IBX, oxidation

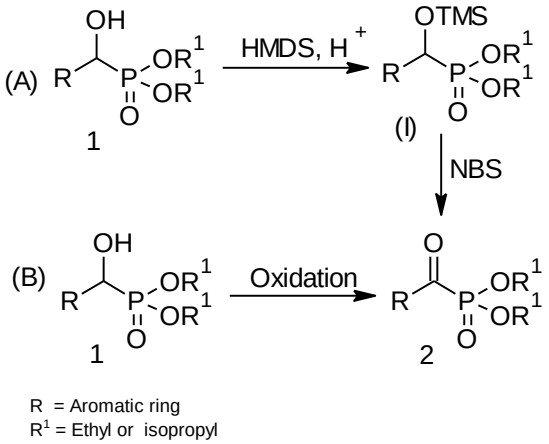
 ©AUTHOR(S)

Introduction

In organophosphorus chemistry, phosphonates are interesting complements to phosphates in terms of biological activity.[1] α-Ketophosphonates act as, mimic of phosphoserine in drug development process[2], as enzyme inhibitors[3] and inhibitors of PTPIB.[4] The α-ketophosphonates constitute as an important class of organophosphonates and are fascinating as well as versatile molecules in organic synthesis.[5] Apart from their possible derivatization to hydrazones,[6] oximes[7] as well as imines[8] they can be reduced to corresponding α-hydroxyphosphonates,[9,10] and can be used as acylating agents and in the Wittig reaction[11]. They can serve as substrates in stereoselective aldol,[12,13] Mukaiyama[14] and in retro Diels-Alder reaction.[15,16]

Michaelis-Arbuzov reaction between an acid chloride and trialkylphosphite is a general method for the preparation of α-ketophosphonates.[17,18] However, the method is suitable mainly for simple aromatic as well as aliphatic acid chlorides. Alternatively, they can also be prepared by the oxidation of an easily accessible α-hydroxyphosphonate. Our interest in the synthesis of α-ketophosphonates stems from an earlier report on the synthesis of α-hydroxyphosphonates from our laboratory.[19] In continuation of the same, we planned to undertake the synthesis of α-ketophosphonates by oxidation of α-hydroxyphosphonates.

A literature survey revealed that the oxidation protocols reported to this aim mostly employ either high valent metal oxide (MnO_2,[20] CrO_3[21]) or their mineral salts ($KMnO_4$,[22] ZnDC[23], PCC,[24] PDC[25] and QCC[26]). However, these protocols are plagued with the necessity of more than a stoichiometric amount of toxic metal salts coupled with the generation of inorganic waste and these facts are the matters of serious concern in the context of environmental compatibility. To circumvent these issues we had developed a conceptually different protocol for the synthesis of α-ketophosphonates by oxidation of corresponding α-trimethylsilyloxy phosphonates under free-radical conditions[27] (Scheme 1A). However, the essentiality of the prior synthesis of α-trimethylsilyloxy phosphonates and reflux conditions remains to be the major limiting factors of this protocol. Consequently, there still remains scope for further innovation towards operational simplicity, milder reaction conditions and shorter reaction times coupled with the avoidance of toxic metal salts in the oxidation of α-hydroxyphosphonates to α-ketophosphonates. With our continued interest in the development of newer synthetic methodologies, we set out to develop a practical method for the oxidation of α-hydroxyphosphonates to α-ketophosphonates (Scheme 1B).



Scheme 1. Oxidation of α-hydroxyphosphonates to α-ketophosphonates

 ©**AUTHOR(S)**

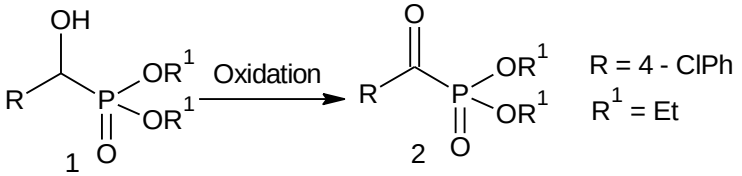
Results and Discussion

A great variety of oxidants bear testimony in the literature for the oxidation of alcohols. However, the very high sensitivity of C(O)-P bond in the resultant α-ketophosphonates towards hydrolysis poses limitations in the selection of proper oxidant as well as the reaction conditions. Keeping this particular limitation in mind we planned to develop a metal-free protocol for the synthesis of α-ketophosphonates.

It is well known that, oxone is a stable 2:1:1 ternary composite of $KHSO_5$, K_2SO_4 and $KHSO_4$ and it's use in various organic transformations is well documented. We have reported earlier the use of oxone in the oxidation of sulfides to sulfoxides as well as sulfones,[28] in the oxidation of hydrazides to diacylhydrazines.[29] However, the use of water being essential in oxone mediated oxidation of alcohols and the same being detrimental in the oxidation of α-hydroxyphosphonates, we focused our search on the reports on the use of water insoluble oxone derivatives in the oxidation of alcohols. It was revealed that two derivatives of oxone *viz.* tetrabutylammoniumperoxymonosulfate (TBAP) and benzyltriphenylphosphonium peroxymonosulfate (BTPP), have earlier been reported in the oxidation of alcohols.[30-34] However, these reagents have not been explored in the oxidation of α-hydroxy phosphonates. Hence, two model reactions were initially performed using diethyl [(4-chlorophenyl) (hydroxy) methyl] phosphonate, **1a,** as the substrate. Thus, to a well stirred solution of **1a** (1mmol) in dry acetonitrile (5 mL) was added TBAP or BTPP (300 mg). Stirring was continued and the reaction was monitored by TLC. However, both these oxidants failed to furnish desired α-ketophosphonate, **2a**, in acceptable yield at ambient temperature. Heating the same reaction mixture under reflux was also not beneficial in driving the reaction to completion (entry 1, 2, Table 1). During our search on protocols for the oxidation of alcohols under heterogeneous conditions, we came across an interesting report on the use of silver carbonate supported on cetrimide to this effect.[35] However, when the model reaction was performed using the reaction conditions reported for the oxidation of alcohols,[35] the catalyst failed to furnish desired α-ketophosphonate, **2a**, in acceptable yield (entry 3, Table 1**).** All these results prompted us to search for other oxidants for this oxidative transformation.

In recent years, the use of hypervalent iodine reagents such as, Dess Martin periodinane, as well as its cheaper precursor, *viz*. *o*-iodoxybezoic acid (IBX) have become the reagents of choice in the oxidation of alcohols and in different areas of organic synthesis.[36] Until recently, the practical utility of IBX was limited owing to its insolubility in common organic solvents. However, there are now reports on the use of IBX for the oxidation of alcohols in common organic solvents.[37] This prompted us to test the efficacy of IBX in the oxidation of α-hydroxyphosphonates. Thus, a well stirred mixture of α-hydroxyphosphonate, **1a**, and IBX (1 mmol, each) was allowed to reflux in dry acetonitrile (5 mL) and the reaction was monitored by TLC. No appreciable conversion of α-hydroxyphosphonate, **1a**, to ketophosphonate, **2a,** was noticed (entry 4, Table 1). The reaction was then repeated using double as well as triple equivalents of IBX in acetonitrile as well as ethyl acetate as the reaction media. Although a noticeable increase in the yield of expected α-ketophosphonate, **2a**, was observed, even after prolonged heating the reaction did not go to completion (Entry 5, 6; Table 1).

Table 1: Screening of oxidants in oxidation of α-hydroxyphosphonate, **1a**.



Entry	Oxidant (equiv.) / (mg)	Conditions	Time (h)	Yield[b] (%)
1	TBAP (300)	DCM , RT; reflux	12, 6	60, 70

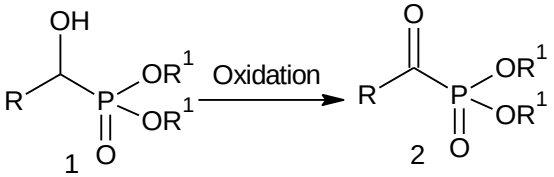
 ©**AUTHOR(S)**

2	BTPP(300 mg)	DCM, RT; reflux	12, 6	55, 75
3	Ag_2CO_3-Cetrimide(500 mg)	Benzene, reflux	6, 12	60, 75
4	IBX (1 equiv.)	MeCN, reflux	6	40
5	IBX(2 equiv.)	MeCN, reflux	6	70
6	IBX(3 equiv.)	EtOAc, reflux	6	85
7	IBX – BTPP (1:1 equiv.)	MeCN, reflux	3	55
8	IBX – BTPP (1:3 equiv.)	MeCN, reflux	3	95
9	DMP (1: 1 equiv.)	CH_2Cl_2, rt	10[c]	97
a: reaction conditions: α-hydroxyphosphonate, **1a** (1 mmol),oxidant, solvent; c: Yields refer to the isolated products; c: time in minutes				

A focused literature survey on the use of IBX in the oxidation of alcohols under anhydrous conditions revealed that there were reports on the use of IBX – BTPP combination in the oxidation of alcohols.[38-45] Based upon these studies it was planned to explore this reagent-oxidant combination in the oxidation of **1a**. Accordingly, a model reaction was carried wherein a mixture of **1a** (1mmol)**,** IBX (0.1 mmol) and BTPP (1 mmol) in dry acetonitrile (5 mL) was stirred under reflux conditions. We did not notice any appreciable progress in the reaction (entry 7, Table 1). However, with an increase in the proportion of BTPP from one equivalent to three equivalents, the desired ketophosphonate, **2a**, resulted in excellent yield (entry 8, Table 1). At this stage, it is worthy to note that although we were successful in obtaining the desired α-ketophosphonate, **2a,** in excellent yield and in an acceptable time, the main limitations of using IBX – BTPP combination were associated with very high proportion of BTPP, it's high molecular weight, cost and, the reflux conditions. To circumvent these limitations, we planned to test the suitability of another hypervalent oxidant *viz*. Dess Martin periodinane, DMP, in the oxidation of α-hydroxyphosphonates. We can disclose that simple stirring together at ambient temperature a solution of **1a,** and Dess-Marin periodinane (1:1 equiv.) in dry acetonitrile or dichloromethane (5 mL) afforded the desired α-ketophosphonate, **2a,** in excellent yield in a very short time (entry 9, Table 1).

With a view to establish the generality of the reaction conditions and to explore the scope of the developed protocol, variety of α-hydroxyphosphonates having electron donating as well as electron withdrawing substituents were shown to undergo smooth oxidation to furnish corresponding α-ketophosphonates in excellent yield (Table 2). Similarly, the α-hydroxy phosphonates derived from heterocyclic as well as conjugated aldehyde viz. cinnamaldehyde also furnished corresponding α-ketophosphonate. In general the reactions were fast and no undesirable products were detected.

Table 2: Dess Martin periodinane mediated oxidation of α-hydroxy phosphonates



Entry	Product 2; (R) =	R^1 =	Product [Ref] (2)	Time (min)	Yield (%)
1	4-Cl-C_6H_4	Et	2a[22]	10	98
2	4-Me-C_6H_4	Et	2b[22]	10	98
3	4-$(Me)_2CHC_6H_4$	Et	2c[22]	15	96
4	2,6-$(Me)_2C_6H_3$	Et	2d	15	98

 ©**AUTHOR(S)**

5	3,4-$(OMe)_2C_6H_3$	Et	2e	10	97
6	2,3,4-$(OMe)_3$ -C_6H_2	Et	2f	15	97
7	3-$NO_2C_6H_4$	Et	2g[22]	20	91
8	C_6H_4CH=CH-	Et	2h[25]	15	95
9	4-$C_6H_5CH_2OC_6H_4$	Et	2i	20	91
10	4- CH_2=$CHCH_2OC_6H_4$	Et	2j	20	90
11	2-Thiophenyl	Et	2k	20	90
12	4-Methylphenyl	iso-propyl	2l	15	98
13	4-Fluorophenyl	iso-propyl	2m	20	90
14	2-Thiophenyl	iso-propyl	2n	20	90
a: α-Hydroxyphosphonate: DMP (1:1) in dry CH_2Cl_2 (5 mL), rt; b: Yields refer to isolated products.					

Conclusions

In summary, we have developed a clean and practically simple protocol for the oxidation of α-hydroxyphosphonates to α-ketophosphonates in excellent yields using Dess-Martin periodinane as an efficient oxidizing agent. Ambient reaction conditions, metal-free environment and very short reaction times are the noteworthy features of the developed protocol.

Experimental Section

General. α-Hydroxyphosphonates were prepared by potassium phosphate-catalyzed reaction of respective phosphites with various aldehydes.[13b] ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance-II (300 MHz) spectrometer.

Synthetic procedure for Diethyl (4-chlorobenzoyl) phosphonate, 2a. An equimolar quantity of diethyl [(4-chlorophenyl) (hydroxy) methyl] phosphonate (entry 1, Table 2) and Dess Martin Periodinane (1 mmol, each) were stirred together in dry dichloromethnane (5 mL) at room temperature. Progress of reaction was monitored by TLC. After completion of reaction, the reaction mixture was directly filtered through a short column of silica gel. From the eluent obtained the solvent was removed under vacuum to get pure α- keto phosphonate.

Diethyl (4-methylbenzoyl) phosphonate (2b). Colorless Oil (bp 122-123^{0}C) ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.25 (t, *J* 7 Hz, 6H), 2.43 (s, 3H), 3.69 - 3.80 (m, 4H), 7.27 (d, *J* 8 Hz, 2H). 8.01 (d, *J* 8 Hz, 2H) ppm.^{13}C-NMR (75 MHz, $CDCl_3$)**:** δ 16.68 (d, $^3J_{C\text{-}P}$ 6 Hz, OCH_2CH_3), 22.17, 64.25 (d, $^2J_{C\text{-}P}$ 7.5 Hz, OCH_2CH_3), 127.37, 129.88, 130.312 146.41, 198.45 (d, $^1J_{C\text{-}P}$ 176.6 Hz, ArCO) ppm.

Diethyl (4-isopropylbenzoyl) phosphonate (**2c).** Colorless oil (bp 156 -157^{0}C)^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22 [d, *J* 8 Hz, 6H, $(CH_3)_2$-CH], 1.38 (t, *J* 7 Hz, 6H, 2 x OCH_2CH_3), 2.92 [m, 1H, CH-$(CH_3)_2$], 4.22 (m, 4H, 2 x OCH_2CH_3), 7.24 (d, *J* 7 Hz, 2H, ArH), 8.06 (d, *J* 7 Hz, 2H, ArH) ppm.

Diethyl (2,6-dimethylbenzoyl) phosphonate (2d). Pale yellow oil (bp 102-104^{0}C) ^{1}H -NMR (300 MHz, $CDCl_3$): δ 1.25 (t, *J* 7.2 Hz, 6H, 2 x OCH_2CH_3), 2.25 (s, 6H, 2 x CH_3), 4.08 – 4.23 (m, 4H, 2 x OCH_2CH_3), 6.99 (d, *J* 7.5 Hz, 2H, ArHs), 7.17 (t, *J* 7.5 Hz, 1H, ArH); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 16.24 (d, 3H JC-P = 6 Hz, OCH_2CH_3), 19.24 (2 x CH_3), 64.12 (d, 2JC-P = 6. 75 Hz, OCH_2CH_3), 127.19, 129.81, 134.12, 139.21, 139.94 (ArCs), 212.12 (d, 1JC-P = 165. 50 Hz, ArCO) ppm. Anal. Calcd. for $C_{13}H_{19}O_4P$ (270.27): C 57.77, H 7.09; Found, C 57.69, H 7.02.

Diethyl (3,4-dimethoxybenzoyl) phosphonate (2e). Pale yellow oil(bp 109-110^{0}C) ^{1}H -NMR (300 MHz, $CDCl_3$): δ 1.4 (t, *J* 6 Hz, 6H), 3.96 (s, 3H, $ArOCH_3$), 3.98 (s, 3H, $ArOCH_3$), 4.36 (m, 4H), 6.98 (d, *J* 8 Hz, 1H), 7.62 (s, 1H),

 ©**AUTHOR(S)**

8.16 (d, *J* 8Hz, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 16.03 (2 x OCH_2CH_3), 55.69 ($ArOCH_3$), 60.21 ($ArOCH_3$), 63.84 (2 x OCH_2CH_3), 110.12, 124.11, 126.53, 129.33, 149.03, 154.80, 196.0 (d, 1JC-P = 175 Hz, ArCO) ppm. Anal. Calcd. for $C_{13}H_{19}O_6P$ (302.27): C 51.66, H 6.34; Found, C 51.63, H 6.29.

Diethyl (3,4,5-trimethoxybenzoyl) phosphonate (2f). Dark yellow oil (bp 89-90^{0}C)^{1}H -NMR (300 MHz, $CDCl_3$): δ 1.33 (t, *J* 7.2 Hz, 6H, 2 x OCH_2CH_3), 3.87 (s, 6H, 2 x $ArOCH_3$), 3.89 (s, 3H, $ArOCH_3$), 4.17-4.27 (m, 4H, 2 x OCH_2CH_3), 7.57 (s, 2H, ArHs); ^{13}C-NMR (75 MHz, $CDCl_3$): 16.33 (d, 3JC-P = 5.25 Hz, 2 x OCH_2CH_3), 56.19 ($ArOCH_3$) 60.94 ($ArOCH_3$), 64.01 (d, 2JC-P = 6.9 Hz, 2 x OCH_2CH_3), 107.27, 130.20, 131.07, 153.07, 153.10 (ArCs), 196.94 (d, 1JC-P =174. 75 Hz, ArCO) ppm. Anal. Calcd. for $C_{14}H_{21}O_7P$ (332.29): C 50.60, H 6.37; Found, C 50.54, H 6.39.

Diethyl (3-nitrobenzoyl) phosphonate (2g). Dark yellow oil (bp 168-169^{0}C)^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.31 (t, *J* 6 Hz, 6H), 4.05 - 4.25 (m, 4H),7.61 (t, *J* 8Hz, 1H), 8.36 (m, 2H), 8.87 (brs, 1H) ; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 21.6, 55.69, 127.95, 131.66, 132.60,133.07, 141.66, 164.00, 196.0 (d, $^1J_{C\text{-}P}$ = 174. 75 Hz, ArCO) ppm.

Diethyl (cinnamyl benzoyl) phosphonate (2h). Colorless oil (bp 76 -77^{0}C) ^{1}H -NMR (300 MHz, $CDCl_3$): δ 1.16 (t, *J* 7.2 Hz, 3H), 1.27 (t, *J* 7.2 Hz, 3H), 4.0 - 4.35 (m, 4H), 6.40 (d, *J* 15.6 Hz, 1H, CH=CH), 7.3 - 7.5 (m, 5H, ArH), 7.70 (d, *J* 15.6 Hz, 1H, CH=CH); ^{13}C-NMR (75 MHz, CDCl3): δ 16.36, 29.61, 63.52, 64.53, 117.52, 128.64, 129.64, 130.86, 134.27, 147.00, 194.00 (d, 1JC-P = 175 Hz, ArCO) ppm.

Diethyl (4-benzyloxybenzoyl) phosphonate (**2i).** Colorless oil ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.38 (t, *J* 7 Hz, 6H), 4.27 (q, *J* 7 Hz, 4H), 5.17 (s, 2H), 7.02 (d, *J* 8 Hz, 2H), 7.3 - 7.45 (m, 5H), 8.18 (d, *J* 8 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 20.76, 51.57, 54.12, 68.94, 114.27, 114.87, 118.38, 121.79, 128.05, 129.36, 134.97, 141.53, 162.81, 164.07, 171.01, 195.22 (d, 1JC-P = 173.5 Hz, ArCO) ppm. Anal. Calcd. for $C_{18}H_{21}O_5P$ (348.34): C 62.07, H 6.08; Found, C 62.01, H 6.04.

Diethyl {4-[(prop-2-en-1-yl)oxy]benzoyl}phosphonate (2j). Colorless oil ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.32 - 1.37 (m, 6H, 2 x OCH_2CH_3), 4.23 (q, *J* 7 Hz, 4H, 2 x OCH_2CH_3), 4.62 (d, *J* 7 Hz, 2H, OCH_2) 5.25 - 5.4 (m, 2H, CH_2=CH), 6.0 (m, 1H, CH_2=CH), 6.98 (d, *J* 8 Hz, 2H), 8.28 (d, *J* 8 Hz, 2H) ppm; ^{13}C -NMR ($CDCl_3$, 75 MHz): 16.11 (2 x OCH_2CH_3), 64.01 (2 x OCH_2CH_3), 68.86 (OCH_2), 114.73, 118.22, 128.13, 129.44, 132.01, 132.34, 141.35, 163.85, 195.8 (d, JC-P = 174 Hz, ArCO) ppm. Anal. Calcd. for $C_{14}H_{19}O_5P$ (298.28): C 56.38, H 6.42; Found, C 56.29, H 6.38.

Diethyl (2-thiophenoyl) phosphonate (2k). Pale yellow oil (bp 101-102^{0}C) ^{1}H -NMR (300 MHz, $CDCl_3$): δ 1.30 (t, *J* 7.2, 6H, 2 x OCH_2CH_3), 4.16 - 4.25 (m, 4H, 2 x OCH_2CH_3), 7.14 (t, *J* 4.5 Hz, 1H, ArH), 7.77 (t, *J* 4.5 Hz, 1H, ArH), 8.35 (d, *J* 3.9, 1H, ArH); ^{13}C -NMR (75 MHz, $CDCl_3$): δ 16.28 (d, 3JC-P = 5. 2 Hz, 2 x OCH_2CH_3), 64.23 (d, 2JC-P = 6. 75 Hz, 2 x OCH_2CH_3), 129.01, 137.18, 137.99, 142.57, 143.64 (ArCs), 190.17 (d, 1JC-P = 182. 25 Hz, ArCO) ppm. Anal. Calcd. for $C_9H_{13}O_4PS$ (248.24): C 43.55, H 5.28, S 12.92 ; Found, C 43.47, H 5.31, S 12.81.

Diisopropyl (4-methylbenzoyl) phosponate (2l). Colorless oil (bp143-145^{0}C) ^{1}H -NMR (300 MHz, $CDCl_3$): δ 1.34 - 1.37 [m, 12H, 2 x $OCH(CH_3)_2$], 2.40 (s, 3H, $ArCH_3$), 4.76 - 4.89 [m, 2H, 2 x $OCH(CH_3)_2$], 7.28 (d, *J* 8.1 Hz, 2H, ArHs), 8.16 (d, *J* 8.1 Hz, 2H, ArHs); ^{13}C -NMR (75 MHz, $CDCl_3$): δ 21.84 ($ArCH_3$), 23.79 [d, 3JC-P = 4.5 Hz, $OCH(CH_3)_2$] 24.06 [d, 3JC-P = 4.5 Hz, $OCH(CH_3)_2$], 73.04 [d, 2JC-P = 7.5 Hz, $OCH(CH_3)_2$], 129.45, 130.02, 132.89, 133.74, 145.75, 198.70 (d, 1JC-P = 175. 50 Hz, ArCO) ppm. Anal. Calcd. for $C_{14}H_{21}O_4P$ (284.29): C 59.15, H 7.45; Found, C 59.19, H 7.47.

Diisopropyl (4-fluorobenzoyl) phosphonate (2m). Pale yellow oil (bp 90-92^{0}C) ^{1}H -NMR (300 MHz, $CDCl_3$): δ 1.33 – 1.36 [m, 12H, 2 x $OCH(CH_3)_2$], 4.21- 4.30 [m, 1H, $OCH(CH_3)_2$], 4.75 - 4.88 [m, 1H, $OCH(CH_3)_2$], 7.12 - 7.18 (m, 2H, ArHs), 8.28 – 8.33 (m, 2H, ArHs) ppm; ^{13}C -NMR (75 MHz, $CDCl_3$): 23.78 [d, 3JC-P = 4.5 Hz, $OCH(CH_3)_2$], 24.06 [d, 3JC-P = 4.5 Hz, $OCH(CH_3)_2$], 73.30 [d, 2JC-P = 7.5 Hz, $OCH(CH_3)_2$], 115.87, 116.16, 132.89, 132.82, 164.81, 168.23, 197. 72 (d, 1JC-P = 178. 50 Hz, ArCO) ppm. Anal. Calcd. for $C_{13}H_{18}FO_4P$ (288.26): C 54.17, H 6.29; Found, C 54.10, H 6.21.

 ©AUTHOR(S)

Diisopropyl (2-thiophenoyl) phosphonate (2n). Pale yellow oil (bp 84-85^{0}C)^{1}H -NMR (300 MHz, $CDCl_3$): δ1.31-1.34 [m, 12H, 2 x $OCH(CH_3)_2$], 4.76 - 4.84 [m, 2H, 2 x $OCH(CH_3)_2$], 7.16 (t, 1H, ArH), 7.76 - 7.80 (m, 1H, ArH), 8.38 (t, 1H, ArH); ^{13}C -NMR (75 MHz, $CDCl_3$): 23.77 [d, 3JC-P = 4.5 Hz $OCH(CH_3)_2$] 23.96 [d, 3JC-P = 4.5 Hz, $OCH(CH_3)_2$], 73.37 [d, 2JC-P = 7.5 Hz, $OCH(CH_3)_2$], 128.89, 136.78, 137.78, 142.72, 143.79, 191.03 (d, 1JC-P = 183.75 Hz, ArCO) ppm. Anal. Calcd. for $C_{11}H_{17}O_4PS$ (276.29): C 47.82, H 6.20, S 11.61; Found, C 47.74, H 6.16, S 11.49.

Acknowledgements

UVD thanks UGC, New Delhi for financial support [F. 43-221/ 2014 (SR)].

References

1. Oertell, K.; Kashemirov, B. A.; Negahbani, A.; Minard, C.; Haratipour, P.; Alnajjar, K. S.; Sweasy, J. B.; Batra, V. K.; Beard, W. A.; Wilson, S. H.; McKenna, C. E.;Goodman, M. F. *Biochemistry* **2018,** *57*, 3925-3933. http://dx.doi.org/10.1021/acs.biochem.8b00417
2. Panigrahi, K.; Eggen, M. ; Maeng, J. H. ; Shen, Q. ; Berkowitz, D. B. *Chemistry & Biology* **2009**, *16 (9)*, 928-936. https://doi.org/10.1016/j.chembiol.2009.08.008
3. P, Kaushik. ; Applegate, G. A. ; Malik, G. ; Berkowitz, D. B. *J. Am. Chem. Soc.* **2015**, *137 (10),* 3600 https://doi.org/10.1021/jacs.5b00022
4. P, Kaushik. ; Xiang, F. ; Masato, K. ; Berkowitz, D. B. *Org. Lett.* **2019**, *21 (24),* 9846-9851. https://doi.org/10.1021/acs.orglett.9b03707
5.Engel, R. *Chem. Rev.* **1977**, *77*, 349-367. https://doi.org/10.1021/cr60307a003
6. Scherer, H.; Hartmann, A.; Regitz, M.; Tunggal, B. D.; Gunther, H. Carbene, V. *Chem. Ber.* **1972**, *105,* 3357-3381. https://doi.org/10.1002/cber.19721051024
7. Bruer, E.; Karaman, R. Golblum, A.; Gibson, D.; Leader, H.; Potter, B. V. L.; Cummins, J. H. *J. Chem. Soc., Perkin Trans. I* **1988**, 3047-3057. http://dx.doi.org/10.1039/P19880003047
8. Karaman, R. Golblum, A.; Bruer, E.; Leader, H. *J. Chem. Soc. Perkin Trans. I* **1989**, 765-774. http://dx.doi.org/10.1039/P19890000765
9. Gajda, T. *Tetrahedron Asymm.* **1994**, *5*, 1965-1972. http://dx.doi.org/10.1016/S0957-4166(00)_10.1016/S0957-4166(00)86271-0
10. Meier, C.; Laux, W. H. G.; Bats, J. W. *Liebigs Ann.* **1995**, 1963-1979. https://doi.org/10.1002/jlac.1995199511276
11. Yamashita, M.; Kojima, M.; Yoshida, H.; Ogata, T.; Inokawa, S. *Bull. Chem. Soc. Jpn.* **1980**, *53,* 1625-1628. https://doi.org/10.1246/bcsj.53.1625
12. Longmire, C.; Evans, S. A. *J. Chem. Soc. Chem. Commun.***1990***,* 922-923. https://doi.org/10.1039/C39900000922
13. Gordon, N. J.; Evans, S. A. Jr. *J. Org. Chem*. **1993**, *58,* 5293 - 5294. http://dx.doi.org/10.1021/jo00072a002.
14. Telan, L. A.; Poon, C. D.; Evans, S. A. Jr. *J. Org. Chem* **1996***, 61,* 7455-7462.

 ©AUTHOR(S)

http://dx.doi.org/10.1021/jo9510853.
15. Schuster, T.; Evans, S. A. Jr. *Phosphorus, Sulfur, Silicon Relat. Elem.***1995**, *103*, 259-271.
https://doi.org/10.1080/10426509508027385
16. Evans, D. A.; Johnson, J. S. *J. Am. Chem. Soc.***1998**, *120*, 4895-4896.
http://dx.doi.org/10.1021/ja980423p.
17. Berlin, K. D., Hellwege, D. M.; Nagabhushnam, M. *J. Org. Chem*. **1965**, 1265-1267.
http://dx.doi.org/10.1021/jo01015a519.
18. Berlin, K. D.; Taylor, H. A. *J. Am. Chem. Soc.* **1964**, *86*, 3862 - 3866.
http://dx.doi.org/10.1021 / ja01072a053.
19. Kulkarni, M. A.; Lad, U. P.; Desai, U. V.; Mitragotri, S. D.; Wadgaonkar, *C. R. Chimie* **2013,** *16,* 148-152.
https://doi.org/10.1016/j.crci.2012.10.009
20. Liao, Y.; Shabany, H.; Spilling, C.D. *Tetrahedron Lett.***1998**, *39*, 8389-8362.
https://doi.org/10.1016/S0040-4039(98)01933-9
21. Kaboudin, B. *Tetrahedron Lett.* **2000**, *41*, 3169-3171.
https://doi.org/10.1016/S0040-4039(00)00323-3
22. Firozabadi, H.; Iranpoor, N.; Sobhani, S.; Saradarian, A. R. *Tetrahedron Lett.* **2001**, *42*, 4369-4371.
https://doi.org/10.1016/S0040-4039(01)00712-2
23. Firozabadi, H.; Iranpoor, N.; Sobhani, S. *Tetrahedron Lett.* **2002,** *43*, 477-480.
https://doi.org/10.1016/S0040-4039(01)02146-3
24. Firozabadi, H.; Iranpoor, N.; Sobhani, S. *Phosphorus, Sulfur, Silicon and related element* **2004**, *179*, 1483–1491;
https://doi.org/10.1080/10426500490463925
25. Firozabadi, H.; Iranpoor, N.; Sobhani, S. *Synth. Commun*. **2004**, *34*, 1463-1471.
https://doi.org/10.1081/SCC-120030697
26. Kluger, R.; Pick, D. C.; Chin, J. *Can. J. Chem*. **1978**, *56,* 1792-1995.
https://doi.org/10.1139/v78-291
27. Mitragotri, S. D. Ph. D. Thesis, Shivaji University, Kolhapur. 2009.
28. Kupwade, R. V.; khot, S. S.; Lad, U. P.; Desai, U. V.; Wadgaonkar, P. P. *Res Chem. Intermed.* **2017**, *43*, 6875-6888.
http://dx.doi.org/10.1007/s11164-017-3026-0;
29. Kulkarni, P. P.; Kadam, A. J.; Desai, U. V.; Mane, R. B.; Wadgaonkar, P. P. *J. Chem. Res.* **2000***,* 184-185.
http://dx.doi.org/10.3184/030823400103166887.;
30. Bragd, P. L.; Besemer, A. C.; van Bekkum, H. *Carbohydr. Pol.* ***2002****, 49*, 397-406.
https://doi.org/10.1016/S0144-8617(01)00344-7
31. Frigerio, M.; Santagostino, M.; Sputore, S. *J. Org. Chem.* **1999**, *64*, 4537-4538.
http://dx.doi.org/10.1021/jo9824596.
32. (a) Lei, Z.; Yang, Y.; Bai, X. *Adv. Synth. Catal.* **2006**, *348*, 877-880.
https://doi.org/10.1002/adsc.200505356
33. Hajipour; A. R.; Mallakpour, S. E.; Adibi, H. *Phosphorus, Sulfur, Silicon Relat. Elem.* **2000**, *167*(1), 71-79.
http://dx.doi.org/10.1080/10426500008082388;
34. Hajipour; A. R.; Mallakpour; S. E.; Adibi, H. *Chem. Lett.* 2000, 29, 460-461.
https://doi.org/10.1246/cl.2000.460
35. Fetizon, M.; Golfier, M. *C. R. Acad. Sc. Paris (C)* **1968**, *267*, 900-903.
36. Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2002**, *102*, 2523-2584.

 ©AUTHOR(S)

http://dx.doi.org/10.1021/cr010003+;
37.Dess, D. E.; Martin, J. C. *J. Org. Chem.***1983**, *48*, 4155-4156.
http://dx.doi.org/10.1021/jo00170a070;
38. Dess, D. E.; Wilson, S. R.; Martin, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 2488-2495.
http://dx.doi.org/10.1021/ja00059a052.
39. Yadav, J. S.; Reddy, B. V. S.; Basak, A. K.; Venkat Narsaiah, *Tetrahedron* **2004**, *60*, 2131-2135.
https://doi.org/10.1016/j.tet.2003.12.056
40. Parlow, J. J.; Case, B. L.; South, M. S. *Tetrahedron* **1999**, *55*, 6785-6796.
https://doi.org/10.1016/S0040-4020(99)00342-7
41. Zhdankin, V. V. *Chem. Rev.* **2008,** *108,* 5299-5358.
http://dx.doi.org/10.1021/cr800332c;
42. Ladziata, U.; Zhdankin, V. V. *Arkivoc* **2006**, *9,* 26-58.
https://doi.org/10.3998/ark.5550190.0007.903
43. Maiti, A.; Yadav, J. S. *Synth. Commun.* **2001**, *31*, 1499-1506.
http://dx.doi.org/10.1081/SCC-100104061;
44. Nicolaou, K. C.; Zhong, Y.L.; Baran, P. S. *J. Am. Chem. Soc.* **2000**, *122*, 7596-7597.
http://dx.doi.org/10.1021/ja001825b;
45. Nicolaou, K. C.; Montagnon, T.; Baran, P. S.; Zhong, Y. L. *J. Am. Chem. Soc.* **2002**, *124*, 2245-2258.
http://dx.doi.org/10.1021/ja012127+;

This paper is an open access article distributed under the terms of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/)