New Annulation Techniques; Condensations of Phosphonium Ylides and Substituted 2*H*-Pyran-5-carboxylates; Preparation of Cyclohexenonedicarboxylates and Cyclohexadienedicarboxylates

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Substituted alkyl 2*H*-pyran-5-carboxylates condensed with alkyl 3-oxo-4-(triphenylphosphoranylidene)butanoate and alkyl 4-(triphenylphosphoranylidene)-2-butenoate to form substituted 2-vinyl-6-oxo-4-cyclohexene-1,3-dicarboxylates, some of which showed ecto-parasiticidal activity in pets and cattle, and substituted 2-vinyl-3,5-cyclohexadiene-1,3-dicarboxylates, respectively. The last mentioned product is in marked contrast to the product obtained using the corresponding arsonium analogue.

Keywords: Alkyl 2*H*-pyran-5-carboxylates; Methyl 3-oxo-4-(triphenylphosphoranylidene)butanoate; Methyl 4-(triphenylphosphoranylidene)-2-butenoate; 2-Vinyl-6-oxo-4-cyclohexene-1,3-dicarboxylate; 2-Vinyl-3,5-cyclohexadiene-1,3-dicarboxylate.

INTRODUCTION

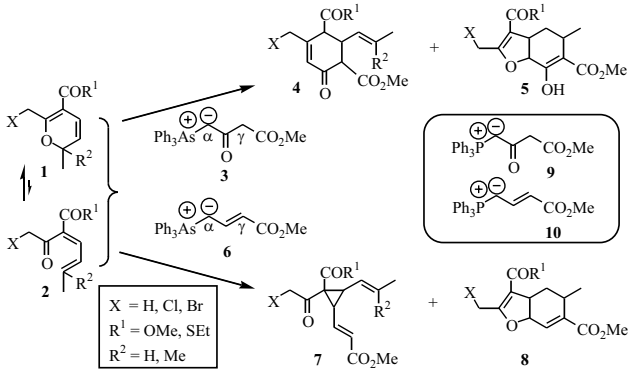
New annulation techniques for the construction of substituted cyclohexenones[1] and substituted cyclohexadienes[2] are important in organic synthesis. Recently, we described the condensations of arsonium ylides and 2*H*-pyran-5-carboxylates **1**.[3,4,5,6] 2*H*-pyran-5-carboxylates **1**[7] have the unique ability to undergo reversible electrocyclic ring opening to the ketodiene **2**[8] making these compounds available for Michael attack. For example, methyl 3-oxo-4-(triphenylarsoranylidene)butanoate **3** reacted with 2*H*-pyran-5-carboxylates **1** and gave mainly cyclohexenonedicarboxylates **4** and tetrahydrobenzofurandicarboxylates **5** (R^2 = H) as a minor byproduct[4] (Scheme I). On the other hand, methyl 4-(triphenylarsoranylidene)but-2-enoate **6** reacted with 2*H*-pyran-5-carboxylates **1** and gave mainly divinylcyclopropanecarboxylates **7**.[5] Tetrahydrobenzofurandicarboxylates **8** (R^2 = H) were in some cases also formed as a byproduct. (Scheme I).

In this paper we report on the Michael-Wittig condensations of the phosphonium ylides namely, methyl 3-oxo-4-(triphenylphosphoranylidene)butanoate **9a**–**9c** and ethyl 4-(triphenylphosphoranylidene)but-2-enoate **10** with substituted 2*H*-pyran-5-carboxylates **1**.

RESULTS AND DISCUSSION

Although the arsonium ylide **3** reacted with 2*H*-pyran-5-carboxylates **1** at room temperature,[4] alkyl 3-oxo-4-(triphenylphosphoranylidene)butanoates **9a**, **9b** and **9c**[9] reacted with 2*H*-pyran-5-carboxylates **1a-1f** in benzene only above 60 °C to form substituted dialkyl 2-vinyl-6-oxo-4-cyclohexene-1,3-dicarboxylates **4a-4f** in a mixture of three keto diastereomers and one or two enol diastereomers (Scheme II).[4] Some retro-aldol took place with conjugated 2*H*-pyran-5-carboxylates **1a-1c**. No tetrahydrobenzofurans **5**[4] were isolated. The mechanism of this reaction can be formulated as being the result of an initial Michael attack of the γ-ylide form of **9a** (**9b** and **9c**) on the ketoester **2**. This is followed by an intramolecular Wittig condensation and expulsion of Ph_3P=O to give **4a**,[10] **4b**, **4c**,[11] **4d**,[4] **4e**[4] and **4f** (Table 1). Apart from the esters of the phosphonium ylide **9a-9c**,[9] few other

Scheme I Condensation of arsonium ylids **3** and **6** and 2*H*-pyran-5-carboxylates **1**



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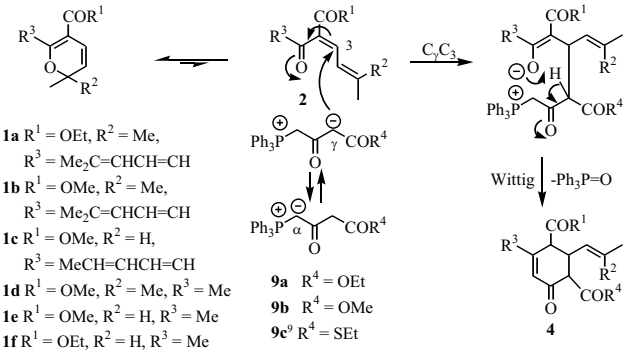
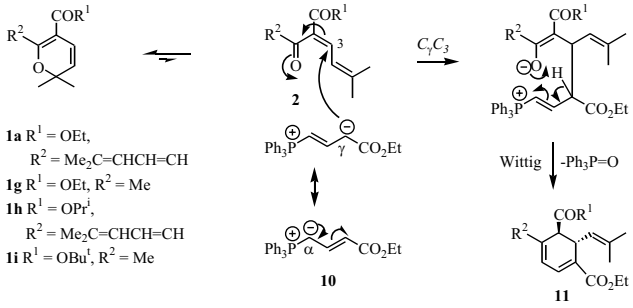
Scheme II Condensation of phosphonium ylide **9a**-**9c** with 2*H*-pyran-5-carboxylates **1**



Scheme III Condensation of phosphonium ylide **10** with 2*H*-pyran-5-carboxylates **1**



phosphonium ylides are known that have been used for Michael-Wittig condensations for the production of cyclohexenone derivatives.[12] No further condensation products were identified.[13] Biological screening tests revealed that cyclohexenonedicarboxylates **4d** and **4e** showed some activity against ectoparasites in pets and cattle.

The Michael-Wittig condensation is now a well-established useful synthetic reaction for the construction of 1,3-cyclohexadienes.[14] In this study we have found that alkyl 4-(triphenylphosphoranylidene)-2-butenoate **10** reacted with 2*H*-pyran-5-carboxylates **1** in benzene at 60 °C to form substituted cyclohexa-3,5-diene-1,3-dicarboxylates **11** (Scheme III). This is in sharp contrast to the condensation of the corresponding arsonium ylide **6** which gave 2,3-divinylcyclopropane-1-carboxylates **7**.[5] A solution of ethyl 2,2,6-trimethyl-2*H*-pyran-5-carboxylate **1g** was added to the phosphonium ylide **10** in benzene and refluxed for 3 hours to give the substituted 3,5-cyclohexadiene-1,3-dicarboxylate **11g** in a modest yield of 41% (Table 2). A *Cγ*-*C*$_3$-Michael-attack of the γ-ylide of **10** on the ketodiene valence-tautomer of **1g** followed by an intramolecular Wittig condensation and elimination of triphenylphosphine oxide furnished the 3,5-cyclohexadiene-1,3-dicarboxylate **11g**. The small coupling constant of e.g. **11g** (J = 1.2 Hz) of the two aliphatic protons in the ring is consistent with the proposed stereochemistry of **11**.[15]

Table 2. Condensation Products Obtained from the Condensation of Phosphonium Ylide **10** with 2*H*-pyran-5-carboxylates **1**

No	R^1	R^2	Yield (%)
11a	OEt	Me_2C=CHCH=CH	27
11g	OEt	Me	41
11h	OPr^i	Me_2C=CHCH=CH	25
11i	OBu^t	Me	49

EXPERIMENTAL SECTION

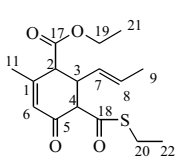
All reactions were carried out in a nitrogen atmosphere. ^{1}H NMR and ^{13}C NMR were recorded on a Varian FT-80 at 80 and 20 MHz, respectively, or on a Varian Gemini 200 spectrometer at 200 MHz and 50.3 MHz, respectively, in $CDCl_3$ with TMS as an internal standard for ^{1}H NMR. High resolution electron ionization (EI) mass spectra were obtained from a Varian MAT 311 A instrument and high resolution chemical ionization spectra (CI) using ammonia, were obtained from a

Table 1. Condensation Products Obtained from the Condensation of Phosphonium Ylids **9a–9c** with 2*H*-pyran-5-carboxylates **1**

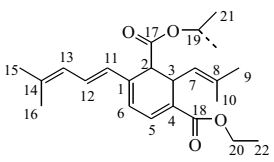
No	R^1	R^2	R^3	R^4	Reaction conditions	Yield (%)	Ratio
4a[10]	OEt	Me	Me_2C=CHCH=CH	OEt	3 h, 130 °C, neat	31[a]	9:22[d]
4b	OMe	Me	Me_2C=CHCH=CH	OMe	7 h, 75 °C, C_6H_6	35[b]	12:23[d]
4c[11]	OMe	H	MeCH=CHCH=CH	OMe	7 h, 70 °C, C_6H_6	23[c]	7:16[d]
4d[4]	OMe	Me	Me	OMe	5 h, 75 °C, C_6H_6	24	16:5:4[e]
4e[4]	OMe	H	Me	OMe	4 h, 75 °C, C_6H_6	33	8:3:1:1[e]
4f	OEt	H	Me	SEt	5 h, 70 °C, C_6H_6	3	(-)

[a,b,c] 4%, 16% and 35% yield of retro-aldol products namely ethyl-, methyl 7-methyl-3-oxo-4,6-octadienoate[11] and methyl 3-oxo-4,6-octadienoate[11] of respectively 2*H*-pyrans **4a**, **4b** and **4c**. [d] Ratio enol:keto of **4a**, **4b** and **4c**. [e] Ratio ketodiesters of **4d** and **4e**.

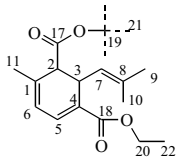
Table 3. ^{13}C Chemical Shifts of Compounds **4f**, **11a**, **11b**, **11c** and **11d**[a,e]



4f



11a, **11h**



11g, **11i**

No	**4f**[b]	**11a**[c]	**11g**[c]	**11h**[b]	**11i**[b]
1	146.37	138.73	138.24	138.81	138.77
2	51.49	46.23	51.06	46.40	51.72
3	38.67	34.99	34.44	34.92	34.17
4	64.95	129.35	128.40	131.81	127.85
5	195.45	131.00	131.54	130.95	131.55
6	126.67	125.96	121.14	125.91	120.56
7	132.54	123.21*[d]	123.59	123.30*[d]	123.33
8	121.54	133.87	133.57	133.84	133.31
9, 15	18.23	25.87, 26.30	25.84	25.95, 26.41	25.71
10, 16		18.30, 18.72	18.18	18.31, 18.76	17.97
11	23.23	128.27	23.86	128.29	23.74
12		132.07		132.15	
13		123.84*		123.86*	
14		137.69		137.81	
17	164.55	171.46	171.19	171.07	170.55
18	191.81	166.41	166.40	166.52	166.53
19, 20	61.62	60.28, 60.82	60.08, 60.70	68.19, 60.32	80.75 59.99
21, 22	14.67, 14.50	14.12, 14.28	14.15, 14.31	21.69, 14.32	27.77 14.11

[a] See Schemes II and III for compound numbers. At room temperature in $CDCl_3$ (δ in ppm). [b] at 50 MHz. [c] at 20 MHz. [d] Signals *can be interchanged. [e] NMR data of compounds **4d** and **4e** are reported in the experimental and gave the same chemical shifts as reported previously.[4]

Kratos Concept ISQ instrument. Ultraviolet absorbance was measured as solutions in 96% EtOH on a Varian SuperScan 3 spectrophotometer or on a Shimadzu UV-150 spectrophotometer. Infrared spectra were obtained on a Hitachi 270-30 FTIR spectrophotometer (film, NaCl plates). Microanalyses were performed by Microanalytisches Labor Pascher (Bonn, Germany) or using a Carlo Erba, CHNS-O EA 1108 Elemental Analyser. Column chromatography was performed using Merck Si-60 (40-63 mm) silica gel. Bulb-to-bulb distillations (bp) were carried out on a Buchi 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. 2*H*-Pyran-5-carboxylates **1** were synthesised from β-ketoesters and α,β-unsaturated aldehydes.[7]

Condensation of methyl 2,2-dimethyl-6-(4-methylpenta-1,3-dienyl)-2*H*-pyran-5-carboxylate 1b and methyl 3-oxo-4-(triphenylphosphoranylidene)-butanoate 9b[11]

A mixture of methyl 3-oxo-4-(triphenylphosphoranylidene)butanoate **9b** (4.40 g, 10.6 mmol) and methyl 2,2-dimethyl-6-(4-methylpenta-1,3-dienyl)-2*H*-pyran-5-carboxylate **1b** (2.36 g, 9.50 mol) in benzene (5 mL) was refluxed for 7 hours in the presence of magnesium sulfate (4.00 g, 33.0 mmol) and hydroquinone (0.11 g, 1.0 mmol). The reaction mixture was diluted with benzene:diethyl ether (2:3) (50 mL) and filtered over silica gel. The filtrate was evaporated and the residue chromatographed over silica gel and eluted with diethyl ether:light petroleum (1:24), (2:23) and (3:22) to (1:4) to give respectively the recovered 2*H*-pyran-5-carboxylate **1b** (0.23 g, 9.8%); methyl 7-methyl-3-oxo-octa-4,6-dienoate (0.28 g, 16.2 %) and (1*E*) dimethyl 6-(4-methylpenta-1,3-dienyl)-2-(2-methylprop-1-enyl)-4-oxocyclohex-5-ene-1,3-dicarboxylate **4b** (0.53 g, 35.2%) in equilibrium with (1*E*) dimethyl 4-hydroxy-6-(4-methylpenta-1,3-dienyl)-2-(2-methylprop-1-enyl)cyclohexa-3,5-diene-1,3-dicarboxylate tautomer. Compound **4b** had identical spectroscopic measurements with **4b** isolated from the condensation of 3-methyl-2-butenal and phosphonium ylide **9b**.[11]

Condensation of methyl 2-methyl-6-(penta-1,3-dienyl)-2*H*-pyran-5-carboxylate 1c and methyl 3-oxo-4-(triphenylphosphoranylidene)butanoate 9b

A mixture of methyl 3-oxo-4-(triphenylphosphoranylidene)butanoate **9b** (13.9 g, 31.3 mmol) and methyl 2-methyl-6-(penta-1,3-dienyl)-2*H*-pyran-5-carboxylate **1c** (3.45 g, 15.7 mol) in benzene (20 mL) was refluxed for 4 hours in the presence of sodium hydride (5 mg) and hydroquinone (1.70 g, 15.4 mmol). The reaction mixture was diluted with benzene (40 mL) and filtered over silica gel. The filtrate was evaporated and the residue chromatographed over silica gel and eluted with diethyl ether:light petroleum (40-60 °C) (1:24), (2:23) and (3:22) to (1:4) to give respectively the recovered 2*H*-pyran-5-carboxylate **1c** (0.03 g, 0.9%); methyl 3-oxoocta-4,6-dienoate (0.93 g, 35.1 %) and (1*E*) dimethyl 6-(penta-1,3-dienyl)-2-(prop-1-enyl)-4-oxocyclohex-5-ene-1,3-dicarboxylate **4c** (1.13 g, 22.6%) in equilibrium with (1*E*) dimethyl 4-hydroxy-6-(penta-1,3-dienyl)-2-(prop-1-enyl)cyclohexa-3,5-diene-1,3-dicarboxylate tautomer. Compound **4c** had identical spectroscopic measurements with **4c** isolated from the condensation of crotonaldehyde and phosphonium ylide **9b**.[11]

Table 4. ^{1}H Chemical Shifts of Compounds (Structures Depicted with Table 3) **4f**, **11a**, **11g**, **11h** and **11i**[a,d]

No	**4f**[b]	*J*	**11a**[c]	*J*	**11g**[c]	*J*	**11h**[b]	*J*	**11i**[b]	*J*
2	2.97	m	3.34	d, 1.2	2.84	d, 1.2	3.35	d, 1.2	2.77	s
3	2.2-2.4	m	3.9-4.4	m	3.9-4.3	m	4.06	d, 11.0	4.01	d, 10.3
4	3.82	d, 6.9								
5			6.99	d, 5.8	6.90	dd, 5.8, 0.5	7.05	d, 6.1	6.89	d, 5.7
6	5.92	s	6.09	d, 5.8	5.95	dq, 5.8, 1.3	6.15	d, 6.1	5.93	dd, 5.7, 1.4
7	5.38	ddm, 15.0, 6.4	4.98	dm, 9.5	5.06	dm, 10.2	5.00	dm, 9.9	5.00	dm, 10.3
8	5.59	dq, 15.0, 6.7								
9	1.66	d, 6.4	1.62	2x s	1.64	d, 1.3	1.64	d, 1.3	1.61	s
15			1.85				1.91	s		
10			1.85	2x s	1.81	d, 1.4	1.82	2x s	1.76	s
16							1.83			
11	2.03	s	6.18	d, 15.0	1.94	d, 1.3	6.25	d, 15.3	1.90	s
12			6.57	dd, 15.0, 10.2			6.60	dd, 15.3, 10.7		
13			5.87	dm, 10.2			5.93	dm, 10.7		
19	4.16	q, 7.1	4.06	2x q, 7.0	4.09	2x q, 7.1	4.96	h, 6.2	-	-
20	2.94	q, 7.4	4.15		4.15		4.17	q, 7.2	4.13	q, 7.2
21	1.24	t, 7.1	1.17	2x t, 7.0	1.20	2x t, 7.1	1.18	d, 6.2	1.38	s
22	1.28	t, 7.4	1.26		1.24		1.26	t, 7.2	1.23	t, 7.2

[a] At room temperature in $CDCl_3$ (δ in ppm). [b] at 200 MHz. [c] at 80 MHz. [d] NMR data of compounds **4d** and **4e** is reported in the experimental and gives the same chemical shifts as reported previously.[4]

Condensation of methyl 2,2,6-trimethyl-2*H*-pyran-5-carboxylate 1d and methyl 3-oxo-4-(triphenylphosphoranylidene)butanoate 9b

A mixture of methyl 3-oxo-4-(triphenylphosphoranylidene)butanoate **9a** (2.80 g, 6.74 mmol) and methyl 2,2,6-trimethyl-2*H*-pyran-5-carboxylate **1d** (1.15 g, 6.31 mol) in benzene (10 mL) was heated for 5 hours at 75 °C in the presence of hydroquinone (1.00 g, 9.08 mmol). The reaction mixture was diluted with light petroleum:diethyl ether (1:1) (50 mL) and filtered over silica gel. The filtrate was evaporated and the residue chromatographed over silica gel and eluted with diethyl ether:light petroleum (40-60 °C) (1:19), (1:9) and (1:3) to give recovered 2,6,6-trimethyl-2*H*-pyram-5-carboxylate **1d** (80 mg, 7.0%), 3-(methoxycarbonyl)-6-methylhepta-3,5-diene (30 mg, 2.6%) and dimethyl 6-methyl-2-(2-methylprop-1-enyl)-4-oxocyclohex-5-ene-1,3-dicarboxylate [4] **4d** (0.42 g, 23.8%). bp 125 °C (airbath) at 10^{-5} mm Hg. λ_{max} = 231, 316 (ε = 11270, 1660). ^{1}H NMR (major keto isomer, 64%): δ 1.64 (3H, d, *J* = 1.5 Hz), 1.68 (3H, d, *J* = 1.4 Hz), 1.96 (3H, d, *J* = 3.6 Hz), 3.17 (1H, dd, *J* = 12.5, 0.4 Hz), 3.53-3.85 (2H, m), 3.69 and 3.71 (6H, 2s), 4.95 (1H, dm, *J* = 9.7 Hz), 6.01 (1H, sm); ^{13}C NMR: δ 17.85 (CH_3), 21.89 (CH_3), 25.78 (CH_3), 40.70 (CH), 51.78 and 52.03 (2x MeO), 53.11 (CH), 58.56 (CH), 122.50 (CH), 127.27 (CH), 137.31 (C) 157.09 (C), 169.45 (C=O), 171.53 (C=O), 192.28 (C=O); HRMS (EI) calcd. for $C_{15}H_{20}O_5$ *m/z* 280.1311, found 280.1309. Anal. Calcd. for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.09; H, 7.32. This compound **4d** was identical to **4d** obtained from the condensation of **1d** and the arsonium ylide **3**.[4]

Condensation of methyl 2,6-dimethyl-2*H*-pyran-5-carboxylate 1e and methyl 3-oxo-4-(triphenylphosphoranylidene)butanoate 9a

A mixture of methyl 3-oxo-4-(triphenylphosphoranylidene)butanoate **9a** (2.80 g, 6.74 mmol) and methyl 2,6-dimethyl-2*H*-pyran-5-carboxylate **1e** (0.90 g, 5.35 mol) in benzene (6 mL) was heated for 4 hours at 75 °C in the presence of hydroquinone (0.90 g, 8.17 mmol). The reaction mixture was diluted with light petroleum:diethyl ether (1:1) (50 mL) and filtered over silica gel. The filtrate was evaporated and the residue chromatographed over silica gel and eluted with diethyl ether:light petroleum (1:3) to give dimethyl 6-methyl-2-(prop-1-enyl)-4-oxocyclohex-5-ene-1,3-dicarboxylate[4] **4e** (0.47 g, 33.0%). bp 115 °C (airbath) at 10^{-5} mm Hg. λ_{max} = 229, 317 (ε = 11060, 860). ^{1}H NMR (major keto isomer, 62%): δ 1.63 (3H, d, *J* = 5, 1.5 Hz), 1.92 (3H, s), 2.95-3.9 (3H, m), 3.71 and 3.68 (6H, 2s), 5.1-5.6 (2H, m), 5.93 (1H, sm). ^{13}C NMR: δ 17.88 (CH_3), 22.08 (CH_3), 44.55 (CH), 52.04 and 52.16 (2x MeO), 52.99 (CH), 58.25 (CH), 127.37 (CH), 128.36 (CH), 130.25 (CH), 156.74 (C), 169.38 (C=O), 171.37 (C=O), 192.19 (C=O); HRMS (EI) calcd. for $C_{14}H_{18}O_5$ *m/z* 266.1154, found 266.1153. Anal. Calcd. for $C_{14}H_{18}O_5$: C, 63.14; H, 6.81. Found: C, 62.78; H, 6.89. This compound **4e** gave identical data to **4e** obtained from the condensation of

1e and the arsonium ylide **3**.[4]

Condensation of ethyl 2,6-trimethyl-2*H*-pyran-5-carboxylate 1f and S-ethyl 3-oxo-4-(triphenylphosphoranylidene)butanoate 9c[9]

A mixture of crude *S*-Ethyl 3-oxo-4-(triphenylphosphoranylidene)butanoate **9c**[9] (15 g, 0.037 mol) and ethyl 2,6-trimethyl-2*H*-pyran-5-carboxylate **1f** (1.1 g, mol) in benzene (150 mL) was heated for 6 hours at 75 °C in the presence of hydroquinone (0.90 g, 8.17 mmol). The mixture was diluted with light petroleum:diethyl ether (1:1) (50 mL) and filtered over silica gel. The filtrate was evaporated and the residue chromatographed over silica gel and eluted with diethyl ether:light petroleum (1:9) and (3:7) to give respectively uncharacterized sulphurous compounds including some unreacted 2*H*-pyran-5-carboxylate **1f** and 1-ethyl,3-*S*-Ethyl 6-methyl-2-(prop-1-enyl)-4-oxocyclohex-5-ene-1,3-dicarboxylate **4f** (0.35 g, 3.1 %). bp 115 °C (airbath) at 10^{-2} mm Hg. λ_{max} = 206 (sh), 234, 344 (ε = 7300, 9900, 2700). IR λ_{max} (film) = 2978 (m), 2933 (m), 1733 (s), 1666 (s), 1634 (m), 1582 (s), 1445 (m), 1378 (m), 1191 (s), 1158 (m), 1032 (m), 967 (m) cm^{-1}. HRMS (EI) calcd. for $C_{16}H_{22}O_4S$ *m/z* 310.1239, found 310.1243. MS: 310 (10), 282 (5), 249 (50), 221 (10), 175 (20), 95 (100). Anal. Calcd. for $C_{16}H_{22}O_4S$: C, 61.91; H, 7.14; S, 10.33. Found: C, 61.82; H, 7.41; S, 10.01.

Condensation of ethyl 2,2-dimethyl-6-(4-methylpenta-1,3-dienyl)-2*H*-pyran-5-carboxylate 1a and ethyl 4-(triphenylphosphoranylidene)but-3-enoate 10

A mixture of ethyl 4-(triphenylphosphoranylidene)-but-3-enoate **10** (5.0 g, 13.3 mmol) and ethyl 2,2-dimethyl-6-(4-methylpenta-1,3-dienyl)-2*H*-pyran-5-carboxylate **1a** (1.25 g, 6.37 mol) in benzene (10 mL) was heated for 15 hours at 75 °C in the presence of hydroquinone (0.11 g, 1.0 mmol). The reaction mixture was diluted with benzene: diethyl ether (1:1) (50 mL) and filtered over silica gel. The filtrate was evaporated and the residue chromatographed over silica gel and eluted with diethyl ether:light petroleum (40-60 °C) (1:19) to give (1*E*) diethyl 6-(4-methylpenta-1,3-dienyl)-2-(2-methylprop-1-enyl)-3,5-cyclohexadiene-1,3-dicarboxylate **11a** (0.18 g, 27.4%). bp 120 °C (airbath) at 0.04 mm Hg. λ_{max} = 371, 248 (ε = 19750, 10390). HRMS (EI) calcd. for $C_{22}H_{30}O_4$ *m/z* 358.2144, found 358.2167. Anal. Calcd. for $C_{22}H_{30}O_4$: C, 72.70; H, 7.93. Found: C, 72.59; H, 8.07.

Condensation of ethyl 2,2,6-trimethyl-2*H*-pyran-5-carboxylate 1g and ethyl 4-(triphenylphosphoranylidene)but-3-enoate 10

A mixture of ethyl 4-(triphenylphosphoranylidene)-but-3-enoate **10** (0.70 g, 1.87 mmol) and ethyl 2,2,6-trimethyl-2*H*-pyran-5-carboxylate **1g** (0.48 g, 1.83 mmol) in benzene (5 mL) was refluxed for 8 hours in the presence of hydroquinone (0.1 g, 0.91 mmol). The reaction mixture was diluted with light petroleum:diethyl ether (1:1) (100 mL) and filtered over silica gel. The filtrate was evaporated and the residue chromatographed over silica gel and eluted with diethyl ether:light petroleum (40-60 °C) (3:17), diethyl 6-methyl-2-(2-methylprop-1-enyl)-3,5-cyclohexadiene-1,3-dicarboxylate **11g** 0.76 g, 40.8%). bp 125 °C (airbath) at 0.04 mm Hg. λ_{max} = 296 (ε = 7030). HRMS (EI) calcd. for $C_{17}H_{24}O_4$ *m/z* 292.1674, found 292.1702. Anal. Calcd. for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 69.55; H, 8.22.

Condensation of 1-methylethyl 2,2-dimethyl-6-(4-methylpenta-1,3-dienyl)-2*H*-pyran-5-carboxylate 1h and ethyl 4-(triphenylphosphoranylidene)but-3-enoate 10

A mixture of ethyl 4-(triphenylphosphoranylidene)but-3-enoate **10** (0.55 g, 1.47 mmol) and 1-methylethyl 2,2-dimethyl-6-(4-methylpenta-1,3-dienyl)-2*H*-pyran-5-carboxyl ate **1h** (0.25 g, 0.905 mmol) in benzene (1 mL) was heated for 75 minutes at 75 °C in the presence of hydroquinone (0.11 g, 1.0 mmol). The reaction mixture was diluted with light petroleum:ethyl acetate (1:1) (50 mL) and filtered over silica gel. The filtrate was evaporated and the residue chromatographed over silica gel and eluted with ethyl acetate:light petroleum (40-60 °C) (1:9), (1*E*) 3-(1-methylethyl),1-ethyl 6-(4-methylpenta-1,3-dienyl)-2-(2-methylprop-1-enyl)-3,5-cyclohexadiene-1,3-dicarboxylate **11h** (0.085 g, 25.2%). IR (cm^{-1}): ν_{max} 2983 (s); 2933 (s); 2875 (m); 1730 (s); 1710 (s); 1631 (m); 1448 (m); 1375 (m); 1259 (s); 1108 (s).

Condensation of 1,1-Dimethylethyl 2,2,6-trimethyl-2*H*-pyran-5-carboxylate 1i and ethyl 4-(triphenylphosphoranylidene)but-3-enoate 10

A mixture of ethyl 4-(triphenylphosphoranylidene)-but-3-enoate **10** (0.48 g, 1.28 mmol) and *t*-butyl 2,2,6-trimethyl-2*H*-pyran-5-carboxylate **1i** (0.17 g, 0.7578 mmol) in benzene (1 mL) was heated at 75 °C for 2 hours in the presence of hydroquinone (0.1 g, 0.91 mmol). The reaction mixture was diluted with light petroleum:ethyl acetate (1:1) (100 mL) and filtered over silica gel. The filtrate was evaporated and the residue chromatographed over silica gel and eluted with ethyl acetate:light petroleum (40-60 °C) (1:9) to give 3-(1,1-dimethylethyl)-1-ethyl 6-methyl-2-(2-methylprop-1-enyl)-3,5-cyclohexadiene-1,3-dicarboxylate **11i** (0.12 g, 49.4%). bp 125 °C (airbath) at 0.04 mm Hg. λ_{max} = 299.5. IR (cm^{-1}): ν_{max} 2984 (s), 2960 (s), 1710 (s), 1706 (s), 1615 (m), 1590 (m), 1445 (m), 1368 (m), 1263 (s), 1142 (s), 842 (m),

757 (m). Found: MH^+ (LSIMS), 321.20596. $C_{19}H_{29}O_4$ requires M, 321.20659.

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