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γ Condensation of an Allylic Phosphonium Ylide

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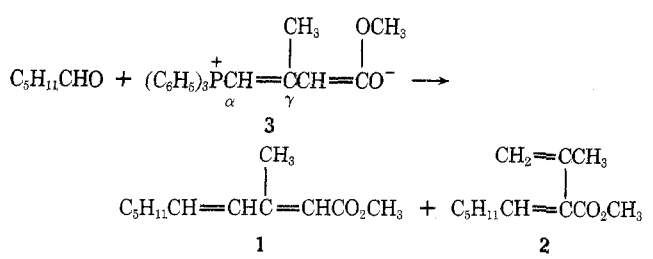
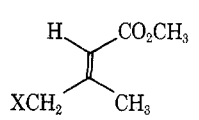
The Wittig reaction of (*E*)-3-methoxycarbonyl-2-methylallyltriphenylphosphonium bromide with *n*-hexanal furnished all four geometric isomers of methyl 3-methyl-2,4-decadienoate, the normal α-condensation product, and both geometric isomers of methyl 2-isopropenyl-2-octenoate, the unprecedented γ-condensation product. The α:γ product ratio varied from 1:9 to 9:1 in response to the tertiary amine base and the group IIB metal halide present. In contrast, the analogous trans phosphonate provided only the trans-2,trans-4 and the cis-2,trans-4 isomers of the α-condensation product in 6:1 ratio.

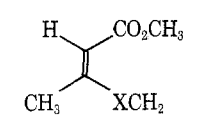
Aldehydes normally condense with allylic phosphonium ylides at the ylide α-carbon atom.[1-5] The Wittig reaction of *n*-hexanal with the stabilized allylic phosphonium ylide **3**, however, generates not only all four geometric isomers of methyl 3-methyl-2,4-decadienoate (**1**), the normal α-condensation product, but also both geometric isomers of methyl 2-isopropenyl 2-octenoate (**2**), the unprecedented γ-condensation product. Under the appropriate reaction conditions, either ester can be produced in >90% relative yield.



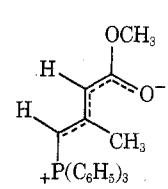
The crystalline trans phosphonium bromide[2,3] **7e** was obtained in 84% yield on heating equimolar quantities of methyl 4-bromo-3-methyl-2-butenoate (**6e:6z** = 86:14) and triphenylphosphine in acetonitrile. This salt slowly isomerized in dry dimethyl sulfoxide near 25°; the isomer ratio at equilibrium was **7e:7z** = 47:53. Treatment of the trans phosphonium salt **7e** with excess sodium hydroxide furnished the phosphonium ylide **3** as yellow crystals in 68% yield. A $CDCl_3$ solution of this ylide near 25° contained two isomeric species in 2:1 ratio. The major and minor species are assigned the structures **3z** and **3e**, respectively,



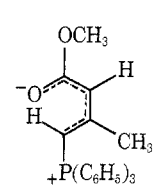
4e, X = OH
5e, X = O_3P
6e, X = Br
7e, X = $P^+(C_6H_5)_3Br^-$
8e, X = $PO(OC_2H_5)_2$



6z, X = Br
7z, X = $P^+(C_6H_5)_3Br^-$
8z, X = $PO(OC_2H_5)_2$

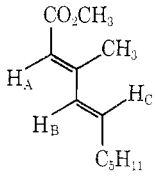


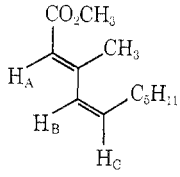
3e

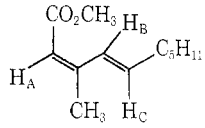


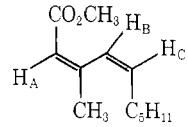
3z

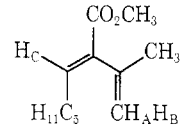
Table I
Infrared, Nmr, and Glc Data for Esters 1 and 2

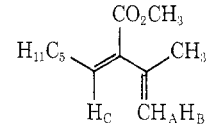

1ee


1ez


1ze


1zz


2e


2z

Compd	Ir, λ_{max} (CCl4), μ (intensity) $\nu_{C=O}$	$\nu_{C=C}$	$\nu_{=CH}$[a]	Nmr (CCl4), δ (ppm), multiplicity, and J (Hz) CCH_3 (b s, 3 H)	OCH_3 (s, 3 H)	H_A (b s)	H_B (1 H)	H_C (1 H)	Glc[b]
1ee	5.81 (s)	6.10 (w), 6.19 (m)	10.36 (m)	2.25	3.65	5.63	6.08, s	6.08, m	100
1ez	5.79 (s)	6.11 (w), 6.24 (w)		2.23	3.66	5.63	5.85, d, 12	5.55, d, 12, t, 7	61
1ze	5.81 (s)	6.10 (m), 6.24 (m)	10.22 (m)	1.97	3.64	5.55	7.63, d, 15.5	6.05, d, 15.5, t, 7	91
1zz				1.80	3.71		7.40, m		65
2e	5.78 (s)	6.12 (w)	11.09 (m)	1.85	3.67	4.68	5.07, b s	6.69, t, 7.5	38
2z	5.76 (s)	6.15 (w)	11.26 (m)	1.87	3.73	4.80	4.92, b s	5.71, t, 7.5	42

[a] Ethylenic out-of-plane wagging mode. [b] Relative retention time on column A at 170°; the retention time of **1ee** was 28.1 min.

Table II
Formation of the Esters 1 and 2 from the Trans Phosphonium Salt 7e and *n*-Hexanal

Reactant, ratio[a] Amine	Halide	DMF[b]	Time,[c] hr	Yield, %	Relative glc yield, % 1ee	1ez	1ze	1zz	2e	2z	1:2
3[d]			0.5	65	12	7	17	6	47	10	42:57
DBN, 1.05		1.5	2.3	73[e]	11	16	12	4	40	12	43:52
DBN, 1.0	$ZnCl_2$, 1.0	2.0	48	72	29	9	5	4	37	16	47:53
DBN, 1.0	CdI_2, 1.0	2.0	50	76	23	15	11	13	27	11	62:38
DBN, 1.0	CdI_2, 2.0	2.0	45	68	35	20	16	21	4	2	92:6
DIEA, 1.0	CdI_2, 1.0	4.0	12	26	45	20	21	4	4	1	90:5
DBN, 1.0	$HgCl_2$, 1.0	2.0	50	74	4	10	5	5	53	20	24:73
DIEA, 1.05		1.0	170[f]	74	2	2	3	2	68	22	9:90
DIEA, 1.01		2.0	370[g]	75	3	2	2	1	69	23	8:92

[a] Millimoles per millimole of *n*-hexanal. [b] Milliliters of dry dimethylformamide per millimole of *n*-hexanal. [c] Clear yellow-orange solution of *n*-hexanal (1.00 mmol), **7e** (1.00 mmol), amine, and halide in DMF was stirred at 25°, except as noted. [d] Solution of the ylide **3** (1.12 mmol) and *n*-hexanal (1.00 mmol) in CH_2Cl_2 (12 ml). [e] Substitution of dry dimethyl sulfoxide for DMF gave a product mixture of identical composition in 57% yield. [f] The salt **7e** (1.10 mmol) remained undissolved in part for about 26 hr. [g] Reaction temperature was 0–5°; the mixture remained heterogeneous for several days.

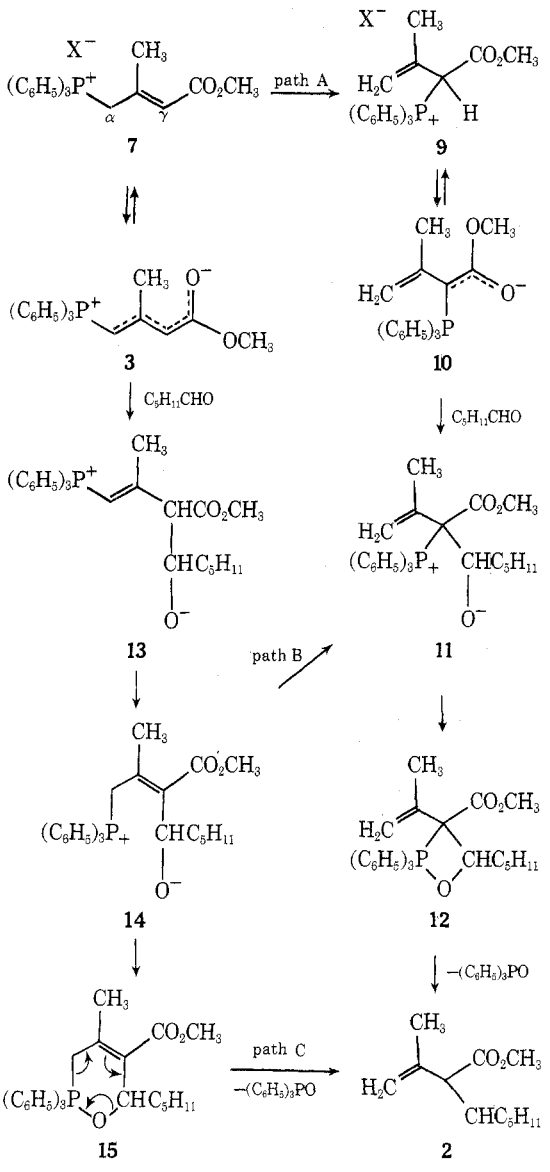
in analogy with the conformers observed by Howe[5] for the homologous *O*-ethyl phosphonium ylide.[6]

Reaction of *n*-hexanal with a dichloromethane solution of the phosphorane **3** for 30 min at 25° afforded in 65% yield a mixture of six isomeric esters. Preparative gas–liquid chromatography provided five fractions, four of which contained >93% of a single isomer by glc assay; the fifth fraction consisted of the esters **1ez** and **1zz** in the ratio 84:14. Each fraction was characterized by infrared and nmr spectroscopy; the distinguishing data are given in Table I.[7] Isomers of the linearly conjugated dienoate **1** exhibited two olefinic stretching vibrations; both isomers of the cross-conjugated dienoate **2** showed only one. The out-of-plane wagging deformation of the ethylenic hydrogens was observed near 10.3 μ for the vicinal trans-4 hydrogens of **1ee** and **1ze** and near 11.2 μ for the isopropenyl methylene groups of **2e** and **2z**. The methoxycarbonyl group deshielded proton H_B of the cis-2 isomers of **1**, the C(3)-methyl protons of the trans-2 isomers of **1**, and the H_C proton of **2e** and the trans-4 isomers of **1**.

The same six isomers were formed in essentially the same ratio both from the preformed ylide **3** and by generation of this ylide *in situ* by deprotonation of the trans phosphonium bromide **7e** with 1,5-diaza-5-bicyclo-[4.3.0]nonene (DBN) in dimethylformamide (DMF) (see Table II). The presence of zinc chloride caused little change in this product ratio. Cadmium iodide, however, favored formation of the α-condensation product; ester **1** constituted more than 90% of the product mixture when diisopropylethylamine (DIEA) was used with an equimolar amount of cadmium iodide or when DBN was employed with 2 equiv of the iodide. In contrast, the cross-conjugated ester **2** comprised 73% of the product mixture when DBN was used with an equimolar amount of mercuric chloride. Finally, when a DMF slurry of the crystalline, sparingly soluble trans phosphonium salt **7e** was treated with *n*-hexanal and the weaker base DIEA, the γ-condensation product **2** was formed in >90% relative yield at both 0 and 25°.

Substantial precedent[1] exists for formation of the α-condensation product **1** by electrophilic attack of *n*-hexanal at the α carbon of ylide **3** and fragmentation of the adduct *via* a cyclic four-center phosphorane. Formally, generation of the γ-condensation product **2** involves electrophilic attack of *n*-hexanal at the γ carbon and double-bond formation with loss of triphenylphosphine oxide. Three possible mechanisms for γ condensation are shown in Scheme I. Path A would involve allylic rearrangement of the triphenylphosphorus moiety before normal Wittig condensation. Thus isomerization of the allylic ylide **3** *via* the phosphonium salts **7** and **9** would give the ylide **10**, which would condense with the aldehyde through the cyclic four-center phosphorane **12**.[8] Path B would involve attachment of *n*-hexanal to the γ carbon of allylic ylide **3**,[9] tautomerization of the initial adduct **13**, allylic rearrangement of the triphenylphosphorus group of the adduct **14**, and elimination of triphenylphosphine oxide from the resulting betaine **11** as in path A. Finally, path C would

Scheme I



avoid the unprecedented allylic rearrangement of the triphenylphosphorus group required by path A or B. Thus the zwitterion **14** obtained by tautomerization of the initial γ adduct **13** would directly fragment to the observed γ-condensation product **2** and triphenylphosphine oxide *via* the cyclic six-center phosphorane **15**. The present data are explicable by competition of any of these pathways for γ condensation with the usual Wittig pathway for α condensation.

Aldehydes normally condense with stabilized phosphonate carbanions to form predominantly the trans olefin.[10,11] Pattenden and Weedon[12] reported that the allylic trans phosphonate **8e** condenses position specifically and stereospecifically with *trans*-geranial and benzaldehyde to form only the all-trans esters. In contrast, the allylic cis phosphonate **8z** was observed to condense position specifically but not stereospecifically with propanal, benzaldehyde, and *trans*-geranial; in each case the product ratio of the cis-2,trans-4 isomer to the trans-2,trans-4 isomer was 1:3.

The trans phosphonate[12] **8e** is formed in 96% yield by heating an equimolar mixture of the trans bromo ester **6e** and triethyl phosphite at 165–170° for 5 min. The stereochemical purity of the phosphonate is strictly dependent on that of the bromo ester, since neither compound is isomerized under the conditions of this Arbuzov reaction.[13] Free-radical bromination[14-19] of methyl 3-methylbutenoate with *N*-bromosuccinimide afforded a mixture of the starting ester, the trans bromo ester **6e**, the cis bromo ester **6z**, and methyl 4-bromo-3-bromomethyl-2-butenoate (**16**) in the ratio 12:42:37:11 by nmr assay. Fractional distillation of this mixture through a Teflon spinning band column provided the pure trans bromo ester in 17% yield. Alternatively, free-radical bromination of 3-methyl-2-butenoic acid afforded a similar mixture of bromo acids from which the trans bromo acid can be obtained either by crystallization[19] from hydrocarbon solvents or by selective lactonization[20] of the cis bromo acids with aqueous alkali; subsequent esterification furnishes the trans bromo ester **6e** in low overall yield. As both of these routes require the purification of lachrymatory allylic bromides that can cause pronounced dermatitis on contact with the skin, a third route to the trans bromo ester was developed that avoids the purification of allylic bromide intermediates.

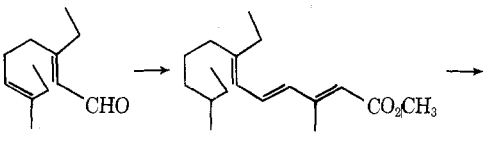
Table III
Formation of the Bromo Ester 6e from the Hydroxy Ester 4e *via* the Phosphite 5e

Time, hr (temp, °C)[a]	Product distribution,[b] mol % 4e	5e	6e
1.3 (0)	26	49	25
6.0 (0)	4	55	41
13.5 (0)	2	46	52
19 (0)	0	39	61
32 (0)	0	25	75
32 (0), 12 (20)	0	10	90

[a] Solution of **4e** (3.0 mmol), PBr_3 (1.1 mmol), and ether (30 ml) under argon. [b] By nmr assay.

The trans hydroxy ester **4e**, prepared in good yield by the method of Epstein and Sonntag,[21] was treated[22] with phosphorus tribromide in 1:1 ether–hexane for 6 hr at 25° to produce the pure trans bromo ester **6e** in 83% yield.[23] This reaction proceeds *via* the trans phosphite **5e**, which is formed in ether faster than it is converted to the bromide (Table III). The trans bromo ester prepared in this manner contained none of the cis isomer by nmr assay.

Treatment of the trans phosphonate **8e** with *n*-hexanal and lithium diisopropylamide for 6 hr below −50° provided isomers **lee** and **lze** in the ratio 86:14, respectively. The 4,5 double bond was formed stereospecifically, since neither of the cis-4 isomers was detected in the product mixture. The partial loss of the trans-2 stereochemistry is evidently due to the nature of the phosphonate carbanion, since the recovered phosphonate **5** was extensively isomerized (cis:trans 63:37). Under carefully selected conditions, however, loss of the trans-2 stereochemistry can be suppressed. Thus during the synthesis[24] of the dehydro analog **18** of the C_{18}-Cecropia juvenile hormone, Wittig reaction of the trans phosphonate **8e** with the appropriate aldehyde provided the trans-2,trans-4,trans-6,cis-10 isomer of the tetraene **17** in about 99% purity under carefully chosen reaction conditions.



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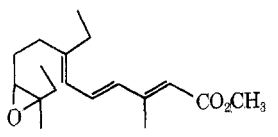

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Table IV
Nmr Data for Eight Compounds of the Type $XCH_2C(CH_3)=CHCO_2CH_3$

Compd	X	Chemical shift (ppm), multiplicity, and coupling constant (Hz)				
		CCH_3 (3 H)	OCH_3 (3 H)	CH_2 (2 H)	=CH (1 H)	X
4e	OH	2.02, d, 1	3.67, s	4.05, d, 2	5.90, m	4.65, s, 1 H
5e	O_3P	2.13, b, s	3.69, s	4.54, b d, 9	5.90, m	
6e	Br	2.26, d, 1.5	3.69, s	3.95, s	5.89, b s	
7e	$P(C_6H_5)_3Br$	2.02, d, 3, d, 1	3.62, s	5.04, b d, 16	5.87, b d, 5	7.6–8.1, m, 15 H
8e	$PO(OC_2H_5)_2$	2.25, d, 3.4, d, 1.3	3.65, s	2.67, d, 23.5, d, 0.7	6.74, b d, 5.5	1.29, 6 H, t, 7.0; 4.06, 4 H, d, 8.5, q, 7.0
6z	Br	2.05, d, 1.5	3.69, s	4.54, s	5.70, b s	
7z	$P(C_6H_5)_3Br$	2.12, d, 3.5, d, 1	3.37, s	5.53, b d, 18	5.86, b d, 5	7.6–8.1, m, 15 H
8z	$PO(OC_2H_5)_2$	2.03, d, 3.6, d, 3	3.65, s	3.37, b d, 24.5	6.74, b d, 5.5	1.27, 6 H, t, 7.0; 4.03, 4 H, d, 8, q, 7.0

Experimental Section

Melting points and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 137 Infracord spectrophotometer. Nuclear magnetic resonance (nmr) spectra were measured with a Varian Associates A-60 spectrometer; chemical shifts are expressed in parts per million (ppm) downfield from internal tetramethylsilane (b = broad). The infrared and nmr spectra were observed in CCl_4 solution. Mass spectra were obsetved in these laboratories with an AEI-MS 9 spectrometer at 70 eV.

Analytical gas–liquid phase chromatography (glc) was performed with column A, a stainless-steel column (15 ft × 0.125 in.) containing 10% Carbowax 20M on Diatoport S (80–100 mesh), on a Hewlett-Packard (F & M) research gas chromatograph, Model 5750, using flame ionization detectors and prepurified nitrogen (30 ml/min) as the carrier gas. Product percentages were calculated from peak-area ratios without correction for detector response. Preparative glc was conducted with column B, a brass column (12 ft × 0.375 in.) containing 16% Carbowax 20M on Diatoport S (60–80 mesh), on a Wilkins Aerograph Model A-700 instrument using thermal conductivity detectors and helium (200 ml/min) as the carrier gas.

Diisopropylamine and hexamethylphosphoric triamide (HMPA) were dried by distillation from calcium hydride; tetrahydrofuran (THF) was freshly distilled from lithium aluminum hydride; and *n*-hexanal, bp 32–34° (1 Torr), was freshly distilled from sodium sulfate.

Methyl (*E*)-4-Bromo-3-methyl-2-butenoate (6e). A. Bromination of Methyl 3-Methyl-2-butenoate. *N*-Bromosuccinimide (46.0 g, 0.258 mol) was added to a solution of methyl 3-methyl-2-butenoate, bp 73.5° (88 Torr) (28.5 g, 0.250 mol), and azobis(isobutyronitrile) (0.41 g, 2.5 mmol) in CCl_4 (250 ml). The slurry was heated at reflux for 10 hr, cooled, and filtered to remove solid succinimide (25.43 g, 99% yield). The filtrate contained four esters by nmr assay, compound (rel mol %): the trans bromo ester **6e** (42), the cis bromo ester **6z** (37), the dibromo ester **16** (11), and the starting ester (10). It was freed of solvent and distilled through a 45-cm stainless-steel spinning-band column to provide the bromo ester **6** (*E*:*Z* = 23:77, 12.4 g, 26% yield), bp[25] 56 (2.2 Torr)–64° (3.5 Torr). As the isomers of **6** were not separated under these conditions, the undistilled material was filtered and distilled without column to give a colorless liquid (26.2 g, 51% yield), bp 40–70° (0.1 Torr), consisting of **6e**:**6z**:**16** (71:12:17).

This mixture was redistilled at reduced pressure through an annular 60-cm Teflon spinning-band column. The first fraction (0.2 g, 4% yield) was the cis bromo ester **6z**, pure by nmr assay: bp 83–89° (9 Torr); ir 5.79 (s, C=O), 6.07 (m, C=C), 6.94 (w, sh), 6.99 (m), 7.29 (m, CCH_3), 7.40 (m, CO_2CH_3), 7.88 (m, sh), 8.00 (s, CO), 8.22 (m), 8.41 (m), 8.62 (vs, CO), 9.60 (m), 10.07 (w), 10.82 (w), 11.25 (w, sh), and 11.58 μ (m); nmr, see Table IV; mass spectrum *m/e* 191.9875 (calcd for $C_6H_9BrO_2$, 191.9786).

After many intermediate fractions, several fractions afforded the trans bromo ester **6e** (8.0 g, 16.5% yield), pure by nmr assay, as a colorless liquid: bp 67–68° (0.45 Torr) [lit.[19] bp 82–83° (10 Torr)]; ir 5.78 (s, C=O), 6.08 (m, C=C), 6.99 (m), 7.26 (w, CCH_3), 7.39 (m, CO_2CH_3), 7.81 (w), 8.11 (s, CO), 8.27 (m), 8.62 (vs, CO), 8.81 (m), 9.66 (m), 10.78 (w), 11.31 (w), and 11.63 μ (w); nmr, see Table IV; mass spectrum *m/e* 191.9781 (calcd for $C_6H_9BrO_2$, 191.9786).

The residual red-black liquid (9.5 g) was mostly 4-hydroxy-3-methyl-2-butenoic acid lactone (**19**) and 4-hydroxy-3-bromomethyl-2-butenoic acid lactone (**20**) by ir and nmr characterization: ir 5.59 (s, C=O), 5.69 (vs, C=O), and 6.08 μ (w, C=C). They were evidently formed during distillation by thermal elimination of CH_3Br from the cis bromo ester **6z** and the dibromo ester **16**, respectively. Nmr data for **16** follow: 3.74 (s, 3, OCH_3), 4.16 (s, 2, trans CH_2), 4.74 (s, 2, cis CH_2), and 6.07 ppm (m, 1, CH=C). **19** nmr: 2.11 (b s, 3, CH_3), 4.69 (b s, 2, CH_2O), and 5.74 ppm (m, 1, CH=C) (lit.[21] 2.12, 4.73, and 5.78 ppm). **20** nmr: 4.34 (b s, 2, CH_2O), 5.90 (b s, 2, CH_2Br), and 6.07 ppm (m, 1, CH=C).

B. Bromination of Methyl (*E*)-4-Hydroxy-3-methyl-2-butenoate (4e). A solution of the trans hydroxy ester[21] **4e**, bp 77° (0.27 Torr), in hexane (100 ml) and ether (100 ml) was stirred under argon at −10° and was treated dropwise over 2 min with phosphorous tribromide (3.0 g, 1.11 mmol, 1.1 equiv). The solution was stirred in the dark for 6.0 hr at 25°, washed with aqueous sodium bicarbonate and brine, dried, and freed of solvent. The residual colorless liquid (4.90 g, 83% yield), the pure trans bromo ester **6e** by nmr assay,[26] was used without further purification.

(*E*)-3-Methoxycarbonyl-2-methylallyltriphenylphosphonium Bromide (7e). A solution of the bromo ester **6** (*E*:*Z* = 86:14; 3.01 g, 15.6 mmol) and triphenylphosphine (4.10 g, 15.6 mmol) in acetonitrile (50 ml) was heated at reflux for 20 min, cooled, and allowed to stand at 25° for 6 hr. A white, crystalline solid was obtained in two crops (3.44 and 1.72 g, 84% combined yield) that was the pure trans phosphonium bromide by nmr assay: mp 183–184° with prior sintering and decomposition to a red liquid (lit.[2] mp 160°, lit.[3] mp 179°); ir 5.82 (s, C=O), 6.09 (m, C=C), 6.20, 6.31, and 6.77 (all w), 6.98 (vs), 7.26 and 7.39 (w), 8.2 (s, broad), 8.70 (s), 9.02 (vs), 9.7 (w), 10.02 (m), 11.36 (w), and 14.75 μ (s, C_6H_5); nmr, see Table IV.

Dilution of the remaining solution with hexane precipitated a white solid, about 90% of which was the cis phosphonium bromide **7z** by nmr assay; for nmr, see Table IV.

An 0.22 *M* solution of trans phosphonium bromide **7e** in dry dimethyl sulfoxide was kept near 25°; the isomer ratio after 7 and 31 days was *E*:*Z* = 47:53 by nmr assay.

(3-Methoxycarbonyl-2-methylallylidene)triphenylphosphorane (3). A solution of the trans phosphonium bromide **7e** (0.495 g, 1.09 mmol) in acetonitrile (5 ml) was shaken with 40% aqueous sodium hydroxide (1.0 ml) for 5 min. The organic phase was washed with brine (1 ml) and freed of solvent. The residual viscous orange liquid (0.36 g) was crystallized from ethyl acetate to furnish yellow crystals (0.275 g, 68% yield) that sintered near 120° and melted near 135° to a deep red liquid. A solution of these crystals in $CDCl_3$ contained two isomers in 2:1 ratio by nmr spectroscopy: broadened methyl singlets at 1.67 (CCH_3, major), 2.50 (CCH_3, minor), 3.40 (OCH_3, minor), and 3.57 ppm (OCH_3, major), olefinic multiplets at 3.2–3.7 and 4.6–5.0 ppm, and an aromatic multiplet at 7.1–7.9 ppm.

Diethyl (*E*)-3-Methoxycarbonyl-2-methylallylphosphonate (8e). A mixture of the trans bromo ester **6e** (1.67 g, 8.65 mmol) and redistilled triethyl phosphite (1.45 g, 8.7 mmol) was heated at 165–170° for 5 min. The resulting material was vacuum distilled through a 5-cm Vigreux column to provide the trans phosphonate **8e** (2.09 g, 96%), pure by nmr assay,[27] as a colorless liquid: bp 112° (0.12 Torr), 117–119° (0.35 Torr) [lit.[28] bp 118–120° (0.55 Torr), lit.[29] bp 120–122° (0.6 Torr)]; ir 5.79 (s, C=O), 6.05 (m, C=C), 6.99 (m), 7.21 (m), 7.38 (m), 7.99 (s), 8.27 (s), 8.68 (s), 9.11 (m), 9.47 (s), 9.71 (vs), 10.35 (s), and 11.38 μ (m); nmr, see Table IV; mass spectrum *m/e* 250.0968 (calcd for $C_{10}H_{19}O_5P$, 250.0970).

Isomerization of the Phosphonate 8. A. With Lithium Diisopropylamide. A solution of diisopropylamine (1.081 g, 10.7 mmol) in dry tetrahydrofuran (12 ml) was cooled under argon to −75°, treated with 1.60 *M* *n*-butyllithium in pentane (Foote Mineral Co.; 6.25 ml, 10.0 mmol), and warmed to 0°. The phosphonate 8 (*E*:*Z* = 55:45; 2.47 g, 9.90 mmol) was added, which immediately colored the solution a deep blood-red. After 10 min at 0° part of this solution was added to 3 *M* aqueous ammonium chloride; extractive work-up furnished the isomers of phosphonate 8 in the ratio *E*:*Z* = 35:65 by nmr assay. After 13 hr at 0° or 15 hr at 0° and 10 hr at 30°, the isomer ratio was *E*:*Z* = 23:77.

B. With Heat. The phosphonate 8 (*E*:*Z* = 86:14) was sealed under argon in a glass tube and heated at 130° for 10 hr; the isomer ratio of the recovered phosphonate was *E*:*Z* = 77:23 by nmr assay.

Methyl 3-Methyl-2,4-decadienoate (1) and Methyl 2-Isopropenyl-2-octenoate (2). Solid trans phosphonium bromide **7e** (1.000 g, 2.20 mmol) and a solution of 1,5-diaza-5-bicyclo[4.3.0]nonene (0.25 ml, 2.1 mmol) in dry dimethylformamide (2.0 ml) was stirred under argon for 5 min at 25°. The resulting clear orange solution was treated with *n*-hexanal (0.24 ml, 2.0 mmol), stirred at 25° for 2.3 hr, diluted with 2:1 hexane–dichloromethane (30 ml), washed with 0.5 *M* aqueous hydrochloric acid, water, 0.5 *M* aqueous sodium bicarbonate, and brine (25 ml each), dried, and freed of solvent. The solid residue, which contained much triphenylphosphine oxide, was triturated with hexane (four 3-ml portions). The hexane triturate was filtered, freed of solvent, and retriturated with hexane (three 1-ml portions). The triturate was filtered and freed of solvent to furnish a clear yellow liquid (0.287 g, 73%) that was a mixture of the ester **1** (four isomers) and the ester **2** (two isomers) by nmr assay. By glc assay this mixture contained the six isomers in the ratio **1ee**:**1ez**:**1ze**:**1zz**:**2e**:**2z** = 11:16:12:4:40:12. The results of eight related experiments are given in Table II.

The product mixtures from several experiments were pooled and separated by preparative glc on column B at 150° into five fractions that were assayed by analytical glc on column A at 170°, isomer (rel %): **1ee** (96) and **1ze** (4); **1ez** (84) and **1zz** (14); **1ze** (94) and **1ee** (6); **2e** (93) and **2z** (7); **2z** (98) and **2e** (2). Diagnostic data from the infrared and nmr spectra of these fractions are given in Table I. The first four fractions gave mass spectral molecular ions at *m*/*e* 196.1452, 196.1450, 196.1443, and 196.1439, respectively (calcd for $C_{12}H_{20}O_2$, *m*/*e* 196.1463).

Methyl 2-Isopropenyl-2-octenoate (2). Solid trans phosphonium bromide **7e** (1,000 g, 2.20 mmol) and a solution of diisopropylethylamine (0.400 ml, 21.1 mmol) and *n*-hexanal (0.24 ml, 2.0 mmol) in dry dimethylformamide (2.0 ml) were stirred under argon at 25° for 170 hr. After 26 hr the initial slurry became a clear yellow solution. The reaction was worked up as described in the previous experiment to provide a clear light yellow liquid (0.288 g, 74% yield) that consisted of the trans isomer **2e**, the cis isomer **2z**, and isomers of the ester **1** in the ratio 68:22:9, respectively, by glc assay.

Methyl (*E*,*E*)- and (*Z*,*E*)-3-Methyl-2,4-decadienoate (1ee and 1ze). A solution of diisopropylamine (0.528 g, 5.24 mmol) in dry THF (5.0 ml) was stirred at −75° under argon and treated with 1.60 *M* *n*-butyllithium in pentane (3.1 ml, 4.95 mmol). The solution was warmed to −60°, diluted with dry HMPA (5.0 ml), and treated with a solution of *n*-hexanal (0.400 g, 4.00 mmol) and the trans phosphonate **8e** (1.10 g, 4.40 mmol) in THF (16 ml) and HMPA (5 ml) precooled to −70°. The reaction solution was stirred for 6.0 hr at −60 to −50° (9:1 acetonitrile–acetone slurry), poured into 0.5 *M* aqueous sodium bicarbonate (50 ml), and extracted with 1:1 hexane–ether. The extracts were washed with 0.5 *M* aqueous sodium bicarbonate and brine, dried, and freed of solvent.

The resulting clear yellow liquid (1.04 g) contained the phosphonate 8 and two isomers of the ester **1** (**1ee**:**1ze** = 9:1) by nmr assay. It was separated into two fractions by chromatography on a 2.0-mm layer of Merck silica gel using dichloromethane as eluent and uv visualization. The faster moving liquid (R_f 0.45–0.75, 0.128 g, 13% recovery) was the phosphonate 8 (*E*:*Z* = 37:63) by nmr assay. The slower moving liquid (R_f 0–0.45, 0.378 g, 48% yield) consisted of only two isomers of the ester 1 in the ratio **1ee**:**1ze** = 86:14 by glc assay.

Registry No.—**1ee**, 50428-75-6; **1ez**, 50428-76-7; **1ze**, 50428-77-8; **1zz**, 50428-78-9; **2e**, 50428-79-0; **2z**, 50428-80-3; **3e**, 50432-30-9; **3z**, 50432-31-0; **4e**, 13866-57-4; **5e**, 50428-82-5; **6e**, 19041-17-9; **6z**, 27652-13-7; **7e**, 50557-81-8; **7z**, 50557-82-9; **8e**, 19945-56-3; **8z**, 19945-48-3; 16, 50428-87-0.

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