

**Dimethyl (2-Oxo-4-methyl-3-pentenyl)phosphonate as a Precursor of  $\alpha,\alpha'$ -Dienones. Short Syntheses of ( $\pm$ )- $\alpha$ -Atlantone and ( $\pm$ )-*ar*-Turmerone**

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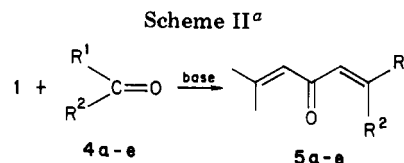
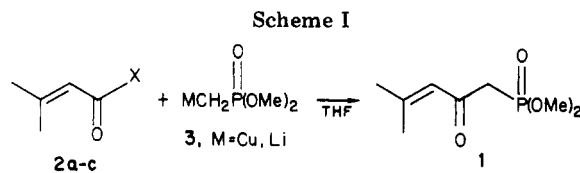
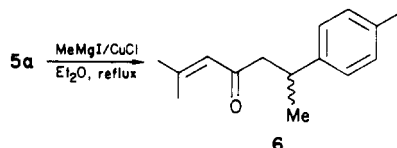
The reactions of phosphonate carbanions with carbonyl compounds<sup>1</sup> to form olefins have become among the most important methods in organic synthesis. Because of the versatility of the technique, various kinds of phosphonates have been developed<sup>2</sup> including  $\beta$ -keto phosphonates<sup>3</sup> which were often used for the synthesis of naturally occurring compounds.<sup>4</sup> While a few reports<sup>5</sup> about the synthesis of  $\gamma,\delta$ -unsaturated- $\beta$ -keto phosphonates have appeared recently, their synthetic utility has not been studied. We report in this paper a simple synthesis of dimethyl (2-oxo-4-methyl-3-pentenyl)phosphonate (1) as a precursor of  $\alpha,\alpha'$ -dienones and short syntheses of ( $\pm$ )- $\alpha$ -atlantone and ( $\pm$ )-*ar*-turmerone using this phosphonate.

The phosphonate 1 was prepared from the reaction of 3,3-dimethylacrylic acid derivatives 2a-c with (dimethylphosphono)methanide 3 in 23-60% yields (Scheme I). The combination of the copper reagent 3 (M = Cu)<sup>6</sup> and senecyl chloride (2a) gave the best yield of 1. On the other hand, the reactions of the lithium reagent 3 (M = Li)<sup>7</sup> with the ethyl ester 2b or the imidazolide 2c both resulted in poor yields as shown in Table I.

The carbanion of 1 was readily generated by the action of sodium hydride in 1,2-dimethoxyethane (DME) or sodium ethoxide in ethanol, respectively, and was reacted with carbonyl compounds 4a-e to afford  $\alpha,\alpha'$ -dienones 5a-e in moderate yields via the Horner-Emmons reaction (Scheme II). The results are summarized in Table II.

In these reactions, the use of sodium hydride and DME gave better yields of dienones. Only the *E* isomers were obtained from the aldehydes, and predominantly the *E* isomers were obtained from the ketones. Unfortunately, styrene oxide did not react with the carbanion 1 in spite of prolonged reaction times.

The phosphonate 1 and dienones 5 were expected to be the versatile intermediates for simple terpenoids because of the presence of 2-methyl-1-propenyl groups in the molecules. When 1-methyl-4-acetyl-1-cyclohexene (4e) was employed as a carbonyl compound in the reaction of 1, ( $\pm$ )- $\alpha$ -atlantone (5e), an important odor constituent of the oils of various *Cedrus* species, was easily obtained. Dienone 5a was also converted to ( $\pm$ )-*ar*-turmerone (6),



<sup>a</sup> 4a, R<sup>1</sup> = *p*-MeC<sub>6</sub>H<sub>4</sub>; R<sup>2</sup> = H. 4b, R<sup>1</sup> = C<sub>6</sub>H<sub>5</sub>; R<sup>2</sup> = H.  
4c, R<sup>1</sup> = Me<sub>2</sub>CH; R<sup>2</sup> = H. 4d, R<sup>1</sup> = Et; R<sup>2</sup> = Me. 4e,  
R<sup>1</sup> = Me-C<sub>6</sub>H<sub>4</sub>-; R<sup>2</sup> = Me.

Table I. Preparation of Phosphonate 1

	X	M	reactn temp., °C	yield, <sup>a</sup> %
2a	Cl	Cu <sup>b</sup>	-50 to -35	60
		Li	-76	c
2b	OEt	Li	-76	44
2c		Li	-76	23

<sup>a</sup> Isolated yields. <sup>b</sup> Generated from dimethyl  $\alpha$ -lithiomethane-phosphonate and copper(I) iodide. <sup>c</sup> Because of impurity 1 could not be isolated.

chief component of the essential oil from the rhizomes of *Curcuma Longa* Linn, in 98% crude yield by the addition of methylmagnesium iodide in the presence of copper(I) chloride to 5a. These syntheses represent a short and convenient route to the synthetic materials which exhibit spectral data in agreement with the previously published data.<sup>8</sup>

### Experimental Section

All reactions were carried out under a nitrogen atmosphere. Melting points and boiling points were uncorrected. <sup>1</sup>H NMR spectra were taken in CCl<sub>4</sub> (internal Me<sub>4</sub>Si) on a JEOL JNNC-60HL. Mass spectra were obtained from a JEOL JMS-01SG-2 spectrometer on-line to a JEOL JEC-6 spectrum computer. IR spectra were recorded on a JASCO IRA-1 spectrometer.

**Dimethyl (2-Oxo-4-methyl-3-pentenyl)phosphonate (1).** To a solution of dimethyl methanephosphonate (11.16 g, 90 mmol) in 90 mL of THF was added dropwise a *n*-butyllithium in hexane solution (66.3 mL, 108 mmol) at -76 °C. After stirring for 30 min, the temperature of the mixture was raised to -40 °C and copper(I) iodide (17.16 g, 90 mmol) was added in one portion. Keeping temperature below -35 °C, senecyl chloride (2a) (10.68 g, 90 mmol) was added dropwise and the mixture was stirred for 1 h. After standing overnight at room temperature and the addition of dichloromethane, the resulting precipitate was removed. The filtrate was concentrated and the residue was diluted with dichloromethane again. This solution was washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent and distillation gave the phosphonate 1 (11.09 g, 60% yield) as a colorless liquid. bp 113-118 °C (1 mmHg); IR 1680 (C=O) 1610 (C=C) 1250 (P=O) cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  1.94 (s, 3 H, (CH<sub>3</sub>)<sub>2</sub>C=CHCO, methyl trans to carbonyl), 2.18 (s, 3 H, (CH<sub>3</sub>)<sub>2</sub>C=CHCO, methyl cis to carbonyl), 3.05 (d, 2 H, P(O)CH<sub>2</sub>CO, *J*<sub>HP</sub> = 11.23 Hz), 6.21 (m, 1 H, vinyl proton); MS calcd for C<sub>8</sub>H<sub>15</sub>O<sub>4</sub>P, 206.07189 (found, 206.07201). Anal. Calcd for C<sub>8</sub>H<sub>15</sub>O<sub>4</sub>P: C, 46.60; H, 7.33. Found: C, 46.68; H, 7.45.

**Synthesis of  $\alpha,\alpha'$ -Dienones 5a-e. (*E*)-1-(4-Methylphenyl)-3-oxo-5-methyl-1,4-hexadiene (5a).** To a suspension of sodium hydride (60% in oil, 0.194 g, 4.83 mmol) in 2 mL of DME was added dropwise the phosphonate 1 (1.00 g, 4.83 mmol) in 2 mL of DME. After the evolution of hydrogen ceased, *p*-

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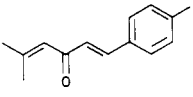
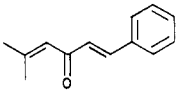
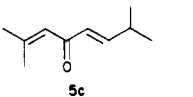
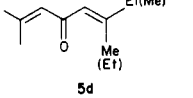
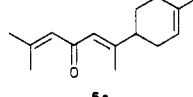
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Table II.  $\alpha,\alpha'$ -Dienones 5a-e from the Reactions of 1 and Carbonyl Compounds 4a-e

carbonyl compound	product	base/solvent <sup>a</sup>	reactn temp, °C	yield, <sup>b</sup> %	config <sup>c</sup>
4a		NaH/DME EtONa/EtOH	70 78	54 40	E
4b		NaH/DME EtONa/EtOH	70 78	69 46	E
4c		NaH/DME	70	73	E
4d		NaH/DME	70	69	E/Z = 60/40
4e		NaH/DME	70	52	E

<sup>a</sup> All reactions were carried out under nitrogen atmosphere for 3 h. <sup>b</sup> Isolated yields and based on phosphonate 1.

<sup>c</sup> Determined by <sup>1</sup>H NMR.

tolualdenide (0.58 g, 4.83 mmol) in 2 mL of DME was added. The reaction mixture was heated with stirring at 70 °C for 3 h. The solvent was removed and the residue was dissolved in ether. After being washed with brine and drying over Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated. Kugelrohr distillation at 150 °C (1 mmHg) gave the dienone 5a (0.52 g, 54% yield) as pale yellow crystal: mp 72–73 °C (lit. mp 73.5–75 °C);<sup>9</sup> <sup>1</sup>H NMR δ 1.91, 2.16 (s, 6 H, (CH<sub>3</sub>)<sub>2</sub>C=CHCO), 2.33 (s, 3 H, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 6.21 (m, 1 H, (CH<sub>3</sub>)<sub>2</sub>C=CHCO), 6.61 (d, 1 H, COCH=CHAr, *J* = 16.5 Hz), 7.10 (d, 2 H, aromatic protons, *J* = 8.25 Hz), 7.40 (d, 2 H, aromatic protons, *J* = 8.25 Hz), 7.46 (d, 1 H, COCH=CHAr, *J* = 16.5 Hz); MS, *m/e* 200 (M<sup>+</sup>). Anal. Calcd for C<sub>14</sub>H<sub>16</sub>O: C, 83.96 H, 8.05. Found: C, 84.20; H, 8.05.

The following  $\alpha,\alpha'$ -dienones 5b–e were obtained from the same process as described above. The yields are listed in Table II.

(*E*)-1-Phenyl-3-oxo-5-methyl-1,4-hexadiene (5b): bp 150 °C (oven temperature) at 1 mmHg; <sup>1</sup>H NMR δ 1.80, 2.18 (s, 6 H, (CH<sub>3</sub>)<sub>2</sub>C=CHCO), 6.20 (m, 1 H, (CH<sub>3</sub>)<sub>2</sub>CHCO), 6.63 (d, 1 H, COCH=CHPh, *J* = 16.5 Hz), 7.41 (d, 1 H, COCH=CHPh, *J* = 16.5 Hz), 7.15–7.55 (m, 5 H, aromatic protons); MS calcd for C<sub>13</sub>H<sub>14</sub>O, 186.10441 (found 186.10351).

2,7-Dimethyl-4-oxo-2,5-octadiene (5c): bp 90 °C (oven temperature) at 1 mmHg; <sup>1</sup>H NMR δ 1.08 (d, 6 H, (CH<sub>3</sub>)<sub>2</sub>CH, *J* = 7 Hz), 1.89, 2.09 (s, 6 H, (CH<sub>3</sub>)<sub>2</sub>C=CHCO), 2.36 (m, 1 H, (CH<sub>3</sub>)<sub>2</sub>CH, *J* = 7.5 Hz), 5.86 (d, 1 H, COCH=CHCH(CH<sub>3</sub>)<sub>2</sub>, *J* = 16.5 Hz), 6.02 (m, 1 H, (CH<sub>3</sub>)<sub>2</sub>C=CHCO), 6.58 (dd, 1 H, COCH=CHCH=CHCH(CH<sub>3</sub>)<sub>2</sub>, *J* = 7.5, 16.5 Hz); MS calcd for C<sub>10</sub>H<sub>16</sub>O; 152.12006 (found, 152.11746).

2,6-Dimethyl-4-oxo-2,5-octadiene (5d): bp 100 °C (oven temperature) at 1 mmHg; <sup>1</sup>H NMR δ 1.55–2.40 [m, 19 H, including δ 1.66 (br s, CH=C(CH<sub>3</sub>)CH<sub>2</sub>), 1.85 (br s, COCH=C(CH<sub>3</sub>)<sub>2</sub>, methyl trans to carbonyl), 2.13 (br s, C(CH<sub>3</sub>)=CHCOCH=C(CH<sub>3</sub>)<sub>2</sub>, two methyl cis to carbonyl)], 5.34 (m, 1 H, CH=C(CH<sub>3</sub>)CH<sub>2</sub>), 6.01 (br s, 2 H, C=CHCOCH=C); MS, *m/e* 218 (M<sup>+</sup>); [α]<sub>D</sub><sup>25</sup> +3° (C 0.74, EtOH).

(±)-α-Atlantone (5e): bp 150 °C (oven temperature) at 1 mmHg; <sup>1</sup>H NMR δ 1.55–2.40 [m, 19 H, including δ 1.66 (br s, CH=C(CH<sub>3</sub>)CH<sub>2</sub>), 1.85 (br s, COCH=C(CH<sub>3</sub>)<sub>2</sub>, methyl trans to carbonyl), 2.13 (br s, C(CH<sub>3</sub>)=CHCOCH=C(CH<sub>3</sub>)<sub>2</sub>, two methyl cis to carbonyl)], 5.34 (m, 1 H, CH=C(CH<sub>3</sub>)CH<sub>2</sub>), 6.01 (br s, 2 H, C=CHCOCH=C); MS, *m/e* 218 (M<sup>+</sup>); [α]<sub>D</sub><sup>25</sup> +3° (C 0.74, EtOH).

(±)-*ar*-Turmerone (6). To a suspension of magnesium turnings (0.12 g, 4.8 mmol) in 20 mL of ether was added methyl iodide (0.35 mL, 4.8 mmol) in 10 mL of ether, and the reaction mixture was refluxed for 30 min. After the addition of copper(I) chloride (0.04 g, 0.4 mmol) and the dienone 5a (0.8 g, 4 mmol), the solution was refluxed for 50 min and treated with saturated ammonium chloride solution. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the removal of ether afforded 6 (0.85 g, 98% yield). This sample was found to be almost pure on the basis of <sup>1</sup>H NMR spectrum. Kugelrohr distillation resulted in a significant loss of material due to thermal lability (0.20 g): bp 85 °C (oven temperature) at 0.5 mmHg; <sup>1</sup>H NMR δ 1.24 (d, 3 H, CH<sub>3</sub>CHAr, *J* = 6.0 Hz), 1.83 (s, 3 H, (CH<sub>3</sub>)<sub>2</sub>C=CHCO, methyl trans to carbonyl), 2.09 (s, 3 H, (CH<sub>3</sub>)<sub>2</sub>C=CHCO, methyl cis to carbonyl), 2.28 (s, 3 H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 6.00 (br s, 1 H, vinyl proton), 7.09 (s, 4 H, aromatic protons); MS, *m/e* 216 (M<sup>+</sup>); [α]<sub>D</sub><sup>30</sup> 0° (c 0.44, EtOH).

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**Registry No.** 1, 95485-29-3; 2a, 3350-78-5; 2b, 638-10-8; 2c, 61985-22-6; 4a, 104-87-0; 4b, 100-52-7; 4c, 78-84-2; 4d, 78-93-3; (±)-4e, 70286-20-3; (*E*)-5a, 73839-46-0; (*E*)-5b, 79629-17-7; (*E*)-5c, 95485-30-6; (*E*)-5d, 95485-31-7; (*E*)-(±)-5e, 56362-49-3; (±)-6, 38142-58-4; dimethyl methanephosphonate, 756-79-6; (*Z*)-5d, 95485-32-8.

### Synthesis of Sulfones by Phase-Transfer Alkylation of Arenesulfinate Salts

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The sulfone group has enjoyed considerable recent popularity in organic synthesis as an activating function which can subsequently be removed under mild conditions.<sup>1</sup> One important method for the preparation of

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