Efficient Approach to 4-Oxo-2-alkenylphosphonates via Regiospecific Friedel−Crafts Acylation

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Treatment of allylic and vinylic phosphonates with excess LiHMDS, followed by addition of chlorotrimethylsilane, afforded α- and γ- silylated allylic phosphonate mixtures. Without separation, these mixtures underwent the Friedel−Crafts reaction and base-promoted isomerization to give 4-oxo-2-alkenylphosphonates, which can serve as building blocks for the construction of polyethylenic chains.

Introduction

The construction of polyethylenic structures, exhibited in natural compounds such as retinoids and cartenoids, by carbon chain elongation of a carbonyl compound has been of great interest over the years.[1] γ-Phosphonocrotonates[2] and protected phosphonoaldehydes[3] appeared to be very useful reagents under the Horner−Wadsworth−Emmons olefination conditions, whereas the preparation and the application of 4-oxo-2-alkenylphosphonates are less known.[4] Recently, we synthesized 4-oxo-2-alkenylphosphonate by γ-acylation of allylic phosphonates utilizing isoxazoline as an intermediate.[5] In the course of our study, it was found that regiospecific acylation at the terminus of an allylic phosphonate containing various substituents remains to be solved, because the substituents are inclined to lessen site selectivity in nucleophilic reactions of allylic phosphonates.[6]

As a result of our efforts to seek a more efficient method, we disclose here the absolute regiospecific synthesis of 4-oxo-2-alkenylphosphonates from variously substituted allylic and vinylic phosphonates, using double bond migration[7] of vinylic phosphonate into allylic phosphonate and the aliphatic Friedel−Crafts acylation of silanes.[8]

Results and Discussion

Our attempts to prepare 4-oxo-2-alkenylphosphonates from easily obtainable starting materials were concentrated on selective γ-acylation of allylphosphonates, and the Friedel−Crafts reaction seemed to be the most appropriate solution. As shown in Scheme 1, α- and γ-silylated allylphosphonates afford respectively 4-oxo-2-alkenylphosphonates (**i**) and 4-oxo-1-alkenylphosphonates (**ii**), which can be easily isomerized to **i**, through electrophilic addition of allylsilanes or vinylsilanes, and a subsequent desilylation process.[9]

In this concept, silylation was carried out by treatment of phosphonates **1** and **2** with excess LiHMDS in THF at −78 °C followed by addition of chlorotrimethylsilane. Not only allylic phosphonates,[10] but also vinylic phosphonates,[11] which were equivalent to allylic phosphonates in the presence of base, were silylated as shown in Scheme 2. It is noteworthy that the employment of vinylic phosphonates expands the range of starting allylic phosphonates. The results of silylation are summarized in Table 1. As expected, silylated allylic phosphonates were obtained as mixtures of α- and γ-silylated products in good yields. The ratios of α-addition products **4** are increased, according to the bulkiness of the γ-substituents. Fortunately, the double bonds of all γ-silylated phosphonates were completely migrated to afford γ-silylated allylic phosphonates **3**. This migration is attributed to different anion-stabilizing power between the phosphonate and silane group.

To diversify silylated allylic phosphonates, α-alkylation of **3** was carried out as shown in Scheme 3. The lithiated derivative of **3a** underwent nucleophilic reaction toward ethyl iodide to give α-alkylated phosphonate **3a′** in a good yield of 90%.

Without any effort to separate α- and γ-silylated mixtures, the resultant phosphonates were acylated by reaction with acyl chloride in the presence of aluminum chloride, followed by treatment of triethylamine to pro vide 4-oxo-2-alkenylphosphonates in excellent yields (Table 2).

As depicted in Scheme 4, the initial products after acylation were mixtures of 4-oxo-2-alkenylphosphonates

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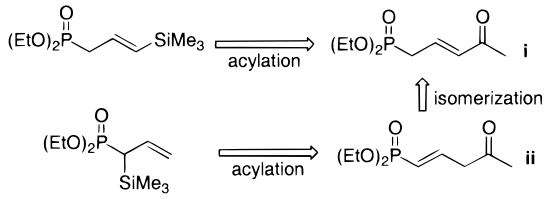
Scheme 1



Scheme 2

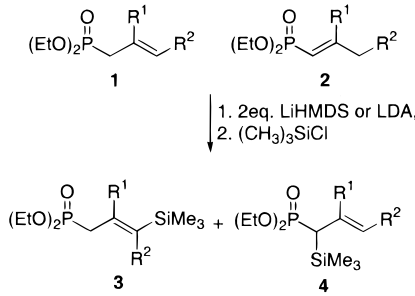
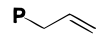
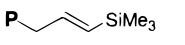
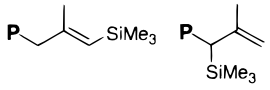
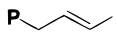
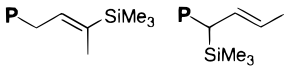
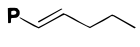
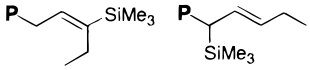
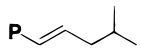
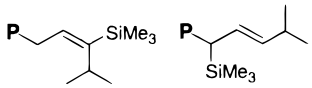
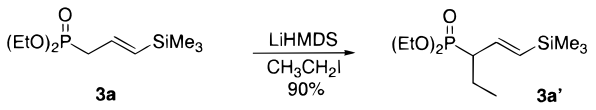


Table 1. Silation of Allylic and Vinylic Phosphonates

starting material **1**, **2**[a]	silylated products **3**, **4**[a]	ratio (γ/α)[b]	yield (%)[c]
 **1a**	 **3a**	–	96
 **1b**	 **3b** **4b**	3:1	84
 **1c**	 **3c** **4c**	2:1	97
 **2a**	 **3d** **4d**	1:9	85
 **2b**	 **3e** **4e**	1:9.6	82

[a] **P** = P(O)(OEt)$_2$. [b] The ratio was determined by ^{1}H NMR analysis. [c] Yield of isolated product.

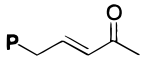
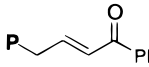
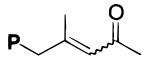
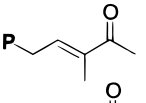
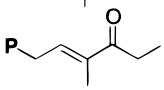
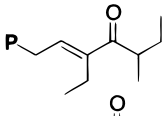
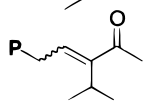
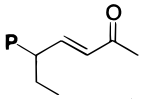
Scheme 3



(**6**) and 4-oxo-1-alkenylphosphonates (**5**), and **5** underwent double bond migration by promotion of triethylamine to give **6**, which is identical to the product from **3**. Only when benzoyl chloride was used as an electrophile (**6b**), the yield of acylation was somewhat low, which seems to be due to the fact that the phenyl group competes with an allyl- or vinylsilane in the Friedel–Crafts reaction. Most products were typically in only the *E* configuration except **6c** and **6g**.[12] The product **6c**

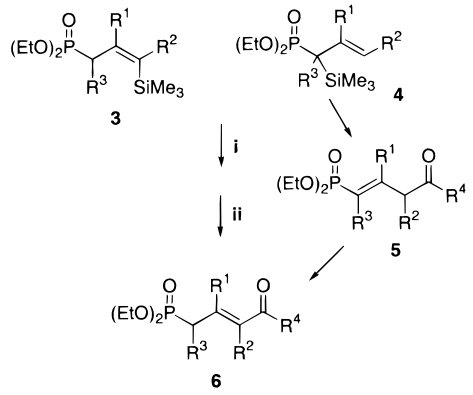
(12) The configurations and the ratios of (*E*)- and (*Z*)-olefins were determined by NOE experiments and ^{1}H NMR analyses. These are described precisely in the Supporting Information.

Table 2. Friedel–Crafts Acylation of α- and γ-Silylated Products and Isomerization

silylated products **3**, **4**[a]	acyl chloride	product **6**[a]		yield (%)[b]
3a	CH_3COCl		**6a**	89
3a	PhCOCl		**6b**	67
3b, 4b	CH_3COCl		**6c**	95[c]
3c, 4c	CH_3COCl		**6d**	98
3c, 4c	CH_3CH_2COCl		**6e**	93
3d, 4d	$CH_3CH_2CH(CH_3)COCl$		**6f**	96
3e, 4e	CH_3COCl		**6g**	97[d]
3a'	CH_3COCl		**6h**	94

[a] **P** = P(O)(OEt)$_2$. [b] Yield of isolated product. [c] The purified product was a mixture of *E*/*Z* isomers in a ratio of 1:1.5. [d] The purified product was a mixture of *E*/*Z* isomers in a ratio of 4.5:1.

Scheme 4



i. $AlCl_3$ / R^4COCl, CH_2Cl_2, 0°C. ii. Et_3N, CH_2Cl_2, 0°C.

bearing a methyl group at the 2-position was obtained as a mixture of *E* and *Z* isomers in a ratio of 1:1.5. The bulky isopropyl group at the 3-position of **6g** led to formation of (*Z*)-olefin as a minority in a ratio of 4.5:1, whereas, for **6f** with a less bulky ethyl group at the same position, the *Z* isomer was not observed at all.

Conclusion

In conclusion, 4-oxo-2-alkenylphosphonates could be obtained from allylic and vinylic phosphonates, which are easily accessible starting materials, using Friedel–Crafts acylation of silanes in good yields. This synthetic route to 4-oxo-2-alkenylphosphonates is so short that the overall yields are high. Also, this result might enlarge the range of regiospecific acylation reactions of various other allyl moieties.

Experimental Section

General Procedures. All reactions were conducted under an atmosphere of N_2 in oven-dried glassware with magnetic stirring. THF was dried over and distilled from sodium metal with benzophenone as the indicator. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS, residual $CHCl_3$, or solvent as an internal standard. The starting materials were synthesized as described in the literature with minor modification.

General Procedure for Silylation of Allylic and Vinylic Phosphonates. To a stirred solution of allylic or vinylic phosphonate (2.0 mmol) in dry THF (10 mL) under N_2 at −78 °C was added the proper base (LiHMDS, 4.0 mL of a 1.0 M solution in THF for allylic phosphonates, 4.0 mmol; LDA, 2.0 mL of a 2.0 M solution in heptane/THF/ethylbenzene for vinylic phosphonates, 4.0 mmol) dropwise. Stirring the mixture for about 1 h was followed by addition of chlorotrimethylsilane (0.244 g, 2.2 mmol). The cooling bath was removed, and the mixture was stirred at rt for 1 h. An aqueous NH_4Cl solution (2 mL) was added, and the resulting solution was extracted with diethyl ether. The combined organic extracts were washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was subjected to silica gel column chromatography (ethyl acetate/hexane, 3:2) to give the silylated allylic phosphonate **3** and/or **4** as a colorless oil.

Diethyl (*E*)-3-Trimethylsilyl-2-propenylphosphonate (3a). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.00 (s, 9H), 1.24 (t, J = 7.1 Hz, 6H), 2.62 (dd, J = 6.2, 21.9 Hz, 2H), 3.95−4.08 (m, 4H), 5.77−5.94 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = −1.5, 16.3 (d, J = 6.0 Hz), 34.7 (d, J = 135.5 Hz), 61.8 (d, J = 6.7 Hz), 134.4 (d, J = 11.0 Hz), 136.8 (d, J = 12.2 Hz).

Alkylation of γ-Silylated Allylphosphonate. To a stirred solution of diethyl 3-trimethylsilyl-2-propenylphosphonate (**3a**; 0.225 g, 0.90 mmol) in anhydrous THF (4 mL) under N_2 at −78 °C was added LiHMDS (0.90 mL of a 1.0 M solution in THF, 0.90 mmol) dropwise. Stirring the mixture for about 1 h was followed by addition of iodoethane (0.12 mL, 1.5 mmol). The cooling bath was removed, and the mixture was allowed to reach rt. After 1 h an aqueous NH_4Cl solution (1 mL) was added, and the resulting solution was extracted with diethyl ether. The combined organic extracts were washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography on a silica gel column using a mixture of ethyl acetate and hexane (1:1) as eluent to give the alkylated product **3a′** (0.226 g, 90%) as a colorless oil.

(*E*)-1-Ethyl-3-trimethylsilyl-2-propenylphosphonate (3a′). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.03 (s, 9H), 0.88 (t, J = 7.4 Hz, 3H), 1.22−1.28 (m, 6H), 1.51−1.64 (m, 1H), 1.76−1.89 (m, 1H), 2.31−2.43 (m, 1H), 3.98−4.09 (m, 4H), 5.78−5.80 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = −1.3, 12.3 (d, J = 15.6 Hz), 16.4 (dd, J = 3.4, 6.0 Hz), 21.3 (d, J = 4.9 Hz), 47.6 (d, J = 134.5 Hz), 61.8 (dd, J = 7.0, 42.5 Hz), 135.8 (d, J = 11.7 Hz), 140.2 (d, J = 9.5 Hz).

General Procedure for Friedel−Crafts Acylation of Silylated Allylic Phosphonates. To a stirred suspension of aluminum chloride (0.202 g, 1.5 mmol) in anhydrous dichloromethane (5 mL) under N_2 at 0 °C was added the proper acyl chloride (1.5 mmol). The solution was stirred until it was clear, after which **3** and/or **4** (1.0 mmol) in anhydrous dichloromethane (3 mL) was added, and the mixture was stirred for 1 h at the same temperature. An aqueous NH_4Cl solution (2 mL) was added, and the resulting solution was extracted with diethyl ether. The combined organic extracts were washed with water, dried over $MgSO_4$, and concentrated in vacuo. The residue was dissolved in dichloromethane (3 mL) and treated with triethylamine (0.14 mL, 1.0 mmol), and the solution was stirred for about 30 min at rt. After removal of triethylamine and solvent under vacuum, the crude product was purified by chromatography on a silica gel column (ethyl acetate/ethanol, 10:1) to give a colorless oil (**6**).

Diethyl (*E*)-4-Oxo-2-pentenylphosphonate (6a). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24 (t, J = 7.1 Hz, 6H), 2.18 (s, 3H), 2.68 (ddd, J = 23.1, 7.9, 1.0 Hz, 2H), 3.98−4.09 (m, 4H), 6.10 (dd, J = 16.0, 4.7 Hz, 1H), 6.57−6.70 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.2 (d, J = 5.9 Hz), 26.8, 30.7 (d, J = 137.6 Hz), 62.2 (d, J = 6.7 Hz), 134.9 (d, J = 13.1 Hz), 136.4 (d, J = 11.1 Hz), 197.4 (d, J = 2.9 Hz). HRMS: m/z (M^+) calcd for $C_9H_{17}O_4P$ 220.0864, found 220.0873.

Diethyl (*E*)-4-Oxo-4-phenyl-2-butenylphosphonate (6b). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25−1.32 (m, 6H), 2.84 (dd, J = 6.8, 22.9 Hz, 2H), 4.03−4.14 (m, 4H), 6.84−7.04 (m, 2H), 7.35−7.56 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.4 (d, J = 5.9 Hz), 31.0 (d, J = 137.2 Hz), 62.3 (d, J = 6.8 Hz), 128.5, 129.9, 130.1, 132.9, 137.5, 189.8. HRMS: m/z (M^+) calcd for $C_{14}H_{19}O_4P$ 282.1021, found 282.1026.

Diethyl 2-Methyl-4-oxo-2-pentenylphosphonate (6c). A mixture of *E* and *Z* stereoisomers was obtained in a ratio of 1:1.5 determined by NOE experiment and ^{1}H NMR analysis. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.23−1.31 (several peaks, 6H), 2.00 (dd, J = 3.8, 1.4 Hz, 3 × 17/27H), 2.14 (s, 3 × 17/27H), 2.15 (s, 3 × 10/27H), 2.22 (dd, J = 3.5, 1.4 Hz, 3 × 10/27H), 2.62 (d, J = 23.6 Hz, 2 × 10/27H), 3.43 (d, J = 25.2 Hz, 2 × 17/27H), 4.01−4.11 (m, 4H), 6.16 (br d, J = 4.8 Hz, 1H). NOE: 6.16 (2.00, 3.0%; 2.22, 0.1%; 2.62, 2.2%; 3.43, 0.9%). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.2 (d, J = 6.3 Hz), 16.3 (d, J = 6.0 Hz), 20.4 (d, J = 2.8 Hz), 26.2 (d, J = 2.1 Hz), 26.3, 31.1 (d, J = 131.5 Hz), 31.7, 31.8, 38.6 (d, J = 133.9 Hz), 61.9 (d, J = 6.5 Hz), 62.1 (d, J = 6.7 Hz), 125.9 (d, J = 11.3 Hz), 127.3 (d, J = 11.5 Hz), 147.8 (d, J = 11.2 Hz), 197.9, 198.0. HRMS: m/z (M^+) calcd for $C_{10}H_{19}O_4P$ 234.1021, found 234.1030.

Diethyl (*E*)-3-Methyl-4-oxo-2-pentenylphosphonate (6d). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24 (t, J = 7.1 Hz, 6H), 1.73 (d, J = 5.0 Hz, 3H), 2.24 (s, 3H), 2.72 (dd, J = 7.9, 23.0 Hz, 2H), 3.99−4.09 (m, 4H), 6.54 (q, J = 8.2 Hz, 1H). NOE: 1.73 (2.72, 5.5%; 6.54, 1.8%). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.2 (d, J = 2.3 Hz), 16.3 (d, J = 5.9 Hz), 25.5, 27.8 (d, J = 137.9 Hz), 62.2 (d, J = 6.8 Hz), 131.3 (d, J = 11.3 Hz), 140.9 (d, J = 13.3 Hz), 198.9 (d, J = 2.9 Hz). HRMS: m/z (M^+) calcd for $C_{10}H_{19}O_4P$ 234.1021, found 234.1014.

Diethyl (*E*)-3-Methyl-4-oxo-2-hexenylphosphonate (6e). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.02 (t, J = 7.2 Hz, 3H), 1.25 (t, J = 7.0 Hz, 6H), 1.76 (d, J = 3.9 Hz, 3H), 2.63 (q, J = 7.2 Hz, 2H), 2.73 (dd, J = 7.9, 23.1 Hz, 2H), 4.00−4.10 (m, 4H), 6.54 (q, J = 8.0 Hz, 1H). NOE: 1.76 (2.73, 4.0%; 6.54, 1.4%). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.5, 11.5 (d, J = 2.2 Hz), 16.3 (d, J = 5.9 Hz), 27.7 (d, J = 138.2 Hz), 30.5, 62.2 (d, J = 6.8 Hz), 129.6 (d, J = 11.2 Hz), 140.3 (d, J = 13.3 Hz), 201.6 (d, J = 2.9 Hz). HRMS: m/z (M^+) calcd for $C_{11}H_{21}O_4P$ 248.1177, found 248.1166.

Diethyl (*E*)-3-Ethyl-5-methyl-4-oxo-2-heptenylphosphonate (6f). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81 (t, J = 7.4 Hz, 3H), 0.91 (t, J = 7.5 Hz, 3H), 1.02 (d, J = 6.8 Hz, 3H), 1.29 (t, J = 7.0 Hz, 6H), 1.26−1.40 (m, 1H), 1.58−1.72 (m, 1H), 2.31 (q, J = 7.5 Hz, 2H), 2.77 (dd, J = 8.0, 23.2 Hz, 2H), 3.08 (sextet, J = 6.7 Hz, 1H), 4.04−4.14 (m, 4H), 6.49 (q, J = 7.5 Hz, 1H). NOE: 2.31 (2.77, 6.3%; 6.49, 1.7%). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.7, 13.4, 16.4 (d, J = 5.9 Hz), 17.1, 19.3, 27.5 (d, J = 137.8 Hz), 40.9, 62.2 (d, J = 6.7 Hz), 128.8 (d, J = 10.7 Hz), 146.3 (d, J = 13.2 Hz), 205.2. HRMS: m/z (M^+) calcd for $C_{14}H_{27}O_4P$ 290.1647, found 290.1635.

Diethyl 3-Isopropyl-4-oxo-2-pentenylphosphonate (6g). A mixture of *E* and *Z* stereoisomers was obtained in a ratio of 4.5:1 determined by NOE experiment and ^{1}H NMR analysis. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (d, J = 6.8 Hz, 2/11 × 3H), 1.15 (d, J = 7.0 Hz, 9/11 × 3H), 1.31 (t, J = 7.1 Hz, 6H), 2.27 (s, 3H), 2.68−2.88 (m, 1H), 2.80 (dd, J = 8.1, 23.3 Hz, 2H), 4.01−4.16 (m, 4H), 6.40 (q, J = 7.6 Hz, 1H). NOE: 1.15 (2.80, 19.2%; 6.40, 3.3%). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.4 (d, J = 5.9 Hz), 20.7 (d, J = 1.9 Hz), 27.2 (d, J = 138.5 Hz), 27.6 (d, J = 15.5 Hz), 62.2 (d, J = 6.8 Hz), 129.8, 150.2, 199.9. HRMS: m/z (M^+) calcd for $C_{12}H_{23}O_4P$ 262.1334, found 262.1331.

Diethyl (*E*)-1-Ethyl-4-oxo-2-pentenylphosphonate (6h). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, J = 7.4 Hz, 3H), 1.25 (dt, J = 2.8, 7.0 Hz, 6H), 1.58−1.70 (m, 1H), 1.87−1.98 (m, 1H), 2.22 (s, 3H), 2.42−2.59 (m, 1H), 3.96−4.09 (m, 4H), 6.11 (dd, J = 16.0, 4.5 Hz, 1H), 6.51−6.61 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.4 (d, J = 15.2 Hz), 16.4 (d, J = 5.3 Hz), 21.4 (d, J = 5.4 Hz), 27.0, 43.8 (d, J = 136.4 Hz), 62.2 (dd, J

= 12.9, 6.9 Hz), 134.2 (d, J = 12.5 Hz), 142.2 (d, J = 9.2 Hz), 197.6. HRMS: m/z (M^+) calcd for $C_{11}H_{21}O_4P$ 248.1177, found 248.1166.

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Supporting Information Available: Copies of ^1H and ^{13}C NMR and HRMS spectra of all compounds **6** and NOE spectra of **6d**, **6e**, **6f**, and **6g** are described in the Experimental Section. This material is available free of charge via the Internet at http://pubs.acs.org.

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