A Facile Synthesis of 2,4-Alkadienoic Esters and 2,4,6-Alkatrienoic Esters via Arsonium Ylides*

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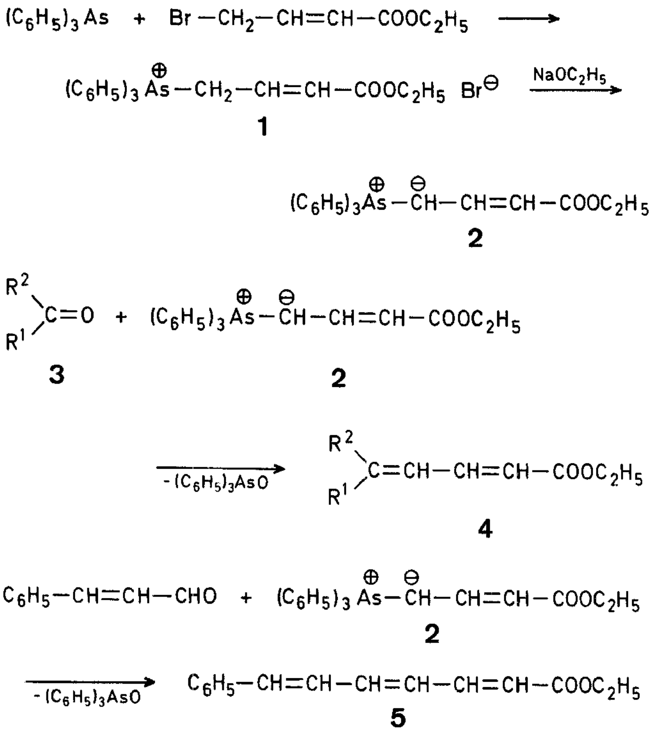
In earlier publications[1], we reported that arsonium ylides bearing an electron-withdrawing substituent in the alkylidene moiety show higher reactivity than the corresponding phosphonium ylides. In view of the biological activity of some polyenes we extended our method to the synthesis of 2,4-alkadienoic esters and 2,4,6-alkatrienoic esters by using 3-ethoxycarbonylallylidenetriphenylarsorane (**2**) as reagent. Arsorane **2** reacts with a variety of ketones as well as aldehydes to afford ethyl 2,4-alkadienoates (**4**) and with cinnamaldehyde to afford ethyl 7-phenyl-2,4,6-heptatrienoate (**5**).



It is worthy of note that 2,4-alkadienoic esters (**4**) have been synthesized from 4-bromocrotonates by Reformatsky reaction; however, attack at the 4-position to give the normal product as well as attack at the 2-position to give the abnormal product was observed[2]. Further, the dehydration of hydroxy esters formed gave rise to mixtures of isomers which were difficult to separate.

Our method is an one-step reaction, the conditions are mild, the yields are good to excellent, and the by-product triphenylarsine oxide can be easily converted to triphenylarsine by conventional reduction[3]. The structures of all products were established by M.S., I.R., and ^1H-N.M.R. spectra. All microanalyses were consistent with the calculated values.

In order to show that the arsonium ylides are indeed more reactive than the corresponding phosphonium ylids, 3-ethoxycarbonylallylidenetriphenylphosphorane was allowed to react with acetone at 35 °C for 24 h; no product was formed at all. Arsoranes react with aldehydes in ~90% yields, while the corresponding phosphoranes react with same aldehydes in much lower yields (for **4a**, 33%; for **4b**, 25%)[4].

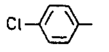
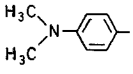
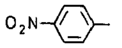
3-Ethoxycarbonylallylidenetriphenylarsorane (**2**) reacts with aromatic aldehydes stereospecifically as evidenced by comparison of the ^1H-N.M.R. spectra of the products with those reported[5]. Products **3a, b, c** are the thermodynamically stable (*E,E*)-isomers. Compound **2** reacts with cinnamaldehyde to give the (*E,E,E*)-isomer of **5**[6] while it reacts with ketones to give two isomers.

The synthesis of methyl (±)-*trans*-chrysanthemate by reaction of methyl 5-methyl-*trans*-2,4-hexadienoate with diphenylsulfonium isopropylide has been reported[7] to proceed with 72.5% yield; the starting dienoate was prepared from methallyl chloride, acetylene, and methanol in the presence of tetracarbonylnickel, but no yield was reported. Our method provides a facile synthesis of the latter compound by a one-step reaction.

3-Ethoxycarbonylallylidenetriphenylarsonium Bromide (1):

A solution of triphenylarsine (120 g; 0.39 mol) and ethyl 4-bromocrotonate (100 g, 0.52 mol) in absolute benzene (60 ml) is stirred at 80 °C for 2 h, and the mixture then allowed to stand for several days.

Table 1. Preparation of Ethyl 2,4-Alkadienoates (**4**) and Ethyl 7-Phenyl-2,4,6-heptatrienoate (**5**)

Product	R^1	R^2	Reaction Conditions Time [h], Temp. [°C]	Yield [%]	m.p. [°C] or b.p. [°C]/torr	Molecular formula[a] or Lit. Data	M.S. *m/e*
4a		H	4, 20°	95	m.p. 75–76°	$C_{13}H_{13}ClO_2$ (236.7)	236, 191, 163, 128
4b		H	4, 20°	95	m.p. 122–123°	123–124°[8]	245, 200, 172, 128
4c		H	4, 20°	85	m.p. 121–122°	m.p. 118–120°[8]	247, 202, 174, 128
4d	CH_3	C_2H_5	12, 35°	45	b.p. 84–85°/4	$C_{10}H_{16}O_2$ (168.2)	168, 139, 123, 95
4e	CH_3	$ClCH_2-$	12, 20°	71	b.p. 102–106°/3	$C_9H_{13}ClO_2$ (188.7)	188, 139, 111, 79
4f	CH_3	CF_3	2, 15°	86	m.p. 177°	$C_9H_{11}F_3O_2$ (208.2)	208, 163, 139, 135
4g	CH_3	CH_3	12, 35°	85	b.p. 85–87°/12	b.p. 81°/6[9]	154, 139, 111, 81
4h	$-(CH_2)_5-$		12, 35°	70	b.p. 98–102°/1	b.p. 143–148°/8[10]	194, 149, 121
5	–		4, 20°	95	m.p. 90–91°	$C_{15}H_{16}O_2$ (228.3)	228, 119, 155, 77

[a] Satisfactory microanalyses obtained: C ±0.30, H ±0.10, N ±0.33; exception: **4g**, C −0.44.

Table 2. Stereochemistry and Spectral Data of Compounds **4** and **5**

Compound	(*E,E*)-Isomer [%]	I.R. ν [cm^{-1}]	^{1}H-N.M.R. (CDCl$_3$/TMS$_{int}$) δ [ppm]
4a	100	1700, 1620, 1230, 840	(*E,E*): 1.31 (t, 3H, $J = 7$ Hz); 4.18 (q, 2H, $J = 7$ Hz); 5.90 (d, 1H, $J = 15$ Hz); 6.7 (m, 2H); 7.2 (m, 5H)
4b	100	1700, 1600, 1230, 810	(*E,E*): 1.31 (t, 3H, $J = 7$ Hz); 3.0 (s, 6H); 4.28 (q, 2H, $J = 7$ Hz); 5.82 (d, 1H, $J = 14$ Hz); 6.7 (m, 4H); 7.27 (m, 3H)
4c	100	1710, 1590, 1330, 850	(*E,E*): 1.27 (t, 3H, $J = 7$ Hz); 4.28 (q, 2H, $J = 7$ Hz); 6.01 (d, 1H, $J = 15$ Hz); 6.9 (m, 2H); 7.4 (m, 3H); 8.17 (d, 2H, $J = 8$ Hz)
4d	71[a]	1700, 1630, 1270	(*E,E*): 1.09 (t, 3H, $J = 7$ Hz); 1.32 (t, 3H, $J = 7$ Hz); 1.93 (s, 3H); 2.19 (q, 2H, $J = 7$ Hz); 4.26 (q, 2H, $J = 7$ Hz); 5.84 (d, 1H, $J = 15$ Hz); 6.04 (d, 1H, $J = 11$ Hz); 7.26 (dd, 1H, $J = 15{,}11$ Hz)
			(*E,Z*): 1.07 (t, 3H, $J = 7$ Hz); 1.32 (t, 3H, $J = 7$ Hz); 1.89 (s, 3H); 2.33 (q, 2H, $J = 7$ Hz); 4.24 (q, 2H, $J = 7$ Hz); 5.80 (d, 1H, $J = 15$ Hz); 5.98 (d, 1H, $J = 11$ Hz); 7.63 (dd, 1H, $J = 15{,}11$ Hz)
4e	25[b]	1700, 1620, 1250	1.00 (t, 3H, $J = 7$ Hz); 1.72 (*E,Z*) + 1.82 (*E,E*) (2s, 3H); 3.88 (s, 2H); 3.92 (q, 2H, $J = 7$ Hz); 5.64 (d, 1H, $J = 15$ Hz); 6.0 (d, 1H, $J = 12$ Hz); 7.27 (dd, 1H, $J = 15, 12$ Hz)
4f	94[b]	1750, 1650, 1200	0.87 (t, 3H, $J = 7$ Hz); 1.30 (*E,Z*) + 1.60 (*E,E*) (2s, 3H); 3.77 (q, 2H, $J = 7$ Hz); 5.70 (d, 1H, $J = 15$ Hz); 6.30 (d, 1H, $J = 11$ Hz); 7.18 (dd, 1H, $J = 15.11$ Hz)
4g	–	1710, 1640, 1280	1.18 (t, 3H, $J = 7$ Hz); 1.92 (s, 6H); 4.18 (q, 2H, $J = 7$ Hz); 5.72 (d, 1H, $J = 15$ Hz); 6.01 (d, 1H, $J = 12$ Hz); 7.67 (dd, 1H, $J = 15, 12$ Hz)
4h	–	1710, 1630, 1270	0.97 (t, 3H, $J = 7$ Hz); 1.32 (s, 6H); 1.90–2.07 (m, 4H); 3.82 (q, 2H, $J = 7$ Hz); 5.43 (d, 1H, $J = 12$ Hz); 5.60 (d, 1H, $J = 8$ Hz); 7.27 (dd, 1H, $J = 12{,}8$ Hz)
5	–	1690, 1600, 1130, 760	1.27 (t, 3H, $J = 7$ Hz); 4.16 (q, 2H, $J = 7$ Hz); 5.82 (d, 1H, $J = 15$ Hz); 6.5–7.5 (m, 10H)

[a] Two isomers were separated by preparative G.L.C. (10% SE-30 on Chromosorb Q at 150 °C).

[b] The ratios of isomers were estimated by the integrated intensities of the ^{1}H-N.M.R. peaks.

The solid is collected by suction and washed with absolute benzene to give pure **1** which is recrystallized from chloroform/ethyl acetate; yield: 180 g (93%); m.p. 151–152 °C.

C$_{24}$H$_{24}$AsBrO$_2$	calc.	C 57.74	H 4.85	Br 16.01
(499.3)	found	57.22	4.78	15.79

3-Ethoxycarbonylallylidenetriphenylarsorane (2):
Sodium (0.81 g, 0.035 g-atom) is allowed to react with absolute ethanol (15 ml) under nitrogen. The solvent is evaporated and absolute ether (100 ml) and the arsonium salt **1** (17.6 g, 0.035 mol) are added at 0 °C. The mixture is stirred for 30 min. The solid is collected by suction and washed with ice water until neutral; yield of **2**: 13.8 g (94%); m.p. 130 °C (dec.).

C$_{24}$H$_{23}$AsO$_2$	calc.	C 68.90	H 5.54
(418.4)	found	68.86	5.43

Ethyl 5-(4-Chlorophenyl)-2,4-pentadienoate (4a); Typical Procedure:
3-Ethoxycarbonylallylidenetriphenylarsorane (**2**; 2.1 g, 5 mmol), 4-chlorobenzaldehyde (**3a**; 0.7 g, 5 mmol), and absolute ether (20 ml) are placed in a flask. The mixture is stirred at 20 °C for 4 h, the white precipitate then collected by suction and washed with absolute ether to give triphenylarsine oxide; yield: 1.60 g (~ 100%). Evaporation of the combined ether solution gives a solid which is recrystallized from ethanol to give ester **4a**; yield: 1.12 g (95%); m.p. 75–76 °C.

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* This paper is our 25th report on the application of elemento-organic compounds of the fifth and sixth groups in organic syntheses.

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