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Regiocontrolled Reactions of Allylphosphonates: Syntheses of 1-[(3-Methoxycarbonyl)-allyl]-vinylphosphonates and 3-Methoxycarbonyl-1,3-dienylphosphonates

Yanchang Shen and Guo-Fang Jiang

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Academia Sinica, 354 Fenglin Lu, Shanghai 200032, China

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ABSTRACT: *'Regiocontrolled syntheses of 3-methoxycarbonyl-1,3-dienylphosphonates and 1-[(3-methoxycarbonyl)-allyl]vinylphosphonates by using different conditions are described.* © 2002 Wiley Periodicals, Inc. Heteroatom Chem 13:373–376, 2002; Published online in Wiley Interscience (www.interscience.wiley.com). DOI 10.1002/hc.10050

INTRODUCTION

The regioselectivity of the application of allylphosphonates in organic synthesis is important, and the regioselectivity of silylation of lithiated allylphosphonates involves the propenyl skeleton. Usually, mixtures of α- and γ-silylated products are obtained. The ratios of α-addition to γ-addition are increased, according to an increase in the bulkiness of the γ-substituents [1,2].

RESULTS AND DISCUSSION

Recently, we reported a new olefination methodology and its application to the regiospecific and stereoselective syntheses of (1*E*,3*Z*)-3-cyanobuta-2,3-dienylphosphonates [3]. In our continuing investigations to explore the new synthetic methodologies for the syntheses of unsaturated phosphonates [4–8], we report here regiocontrolled syntheses of 3-methoxycarbonyl-1,3-dienylphosphonates or 1-[(3-methoxycarbonyl)-allyl]vinylphosphonates by using different conditions (see Scheme 1).

The results are summarized in Table 1.

The catalytic reaction mechanism (speculative) is shown in Scheme 2.

The phosphoryl-stabilized carbanion **5**, generated from the corresponding phosphonate **1** and potassium *tert*-butoxide, reacts with *N*-tosylsulfonyl imines **2** to give the adducts **6**. After hydrogen transfer, **6** affords **7**. Elimination of *p*-toluenesulfonamide anion from **7a** gives 1-[(3-methoxycarbonyl)-allyl]-vinylphosphonates **3**, while from **7b**, 3-methoxycarbonyl-1,3-dienylphosphonates **4**. The *p*-toluenesulfonamide anion abstracts a proton from **1** to give *p*-toluenesulfonamide and regenerates the carbanion **5**. Thus the catalytic cycle is completed.

The regiocontrolled results, depending on the reaction temperature, cannot be rationalized satisfactorily by using the concepts of the kinetic and thermodynamic control of the selectivity, and the detailed mechanism is being pursued.

The configurations of the compounds **3** were ascertained on the basis of their $J_{H,P}$ and $J_{H,H}$ values. It has been reported [9] that $^3J_{cis\text{-}H,P} = 10$–$30$ Hz,

Correspondence to: Yanchang Shen; e-mail: shenyc@pub.sioc.ac.cn.

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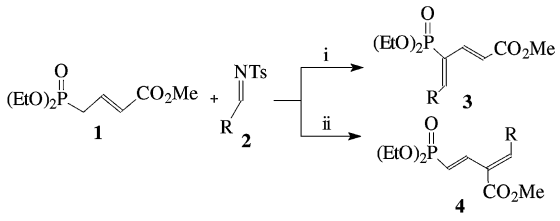


Conditions: (i) DMF, Cat. ^{t}BuOK(20 mol%), 130ºC, 5 min.
(ii) DMF, Cat. ^{t}BuOK(20 mol%), 0ºC, 5 min.

SCHEME 1

$^3J_{\text{trans-K,P}} = 30–50$ Hz. The $J_{H,H}$ of each **3** is equal to ~16 Hz and $^3J_{H,P}$ is equal to ~20 Hz. Thus, the configuration of **3** is ascertained as *E* in the vinyl phosphonate moiety and *E* in the double bond of the side chain. Similarly, the configurations of the compounds **4** were ascertained on the basis of their $J_{H,H}$ and NOSEY spectra. The $J_{H,H}$ is ~17.6, and the NOSEY spectrum shows that the vinyl H at the 2-position is *cis* with respect to the aryl group. Thus, the configuration is ascertained as 1*E*,3*Z* in each **4**.

In summary, this regiocontrolled base-catalyzed olefination methodology of allylic phosphonates is very convenient; the reaction time is short (5 min), the addition can be controlled either to the α or γ position, and the double bond formed is exclusively *E*. The title compounds are useful intermediates in organic syntheses, and are not easily available with existing synthetic methods.

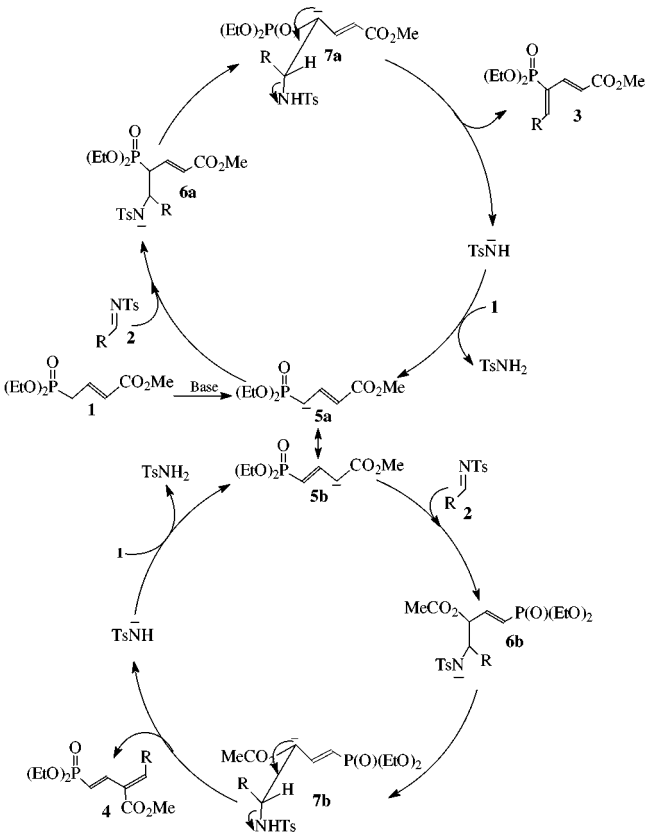
EXPERIMENTAL

The IR spectra of liquid products were determined as films on a Digilab FTS-20E spectrometer. ^{1}H NMR spectra were recorded on a Bruker AM-300 (300 MHz) spectrometer (values in ppm from $SiMe_4$, in $CDCl_3$; *J* values are given in Hz). Mass spectra were measured on a Finnigan GC-MS-4021 mass spectrometer.

TABLE 1 Preparations of 1-[(3-Methoxycarbonyl)-allyl]-vinylphosphonates **3** and 3-Methoxycarbonyl-1,3-dienylphosphonates **4**

Entry	*R*	*Method*[a]	*Yield (%)*[b]	***3:4***[c]
1	4-$CH_3OC_6H_4$	A	83	70:30
2	4-$CH_3OC_6H_4$	B	71	14:86
3	4-$CH_3C_6H_4$	A	77	82:18
4	4-$CH_3C_6H_4$	B	80	27:73
5	C_6H_5	A	79	73:27
6	C_6H_5	B	73	15:85
7	4-$C_2H_5C_6H_4$	A	80	85:15
8	4-$C_2H_5C_6H_4$	B	75	10:90

[a]Method A: DMF, Cat. ^{t}BuOK (20 mol%), 130°C, 5 min; Method B: DMF, Cat. ^{t}BuOK (20 mol%), 0°C, 5 min.
[b]Isolated yields.
[c]Isolated ratio.



SCHEME 2

*Diethyl-3-ethoxycarbonylallylphosphonate (**1**)*

It was prepared according to the known procedure [10].

*Diethyl-2-(aryl)-1-[(3-methoxycarbonyl)-prop-2-enyl]vinylphosphonate (**3a–d**)*

Method A: A mixture of diethyl-3-ethoxycarbonylallylphosphonate (**1**; 0.24 g, 1 mmol), *N*-tosyl aryl imines **2** (1 mmol), potassium *tert*-butoxide (25 mg [95%], 0.2 mmol), and DMF (10 ml) in a capped vessel under nitrogen was heated and stirred at 130°C for 5 min. Thin-layer chromatography showed that the reaction had been completed. The reaction mixture was filtered through a short column of silica gel to remove the precipitate, which was identified as $TsNH_2$. The filtrate was concentrated and chromatographed on silica gel, and eluted with petroleum ether (60–90°C)–ethyl acetate (2:1) to give the major product **3** and then the minor products **4**.

*Diethyl-2-(4-methoxyphenyl)-1-[(3-methoxycarbonyl)-prop-2-enyl]vinylphosphonate (**3a**)*

Oil. IR (neat): $\upsilon = 2990$, 1720, 1620, 1600, 1280, 1250, 1050, 1030, 970 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): $\delta = 7.78$ (d, $J = 21.6$ Hz, 1H), 7.72 (dd, $J = 21.4$, 16.3 Hz, 1H). 7.35 (d, $J = 8.7$ Hz, 2H), 6.93 (d, $J = 8.7$ Hz, 2H), 6.48 (d, $J = 16.1$ Hz, 1H), 4.15–4.06 (m, 4H), 3.82 (s, 3H), 3.75 (s, 3H), 1.32 (t, $J = 7.0$ Hz, 6H). MS: m/z (%) = 354 (M^+, 100), 322 (83), 294 (57), 217 (33), 201 (21), 185 (15). Anal Calc for $C_{17}H_{23}O_6P$ (354.33): C, 57.62; H, 6.54. Found: C, 57.89; H, 6.66.

*Diethyl-2-(4-methylphenyl)-1-[(3-methoxycarbonyl)-prop-2-enyl]vinylphosphonate (**3b**)*

Oil. IR (neat): $\upsilon = 2990$, 1720, 1620, 1610, 1250, 1020, 970 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): $\delta = 7.83$ (d, $J = 22.4$ Hz, 1H), 7.71 (dd, $J = 22.7$, 16.2 Hz, 1H). 7.29 (d, $J = 8.2$ Hz, 2H), 7.22 (d, $J = 8.0$ Hz, 2H), 6.50 (d, $J = 16.2$ Hz, 1H), 4.18–4.08 (m, 4H), 3.75 (s, 3H), 2.37 (s, 3H), 1.33 (t, $J = 7.0$ Hz, 6H). MS: m/z (%) = 338 (M^+, 100), 306 (78), 278 (42), 201 (55), 169 (17), 141 (14). Anal Calc for $C_{17}H_{23}O_5P$ (338.34): C, 60.35; H, 6.85. Found: C, 60.53; H, 7.08.

*Diethyl-2-(phenyl)-1-[(3-methoxycarbonyl)-prop-2-enyl]vinylphosphonate (**3c**)*

Oil. IR (neat): $\upsilon = 2990$, 1720, 1620, 1280, 1250, 1050, 970 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): $\delta = 7.90$ (d, $J = 21.0$ Hz, 1H), 7.75 (dd, $J = 22.5$, 16.2 Hz, 1H). 7.49–7.39 (m, 5H), 6.56 (d, $J = 16.2$ Hz), 1H), 4.30–4.00 (m, 4H), 3.79 (s, 3H), 1.37 (t, $J = 6.9$ Hz, 6H). MS: m/z (%) = 324 (M^+, 100), 292 (72), 264 (31), 209 (11), 187 (64), 155 (16). Anal Calc for $C_{16}H_{21}O_5P$ (324.31): C, 59.26; H, 6.53. Found: C, 59.45; H, 6.63.

*Diethyl-2-(4-ethylphenyl)-1-[(3-methoxycarbonyl)-prop-2-enyl]vinylphosphonate (**3d**)*

Oil. IR (neat): $\upsilon = 2980$, 1720, 1620, 1610, 1280, 1250, 1050, 1020, 970 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): $\delta = 7.86$ (d, $J = 22.2$ Hz, 1H), 7.75 (dd, $J = 22.9$, 16.2 Hz, 1H). 7.34 (d, $J = 8.2$ Hz, 2H), 7.23 (d, $J = 8.6$ Hz, 2H), 6.53 (d, $J = 16.2$ Hz, 1H), 4.20–4.10 (m, 4H), 3.78 (s, 3H), 2.69 (q, $J = 7.6$ Hz, 2H), 1.35 (t, $J = 7.0$ Hz, 6H), 1.26 (t, $J = 7.6$ Hz, 3H). MS: m/z (%) = 352 (M^+, 100), 320 (99), 292 (82), 264 (25), 237 (43), 215 (77), 183 (29), 155 (16). Anal Calc for $C_{18}H_{25}O_5P$ (352.36): C, 61.36; H, 7.15. Found: C, 60.89; H, 7.36.

*Diethyl-4-(4-aryl)-3-(methoxycarbonyl)-but-1,3-dienylphosphonate (**4a–d**)*

Method B: The procedure is similar to the method A but the temperature was kept at 0°C.

*Diethyl-4-(4-methoxyphenyl)-3-(methoxycarbonyl)-but-1,3-dienylphosphonate (**4a**)*

Oil. IR (neat): $\upsilon = 2980$, 1720, 1600, 1260, 1050, 1030, 970 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): $\delta = 7.79$ (d, $J = 2.9$ Hz, 1H), 7.43 (dd, $J = 23.7$, 17.6 Hz, 1H). 7.35 (d, $J = 8.7$ Hz, 2H), 6.91 (d, $J = 8.7$ Hz, 2H), 6.57 (dd, $J = 20.6$, 17.6 Hz, 1H), 4.13–4.03 (m, 4H), 3.81 (s, 6H), 1.31 (t, $J = 7.1$ Hz, 6H). MS: m/z (%) = 354 (M^+, 51), 322 (17), 294 (6), 216 (100), 185 (48), 158 (14), 115 (10). Anal Calc for $C_{17}H_{23}O_6P$ (354.33): C, 57.62; H, 6.54. Found: C, 57.63; H, 6.72.

*Diethyl-4-(4-methylphenyl)-3-(methoxycarbonyl)-but-1,3-dienylphosphonate (**4b**)*

Oil. IR (neat): $\upsilon = 2980$, 1720, 1610, 1250, 1030, 970 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): $\delta = 7.82$ (d, $J = 3.1$ Hz, 1H), 7.41 (dd, $J = 24.4$, 17.6 Hz, 1H). 7.28 (d, $J = 8.0$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 6.57 (dd, $J = 20.6$, 17.6 Hz, 1H), 4.13–4.03 (m, 4H), 3.83 (s, 3H), 2.35 (s, 3H), 1.30 (t, $J = 7.1$ Hz, 6H). MS: m/z (%) = 338 (M^+, 100), 306 (11), 278 (6), 200 (20), 169 (26), 141 (11), 115 (8). Anal Calc for $C_{17}H_{23}O_5P$ (338.34): C, 60.35; H, 6.85. Found: C, 60.50; H, 7.08.

*Diethyl-4-phenyl-3-(methoxycarbonyl)-but-1,3-dienylphosphonate (**4c**)*

Oil. IR (neat): $\upsilon = 2980$, 1720, 1620, 1250, 1220, 1030, 970 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): $\delta = 7.86$ (d, $J = 3.0$Hz, 1H), 7.41 (dd, $J = 21.0$, 17.6 Hz, 1H). 7.40–7.37 (m, 5H), 6.60 (dd, $J = 19.0$, 17.7 Hz), 1H), 4.14–4.05 (m, 4H), 3.87 (s, 3H), 1.32 (t, $J = 7.1$ Hz, 6H). MS: m/z (%) = 324 (M^+, 100), 292 (7), 264 (8), 209 (4), 187 (15), 155 (15). Anal Calc for $C_{16}H_{21}O_5P$ (324.31): C, 59.26; H, 6.53. Found: C, 59.31; H, 6.70.

*Diethyl-4-(4-ethylphenyl)-3-(methoxycarbonyl)-but-1,3-dienylphosphonate (**4d**)*

Oil. IR (neat): $\upsilon = 2980$, 1720, 1610, 1250, 1220, 1050, 1030, 960 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): $\delta = 7.84$ (d, $J = 3.0$ Hz, 1H), 7.43 (dd, $J = 21.0$, 17.6 Hz, 1H). 7.31 (d, $J = 8.2$ Hz, 2H), 7.23 (d, $J = 8.2$ Hz, 2H), 6.58 (dd, $J = 19.1$, 17.6 Hz, 1H), 4.14–4.04 (m, 4H), 3.84 (s, 3H), 2.66 (q, $J = 7.6$ Hz, 2H), 1.31 (t, $J = 7.0$ Hz, 6H), 1.23 (t, $J = 7.6$ Hz, 3H). MS: m/z (%) = 352 (M^+, 100), 320 (23), 292 (9), 214 (79), 183 (52), 155 (21), 111 (17). HRMS Calc for $C_{18}H_{25}O_5P$: 352.1440. Found: 352.1453.

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