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TETRAHEDRON

Preparation of Alkyl 3-methylalka-2,4-dienoates from γ,δ-Unsaturated β-Keto Esters via the Corresponding Conjugated Unsaturated 3-Enol Phosphates.

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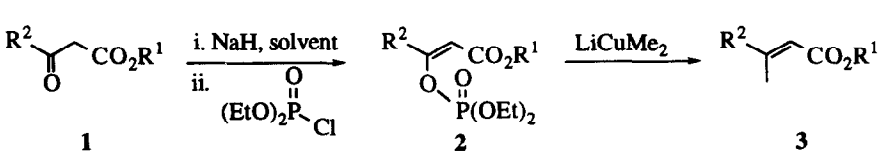
Abstract: Methylation of α,β,γ,δ-unsaturated-β-substituted enol phosphates with lithium dimethyl cuprate gave a mixture of *(2E,4E)*- and *(2Z,4E)* alkyl 3-methylalka-2,4-dienoates and unsubstituted alkyl alka-2,4-dienoates. An improved synthesis is described for ethyl β-safranate and the insect growth regulator hydroprene.

INTRODUCTION

Esters of trienoic acids are found widespread in natural products. For example, an ester of *(2E, 4E, 6E)*-octa-2,4,6-trienoic acid was recently reported.[1] Substituted methyl derivatives of last mentioned esters, like *(2E, 4E, 6E)*-3,7-dimethylocta-2,4,6-trienoic acids, have potential medicinal properties or have been used as retinoids.[2] New syntheses of trienoic acids are still being investigated,[3] while the classical Wittig-Horner-Emmons condensations are very much in use.[4,5] One of us has reported on the synthesis of methyl substituted trienoic esters using condensations of crotonate arsonium ylide and α,β-unsaturated aldehydes.[6]

The stereoselective transformation of β-keto esters **1** into alkyl *(E)*-3-methylalk-2-enoates **3** via *(Z)*-enol phosphates, the [(diethoxyphosphinyl)oxy]-2-alkenoates **2** (Scheme 1), is a useful synthetic technique.[7,8,9] The procedure is normally carried out by deprotonation of the β-keto ester **1** with, for example, sodium hydride in an appropriate solvent like diethyl ether or tetrahydrofuran (THF). The anion is then quenched with diethylphosphorochloridate to give the enol phosphate **2**. Methylation of *(Z)*-enol phosphates **3** with lithium dimethylcuprate gives alkyl *(E)*-3-methylalk-2-enoates **3** (Scheme 1).[7,8,9,10] Although the toxic effects of copper to the environment has recently been in the news,[11] this reaction remains an important tool in organic synthesis.[12]

Scheme 1



1 **2** **3**

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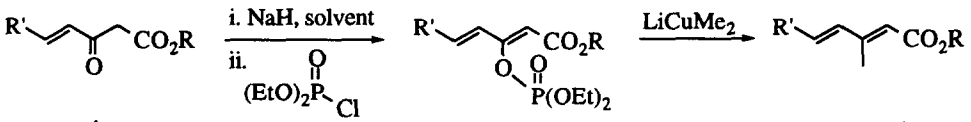
The transformation of *(2Z)*-unsaturated conjugated 3-[(diethoxyphosphinyl)oxy]-2-alkenoates **5**, obtained using the same procedure from the corresponding unsaturated β–keto esters **4**, into 3-methylalka-2,4-alkadienoates **6** is less well known. We[13] and others[14,15] have been interested in this very useful technique, for example in the preparation of insect growth regulators hydroprene **6d(i)**[16,17,18] and alkyl safranate **6e**[19,20] (Scheme 2). In this paper we describe the preparation and transformation of enol phosphates **5** into 3-methylalka-2,4-alkadienoates **6**. and extent this method to include also cyclic compounds.

Scheme 2

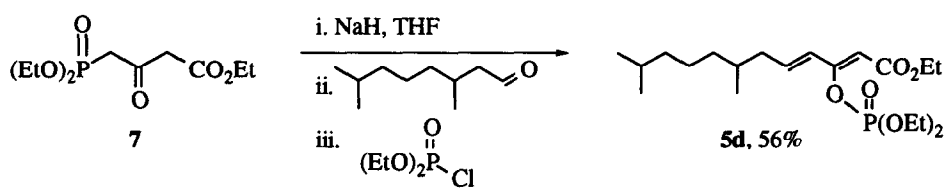


4 **5** **6**

RESULTS

To this end, the β-keto esters **4**[21,22,23] were deprotonated with sodium hydride in THF at 0 °C, and the anion was quenched with diethylphosphorochloridate to give the *(2Z)*-enol phosphates **5** in high yield as viscous colourless or pale yellow oils (Scheme 3). We also investigated the one pot synthesis of acyclic enol phosphates **5** by quenching [$(EtO)_2P(O)Cl$] the Wittig-Horner product obtained from the appropriate aldehyde and the phosphonate **7** in the presence of two equivalentmol sodium hydride[23] (Scheme 4). Thus the enol phosphate **5d** was obtained in a modest yield of 56% or an average yield of 75% for each step. This is an attractive method with better control over the enol stereochemistry and reduces separation and purification procedures.[24]

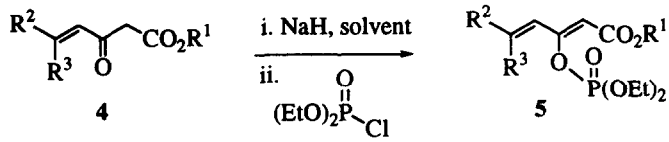
Scheme 4



The enol phosphates **5** were distilled, however, the *(2Z, 4E)*-isomer **5c(i)** isomerized to the *(2E,4E)* isomer **5c(ii)** during distillation. The ^{13}C-NMR values for both these isomers (Table 1) are indicative and partially in agreement with the reported values for *Z*- and *E*-enol phosphates where the ^{13}C chemical shift differences and coupling constants are respectively for: P-O-C=CH-R: *cis* <*trans*: 0.5 - 1.3 ppm, and $J_{PC(2)}$ *cis*: <*trans*: ($J_{PC(2)}$ *trans* 8.6 - 11.9); for P-O-C(-C)=CH-R: *cis* >*trans*: by 0.2 - 1.3 ppm, and $J_{PC(3)}$ *cis*: <*trans*: ($J_{PC(3)\,trans}$ 3.2 - 4.9).[25]

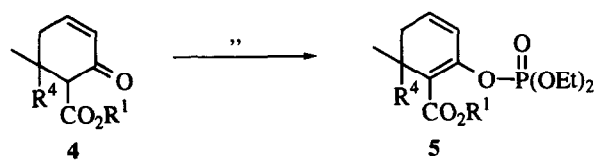
Methylation of *(Z)*-enol phosphates **5** with lithium dimethylcuprate gave apart from the expected alkyl *(2E, 4E)*-3-methylalka-2,4-dienoates **6(i)**, unfortunately also the *(2Z, 4E)*-3-methylalka-2,4-dienoates **6(ii)** isomer in lesser amounts (Scheme 3). Alkylation of the enol phosphate **5d** with copper-catalysed

Scheme 3



4 5

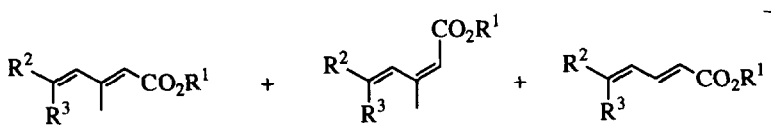
	R^1	R^2	R^3	Yield 5
4a, 5a	Me	CH_3	CH_3	88%
4b, 5b	Me	$CH_3CH{=}CH$	H	76%
4c, 5c	Me	$(CH_3)_2C{=}CH$	H	83%
4d, 5d	Et	$(CH_3)_2CH(CH_2)_3CH(CH_3)CH_2$	H	98%



4 5

	R^1	R^4	Yield 5
4e, 5e	Et	Me	82%
4f, 5f	Et	H	73%

$LiCuMe_2$
Et_2O -65 °C



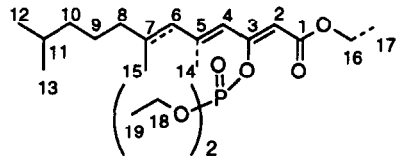
6i 6ii 8

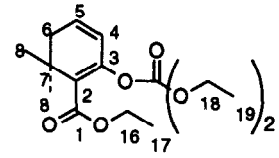
	R^1	R^2	R^3	Yield 6(i)	6(ii)	8
6a, 8a	Me	CH_3	CH_3	39%	27%	9%
6b, 8b	Me	$CH_3CH{=}CH$	H	26%	21%	7%
6c, 8c	Me	$(CH_3)_2C{=}CH$	H	28%	18%	8%
6d, 8d	Et	$(CH_3)_2CH(CH_2)_3CH(CH_3)CH_2$	H	47%	16%	14%

	R^1	R^4	Yield
6e	Et	Me	55%
6f	Me	H	66%

	Yield
8e	10%
8f	9%

Table 1 ^{13}C Chemical shifts (δ_C in ppm) for enol phosphates **5b**, *cis*-**5c**, *trans*-**5c**, **5d**, **5e** and **5f**[a]





No	**5b**		**5c**(*cis*)		**5c**(*trans*)		**5d**		**5e**		**5f**	
		J_{PC}		J_{PC}		J_{PC}		J_{PC}		J_{PC}		J_{PC}
1	164.55	1.9	164.55	1.8	166.31	1.3	163.65	1.9	166.49	1.7	165.52	2.0
2	106.60	1.7	106.43	1.8	104.00	3.3	105.21	5.9	122.07	8.5	116.63	7.5
3	155.87	7.8	156.40	8.1	159.28	8.0	154.48	8.0	144.60	8.0	149.20	7.8
4	123.58	2.2	123.38	2.0	120.39	5.7	124.92	2.0	122.07	1.6	123.04	1.7
5	138.08	1.1	134.48	0.8	133.96	~0	139.31	~0	131.82	0.7	133.88	0.8
6	130.87	~0	124.99	~0	125.37		39.42		39.18	~0	30.39	
7	136.32		143.03		143.69		32.20		34.69		28.28	
8	18.53		26.34		26.48		36.07		25.85		17.85	
9							23.99					
10							38.39					
11							27.12					
12							21.84					
13							21.75					
15			18.80		18.82		18.70					
17	51.04		50.91		51.16		59.80		60.42		60.20	
18							14.29		14.29		14.29	
19	64.79	6.0	64.74	6.0	64.86	6.1	63.78	6.1	64.55	6.3	64.54	6.1
20	16.15	6.9	16.19	7.2	16.17	6.9	15.29	7.0	16.09	6.4	16.17	6.8

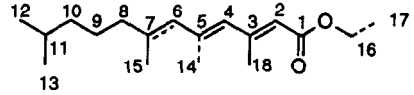
a. At 20 MHz in $CDCl_3$ and J_{PC} measured in Hz.

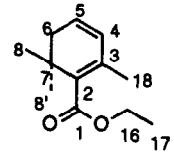
Table 2 ^{1}H Chemical shifts (δ_H in ppm) for enol phosphates **5a**, **5b**, **5c**, **5d** **5e** and **5f**.[a]

No	**5a**		**5b**		**5c**		**5d**		**5e**		**5f**	
		J_{HH}		J_{HH}		J_{HH}		J_{HH}		J_{HH}		J_{HH}
2	5.33	~0	5.51	*d*	5.50	*d*	5.46	*e*				
4	5.85	~0	5.94	d, 16	5.92	d, 15.1	5.90	d, 15.4	6.20	d, 10.0	6.13-6.16	m
5			6.85	dm, 16.0	7.24	dd, 15.1, 11.5	6.52	dd, 15.4, 7.4	5.96	dt, 10.0, 3.9	,,	,,
6	1.88	d, 1.3	6.05-6.15	m	5.94	d, 11.5	1.95-2.15	dm, 7.4	2.18	d, 3.9	1.97-2.49	m
7			6.05-6.15	m			1.47-1.80	m			2.86	q, 6.8
8			1.83	d, 5.1	1.86	sm	1.05-1.44	m	1.18	s	1.06	d, 6.8
9							1.05-1.44	m				
10							1.05-1.44	m				
12,13							0.86	d, 6.1				
14	1.93	d, 1.3										
15					1.86	sm	0.88	d, 5.9				
16	3.76		3.71		3.71		4.30	q, 7.0	4.23	q, 7.1	4.20	q, 7.1
17							1.27	t, 7.0	1.34	t, 7.1	1.30	t, 7.1
18	4.24	q, 7.1[b]	4.25	q, 7.1[b]	4.26	q, 7.1[b]	4.25	q, 7.0,[f]	4.16	q, 7.1[h]	4.20	q, 7.1[h]
19	1.34	t, 7.1[c]	1.35	t, 7.1[c]	1.36	t, 7.1[c]	1.36	t, 7.0, [g]	1.32	t, 7.1	1.33	t, 7.1[i]

[a] At 80 MHz in $CDCl_3$ and J_{HH} measured in Hz and J_{PH} measured in Hz; [b] 7.8 - 8.0 Hz, [c] 1.1 - 1.2 Hz, [d] 1.6 - 1.7 Hz, [e] 0.7 Hz, [f] 7.0 Hz, [g] 1.3 Hz, [h] 8.2 Hz, [i] 1.0 Hz.

Table 3 ^{13}C Chemical shifts (δ_C in ppm) for products **6b(i)**, **6b(ii)**, **6c(i)**, **6c(ii)**, **6d(i)**, **6d(ii)**, **6e** and **6f**.[a,b]





no	6b(i)	6b(ii)	6c(i)	6c(ii)	6d(i)	6d(ii)	6e	6f
1	167.59	166.81	167.51	166.87	167.10	166.37	169.43	168.31
2	118.09	116.18	117.67	115.68	117.82	115.84	131.66	127.13
3	152.90	151.31	153.22	151.71	152.37	151.11	133.60	140.93
4	133.24*,[c]	127.49	125.53	127.26	134.96	128.93	128.22	129.75
5	133.79*	133.90*	133.17	132.48	135.92	137.84	128.22	130.13
6	131.59	132.38*	131.16	126.15	40.67	40.90	39.61	30.82
7	135.08	136.34	140.06	140.56	33.27	33.32	33.39	20.81
8	18.49	18.48	26.45	26.34	37.03	37.12	25.93	27.58
9					24.88	24.86		
10					39.32	39.29		
11					28.02	28.01		
12					22.62	22.69		
13					,,	22.61		
15			18.67	18.71	19.64	19.53		
16	50.95	50.85	50.77	50.86	59.45	59.53	59.83	59.81
17					14.37	14.37	14.41	14.45
18	13.79	20.85	13.8	20.98	13.88	19.68	19.53	17.88

[a] At 20 MHz in $CDCl_3$. [b] For compounds **8b**, **8c** and **8f** ^{13}C-NMR data were identical to those obtained via other methods, see ref. 6. [c] signals with * can be interchanged.

Table 4 ^{1}H Chemical shifts (δ_H in ppm) for products **6a(i)**, **6a(i)**, **6b(i)**, **6b(ii)**, **6c(i)**, **6c(ii)**, **6f**, **6d(i)**, **6d(ii)**, **6e** and **8e**[a]

no	**6a(i)**		**6a(ii)**		**6b(i)**		**6b(ii)**		**6c(i)**[4,5]		**6c(ii)**		**6f**	
		J_{HH}		J_{HH}		J_{HH}		J_{HH}		J_{HH}		J_{HH}		J_{HH}
2	5.73	sm	5.65	sm	5.74	sm	5.63	sm	5.74	s	5.60	sm		
4	5.71	m	6.45	m	7.61	d, 15.0	5.83-6.50	m	6.13	d, 15.5	7.63	d, 15.4	5,87-5.91	sm
5					5.92-6.72	m	„	„	6.84	dd, 15.5, 11.5	6.82	dd, 15.4, 10.9	„	„
6	1.83	sm	2.02	dm, 1.4	„	„	„	„	5.95	d, 11.5	6.04	10.9	1.85-2.95	m
7					„	„	„	„					„	„
8					1.82	d, 6.5	1.82	d, 5.5	1.83	sm	1.84	sm	0.98	d, 6.9
14	1.83	sm	1.86	d, 1.4										
15									1.85	sm	1.84	sm		
16	3.69	s	3.66	s	3.69	s	3.69	s	3.68	s	3.68	s	4.12	q, 7.1
17													1.30	t, 7.1
18	2.23	d, 0.6	1.74	d, 1.3	2.28	d, 1.2	2.00	d, 1.3	2.33	d, 1.2	2.04	d, 1.1	2.12	d, 0.5

No	**6d(i)**		**6d(ii)**		**6e**		**8e**[b]	
		J_{HH}		J_{HH}		J_{HH}		J_{HH}
2	5.74	sm	5.59	sm				
3							6.68	sm
4	6.04-6.15	m	7.57	d, 15.9	5.82-5.88	sm	5.99	sm
5	„	„	6.11	dt, 15.9, 7.0	„	„	„	„
6	1.90-2.30	m	1.90-2.30	m	2.08-2.12	m	2.18	sm
7	1.30-1.70	m	1.30-1.70	m				
8,(9,10)	1.10-1.40	m	1.10-1.40	m	1.11	s	1.23	s
11	1.30-1.70	m	1.30-1.70	m				
12;13	0.86	d, 6.0	0.86	d, 6.0				
15	0.86	d, 6.0	0.88	d, 6.2				
16	4.15	q, 7.1	4.14	q, 7.1	4.25	q, 7.1	4.18	q, 7.1
17	1.27	t, 7.1	1.27	t, 7.1	1.29	t, 7.1	1.32	t, 7.1
18	2.25	d, 1.1	1.98	d, 1.2	1.81	s		

[a] At 80 MHz in $CDCl_3$ and J_{HH} measured in Hz. [b] For compounds **8b**, **8c** and **8f** ^{1}H-NMR data were identical to those obtained via other methods see ref. 6.

methylmagnesium chloride gave even more of the *cis*-hydroprene **6d(ii)**. A wealth of information is available on cuprate-alkene π-complexes.[26] In general, reduction during cuprate addition is now well known.[27] Reduction of enol phosphate substitution is also found[28] and it is believed to follow a single electron transfer mechanism.[29] It was therefore not a surprise to find that with our conjugated enol phosphates **5** lithium dimethylcuprate addition led to a substantial amount of reduction to **8** (Scheme 3). Lowering the reaction temperature to -95 °C and/or changing the solvent (THF, ether:THF, ether:DMPU)[30] had little effect on the ratio **6(i)**:**6(ii)**:**8**. Compounds **6a** are often used in synthesis,[31] derivatives of **6c(i)**[32,33] and **6c(ii)**[34,35] have been found in nature and synthesized[4,5] or used for further preparations. Of the cyclic compounds **6e** and **6f**, Michael-Wittig condensations are still in use for **6e**,[36] and some preparations of **6f** are known.[37,38]

In conclusion, we have explored the lithium dimethylcuprate alkylation of conjugated enol phosphates **5** and found that isomerization and a substantial amount of cuprate-induced reduction of enol phosphate **5** took place. However, our method for the transformation of unsaturated β-keto esters into 3-methyl conjugated 2,4-alkadienoates **6** still offers an attractive alternative especially for the acyclic compounds which is merely a two-step process from the phosphonate **7**.

EXPERIMENTAL SECTION

All reactions were carried under nitrogen. ^{1}H-NMR and ^{13}C-NMR were recorded on a Varian FT-80 at respectively 80 or 20 MHz in $CDCl_3$ with TMS as an internal standard for ^{1}H-NMR. High resolution electron ionization (EI) mass spectra were obtained from a Varian MAT 311 A. UV absorbance was measured as solutions in 96% EtOH on a Varian SuperScan 3. Microanalyses were performed by Microanalytisches Labor Pascher. Column chromatography was performed using Merck Si-60 (40-63mm) silica gel. Bulb-to-bulb distillations (b.p.) were carried out on a Büchi GKR-51 apparatus. Diethyl ether (ether) and tetrahydrofuran (THF) were dried (sodium) and distilled from $LiAlH_4$. Light petroleum refers to the fraction between 40 - 60 °C.

1. Preparation of alkyl substituted-3-([diethoxyphosphinyl]oxy)-2,4-dienoates **5**.

(a) General procedure for the preparation of conjugated enol phosphates **5** from alkyl 3-oxoalk-4-enoates **4**.

Alkyl 3-oxo-4-alkenoate **4** (5 mmol) in anhydrous tetrahydrofuran (15 mL) was added within 5 minutes to an oil free suspension sodium hydride (170 mg, 7.08 mmol) in THF (25 mL) at 0 °C for 15 minutes. The reaction mixture was quenched with diethylphosphorochloridate (1.10 g, 6.18 mmol) at 0 °C and stirred for another 15 - 25 minutes at 0 °C or at room temperature and monitored by TLC. The solution was diluted with diethyl ether (20 mL) and the white suspension sodium chloride filtered on a layer of *Celite* or powdered $MgSO_4$ and silica gel. The evaporated residue was chromatographed on silica gel with diethyl ether:light petroleum (24:1), (9:1), (4:1) or (11:9), depending on the polarity of the enol phosphate, to give pure *(2Z)*-alkyl 3-([diethoxyphosphinyl]oxy)-2,4-dienoate **5**.

(i). Methyl 5-methyl-3-oxohex-4-enoate **4a** gave *(2Z)*-methyl 3-([diethoxyphosphinyl]oxy)-5-methylhexa-2,4-dienoate **5a** (88%), b.p. 105 - 110 °C at 10^{-5} mm Hg; (Found: C, 49.32; H, 7.30. P, 10.1. $C_{12}H_{21}O_6P$ requires C, 49.31; H, 7.24, P, 10.6%); λ_{max} (EtOH)/nm 262 (ε = 13000); [Found: M^+(EI), 292.1090. $C_{12}H_{21}O_6P$ requires *M*, 292.1076].

(ii). *(4E, 6E)*-Methyl 3-oxoocta-4,6-dienoate **4b** gave *(2Z, 4E, 6E)*-methyl 3-([diethoxyphosphinyl]-oxy)octa-2,4,6-trienoate **5b** (76%), b.p. 140 °C at 10^{-5} mm Hg; (Found: C, 51.18; H, 6.94; P, 10.1. $C_{13}H_{21}O_6P$ requires C, 51.32; H, 6.96; P, 10.18%); λ_{max} (EtOH)/nm 296 (ε = 34000); [Found: M^+(EI), 304.1087. $C_{13}H_{21}O_6P$ requires *M*, 304.1076].

(iii). *(4E)*-Methyl 7-methyl-3-oxoocta-4,6-dienoate **4c** gave *(2Z, 4E)*-methyl 3-([diethoxyphosphinyl]-oxy)-7-methylocta-2,4,6-trienoate **5c** (83%), b.p. 145 °C at 10^{-5} mm Hg; (Found: C, 52.67; H, 7.38. $C_{14}H_{23}O_6P$ requires C, 52.83; H, 7.28%);λ_{max} (EtOH)/nm 313, 214 (ε = 30100, 5000); [Found: M^+(EI), 318.1203. $C_{14}H_{23}O_6P$ requires *M*, 318.1232]; *m/z* (EI); 318 (M^+, 16%), 286 (31), 164 (18), 155 (100), 133 (28), 132 (48).

(iv). *(4E)*-Ethyl 7,11-dimethyl-3-oxododec-4-enoate **4d** gave *(2Z, 4E)*-ethyl 3-([diethoxyphosphinyl]-oxy)-7,11-dimethyldodeca-2,4-dienoate **5d** (98%), b.p. 150 °C at 10^{-5} mm Hg; (Found: C, 59.24; H, 9.30, P, 7.29. $C_{20}H_{37}O_6P$ requires C, 59.39; H, 9.22, P, 7.66%); λ_{max} (EtOH)/nm 259 (ε = 24800); [Found: M^+(EI), 404.2323. $C_{20}H_{37}O_6P$ requires *M*, 404.2327]

(v). Ethyl 6,6-dimethyl-2-oxocyclohex-3-ene-1-carboxylate **4e** gave ethyl 2-([diethoxyphosphinyl]oxy)-6,6-dimethylcyclohexa-1,3-diene-1-carboxylate **5e** (82%), b.p. 125 °C at 10^{-5} mm Hg; (Found: C, 54.43; H, 7.73. P, 8.85. $C_{15}H_{25}O_6P$ requires C, 54.21; H, 7.58, P, 9.32%); λ_{max} (EtOH)/nm 273 (ε = 5400); [Found: M^+(EI), 332.1364. $C_{15}H_{25}O_6P$ requires *M*, 332.1388].

vi). Ethyl 6-methyl-2-oxocyclohex-3-ene-1-carboxylate **4f** gave ethyl 2-([diethoxyphosphinyl]oxy)-6-methylcyclohexa-1,3-diene-1-carboxylate **5f** (73%), b.p. 125 °C at 10^{-5} mm Hg; (Found: C, 52.58; H, 7.54. P, 9.64. $C_{14}H_{23}O_6P$ requires C, 52.83; H, 7.28, P, 9.73%); λ_{max} (EtOH)/nm 286 (ε = 7400); [Found: M^+(EI), 318.1219. $C_{14}H_{23}O_6P$ requires *M*, 318.1232]; *m/z* (EI); 318 (M^+, 58%), 303 (12), 257 (88), 229 (90), 201 (100).

(b) One-pot procedure for the preparation of conjugated enol phosphates **5** from α,β-conjugated aldehydes and alkyl 4-(dialkoxyphosphinyl)-3-oxobutanoate **7**.

Alkyl 4-(dialkoxyphosphinyl)-3-oxobutanoate **7** (7.5 mmol) in THF (15 mL) was added to an oil free suspension sodium hydride (16.7 mmol) in THF (15 mL) at 0 °C and was then stirred at 28 °C for 15 minutes. Aldehyde (8 mmol) in THF (10 mL) was added within 10 minutes to the monoanion of the phosphonate at 0 °C and then stirred for 40 minutes at room temperature. A slow evolution of hydrogen evolved. Diethylphosphorochloridate (8 mmol) was added neat to the reaction mixture and the solution stirred for 20 to 40 minutes at room temperature and monitored by TLC. The mixture was diluted with ether (100 mL) and filtered over *Celite* and silica gel. The evaporated residue was chromatographed on silica gel.

(i) Methyl 3-([diethoxyphosphinyl]oxy)octa-2,4,6-trienoate **5b** (47%)

(ii) Methyl 3-([diethoxyphosphinyl]oxy)-7-methylocta-2,4,6-trienoate **5c** (42%)

(iii) Ethyl 3-([diethoxyphosphinyl]oxy)-7,11-dimethyldodeca-2,4-dienoate **5d** (56%)

2. General procedure for the alkylation of conjugated enol phosphates 5 with lithium dimethylcuprate. Preparation of Alkyl 3-methylalka-2,4-dienoates 6.

Methyllithium (15 mmol) in ether (18 mL) was added within 5 minutes to a suspension of powdered copper (I) iodide (7 mmol) in ether (10 mL) at 0 °C and stirred until a clear solution resulted. Alkyl 3-([diethoxyphosphinyl]oxy)alka-2,4-dienoate **5** (3.5 mmol) in diethyl ether (3 mL) was added within 5 minutes to the lithium dimethylcuprate solution at -65 °C. and stirred for 10 to 20 minutes and monitored by

TLC. The reaction mixture was treated with a saturated aqueous solution ammonium chloride (20 mL) and allowed to come to room temperature. Extraction with diethyl ether followed by chromatography of the dried evaporated residue on silica gel gave after elution with diethyl ether:light petroleum (1:49) or (1:19) alkyl 3-methylalka-2,4-dienoates **6**.

(i). *(2Z)*-Methyl 3-([diethoxyphosphinyl]oxy)-5-methylhexa-2,4-dienoate **5a** gave *(2E)*-methyl 3,5-dimethylhexa-2,4-dienoate **6a(i)** (39%) b.p. 80 °C at 15 mm Hg; and *(2Z)*-**6a(ii)** (27%) b.p. 80 °C at 15 mm Hg; (Found [mixture]: C, 70.14; H, 9.15. $C_9H_{14}O_2$ requires C, 70.10; H, 9.15%); λ_{max} (EtOH)/nm *(2E)*-**6a(i)** 269 (ε = 12200), *(2Z)*- **6a(ii)** 274 (ε = 8100); [Found (mixture): M^+(EI), 154.0996. $C_9H_{14}O_2$ requires *M*, 154.0994]; and *(2E)* methyl hexa-2,4-dienoate **8a** (9%), b.p. 55 °C at 18 mm Hg.

(ii). *(2Z, 4E, 6E)*-Methyl 3-([diethoxyphosphinyl]oxy)octa-2,4,6-trienoate **5b** gave *(2E, 4E, 6E)*-methyl 3-methylocta-2,4,6-trienoate **6b(i)** (26%) b.p. 65 °C at 0.05 mm Hg; and *(2Z, 4E, 6E)*-**6b(ii)** (21%); b.p. 65 °C at 0.05 mm Hg; λ_{max} (EtOH)/nm *(2E, 4E, 6E)*-**6b(i)** 297 (ε = 26800), *(2Z,4E, 6E)*-**6b(ii)** 298 (ε = 31600); [Found (mixture): M^+(EI), 166.0987. $C_{10}H_{14}O_2$ requires *M*, 166.0994]; and *(2E, 4E, 6E)* methyl 2,4,6-octatrienoate **8(b)**[6] (7%), m.p. 54 °C at 0.05 mm Hg; λ_{max} (EtOH)/nm *(2E, 4E, 6E)*-**8(b)** 298 (ε = 34200), [Found: M^+(EI), 152.0842. $C_9H_{12}O_2$ requires *M*, 152.0837].

(iii). *(2Z, 4E)*-Methyl 3-([diethoxyphosphinyl]oxy)-7-methylocta-2,4,6-trienoate **5c** gave *(2E, 4E)*-methyl 3,7-dimethylocta-2,4,6-trienoate **6c(i)** (28%) b.p. 60 °C at 0.01 mm Hg; and *(2Z, 4E)* **6c(ii)** (18%), b.p. 95 °C at 1.5 mm Hg; (Found[mixture]: C, 72.88; H, 8.95. $C_{11}H_{16}O_2$ requires C, 73.30; H, 8.95%); λ_{max} (EtOH)/nm *(2E,4E)*-**6c(i)** 309 (ε = 32200), *(2Z,4E)*-**6c(ii)** 312 (ε = 25800); [Found (mixture): M^+(EI), 180.1146. $C_{11}H_{16}O_2$ requires *M*, 180.1150]; *m/z* (EI); 180 (M^+, 27%), 121 (100), 106 (12), 105 (46); and *(2E, 4E)* methyl 7-methylocta-2,4,6-trienoate **8c**[6] (8%), b.p. 80 °C at 1.5 mm Hg; [Found: M^+(EI), 166.0987. $C_{10}H_{14}O_2$ requires *M*, 166.0994].

(iv) *(2Z, 4E)*-Ethyl 3-([diethoxyphosphinyl]oxy)-7,11-dimethyldodeca-2,4-dienoate **5d** gave *(2E, 4E)*-ethyl 3,7,11-trimethyldodeca-2,4-dienoate **6d(i)** (47%) b.p. 90 °C at 0.01 mm Hg; and *(2Z, 4E)* -**6d(ii)** (16%), b.p. 95 °C at 1.5 mm Hg; (Found [mixture]: C, 76.64; H, 11.38. $C_{17}H_{30}O_2$ requires C, 76.64; H, 11.35%); λ_{max} (EtOH)/nm *(2E,4E)*-**6d(i)** 264 (ε = 33900), *(2Z,4E)*-**6d(ii)** 264 (ε = 18100); [Found (mixture): M^+(EI), 266.2262. $C_{17}H_{30}O_2$ requires *M*, 266.2245]; *m/z* (EI); 266 (M^+, 11%), 139 (100), 111 (30); and *(2E, 4E)* -ethyl 7,11-dimethyl-2,4,-dodecadienoate **8d** (14%), b.p. 90 °C at 0.01 mm Hg.

(v). Ethyl 2-([diethoxyphosphinyl]oxy)-6,6-dimethylcyclohexa-1,3-diene-1-carboxylate **5e** gave ethyl 2,6,6-trimethylcyclohexa-1,3-diene-1-carboxylate **6e** (55%) b.p. 55 °C at 2 mm Hg; (Found: C, 73.85; H, 9.35. $C_{12}H_{18}O_2$ requires C, 74.19; H, 9.34%); λ_{max} (EtOH)/nm 274 (ε = 6800); [Found: M^+(EI), 194.1313. $C_{12}H_{18}O_2$ requires *M*, 194.1307], and ethyl 6,6-dimethylcyclohexa-1,3-diene-1-carboxylate **8e** (10%).

(vi). Ethyl 2-([diethoxyphosphinyl]oxy)-6-methylcyclohexa-1,3-diene-1-carboxylate **5f** gave ethyl 2,6-dimethylcyclohexa-1,3-diene-1-carboxylate **6f** (66%) b.p. 55 °C at 2 mm Hg; (Found: C, 72.79; H, 9.05. $C_{11}H_{16}O_2$ requires C, 73.30; H, 8.95%); λ_{max} (EtOH)/nm 289; [Found: M^+(EI), 180.1153. $C_{11}H_{16}O_2$ requires *M*, 180.1150], and ethyl 6-methylcyclohexa-1,3-diene-1-carboxylate **8f** (9%).[6]

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