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Condensations of Ethyl 3-Ethoxy-4-(triphenylphosphoranylidene)-2-butenoate with α,β-Unsaturated Carbonyl Compounds

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Summary. *Wittig* condensations of α,β-unsaturated carbonyl compounds with ethyl 3-ethoxy-4-(triphenylphosphoranylidene)-2-butenoate gave good to high yields of (2*E*,4*E*,6*E*)-ethyl 3-ethoxy-2,4,6-alkatrienoates. Some of last mentioned compounds were almost quatitatively hydrolysed to (4*E*,6*E*)-ethyl 3-oxo-4,6-alkadienoates. This method can therefore be used as an attractive alternative for the preparation of unsaturated conjugated β-keto esters previously prepared in very low yields from α,β-unsaturated carbonyl compounds and ethyl 3-oxo-4-(triphenylphosphoranylidene)butanoate.

Keywords. Ethyl 3-ethoxy-2,4,6-alkatrienoates; Ethyl 3-ethoxy-4-(triphenylphosphoranylidene)-2-butenoate; Unsaturated-β-ketoesters; *Wittig* condensations.

Introduction

For quite some time we have been interested in the synthetic capabilities of esters of 3-oxo-4-(triphenylphosphoranylidene)-butanoate (**1**) (Scheme 1) [1, 2]. Thus, *Wittig* condensations of the phosphonium ylide **1** with α,β-unsaturated carbonyl compounds **2**, gave poor yields of (4*E*,6*E*)-ethyl 3-oxo-2,4-alkadienoates **3** (Scheme 1). The low yield of unsaturated conjugated β-keto esters **3** was due to further condensation reactions of **3** with carbonyl compounds **2**, like aldol condensations and subsequent *Michael-Wittig* condensations of these aldol products with the ylide **1** [2, 3]. However, under certain conditions this ylide **1** can be manipulated into useful *Michael-Wittig* condensations with α,β-unsaturated carbonyl compounds **2** to form substituted 3-cyclohexen-2-one-1-carboxylates, for example with 2-butenal (**2b**), ethyl 6-methyl-2-oxocyclohex-3-ene-1-carboxylate (**9**) is obtained (Scheme 1) [4]. In this paper we describe the condensation of ethyl

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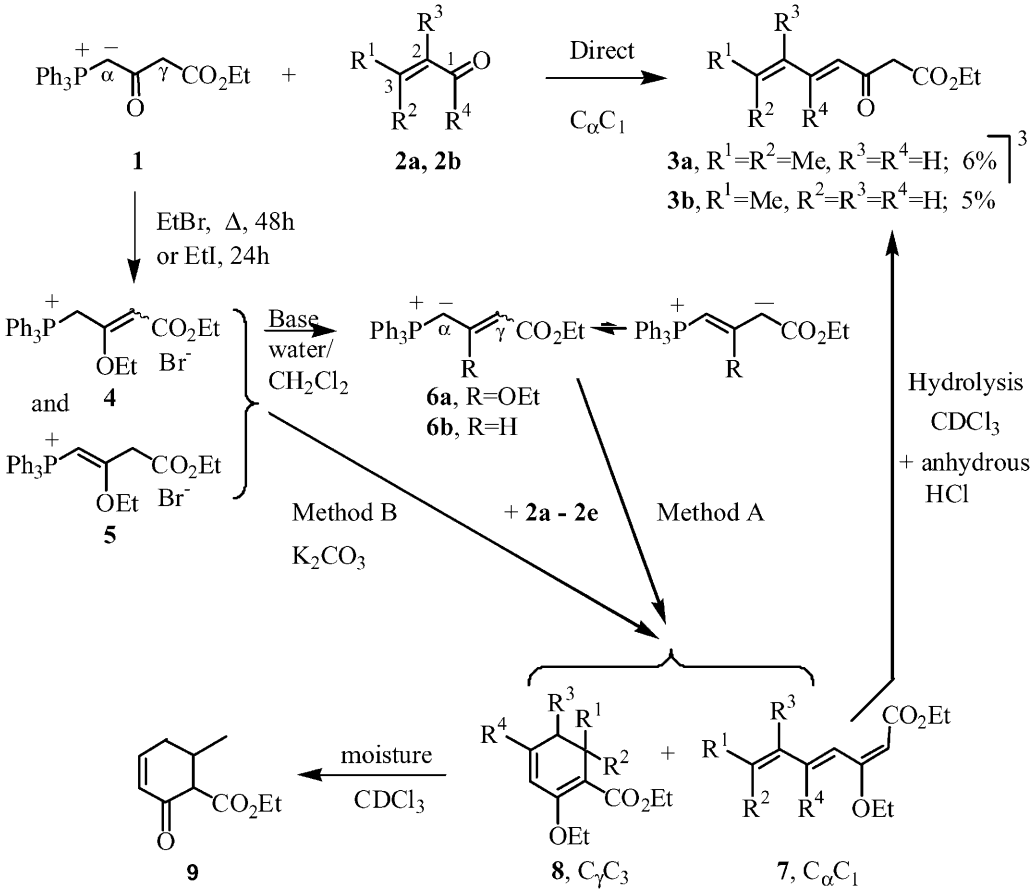

	R^1	R^2	R^3	R^4	Method A		Method B	
					7	**8**	**7**	**8**
a	Me	Me	H	H	93%	0%	75%	0%
b	Me	H	H	H	61%	3%[a]	27%	8%
c	H	H	Me	H	81%	0%	–[b]	–[b]
d	Me	H	Me	Me	0%	0%	0%	0%
e	$(CH_3)_2C{=}CH(CH_2)_2$	Me	H	H	53%	0%	48%	0%

[a] Isolated as the hydrolysed product **9**; [b] not carried out

Scheme 1. Condensations of ethyl 3-ethoxy-4-(triphenylphosphoranylidene)-2-butenoate with α,β-unsaturated carbonyl compounds

3-ethoxy-4-(triphenylphosphoranylidene)-2-butenoate (**6a**) [5–8] with α,β-unsaturated carbonyl compounds **2** (Scheme 1) as an attractive alternative for the synthesis of 3-oxo-4,6-alkadienoates **3**. *Bestmann et al.* introduced the ethoxy phosphonium ylide **6a** some thirty years ago [5–8]. Only in the last fifteen years was there a renewed interest in this ylide **6a** [9–22]. Some classical *Wittig* condensation reactions were carried out [7, 9, 15, 17, 19, 22, 25, 26] and novel cyclisations to five membered-[10, 12–14, 16, 18, 23], six membered unsaturated

carbocyclic rings [16] and aromatics [20, 21]. Cyclopropanations of the corresponding arsonium ylide [19] were documented. The phosphonium salt **4** was prepared by *Bestmann* from 1,1-diethoxyvinyl-2-(triphenylphosphoranylidene) [5–8]; However, *Hudson* prepared the phosphonium salt **4** from triphenylphosphine and ethyl γ-bromo-3-ethoxycrotonate [9]. We have found that the reaction of ethyl bromide with ethyl 3-oxo-4-(triphenylphosphoranylidene) butanoate (**1**) gave apart from **4** also the vinylic salt **5** [27].

Results and Discussion

Condensation of ethyl 3-ethoxy-4-(triphenylphosphoranylidene)-2-butenoate (**6a**) and 3-methylbut-2-enal (**2a**) in benzene gave the classical *Wittig* product ethyl 3-ethoxy-7-methyl-2,4,6-octatrienoate (**7a**) as a 9:1 mixture of (2*E*,4*E*) and (2*E*,4*Z*) geometric isomers in a high yield of 93% [28]. This compound **7a** easily hydrolysed with HCl in $CDCl_3$ with little water to give only (2*E*,4*E*)-ethyl 7-methyl-3-oxo-4,6-octadienoate (**3a**). The condensation of **6a** with 2-butenal (**2b**) gave the *Wittig* product **7b** (61%) as a 4:1 mixture of (2*E*,4*E*,6*E*) and (2*E*,4*Z*,6*E*) isomers. Recently, a similar result with a different ester of **6a** was obtained [29]. Ethyl 4-(triphenylphosphoranylidene)-2-butanoate (**6b**) is well known to undergo *Michael-Wittig* condensations with for example 2-butenal **2b** [30]. However, the ylide **6a** gave only some of the *Michael-Wittig* product **8b**. Last mentioned compound **8b** was very labile and in the presence of HCl in chloroform, hydrolysed to the corresponding cyclic β-keto ester: ethyl 6-methyl-2-oxocyclohex-3-ene-1-carboxylate (**9**). Eluation of **9** seems to suggest that partially hydrolyses of **8b** to **9** must have taken place on silica gel during chromatography. It is interesting to note that condensation of 2-butenal (**2b**) with the *in situ* generated phosphonium ylide **6a**, from a mixture of the allylic-**4** and vinylic phosphonium **5** salts and potassium carbonate, gave a lower overall yield but mainly the (2*E*,4*E*,6*E*) geometric isomer of ethyl 3-ethoxy-2,4,6-octatrienoate (**7b**), and none of the (2*E*,4*Z*,6*E*) isomer. This method gave also a higher yield of the cyclic ester **8b**. The higher yields that are obtained using the isolated phosphonium ylide **6a** as compared to the use of the *in situ* formed phosphonium ylide **6a**, seems to be a general outcome for 3-methyl-2-butenal (**2a**) and 2-methylpropenal (**2c**) condensations as well. In our hands, conjugated ketones 4-methyl-3-penten-2-one and 3-methyl-3-penten-2-one (**2d**) did not condense with the ylide **6a**. A similar result has also been communicated before, namely that methylvinylketone condensed with **6a** only in very low yields ($<10\%$) [16].

Experimental

All reactions were carried out under nitrogen. ^{1}H-NMR (δ, ppm, with $SiMe_4$ as an internal standard) and ^{13}C-NMR (δ, ppm) were recorded on a Varian Gemini 200 spectrometer at 200 MHz and 50.3 MHz, or on a Varian FT-80 at 80 MHz and 20 MHz respectively as indicated. High resolution electron ionization (EI) mass spectra were obtained from a Varian MAT 311 A instrument. Infrared spectra were obtained on a Hitachi 270-30 FTIR spectrophotometer (film, NaCl plates). Ultraviolet absorbance was measured as solutions in 96% EtOH on a Varian SuperScan 3 spectrophotometer or on a Shimadzu UV-150 spectrophotometer. Microanalyses were performed by Microanalytisches Labor Pascher (Bonn, Germany). Column chromatography was performed using Merck Si-60 (40–63 mm)

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 and distilled from $LiAlH_4$. Light petroleum is the fraction between 40–60°C.

Condensations of ethyl 3-ethoxy-4-(triphenylphosphoranylidene)but-2-enoate (**6a**) *with unsaturated carbonyl compounds*

With 3-methyl-2-butenal (**2a**) (Method A)

Ethyl 3-ethoxy-4-(triphenylphosphoranylidene)but-2-enoate (**6a**) (3.0 g, 7.17 mmol) in benzene (5 cm^3) was treated with 3-methyl-2-butenal **2a** (1.0 g, 11.9 mmol) and heated for 11 h at 75°C. The reaction mixture was diluted with light petroleum (10 cm^3) and filtered over silica gel. The filtrate was concentrated and chromatographed over silica gel and eluted with diethyl ether:light petroleum 1:9 to give a (9:1) mixture of (2*E*,4*E*)- and (2*E*,4*Z*)-ethyl 3-ethoxy-7-methylocta-2,4,6-trienoate (**7a**) (1.49 g, 93%), bp 110°C/0.05 mm Hg. λ_{max} (EtOH)/nm: 308, 218 (ε/$dm^3\,dm^{-1}\,cm^{-1}$ 28700, 7300); HRMS (EI) calcd. for $C_{13}H_{20}O_3$ (M^+) $m/z = 224.1412$, found 224.1428; ^{1}H NMR ($CDCl_3$, 80 MHz): $\delta = 1.21$ (t, $J = 7.1$ Hz, 3H), 1.33 (t, $J = 7.0$ Hz, 3H), 1.78 (sm, 6H), 3.83 (q, $J = 7.0$ Hz, 2H), 4.07 (q, $J = 7.1$ Hz, 2H), 4.95 (s, 1H), 5.97 (dm, $J = 11.0$ Hz, 1H), 7.13 (dd, $J = 15.3$, 11.0 Hz, 1H), 7.31 (d, $J = 15.3$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 20 MHz): $\delta = 14.0$, 14.1, 18.6, 26.4 (4×CH_3), 59.0, 63.3 (2×CH_2), 91.1 (C2), 121.1 (C4), 125.2 (C6), 131.6 (C5), 141.2 (C7), 166.4, 167.2 (C1, C3); IR (cm^{-1}): $\nu = 3080$ w, 2984 s, 2940 s, 2870 s, 1701 s, 1621 s, 1566 s, 1480 m, 1446 s, 1378 s, 1280 s, 1254 s, 1141 s, 1064 s, 989 m, 809 m.

With 3-methyl-2-butenal (**2a**) (Method B)

[2-Ethoxy-3-(ethoxycarbonyl)prop-2-enyl]triphenylphosphonium bromide (**4**) (+**5**) (0.7 g, 1.353 mmol) in chloroform (10 cm^3) was treated with 3-methyl-2-butenal (**2a**) (0.25 g, 2.98 mmol) and the reaction mixture heated for 6 h at 60°C in the presence of potassium carbonate (2.00 g). The reaction mixture was diluted with light petroleum (10 cm^3) and filtered over silica gel. The filtrate was concentrated and chromatographed over silica gel and eluted with ethyl acetate:light petroleum 1:9 to give (2*E*,4*E*)-ethyl 3-ethoxy-7-methylocta-2,4,6-trienoate (**7a**) (0.228 g, 75.2%) with only traces of the (2*E*,4*Z*) isomer. Hydrolysis of **7a** with little aqueous HCl in $CDCl_3$ occurred instantaneously and gave ethyl 7-methyl-3-oxoocta-2,4-dienoate (**3a**). ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 1.28$ (t, $J = 7.0$ Hz, 3H), 1.93 (sm, 6H), 3.59 (s, 2H), 4.21 (q, $J = 7.0$ Hz, 2H), 6.03 (dm, $J = 11.5$ Hz, 1H), 6.12 (d, $J = 15.3$ Hz, 1H), 7.53 (dd, $J = 15.3$, 11.5 Hz, 1H); this compound was identical with **3a** obtained before [3].

With 2-butenal (**2b**) (Method A)

Ethyl 3-ethoxy-4-(triphenylphosphoranylidene)but-2-enoate (**6a**) (2.0 g, 4.78 mmol) in *THF* (10 cm^3) was treated with 2-butenal (**2a**) (0.25 g, 3.57 mmol) and heated for 16 h at 60°C. The reaction mixture was diluted with light petroleum (20 cm^3) and filtered over silica gel. The filtrate was concentrated and chromatographed over silica gel and eluted with diethyl ether:light petroleum 1:9 to give a (4:1) mixture of (2*E*,4*E*,6*E*)- and (2*E*,4*Z*,6*E*)-ethyl 3-ethoxyocta-2,4,6-trienoate (**7b**) (0.46 g, 61%). λ_{max} (EtOH)/nm: 296.5, 215 (ε/$dm^3\,dm^{-1}\,cm^{-1}$ 26300, 8200); HRMS (EI) calcd. for $C_{12}H_{18}O_3$ (M^+) $m/z = 210.1256$, found 210.1238; ^{1}H NMR ($CDCl_3$, 200 MHz) (2*E*,4*E*,6*E*-isomer): $\delta = 1.23$ (t, $J = 7.1$ Hz, 3H), 1.34 (t, $J = 7.0$ Hz, 3H), 1.78 (d, $J = 6.6$ Hz, 3H), 3.84 (q, $J = 7.0$ Hz, 2H), 4.11 (q, $J = 7.1$ Hz, 2H), 4.99 (s, 1H), 5.92 (dq, $J = 15.0$, 6.6 Hz, 1H), 6.21 (ddm, $J = 15.0$, 10.5 Hz, 1H), 6.88 (dd, $J = 15.3$, 10.5 Hz, 1H), 7.34 (d, $J = 15.3$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 20 MHz) (2*E*,4*E*,6*E*)-isomer): $\delta = 14.0$, 14.2 (2 × OCH_2CH_3), 18.3 (CH_3), 59.1 (OCH_2CH3), 63.4 ($CO_2CH_2CH_3$), 91.5 (C2), 121.4 (C4), 131.4 (C6), 134.7 (C7), 135.6 (C5), 166.2, 167.2 (2 × –C=); IR (cm^{-1}): $\nu = 3070$ w,

2986 s, 2940 s, 1704 s, 1621 s, 1568 s, 1445 s, 1382 s, 1278 s, 1220 m, 1142 s, 1059 s, 995 m, 810 m. After further elution, ethyl 6-methyl-2-oxocyclohex-3-ene-1-carboxylate (**9**) (25 mg, 3%) was isolated. ^{1}H NMR ($CDCl_3$, 200 MHz) $\delta = 1.03$ (d, $J = 6.4$ Hz, 3H), 1.24 (t, $J = 7.0$ Hz, 3H), 2.65–2.35 and 2.2–2.0 (2m, 2H), 3.06 (d, $J = 11.7$ Hz, 1H), 4.19 (q, $J = 7.0$ Hz, 2H), 6.01 (ddd, $J = 10.1$, 2.6, 1.0 Hz, 1H), 6.95 (ddd, $J = 10.1$, 5.8, 2.8 Hz, 1H), 6.88 (dd, $J = 15.3$, 10.5 Hz, 1H), 7.34 (d, $J = 15.3$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 20 MHz): $\delta = 14.1$ (OCH_2CH_3), 19.7 (CH_3), 32.8, 33.1 (C5 and C6), 60.9 (C1), 61.6 ($CO_2CH_2CH_3$), 128.6 (C3), 149.9 (C4), 169.9 (CO_2Et), 194.6 (C2) [4]. Hydrolysis of **7b** with little aqueous HCl in $CDCl_3$ occurred instantaneously and gave ethyl 3-oxoocta-2,4-dienoate (**3b**). ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 1.29$ (t, $J = 7.0$ Hz, 3H), 1.90 (d, $J = 6.4$ Hz, 3H), 3.60 (s, 2H), 4.22 (q, $J = 7.0$ Hz, 2H), 6.14 (d, $J = 11.5$ Hz, 1H), 6.1–6.4 (m, 1H), 6.95–7.25 (m, 2H); this compound was identical with **3b** obtained before [3].

With 2-butenal (**2b**) (Method B)

[2-Ethoxy-3-(ethoxycarbonyl)prop-2-enyl]-triphenylphosphonium bromide, (0.7 g, 1.353 mmol) in chloroform (10 cm^3) was treated with 2-butenal (**2b**) (0.25 g, 3.57 mmol) and heated for 6 h at 60°C in the presence of potassium carbonate (2.00 g). The reaction mixture was diluted with light petroleum (20 cm^3) and filtered over silica gel. The filtrate was concentrated and chromatographed over silica gel and eluted with ethyl acetate:light petroleum 1:9 to give only (2*E*,4*E*,6*E*) ethyl 3-ethoxyocta-2,4,6-trienoate (**7b**) (0.077 g, 27.1%). Followed by ethyl 2-ethoxy-6-methyl-1,3-cyclohexadiene-1-carboxylate (**8b**) (22 mg, 7.8%); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 1.00$ (d, $J = 6.9$ Hz, 3H), 1.30 (t, $J = 7.0$ Hz, 3H), 1.32 (t, $J = 7.2$ Hz, 3H), 2.07 (ddd, $J = 17.5$, 5.6, 2.1 Hz, 1H), 2.46 (dddd, $J = 17.5$, 8.4, 2.6, 2.3 Hz, 1H), 2.88 (dqm, $J = 6.9$, 5.6 Hz, 1H), 4.20 (q, $J = 7.0$ Hz, 2H), 4.21 (q, $J = 7.2$ Hz, 2H), 6.07 (dd, $J = 9.2$, 2.6 Hz, 1H), 6.10 (ddm, $J = 9.2$, 8.4 Hz, 1H). Followed by ethyl 6-methyl-2-oxocyclohex-3-ene-1-carboxylate (**9**) [4].

With 2-methylpropenal (**2c**)

Ethyl 3-ethoxy-4-(triphenylphosphoranylidene)-but-2-enoate (**6a**) (0.50 g, 1.195 mmol) in *THF* (10 cm^3) was treated with 2-methylpropenal (**2c**) (0.25 g, 3.57 mmol) and heated for 16 h at 60°C. The reaction mixture was diluted with light petroleum (20 cm^3) and filtered over silica gel. The filtrate was concentrated and chromatographed over silica gel and eluted with ethyl acetate:light petroleum 1:9 to give (2*E*,4*E*)-ethyl 3-ethoxy-6-methylhepta-2,4,6-trienoate (**7c**) (4:1) (0.203 g, 80.7%). λ_{max} (EtOH)/nm = 240, ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 1.29$ (t, $J = 7.0$ Hz, 3H), 1.41 (t, $J = 7.0$ Hz, 3H), 1.96 (sm, 3H), 3.91 (q, $J = 7.0$ Hz, 2H), 4.16 (q, $J = 7.0$ Hz, 2H), 5.09 (s, 1H), 5.22 (sm, 2H), 7.04 (d, $J = 15.9$ Hz, 1H), 7.51 (d, $J = 15.9$, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 14.3$, 14.4 (OCH2CH_3), 18.4 (CH_3), 59.5 ($CO_2CH_2CH_3$), 63.7 (OCH_2CH_3), 92.5 (C2), 120.9 (C4), 121.0 (C7), 137.8 (C6), 142.0 (C6), 166.3, 167.6 (C1, C3); IR (cm^{-1}): $\nu = 3080$ w, 2981 s, 2940 s, 1706 s, 1620 s, 1580 s, 1446 s, 1378 s, 1253 s, 1141 s, 1060 s, 990 m, 816 m.

With 3-methylpent-3-en-2-one (**2d**)

Ethyl 3-ethoxy-4-(triphenylphosphoranylidene)but-2-enoate (**6a**) (0.50 g, 1.195 mmol) in *THF* (10 cm^3) was treated with 3-methylpent-3-en-2-one (**2d**) (0.25 g, 3.57 mmol) and heated for 16 h at 60°C. The reaction mixture was diluted with light petroleum (20 cm^3) and filtered over silica gel. The filtrate was concentrated and chromatographed over silica gel and eluted with ethyl acetate:light petroleum 1:9 to give only traces of (2*E*,4*Z*,6*E*)- and mostly the (2*E*,4*E*,6*E*)-isomer of ethyl 3-ethoxy-2,6-dimethylnona-2,4,6-trienoate (20 mg). ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 1.04$ (t, $J = 7.5$ Hz, 3H), 1.27 (t, $J = 7.1$ Hz, 3H), 1.40 (t, $J = 7.0$ Hz, 3H), 1.84 (s, 3H), 2.12 (q, $J = 7.5$ Hz, 2H), 3.90 (q, $J = 7.0$ Hz, 2H), 4.14 (q, $J = 7.1$ Hz, 2H), 5.02 (s, 1H), 6.04 (dm, $J = 10.9$ Hz, 1H), 7.21 (dd, $J = 15.3$, 10.9 Hz, 1H), 7.39 (d, $J = 15.3$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 12.3$ (CH_3CH_2C), 14.3, 14.4

(OCH_2CH_3), 25.7 (CH_3), 32.9 (CCH_2CH_3), 59.4 ($CO_2CH_2CH_3$), 63.6 (OCH_2CH_3), 91.3 (C2), 121.6 (C6), 123.7 (C4), 132.1 (C5), 147.1 (C7), 166.8, 167.8 (C1, C3). This unexpected compound is probably due to some small amounts of 2-methylpent-2-enal being present in 3-methylpent-3-en-2-one.

With 3,7-dimethylocta-2,6-dienal (**2e**)

[2-Ethoxy-3-(ethoxycarbonyl)prop-2-enyl]triphenylphosphonium bromide (**4**) (+**5**) (0.7 g, 1.353 mmol) in $CHCl_3$ (10 cm^3) was treated with 3,7-dimethylocta-2,6-dienal (**2e**) (0.40 g, 2.63 mmol) and heated for 6 h at 60°C in the presence of potassium carbonate (2.00 g). The reaction mixture was diluted with light petroleum (20 cm^3) and filtered over silica gel. The filtrate was concentrated and chromatographed over silica gel and eluted with ethyl acetate:light petroleum 1:9 to give only the (2*E*,4*E*,6*E*)-isomer of ethyl 3-ethoxydodeca-2,4,6,10-tetraenoate (**7e**) (0.19 g, 48.1%). λ_{max} (EtOH)/nm = 304, 239.5; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 1.26$ (t, $J = 7.1$ Hz, 3H), 1.38 (t, $J = 7.0$ Hz, 3H), 1.59 (sm, 3H), 1.66 (sm, 3H), 1.83 (sm, 3H), 2.1–2.3 (m, 4H), 3.89 (q, $J = 7.0$ Hz, 2H), 4.13 (q, $J = 7.1$ Hz, 2H), 5.01 (s, 1H), 5.07 (sm, 1H), 6.04 (d, $J = 11.0$ Hz, 1H), 7.20 (dd, $J = 15.2$, 11.0 Hz, 1H), 7.39 (d, $J = 15.2$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 14.3$, 14.4 (OCH_2CH_3), 17.1, 25.7, 25.4 ($3\times CH_3$), 40.2 ($2\times CH_2$), 59.3 ($CO_2CH_2CH_3$), 63.6 (OCH_2CH_3), 91.4 (C2), 121.7 (C6), 123.6 (C4), 125.1 (C10), 131.8 (C11), 131.9 (C5), 145.1 (C7), 166.7, 167.5 (C1, C3); IR (cm^{-1}): $\nu = 3080$ w, 2980 s, 2934 s, 2880 s, 1710 s, 1617 s, 1563 s, 1446 m, 1377 s, 1282 s, 1142 s, 1066 s, 980 m, 811 m (Method A: 53%).

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