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Lanthanoid-metal-mediated reaction of acylphosphonates: evidence for the formation of an acyllanthanoid complex

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Abstract

The reactions of diethyl acylphosphonates (**1a–e**) with Yb and Sm were examined. Reactivities of Yb to **1a–e** are different from those of Li and Na. Typically, ethyl benzoylphosphonate (**1a**) reacts with Yb metal in tetrahydrofuran–hexamethylphosphoramide to afford diethyl 1,2-diphenyl-2-oxoethyl phosphate (**2a**) and diethyl 1-(diethyl-phosphoryloxy)-1-phenylmethylphosphonate (**3a**). The formations of **2a** and **3a** were explained best by the formation of acylytterbium complexes.

Keywords: Ytterbium; Samarium; Acylphosphonate; Phosphorus

1. Introduction

Many acyl metal complexes are known on transition metals, such as palladium, cobalt, nickel and zirconium [1]. Acyl alkali metal complexes such as acyllithium have been extensively studied [2–4]. An alkyllithium reacts with carbon monoxide to generate an acyllithium, which is unstable and readily reacts with electrophiles or dimerizes to α-ketol. Our first attempts to synthesize an acylytterbium intermediate resulted in complex reaction. Phenylytterbium iodide reacted with carbon monoxide (CO) to give various products [5]. In the lanthanoid chemistry, there are several reports on the reaction via an acyl complex. Kagan and coworkers [6] reported the reactions of acyl chlorides with SmI_2 to afford α-diketones and α-ketols via an acylsamarium species. Evans and coworkers [7] reported the reaction of lanthanoid complexes with CO to afford the corresponding acyllanthanoid complexes which were isolated. Marks and coworkers [8] reported the activation of CO with lanthanoid complexes to afford a carben-like acyl complex [8].

Recently, we reported that the reaction of lanthanoid metals (Yb and Sm) with diaryl ketones such as benzophenone produced the corresponding dianion complexes that react easily with a variety of electrophiles such as ketones, esters, epoxides, nitriles, carbon dioxide and acetylenes producing adducts [9]. We have succeeded in isolating and structurally characterizing the ytterbium(II)-benzophenone dianion complex [10]. However, aliphatic ketones have a lower reactivity and do not react with ytterbium under similar conditions. Our second attempts to synthesize acyllanthanoid complexes are directed towards the hetroatom-bound carbonyl compounds. These activated carbonyl compounds are reactive to lanthanoid metals and react with various electrophiles. In particular, aroyl trimethylsilanes react with ytterbium to give the homocoupling products, diarylacetylenes, selectively [11]. Furthermore, the cross-coupling reaction of ketones with acylsilanes gave the deoxygenatively acylated adducts of ketones [12]. On this basis, we were interested in the reactivities of acyl phosphorous compounds with lanthanoid metals. In this paper we wish to report the

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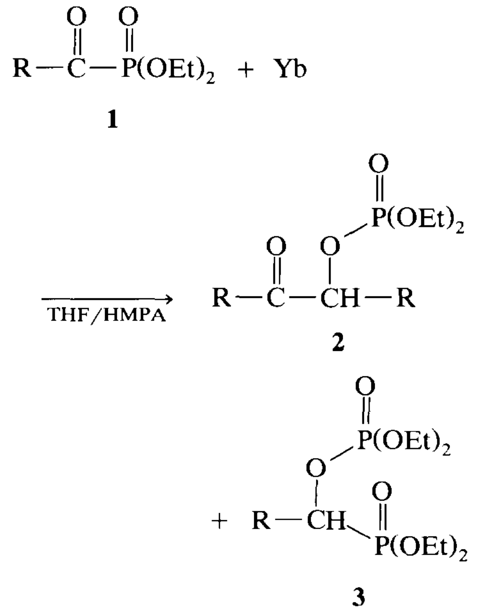
results of the reaction of acylphophonates with ytterbium metal:

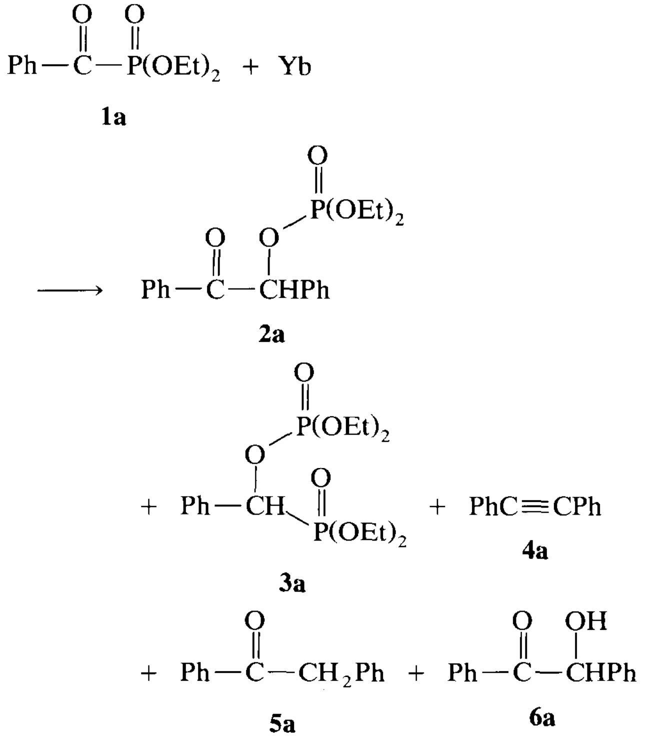


(1)

2. Results and discussion

2.1. Reactions of acylphosphonates with Yb metal

The reaction of diethyl benzoylphosphonate (**1a**) with lanthanoid metals such as Yb was examined. The reaction of **1a** with an equimolar amount of Yb was carried out at −10°C for 30 min in a tetrahydrofuran (THF)–hexamethylphosphoramide (HMPA) (4 : 1) solution. The reaction gave diethyl 1,2-diphenyl-2-oxoethyl phosphate (**2a**), diethyl 1-(diethylphosphoryloxy)-1-phenylmethylphosphonate (**3a**), diphenylacetylene (**4a**), benzyl phenyl ketone (**5a**) and benzoin (**6a**) with 36, 29, 3, 11 and 12% yields respectively:



(2)

Of these products generated, the ketone **5a** and benzoin (**6a**) were also formed in the reaction of benzoyl chloride with SmX_2 (X = I etc.) as depicted by Kagan and coworkers [6]. We have also succeeded the selective synthesis of symmetric acetylene such as **4a** using acylsilanes and Yb [11]. Our attention is focused on the production of **2a** and **3a**. In the lanthanoid chemistry, the formation of **2a** and **3a** from acylphosphonate **1a** is quite new to the best of our knowledge. It is note worthy that the unique phosphorous compounds **2a**

Table 1
Reaction of benzoylphosphonate (**1a**) with rare earth metals [a]

Entry	Metal (equivalent)	Temperature (°C)	Time (h)	Yield [b] (%) of the following products				
				2a	**3a**	**4a**	**5a**	**6a**
1	Yb (1)	Room temperature	1.5	—	—	9	34	24
2	Yb (1)	−10	0.5	36	29	3	11	12
3	Yb (1)	−35	0.5	38	61	—	—	—
4	Yb (1)	−35 [c]	0.5	27	12	—	—	—
5	Yb (1)	−35	24	14	6	11	20	26
6	Yb (0.5)	−35	0.5	32	30	—	—	—
7	Sm (1)	0	1	—	14	—	—	—
8	Li (1)	Room temperature [d]	3	11	18	—	—	—

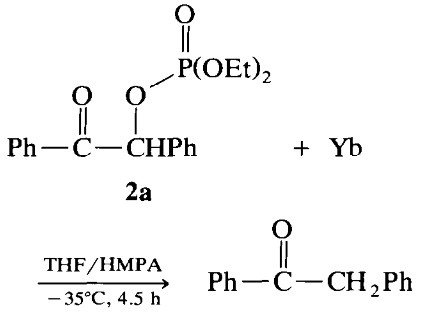
[a] **1a**, 1 mmol; THF, 4 ml; HMPA, 1 ml.

[b] Obtained by GLC.

[c] THF (4 ml).

[d] Diethyl 1,2-diphenyl-2-diethylphosphorylvinyl phosphate (**8**) and diethyl 1,2-diphenyl-2-oxoethylphosphonate (**9**) were also obtained in 40 and 9% yields respectively.

and **3a** are selectively formed by using rare earth metals such as Yb. Therefore the optimization of the reaction conditions for the yields of **2a** and **3a** was studied. The results for the ytterbium-mediated reaction of **1a** under the various conditions are summarized in Table 1. In the reaction at room temperature for 1.5 h, neither **2a** nor **3a** was formed and **4a**, **5a** and **6a** were generated preferentially (entry 1 in Table 1). Of the reaction conditions tested, the reaction at −35°C for 30 min in a THF–HMPA solution gave the best result to afford **2a** and **3a** with 38 and 61% yields respectively, without the formation of **4a**, **5a** and **6a**. The yields of **2a** and **3a** increased and the yields of **4a**, **5a** and **6a** decreased with decreasing temperature (entries 1–3 in Table 1). In the case of THF as the sole solvent, the yields of **2a** and **3a** decreased (entry 4 in Table 1). Therefore the reaction requires donor solvents such as HMPA. Equimolar amounts of Yb metal and **1a** are required for the reaction (entry 3 vs. entry 6 in Table 1). The reaction for the longer reaction time resulted in the lower selectivity (entry 5 in Table 1). A pronounced relationship on the selectivities of **2a** and **3a** was not observed in each case. The control experiment revealed that **5a** was formed from the further reaction of **2a** with Yb metal:

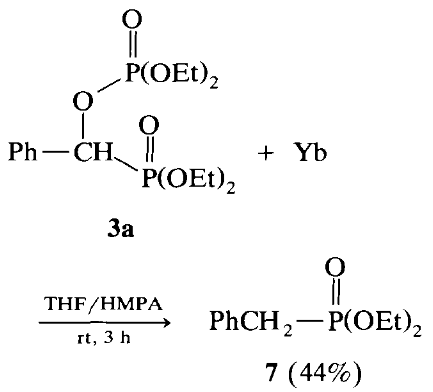


$$\mathrm{Ph{-}C(=O){-}CH(Ph){-}O{-}P(=O)(OEt)_2 + Yb \xrightarrow[-35°C,\ 4.5\ h]{THF/HMPA} Ph{-}C(=O){-}CH_2Ph} \quad (3)$$

2a

5a (75%)

The reaction of **3a** with Yb metal gave diethyl benzylphosphonate (**7**) with a 44% yield:



$$\mathrm{Ph{-}CH(OP(=O)(OEt)_2){-}P(=O)(OEt)_2 + Yb \xrightarrow[rt,\ 3\ h]{THF/HMPA} PhCH_2{-}P(=O)(OEt)_2} \quad (4)$$

3a

7 (44%)

In marked contrast to the above reactions, the use of lithium metal in lieu of Yb metal gave **2a** and **3a** with low yields. From the reaction products, we also detected diethyl 1,2-diphenyl-2-diethylphosphorylvinyl phosphate (**8**) and diethyl 1,2-diphenyl-2-oxoethylphosphonate (**9**) with 40 and 9% yields respectively (entry 8 in Table 1). It is known that the reaction of **1a** with sodium amalgam (Na–Hg) gives diethyl α-hydroxybenzylphosphonate (**10**) [13]. Nevertheless the reaction of **1a** with Yb did not afford **8–10**. Thus the reactivities of Yb to **1a** are different from those of Li and Na.

The representative results for the ytterbium-mediated reaction of various diethyl acylphosphonates (**1a–e**) using the optimized conditions are summarized in Table 2. The reactions of both aromatic and aliphatic acylphosphonates with Yb afforded the corresponding adducts **2a–e** and **3a–e** with moderate yields. Aliphatic acylphosphonates (**1d–e**) have low reactivity to Yb; therefore a higher reaction temperature than in the case of aroylphosphonates was needed (entries 4 and 5 in Table 2). Generally, the yield of **3** is superior to that of **2** under these reaction conditions. In the reaction of acyl chloride with SmI_2, a carbene-like intermediate was depicted by Kagan and coworkers [6]. In order to trap the carbene intermediate, the reaction of diethyl heptenoyl phosphonate (**1e**) having an olefinic moiety was attempted. However, no adduct except for **2e** and **3e** was obtained in the reaction (entry 5 in Table 2).

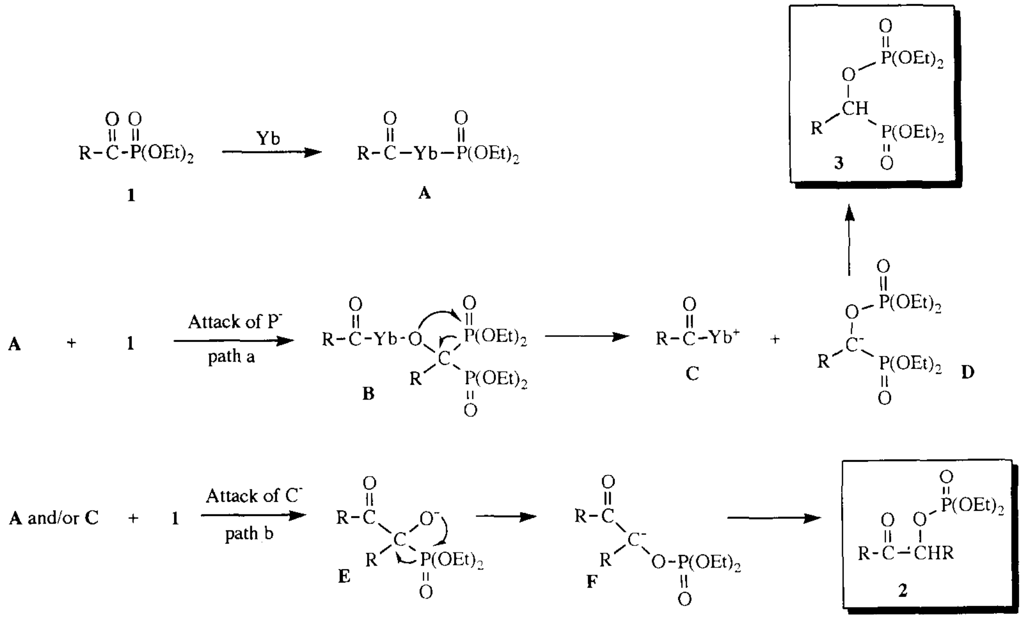
2.2. Reaction mechanism

The possible reaction mechanism of diethyl acylphosphonates with Yb is shown in Scheme 1. The reaction starts by two-electron transfer from Yb metal to the weak C–P bond to afford a phosphoryl acylytterbium(*II*) intermediate **A** [14]. Thus obtained phosphoryl acylytterbium (**A**) reacts with **1** via the following paths a and b. The reaction pathways a and b are the route to the adducts **3** and **2** respectively. In path a, a phosphoryl anion of **A** attacks the carbonyl group of **1** to give an intermediate **B**. Thus the formed **B** would decompose to **D** and an acylytterbium **C** [15]. Phosphoryloxy phosphonate **3** is formed from **D** by quenching with aqueous HCl. Thus the formed **C** and/or acyl carbanions of **A** react with **1** to afford **E** shown in path b. **E** rearranges to **F** which gives α-ketophosphate (**2**).

Table 2
Reaction of diethyl acylphosphonates [a]

Entry	Phosphonate **1** R	Product; yield [b] (%)	
		2	**3**
1	Ph (**1a**)	**2a**; 17(38)	**3a**; 38(61)
2	*p*-Tol (**1b**)	**2b**; 16	**3b**; 31
3	*p*-Anisyl (**1c**)	**2c**; 21	**3c**; 30
4	*n*-Hexyl [c] (**1d**)	**2d**; 10	**3d**; 49
5	CH_2=$CH(CH_2)_4$ [c] (**1e**)	**2e**; 21	**3e**; 28

[a] **1**, 1 mmol; THF, 4 ml; HMPA, 1 ml; −35°C; 30 min.
[b] Isolated yield (obtained by GC).
[c] Room temperature; 12 h.



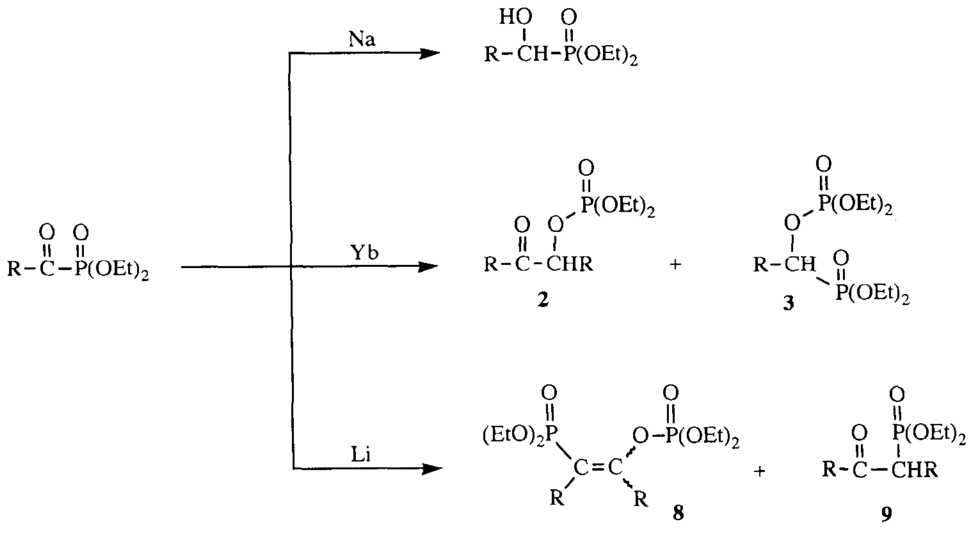
Scheme 1.

In the case of the reaction of **1a** with lithium metal, different products **8** and **9** were generated. We can explain the formation of **8** and **9** by considering the formation of lithium enolate {R(LiO)C=CR-[(PO(OEt)$_2$]}, which generates by the reductive coupling of **1** followed by the elimination of (EtO)$_2$PO$_2$Li.

3. Conclusions

Ytterbium metal undergoes the reaction of acylphosphonate **1a–e** under the mild reaction conditions. The reactivities of Yb to **1** are different from those of Li and Na, as summarized in Scheme 2. Although the redox potential of Yb metal (YbYb^{3+} = -2.27 eV) is lower than those of Li and Na metal (LiLi$^+$ = -3.04 eV; NaNa$^+$ = -2.71 eV), the unique reactivity of Yb may be explained in terms of its strong oxophilicity. That is, lanthanoid metals stabilize the acyl complex, and therefore these reaction of acylphosphonate with Yb metal could proceed via the acylytterbium complex.

In these reactions, the generation of an acylytterbium intermediate was suggested. Unique organic synthesis using the combination of acylphosphonates and Yb metal could be expected.



Scheme 2.

4. Experimental section

4.1. Materials and method

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-270 spectrometer and a Bruker AM-X-400 wb spectrometer in $CDCl_3$ solution unless otherwise noted, and chemical shifts are reported in parts per million on the scale from internal tetramethylsilane. IR spectra were recorded on a Perkin–Elmer 1600 Fourier transform IR and a Hitachi 260-30 spectrophotometer. Analytical evaluation by gas–liquid chromatography (GLC) was done using a analytical column of 1.1 m length and 3.2 mm inside diameter packed with 2% silicone OV-17 on Chromosorb W. Mass spectra were obtained on a Shimadzu gas chromatography (GC)–mass spectroscopy (MS) QP-1000 apparatus using a glass column of 1 m length and 3.2 mm inside diameter packed with 2% silicone OV-17 on Chromosorb W. Elemental analyses were performed on a Yanagimoto MT-2 CHN corder.

THF was distilled from sodium benzophenone ketyl under argon prior to use. HMPA was dried over calcium hydride, distilled under reduced pressure (boiling point, 66°C at 2 Torr), and stored over activated 4A molecular seives under argon. Samarium and ytterbium (40-mesh, Shiga Rare Metal) metals are commercial grade. Diethyl acylphosphonates were prepared by the procedure given in the literature [13].

4.2. General procedure for the reaction of diethyl acylphosphonates with ytterbium metal

In a two-necked 30 ml round-bottomed flask, ytterbium metal (173 mg, 1 mmol) was placed. The flask was flame dried under reduced pressure. To the flask, THF (4 ml), HMPA (1 ml), methyl iodide (3 μl) were successively added at room temperature. Diethyl acylphosphonate (1 mmol) was added at the indicated temperature. The mixture was stirred at the same temperature for several hours. After the reaction, water was added to the reaction mixture. The mixture was extracted with ether (20 ml × 3). The combined ethereal extracts were washed with brine (20 ml), dried over $MgSO_4$ and filtrated. After the removal of solvents, the residue was purified by MPLC (SiO_2, hexane–ethyl acetate–ethanol) to obtain the corresponding adducts **2a**–**e** and **3a**–**e**. The yields of each adduct were calculated by GLC analysis. These results are listed in Tables 1 and 2.

Diethyl 1,2-diphenyl-2-oxoethyl phosphate (2a): pale-yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.14 (dt, $J = 7.0$ Hz, $J_{H-P} = 1.1$ Hz, 3H), 1.32 (dt, $J = 7.0$ Hz, $J_{H-P} = 1.1$ Hz, 3H), 3.91 (dq, $J = 7.0$ Hz, $J_{H-P} = 7.2$ Hz, 2H), 4.18 (dq, $J = 7.0$ Hz, $J_{H-P} = 7.2$ Hz 2H), 6.64 (d, $J_{H-P} = 8.1$ Hz, 1H), 7.27–7.98 (m, 10H). ^{13}C NMR ($CDCl_3$): δ 15.8 (d, $J_{C-P} = 7.4$ Hz), 16.1 (d, $J_{C-P} = 7.4$ Hz), 64.0 (d, $J_{C-P} = 6.1$ Hz), 64.3 (d, $J_{C-P} = 6.1$ Hz), 80.1 (d, $J_{C-P} = 4.9$ Hz), 128.1, 128.6, 129.0, 129.1, 129.3, 133.5, 134.3, 134.9, 193.6 (d, $J_{C-P} = 4.8$ Hz). IR (neat): ν(C=O) 1702, ν(P=O) 1246, ν(P–O–C) 1037, ν(P–O–C) 984 cm^{-1}. MS: m/z 348 (M^+), 243 ($M^+ -$ PhCO), 105 ($PhCO^+$). Anal. Found: C, 62.08; H, 6.06. $C_{18}H_{21}O_5P$ Calc.: C, 62.06; H, 6.07%.

Diethyl 1-(diethylphosphoryloxy)-1-phenylmethylphosphonate (3a): colorless oil. ^{1}H NMR ($CDCl_3$): δ 1.12 (t, $J = 7.0$ Hz, 3H), 1.22 (t, $J = 7.1$ Hz, 3H), 1.27 (t, $J = 7.1$ Hz, 3H), 1.29 (t, $J = 7.1$ Hz, 3H), 3.85–4.18 (m, 8H), 5.55 (dd, $J_{H-P} = 10.6$ and 13.4 Hz, 1H), 7.35–7.40 (m, 3H), 7.51–7.53 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 15.8 (d, $J_{C-P} = 7.3$ Hz), 15.9 (d, $J_{C-P} = 7.4$ Hz), 16.3 (d, $J_{C-P} = 5.7$ Hz), 16.4 (d, $J_{C-P} = 5.7$ Hz), 63.4 (d, $J_{C-P} = 2.8$ Hz), 63.3 (d, $J_{C-P} = 3.1$ Hz), 63.9 (d, $J_{C-P} = 5.7$ Hz), 64.1 (d, $J_{C-P} = 5.6$ Hz), 74.7 (dd, $J_{C-P} = 6.8$ and 172.1 Hz), 128.0 (d, $J_{C-P} = 6.1$ Hz), 128.42, 128.43, 129.0 (d, $J_{C-P} = 2.4$ Hz). IR (neat): ν(P=O) 1259, ν(P–O–C) 1024 cm^{-1}. MS: m/z 380 (M^+), 243 ($M^+ - (EtO)_2PO$); Anal. Found: C, 46.93; H, 7.14. $C_{15}H_{26}O_7P_2$ Calc.: C, 47.37; H, 6.89%.

Diethyl 1,2-di(*p*-tolyl)-2-oxoethyl phosphate (2b): colorless oil. ^{1}H NMR ($CDCl_3$): δ 1.14 (dt, $J = 7.1$ Hz, $J_{H-P} = 0.8$ Hz, 3H), 1.32 (dt, $J = 7.1$ Hz, $J_{H-P} = 0.8$ Hz, 3H), 2.29 (s, 3H), 2.33 (s, 3H), 3.88–3.95 (m, 2H), 4.16–4.24 (m, 2H), 6.62 (d, $J_{H-P} = 7.9$ Hz, 1H), 7.15 (d, $J = 8.1$ Hz, 2H), 7.17 (d, $J = 8.3$ Hz, 2H), 7.38 (d, $J = 8.1$ Hz, 2H), 7.83 (d, $J = 8.3$ Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 15.8 (d, $J_{C-P} = 7.2$ Hz), 16.0 (d, $J_{C-P} = 7.2$ Hz), 21.2, 21.6, 63.9 (d, $J_{C-P} = 6.2$ Hz), 64.3 (d, $J_{C-P} = 5.9$ Hz), 79.9 (d, $J_{C-P} = 4.8$ Hz), 128.1, 129.1, 129.3, 129.8, 131.7, 132.1 (d, $J_{C-P} = 5.0$ Hz), 139.3, 144.5, 193.1 (d, $J_{C-P} = 4.4$ Hz). IR (neat): ν(C=O) 1697, ν(P = O) 1265, ν(P–O–C) 1036 cm^{-1}. MS: m/z 376 (M^+), 361 ($M^+ -$ OEt), 257 ($M^+ - MeC_6H_4CO$), 119 ($MeC_6H_4CO^+$). Anal. Found: C, 63.81; H, 6.68. $C_{20}H_{25}O_5P$ Calc.: C, 63.82; H, 6.69%.

Diethyl 1-(diethylphosphoryloxy)-1-(*p*-tolyl)methylphosphonate (3b): colorless oil. ^{1}H NMR ($CDCl_3$): δ 1.13 (t, $J = 7.0$ Hz, 3H), 1.21–1.31 (m, 9 H), 2.35 (s, 3H), 3.85–4.18 (m, 8H), 5.54 (dd, $J_{H-P} = 10.6$ and 13.1 Hz, 1H), 7.18 (d, $J = 7.9$ Hz, 2H), 7.41 (d, $J = 7.9$ Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 15.8 (d, $J_{C-P} = 7.1$ Hz), 16.0 (d, $J_{C-P} = 7.0$ Hz), 16.3 (d, $J_{C-P} = 5.7$ Hz), 16.4 (d, $J_{C-P} = 5.7$ Hz), 21.2, 63.4 (d, $J_{C-P} = 5.8$ Hz), 63.5 (d, $J_{C-P} = 5.7$ Hz), 63.9 (d, $J_{C-P} = 5.8$ Hz), 64.1 (d, $J_{C-P} = 5.7$ Hz), 74.7 (dd, $J_{C-P} = 7.0$ and 172.9 Hz), 128.0 (d, $J_{C-P} = 6.0$ Hz), 129.1, 130.7, 138.9 (d, $J_{C-P} = 2.6$ Hz). IR (neat): ν(P=O) 1261, ν(P–O–C) 1025 cm^{-1}. MS: m/z 394 (M^+), 257 ($M^+ - (EtO)_2PO$). Anal. Found: C, 48.77; H, 7.37. $C_{16}H_{28}O_7P_2$ Calc.: C, 48.73; H, 7.15%.

Diethyl 1,2-di(*p*-anisyl)-2-oxoethyl phosphate (2c): colorless oil. ^{1}H NMR (CDCl$_3$): δ 1.15 (dt, $J = 7.1$ Hz, $J_{H-P} = 1.0$ Hz, 3H), 1.32 (dt, $J = 7.1$ Hz, $J_{H-P} = 1.0$ Hz, 3H), 3.76 (s, 3H), 3.80 (s, 3H), 3.91 (m, 2H), 4.19 (m, 2H), 6.60 (d, $J_{H-P} = 7.9$ Hz, 1H), 6.86 (d, $J = 8.8$ Hz, 2H), 6.87 (d, $J = 8.8$ Hz, 2H), 7.42 (d, $J = 8.9$ Hz, 2H), 7.92 (d, $J = 8.9$ Hz, 2H). ^{13}C NMR (CDCl$_3$): δ 15.8 (d, $J_{C-P} = 7.1$ Hz), 16.0 (d, $J_{C-P} = 7.1$ Hz), 55.2, 55.4, 63.9 (d, $J_{C-P} = 6.0$ Hz), 64.2 (d, $J_{C-P} = 6.0$ Hz), 79.4 (d, $J_{C-P} = 4.8$ Hz), 113.9, 114.5, 127.1, 127.4, 129.7, 131.3, 160.3, 163.7, 191.9 (d, $J_{C-P} = 4.8$ Hz). IR (neat): ν(C=O) 1690, ν(P=O) 1260, ν(P–O–C) 1035 cm^{-1}. MS: m/z 408 (M$^+$), 363 (M$^+$ − OEt), 273 (M$^+$ − MeOC$_6$H$_4$CO), 135 (MeOC$_6$H$_4$CO$^+$). Anal. Found: C, 58.34; H, 6.27. $C_{20}H_{25}O_7P$ Calc.: C, 58.52; H, 6.17%.

Diethyl 1-(diethylphosphoryloxy)-1-(*p*-anisyl)methylphosphonate (3c): yellow oil. ^{1}H NMR (CDCl$_3$): δ 1.10–1.35 (m, 12H), 3.81 (s, 3H), 3.84–4.20 (m, 8H), 5.50 (dd, $J_{H-P} = 10.6$ and 12.9 Hz, 1H), 6.91 (d, $J = 8.9$ Hz, 2H), 7.47 (d, $J = 8.9$ Hz, 2H). ^{13}C NMR (CDCl$_3$): δ 15.8 (d, $J_{C-P} = 8.5$ Hz), 15.9 (d, $J_{C-P} = 8.5$ Hz), 16.3 (d, $J_{C-P} = 6.1$ Hz), 16.4 (d, $J_{C-P} = 7.3$ Hz), 55.3, 63.4 (d, $J_{C-P} = 6.1$ Hz), 63.8 (d, $J_{C-P} = 4.9$ Hz), 64.1 (d, $J_{C-P} = 6.1$ Hz), 74.4 (dd, $J_{C-P} = 7.1$ and 174.7 Hz), 113.9, 125.6, 129.7 (d, $J_{C-P} = 6.1$ Hz), 160.2 (d, $J_{C-P} = 2.4$ Hz). IR (neat): ν(P=O) 1256, ν(P–O–C) 1025 cm^{-1}. MS: m/z 410 (M$^+$), 273 (M$^+$ −(EtO)$_2$PO), 137 ((EtO)$_2$PO$^+$), 135 (CH$_3$C$_6$H$_4$CO$^+$). Anal. Found: C, 46.78; H, 6.86. $C_{16}H_{28}O_8P_2$ Calc.: C, 46.83; H, 6.87%.

Diethyl 8-oxo-7-tetradecanyl phosphate (2d): colorless oil. ^{1}H NMR (CDCl$_3$): δ 0.87 (t, $J = 6.5$ Hz, 3H), 0.89 (t, $J = 6.6$ Hz, 3H), 1.27–1.43 (m, 22H), 1.61–1.68 (m, 2H), 2.38 (t, $J = 7.5$ Hz, 2H), 4.10–4.19 (m, 4H), 5.28 (ddd, $J_{H-P} = 3.9$, $J = 8.6$ and 10.0 Hz, 1H). ^{13}C NMR (CDCl$_3$): δ 14.0, 16.4 (d, $J_{C-P} = 5.8$ Hz), 16.5 (d, $J_{C-P} = 5.7$ Hz), 22.5, 22.5, 25.0, 25.5, 25.7, 28.8, 29.3, 31.5 (d, $J_{C-P} = 9.9$ Hz), 34.2, 62.6 (d, $J_{C-P} = 5.7$ Hz), 62.7 (d, $J_{C-P} = 6.5$ Hz), 67.4 (d, $J_{C-P} = 167.2$ Hz), 172.8 (d, $J_{C-P} = 4.9$ Hz). IR (neat): ν(C=O) 1745, ν(P=O) 1255, ν(P–O–C) 1026 cm^{-1}. MS: m/z 364 (M$^+$), 113 (C$_6$H$_{13}$CO$^+$), 85 (C$_6$H$_{13}^+$). Anal. Found: C, 59.32; H, 10.23. $C_{18}H_{37}O_5P$ Calc.: C, 59.31; H, 10.23%.

Diethyl 1-(diethylphosphoryloxy)-*n*-heptylphosphonate (3d): yellow oil. ^{1}H NMR (CDCl$_3$): δ 0.88 (t, $J = 6.9$ Hz, 3H), 1.30–1.67 (m, 20H), 1.86–1.91 (m, 2H), 4.41–4.24 (m, 8H), 4.60–4.68 (m, 1H). ^{13}C NMR (CDCl$_3$): δ 14.1, 16.1 (d, $J_{C-P} = 5.1$ Hz), 16.46 (d, $J_{C-P} = 5.3$ Hz), 16.52 (d, $J_{C-P} = 5.1$ Hz), 22.6, 25.3 (d, $J_{C-P} = 10.5$ Hz), 28.9, 31.0 (brs), 31.6, 62.9 (brs), 64.0 (d, $J_{C-P} = 5.8$ Hz), 73.2 (dd, $J_{C-P} = 7.2$ and 169.6 Hz). IR (neat): ν(P=O) 1262, ν(P–O–C) 1026 cm^{-1}. MS: m/z 390 (M$^+$), 251 (M$^+$ −(EtO)$_2$PO). Anal. Found: C, 46.46; H, 8.80. $C_{15}H_{34}O_7P_2$ Calc.: C, 46.38; H, 8.82%.

Diethyl 8-oxo-1,13-tetradecadien-7-yl phosphate (2e): colorless oil. ^{1}H NMR (CDCl$_3$): δ 1.26–2.08 (m, 20H), 2.38 (t, $J = 7.4$ Hz, 2H), 4.13 (q, $J = 7.1$ Hz, 2H), 4.16 (q, $J = 7.1$ Hz, 2H), 4.93–5.03 (m, 4H), 5.27 (dt, $J = 9.3$ Hz, $J_{H-P} = 4.0$ Hz, 1H), 5.74–5.82 (m, 2H). IR (neat): ν(C=O) 1745, ν(P=O) 1255, ν(P–O–C) 1024 cm^{-1}. MS: m/z 152 (C$_6$H$_{11}$COC$_3$H$_6^+$), 111 (C$_6$H$_{11}$CO$^+$), 83 (C$_6$H$_{11}^+$), 55 (C$_4$H$_7^+$).

Diethyl 1-(diethylphosphoryloxy)-6-heptenylphosphonate (3e): yellow oil. ^{1}H NMR (CDCl$_3$): δ 1.33–2.08 (m, 20H), 4.10–4.24 (m, 8H), 4.61–4.64 (m, 1H), 4.92–5.02 (m, 2H), 5.73–5.88 (m, 1H). ^{13}C NMR (CDCl$_3$): δ 15.5 (d, $J_{C-P} = 2.4$ Hz), 15.6 (d, $J_{C-P} = 2.5$ Hz), 15.9 (d, $J_{C-P} = 6.1$ Hz), 16.0 (d, $J_{C-P} = 3.7$ Hz), 24.3 (d, $J_{C-P} = 11.0$ Hz), 27.9, 30.4, 33.0, 62.3 (d, $J_{C-P} = 8.3$ Hz), 63.5 (d, $J_{C-P} = 6.1$ Hz), 72.6 (dd, $J_{C-P} = 6.7$ and 170.3 Hz), 114.1, 138.0. IR (neat) ν(P=O) 1260, ν(P–O–C) 1027 cm^{-1}. MS: m/z 386 (M$^+$). Anal. Found: C, 46.15; H, 8.71. $C_{15}H_{32}O_7P_2$ calc.: C, 46.63; H, 8.34%.

4.3. Control reaction of 2a with Yb

Ytterbium metal (104 mg, 0.6 mmol) was placed in a two-necked 30 ml round-bottomed flask. The flask was flame dried under reduced pressure. To the flask, THF (1.4 ml), HMPA (0.6 ml), methyl iodide (3 μl) were successively added at room temperature. **2a** (0.211 g, 0.6 mmol) in THF (1 ml) solution was added at −35°C. The mixture was stirred at the same temperature for 4.5 h. Water was added to the reaction mixture. The mixture was extracted with ether (20 ml × 3). The combined extracts were washed with brine (20 ml), dried over MgSO$_4$ and filtrated. The crude ketone **5a** was obtained with a 75% yield. The yield of **5a** was calculated by GLC analysis.

4.4. Control reaction of 3a with Yb

As described above, the reaction of **3a** (87 mg, 0.23 mmol) with Yb (87 mg, 0.5 mmol) in THF (2 ml)–HMPA (0.5 ml) was carried out at room temperature for 3 h. The usual work-up followed by MPLC (SiO$_2$, hexane–ethyl acetate–ethanol) purification gave diethyl benzylphosphonate (**7**) with a 44% yield.

Diethyl benzylphosphonate (7): yellow oil. ^{1}H NMR (CDCl$_3$): δ 1.23 (t, $J = 7.0$ Hz, 6H), 3.15 (d, $J_{H-P} = 21.2$ Hz, 2H), 3.85–4.17 (m, 4H), 7.29 (s, 5H). MS: m/z 288 (M$^+$), 199 (M$^+$ − Et), 91 (PhCH$_2^+$).

4.5. Reaction of 1a with lithium metal

The reaction of **1a** (0.63 ml, 3 mmol) with Li (21 mg, 3 mmol) in THF (12 ml)–HMPA (3 ml) was carried out according to the general procedure described above. A mixture of **2a**, **3a**, diethyl 1,2-diphenyl-2-diethylphosphorylvinyl phosphate (**8**) and diethyl 1,2-diphenyl-2-oxoethylphosphonate (**9**) was obtained with 11, 18, 40 and 9% yields respectively.

Diethyl 1,2-diphenyl-2-diethylphosphorylvinyl phosphate (8): pale-yellow oil. ^{13}C NMR ($CDCl_3$): δ 15.6 (d, $J_{C-P} = 7.3$ Hz), 15.8 (d, $J_{C-P} = 7.3$ Hz), 62.0 (d, $J_{C-P} = 6.1$ Hz), 63.7 (d, $J_{C-P} = 6.2$ Hz), 127.3, 127.6, 128.0, 129.9, 134.2. IR (neat): ν(C=C) 1634, ν(P=O) 1257, ν(P–O–C) 1026, 968 cm^{-1}. MS: m/z 286 ($M^+ - P(O)(OEt)_2$), 194 ($PhC{=}C(O)Ph^+$), 178 ($PhC{=}CPh^+$); Anal. Found: C, 56.65; H, 6.60. $C_{22}H_{30}O_7P_2$ calc.: C, 56.41; H, 6.45%.

Diethyl 1,2-diphenyl-2-oxo-ethylphosphonate (9): pale-yellow oil. ^{1}H NMR ($CDCl_3$); δ 1.32 (dt, $J = 7.0$ Hz, $J_{H-P} = 1.1$ Hz, 6H), 4.03 (dq, $J = 7.0$ Hz, $J_{H-P} = 7.2$ Hz, 2H), 4.11 (dq, $J = 7.0$ Hz, $J_{H-P} = 7.2$ Hz, 2H), 5.34 (d, $J_{H-P} = 22.2$ Hz, 1H), 7.26–8.01 (m, 10H). ^{13}C NMR ($CDCl_3$): δ 16.3 ($J_{C-P} = 5.1$ Hz), 54.5 ($J_{C-P} = 38.0$ Hz), 62.1 ($J_{C-P} = 6.1$ Hz), 63.2 ($J_{C-P} = 4.9$ Hz), 127.8, 128.6, 128.7, 128.9, 129.9, 133.2, 136.6, 143.5, 193.5 ($J_{C-P} = 4.9$ Hz). IR (neat): ν(C=O) 1682, ν(P=O) 1250, ν(P–O–C) 1024, 966 cm^{-1}. MS: m/z 332 (M^+), 105 ($PhCO^+$).

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