

singlets at δ 2.23, 1.43, and 1.36, with an integral ratio of 1:3:3. The ^{15}N -nmr spectrum (toluene) showed a single line (0.9 Hz half-width) at 6,082,641.8 Hz.

2-Amino-4-nitro-3,5-di-*tert*-butyltoluene-4- ^{15}N -6-*d*. A sample of **4** (0.24 g) dissolved in 25 ml of ethanol was reduced with hydrogen in the presence of prereduced platinum oxide at atmospheric pressure. The uptake of the requisite amount of hydrogen was rapid, and reaction was complete after 1 hr. The deep yellow crystalline product was isolated by filtration and evaporation of ethanol solvent, 0.20 g. Glpc indicated almost complete conversion of reactant to a single product. The ^1H -nmr spectrum (CCl_4) consisted of two *tert*-butyl singlets at δ 1.32 (9 H) and 1.49 (9 H), an aromatic methyl singlet at 2.18 (3 H), and a broad amine proton band at about 3.8 (2 H). The spectrum of this sample at -60° (DCCl_3) is shown in Figure 3.

Reduction of an unlabeled sample of **4** was carried out in an identical manner. Recrystallization of the product from hexane and sublimation (110° (1 mm)) afforded an analytical sample, mp $104\text{--}106^\circ$.

Anal. Calcd for $\text{C}_{15}\text{H}_{24}\text{N}_2\text{O}_2$: C, 68.14; H, 9.15; N, 10.60. Found: C, 68.22; H, 9.20; N, 10.89.

Nitration of 2,4,6-Tri-*tert*-butylnitrobenzene-2(and 4)-*tert*-butyl- d_9 and Mass Spectral Analysis. Parallel nitrations of 50-mg samples of unlabeled **1** and 1-2(and 4)-*tert*-butyl- d_9 were carried out by mixing the nitro compounds with 2-ml portions of fuming nitric acid at 0° . After a 40-min reaction time, water was added, and the organic products were extracted with toluene. The toluene extracts, after thorough extraction with water and drying over sodium sulfate, were analyzed by direct injection into a gas chromatograph mass spectrometer (LKB Model 9000). Mass spectral data for the products of interest are shown in Figure 1.

Acknowledgment. We wish to thank Professor J. D. Roberts and Dr. F. J. Weigert for their interest and for recording the ^{15}N magnetic resonance spectra reported here. The assistance of Mrs. Inger Lindgren in performing the analysis on the LKB mass spectrometer is gratefully acknowledged. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Reactions and Nuclear Magnetic Resonance Studies of Allylic Wittig Ylides

Robert K. Howe

Contribution from the Monsanto Co., Agricultural Division, Research and Development Department, St. Louis, Missouri 63166. Received October 31, 1970

Abstract: Nmr studies of (3-ethoxycarbonyl-2-methylallylidene)triphenylphosphorane (**9**) reveal that this Wittig ylide exists mainly as two conformers **9a** and **9b** in rapid equilibrium, with the *cis* form **9a** as the major isomer. The ylide condenses with benzaldehyde to give ethyl 3-methyl-5-phenyl-2,4-pentadienoate in which *cis*-2 isomers predominate. Protonation of the ylide, formed from phosphonium salts *cis*-**3** and *trans*-**4**, with aqueous hydrogen bromide regenerates the salts in an 88:12 ratio of **3** and **4**. Hydrolysis of **9** produces triphenylphosphine oxide and a 92:8 mixture of ethyl 3-methyl-3-butenate and ethyl 3-methylcrotonate. (3-Ethoxycarbonylallylidene)triphenylphosphorane (**8**) exists as the two conformers **8a** and **8b**, with the *trans* form **8a** as the major isomer. Ylide **8** condenses with benzaldehyde to produce predominantly *trans*-2 isomers of ethyl 5-phenyl-2,4-pentadienoate.

The phosphonium ylide from either the methyl or ethyl ester of (3-carboxy-2-methylallyl)triphenylphosphonium bromide has been reported to condense with β -ionylidenealdehyde in ethanol to give predominantly *trans*-2 isomers of vitamin A ester.¹ Thus, the observation in the present work that the ylide condenses with benzaldehyde to give mainly *cis*-2 isomers of ethyl 3-methyl-5-phenyl-2,4-pentadienoate prompted further studies of the ylide.

The phosphonium salts **3** and **4** were each obtained in pure form by fractional crystallization of the salt mixtures produced from the reaction of triphenylphosphine with enriched samples of **1** and **2**, respectively. Treatment of either **3** or **4** with base and benzaldehyde gave, within experimental error, the same product ester mixture **5** in which the sum of *cis*-2 isomers amounted to 57–60% (Scheme I). The product mixture was analyzed by integration of the nmr signals of the vinyl methyl groups, which are sufficiently separated in the spectra to allow reasonably accurate assays. The nmr spectra of all the individual esters have been determined

and reported in detail previously.^{2–4} Under similar conditions the ylide from **6**⁵ reacted with benzaldehyde to produce ethyl 5-phenyl-2,4-pentadienoate (**7**) that consisted of 94% *trans*-2 isomers.

The ylide **8** formed from **6** and the ylide **9** formed either from **3** or **4** were prepared and isolated as solids. The infrared spectrum of **8** has strong absorption at 1636 cm^{-1} and very strong absorption at 1530 cm^{-1} , and the ylide **9** has strong absorption at 1632 cm^{-1} and very strong absorption at 1492 cm^{-1} , indicative of extensive delocalization of the carbanionic charge into the carbonyl group of the ylides. The ylides **8** and **9** are

(2) R. H. Wiley, T. H. Crawford, and C. E. Staples, *J. Org. Chem.*, **27**, 1535 (1962).

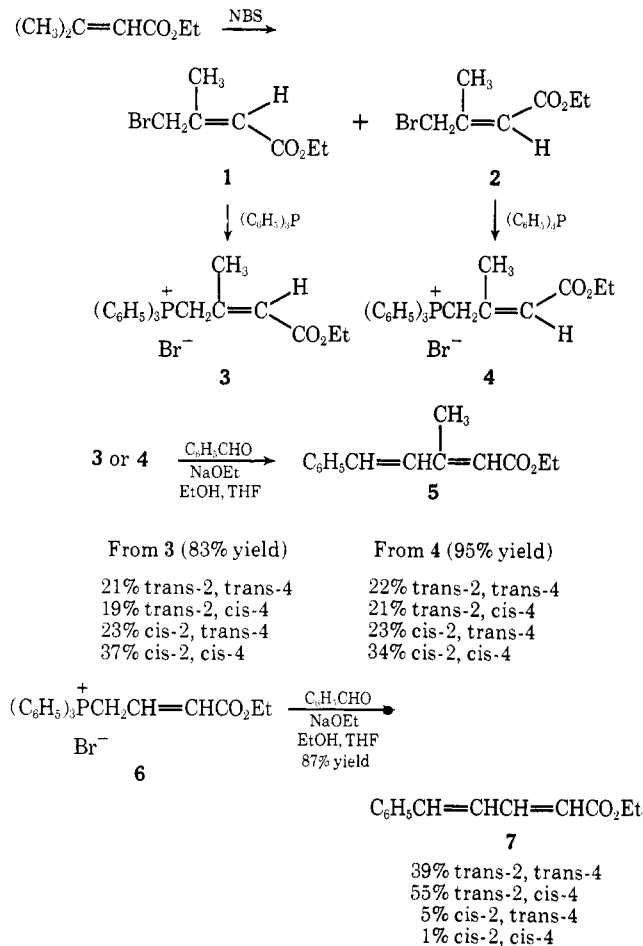
(3) R. H. Wiley, H. C. van der Plas, and N. F. Bray, *ibid.*, **27**, 1989 (1962).

(4) G. Pattenden and B. C. L. Weedon, *J. Chem. Soc. C*, 1997 (1968).

(5) The corresponding methyl ester derivative, (3-methoxycarbonylallyl)triphenylphosphonium bromide, and its ylide have been prepared: (a) F. Bohlmann, *Chem. Ber.*, **90**, 1519 (1957); (b) E. Buchta and F. Andree, *ibid.*, **92**, 3111 (1959); (c) G. Kresze, J. Firl, and H. Braun, *Tetrahedron*, **25**, 4481 (1969). Bohlman prepared methyl 5-aryl-2,4-pentadienoates of unspecified stereochemistry via the reaction of the ylide with aromatic aldehydes. Kresze, *et al.*, found the product mixture from reaction of 9-anthraldehyde and the ylide to consist of 70% methyl 5-(9-anthryl)-*trans,trans*-2,4-pentadienoate and 30% methyl 5-(9-anthryl)-*trans,cis*-2,4-pentadienoate.

(1) (a) G. Wittig and H. Pommer, German Patent 950,552 (1956); (b) H. Pommer, *Angew. Chem.*, **72**, 811 (1960).

Scheme I



vinyllogous analogs of methoxycarbonylmethylenetriphenylphosphorane, which has been shown by nmr⁶ and ir⁷ data to possess considerable enolate⁸ character.

The nmr spectra of **8** and **9** are particularly informative. The data for **8** in chloroform-*d* at 24° and the structure assignments are given in Chart I. The ratio of **8a** to **8b** at 24° is *ca.* 75:25. All coupling constants were verified by proton-proton decoupling, phosphorus-proton decoupling, and spectra obtained at both 60 and 100 MHz (coupling constants field independent). In **8a**, proton H_B is severely deshielded by the negative carbonyl group, and H_A in **8b** is similarly deshielded. Deshielding by a carbonyl group is well known.^{9,10} The dramatic deshielding that can occur due to a proximate oxygen anion is less well known.¹¹ In general, electric charges can significantly alter shielding con-

(6) (a) H. J. Bestmann, G. Joachim, I. Lengyel, J. F. M. Oth, R. Merényi, and H. Weitkamp, *Tetrahedron Lett.*, 3355 (1966); (b) F. J. Randall and A. W. Johnson, *ibid.*, 2841 (1968); (c) H. I. Zelinger, J. P. Snyder, and H. J. Bestmann, *ibid.*, 2199 (1969).

(7) A. J. Speziale and K. W. Ratts, *J. Amer. Chem. Soc.*, **85**, 2790 (1963).

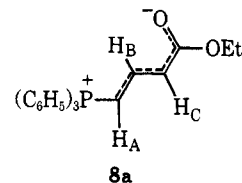
(8) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, pp 62-79.

(9) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance in Organic Chemistry," 2nd ed, Pergamon Press, London, 1969, pp 88-92, 222-223.

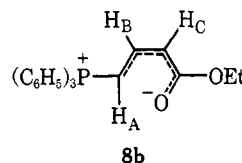
(10) It has been reported (ref 2) that the deshielding effect of a *cis*-carboxylate ion (in pyridine solution) is considerably greater than the deshielding of a *cis*-methoxycarbonyl group (in carbon tetrachloride solution). This is probably due in part, however, to the aromatic induced solvent shift with pyridine; see D. H. Williams, *Tetrahedron Lett.*, 2305 (1965).

(11) S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **87**, 5247 (1965).

Chart I

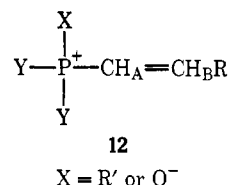
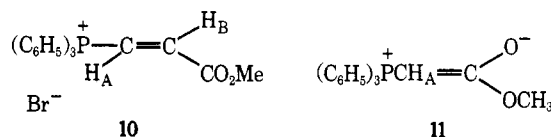


Major isomer, ³¹P at -9.8 ppm; H_A τ 6.27, J_{AB} = 14 Hz, J_{PH} = 22.5 Hz; H_B τ ~2.6, obscured; H_C τ 4.85, J_{BC} = 13 Hz, J_{PH} ≈ 0 Hz; OEt τ 6.00, 8.83



Minor isomer, ³¹P at -12.0 ppm; H_A τ 4.53, J_{AB} = 14.5 Hz, J_{PH} = 26 Hz; H_B τ 3.58, J_{AB} = 14.5 Hz, J_{BC} = 9.5 Hz, J_{PH} = 20 Hz; H_C τ 5.45, J_{BC} = 9.5 Hz, J_{PH} = 3.2 Hz; OEt τ 5.90, 8.74

stants, and the effects can be calculated.¹² Such calculations predict large downfield shifts for H_B in **8a** and for H_A in **8b** due to a partial negative charge on the carbonyl oxygen atom. The PH_A couplings in **8a** and **8b** are consistent with those observed for **10** (*J* = 19.5 Hz),¹³ **11** (*J* = 21.5 Hz),^{6b} and a variety of **12** (*J* =



16-24 Hz).¹⁴ The PH_B coupling in **8b** is consistent with the *cis* PH_B couplings in **10** (*J* = 18.5 Hz)¹³ and **12** (*J* = 13-25 Hz)¹⁴ and is significantly different from the *trans* PH_B couplings in **12** (*J* = 39-50 Hz).¹⁴ The long-range PH_C coupling of 3.2 Hz in **8b** and *ca.* 0 Hz in **8a** further dictates the structural assignments for **8b** and **8a**; the "W" shaped arrangement of connecting bonds¹⁵ in **8b** allows maximum long-range PH_C coupling.¹⁶

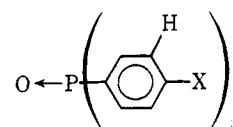
(12) (a) T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963); (b) M. P. Schweizer, S. I. Chan, G. K. Helmkamp, and P. O. P. Ts'o, *J. Amer. Chem. Soc.*, **86**, 696 (1964).

(13) G. Pattenden and B. J. Walker, *J. Chem. Soc. C*, 531 (1969).

(14) (a) J. E. Lancaster, *Spectrochim. Acta, Part A*, **23**, 1449 (1967); (b) G. L. Kenyon and F. H. Westheimer, *J. Amer. Chem. Soc.*, **88**, 3557 (1966).

(15) The planar "W" configuration favors long-range interactions in fully saturated systems, in cases where one or more of the intervening carbon atoms are sp² hybridized, and in systems where one of the connective bonds is a double bond: (a) ref 9, p 338; (b) M. Barfield, *J. Chem. Phys.*, **41**, 3825 (1964); (c) E. W. Garbisch, *J. Amer. Chem. Soc.*, **86**, 5561 (1964).

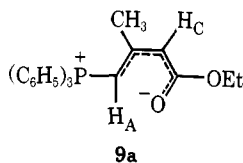
(16) A similar long-range PH coupling (*J* = 2.1-3.4 Hz) has been observed in triarylphosphine oxides between the phosphorus atom and the meta protons: C. E. Griffin, *Tetrahedron*, **20**, 2399 (1964).



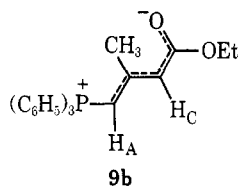
The relative magnitudes of the $H_B H_C$ couplings in **8a** ($J = 13$ Hz) and **8b** ($J = 9.5$ Hz) reveal that H_B and H_C are trans in **8a** and cis in **8b**.¹⁷

The nmr data for **9** in chloroform-*d* at -7° and the structure assignments are given in Chart II. The nmr spectra of the ylide generated from pure **3** and pure **4** at 0° were identical. The ratio of **9a**:**9b** in chloroform-*d*

Chart II



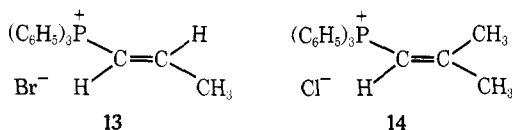
Major isomer, ^{31}P at -12.7 ppm; H_A τ 4.42 doublet, $J_{PH} = 23$ Hz; H_C τ 5.38 doublet, $J_{PH} = 6$ Hz; CH_3 τ 8.40 singlet; OEt τ 5.85, 8.75



Minor isomer, ^{31}P at -9.9 ppm; H_A τ 7.11 doublet, $J_{PH} = 22.5$ Hz; H_C τ 5.59 singlet; CH_3 τ 7.46 doublet, $J_{PCH_3} = 1.5$ Hz; OEt τ 6.07, 8.92

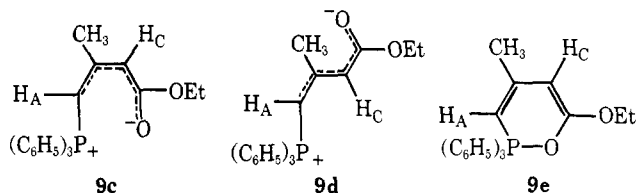
at 24° was *ca.* 70:30 and at -7° was *ca.* 85:15. Although the major isomer **9a** gave sharp signals at 24° , the minor isomer **9b** gave broad peaks due to an exchange phenomenon at 24° ; at -7° the peaks due to **9b** were sharp. Again, coupling constants were verified by proton-proton decoupling, phosphorus-proton decoupling, and spectra run at both 60 and 100 MHz. The data allow unambiguous assignment of structure **9a** to the major isomer. Thus, the observed long-range PH_C coupling of 6 Hz indicates the "W" arrangement of bonds connecting the phosphorus atom and H_C , the pronounced deshielding of H_A indicates it to be cis to the negatively charged carbonyl group, and the similarity of chemical shifts of H_A , H_C , and the ^{31}P atom to the corresponding shifts in **8b** indicates the close stereochemical relationship of **9a** to **8b**.

The observed $\text{P}-\text{CH}_3$ coupling of 1.5 Hz in **9b** but of *ca.* 0 Hz in **9a** and the difference in chemical shifts of H_A and H_C in **9b** compared to H_A and H_C in **8a** makes the assignment of the structure **9b** to the minor isomer less certain. Compounds **13**¹⁸ and **14** provide additional information about cis and trans $\text{P}-\text{CH}_3$ couplings and cis and trans CH_3 shifts in vinylphosphonium salts. The methyl protons of **13** appear at τ 7.63 as a doublet



($J = 6.5$ Hz, vicinal $\text{H}-\text{CH}_3$ coupling) of quartets, $J \simeq 1$ Hz. The quartets could arise from an allylic $\text{H}-\text{CH}_3$ coupling of *ca.* 1 Hz and a $\text{P}-\text{CH}_3$ coupling of *ca.* 2 Hz, or *vice versa*. The trans methyl of **14** appears at τ 7.52 as a slightly broadened singlet, $W_{1/2} = 3$ Hz. The cis methyl of **14** appears at τ 8.18 (shielded by the phenyl

rings) as a doublet, $J_{PCH_3} = 3.0$ Hz, of doublets, $J_{HCH_3} = 1.05$ Hz. Irradiation of the vinyl proton caused sharpening of the lower field methyl group to $W_{1/2} = 1.7$ Hz and collapse of the doublet of doublets for the higher field methyl group to a doublet, $J = 3$ Hz. Since both cis and trans $\text{P}-\text{CH}_3$ couplings can be of the order of 1–3 Hz, the observed $\text{P}-\text{CH}_3$ coupling of 1.5 Hz in the minor isomer of **9** is of little aid in the structure assignment. From the methyl shifts in **13**, **14**, and **9a**, methyl shifts of *ca.* τ 7.5 for **9c**, *ca.* τ 6.5 for **9d** (methyl group



trans to phosphorus and deshielded *ca.* 1 ppm by negative carbonyl group), and *ca.* τ 7.4 for **9b** (cis to phosphorus and deshielded *ca.* 1 ppm by negative carbonyl group) could be expected. While **9c** could experience some electrostatic stabilization, models reveal very severe steric interactions that make the existence of **9c** unlikely. Pentavalent phosphorus atoms exhibit large positive shifts;¹⁹ the observed absence of any ^{31}P resonances at positive shifts in the nmr spectrum of **9** eliminates the possibility of a significant amount of **9e**. Protonation studies of **9** (*vide infra*) indicate that the minor isomer has the CH_3 and CO_2Et groups cis to each other. The chemical shift of the methyl protons rules out a major contribution of **9d**. The observed data for the minor isomer of **9** may result from **9b** alone or from a rapid equilibrium between **9b** and **9d**, with **9d** present only to a small extent (the factors that cause the $\text{P}-\text{CH}_3$ splitting in **9b** but not **9a** and the higher shifts for H_A and H_C in **9b** relative to **8a** remained unexplained).

The broadening of the peaks of **9b** at 24° in chloroform-*d* is due to proton exchange with a trace of protonic impurity, possibly residual phosphonium salt. In benzene-*d*₆ at 24° (**9a**:**9b** ratio of *ca.* 52:48) the peaks due to **9b** were fairly sharp except for the H_A signal, which was still severely broadened. Addition of 1 drop of butyllithium in hexane²⁰ to the benzene-*d*₆ solution resulted in appearance of H_A as a doublet, $J = 22.5$ Hz. The broadening of phosphorus ylide proton spectra due to traces of phosphonium salt has been reported and discussed.^{6b,20}

Only two sets of resonances (major and minor isomers described in Chart II) were found for **9** in chloroform-*d* even at -55° . We suspect that rotations about the $\text{PC}-\text{C}$ and $\text{H}_2\text{C}-\text{CO}_2\text{Et}$ bonds in **8** and **9** have very low activation energies and are rapid relative to the nmr time scale, but that the rotamers shown in Charts I and II predominate (extent unknown) over their P, H_A -exchanged rotamers and O, OEt -exchanged rotamers due to steric effects. Only in the **9b**, **9d** pair of P, H_A -exchanged rotamers are the steric effects favorable for the presence of significant amounts of both P, H_A -exchanged rotamers. The data for compounds of type **11** in which H_A is replaced by various alkyl groups **R** indicate that as the bulk of **R** increases, the propor-

(17) In general, the *trans*-ethylenic coupling constant is greater than the *cis* coupling constant in 1,2-disubstituted olefins: ref 9, pp 301–302.

(18) D. Seyferth and J. Fogel, *J. Organometal. Chem.*, **6**, 205 (1966).

(19) F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968).

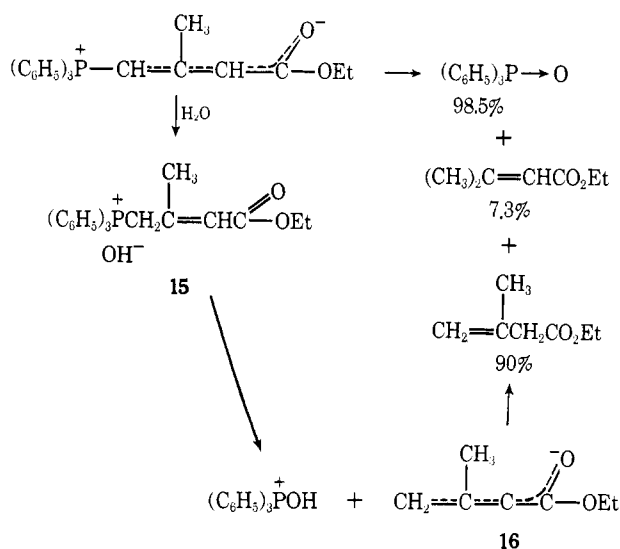
(20) P. Crews, *J. Amer. Chem. Soc.*, **90**, 2961 (1968).

tion of rotamer with O⁻ cis to the R group increases and predominates because of steric effects.^{6c} Thus, the rotamers in Charts I and II could be expected to predominate over their O, OEt-exchanged rotamers.

Protonation at 0° of **9**, generated either from **3** or **4** at 0°, with aqueous hydrogen bromide gave a mixture of salts that consisted of 88 ± 2% **3** and 12 ± 2% **4**, with *ca.* 10% unidentified by-product (methyl signal at τ 8.08). Controls demonstrated the stability of **3** and **4** under the conditions of ylide protonation and salt analysis by nmr spectroscopy.

Hydrolysis of **9** is fairly rapid and produces the products and yields indicated in Chart III. Several plausible pathways exist for the hydrolysis. One of these involves **15** and **16**. Hydroxide ion attack on phosphorus²¹ in **15** could produce **16**, and kinetically con-

Chart III



trolled protonation of **16** could possibly give rise to the observed ratio of nonconjugated to conjugated ester. The ratio did not change, within experimental error, during the course of the hydrolysis. Gas chromatographic analyses of incompletely hydrolyzed mixtures showed a material with the same retention time as triphenylphosphine and showed triphenylphosphine oxide yields in excess of ester yields; apparently, the ylide undergoes pyrolysis in the gc system to form triphenylphosphine and triphenylphosphine oxide.

The replacement of H_B in **8** by a methyl group would be expected to produce a **9a:9b** ratio of greater than 25:75 (at 24°). It is somewhat surprising based on steric effects alone that the ratio of **9a:9b** (at 24°) is as high as 70:30. Since, at 24°, the **9a:9b** ratio of 70:30 in chloroform-*d* changes to 52:48 in benzene, factors such as self-association of ylide molecules and solvation effects must contribute substantially to the **8a:8b** and **9a:9b** ratios.

Reaction of benzaldehyde with **9a** locks the 2-double bond in the *cis* configuration, and similarly **9b** produces a *trans*-2 double bond. The observed formation of 58.5 ± 1.5% *cis*-2 products from **9** at 25–45° indicates that **9a** and **9b** must react with similar rate constants with benzaldehyde.²² The formation of 94% *trans*-2

isomers from **8** indicates that **8a** may react slightly faster than **8b** with benzaldehyde. The stereochemistry of the 4-double bond formed in the reaction depends on the many factors involved in any Wittig reaction. These factors have already been discussed in detail.²³

Experimental Section

Melting points were taken in open capillaries in a Mel-Temp apparatus and are corrected. Boiling points are uncorrected. Infrared spectra were determined with a Beckman IR10 instrument. Nmr spectra at 60 MHz were obtained with a JEOLCO C-60HL spectrometer. Nmr spectra at 100 MHz were obtained on a Varian HA-100 instrument. For nmr spectra of ylides, the CDCl₃ solvent was filtered through basic alumina just prior to use.

(*cis*-3-Ethoxycarbonyl-2-methylallyl)triphenylphosphonium Bromide and (*trans*-3-Ethoxycarbonyl-2-methylallyl)triphenylphosphonium Bromide. A 145-g sample of *ca.* 50:50 mixture of *cis*- and *trans*-ethyl 4-bromo-3-methyl-2-butenolate from NBS treatment of ethyl β -methylcrotonate was subjected to distillation using a Teflon spinning band column. After a slight forerun, 27.2 g of liquid, bp 52–57° (0.7 mm), was collected; this consisted of a 77:23 ratio of *cis* (**1**) to *trans* (**2**) ester mixture with 10% impurities (gc assay on 2 ft 10% SE-52 at 95°). The signals in the nmr spectrum (CDCl₃) of this material due to the major component, the *cis* ester, are τ 4.20 (q, *J* = 1.4 Hz, C=CH), 5.43 (s, CH₂Br), 5.80 (q, *J* = 7 Hz, OCH₂CH₃), 7.93 (d, *J* = 1.4 Hz, CH₃), 8.70 (t, *J* = 7 Hz, OCH₂CH₃).

The pot residue, 90.2 g, consisted of 89% *trans* ester and 11% *cis* ester. The signals due to the *trans* isomer in the nmr spectrum of this material appear at τ 4.02 (unresolved m, *W*_{1/2} = 3.9 Hz, C=CH), 5.81 (q, *J* = 7 Hz, OCH₂CH₃), 6.03 (s, CH₂Br), 7.71 (d, *J* = 1.4 Hz, CH₃), 8.70 (t, *J* = 7 Hz, OCH₂CH₃).

The 27.2 g of *cis*-rich material was treated with 27.4 g (0.80 equiv) of triphenylphosphine in 200 ml of ether at reflux for 1.5 hr. The mixture was cooled; the resultant solid, mp 148° bubble, 185° dec, 22.4 g, consisted of 88% *cis*-phosphonium salt and 12% *trans*-phosphonium salt (nmr assay).

Upon standing overnight, the ether filtrate deposited 14.5 g of solid, mp 153° bubble, 186–187° dec, that consisted of a 95:5 *cis*- to *trans*-phosphonium salt mixture. The first sample was crystallized from acetonitrile–ethyl acetate to give 11.5 g of solid, mp 150° dec, that contained no detectable (<5%) *trans* isomer. Solvated acetonitrile could not be removed by drying at 90° (<1 mm), so the sample was crystallized from chloroform–ether and dried at 90° (<1 mm) to give pure *cis*-phosphonium salt **2**: mp 150° bubble, melt and resolidify, 190° dec; ir (CHCl₃) 1698 (s), 1645 cm⁻¹ (m); nmr (CDCl₃) τ 2.30 (m, 15, ArH), 4.13 (dd, 1, *J*_{PH} = 5.0 Hz, *J*_{HH} = 1.3 Hz, C=CH), 4.43 (d, 2, *J*_{PH} = 18 Hz, CH₂P), 6.15 (q, 2, *J* = 7 Hz, OCH₂CH₃), 7.84 (dd, 3, *J*_{PH} = 3.5 Hz, *J*_{HH} = 1.3 Hz, CH₃), 8.92 (t, 3, *J* = 7 Hz, OCH₂CH₃).

Anal. Calcd for C₂₅H₂₆BrO₂P: C, 63.97; H, 5.58; Br, 17.03. Found: C, 63.79; H, 5.67; Br, 16.85.

The 90 g (0.434 mol) of 89% *trans* ester was treated with 118 g (0.45 mol) of triphenylphosphine in 300 ml of benzene at 50–60° for 1.25 hr and then at 25° overnight. The resultant solid (85% *trans* salt, 15% *cis* salt; nmr assay), 162.3 g, was recrystallized by dissolution in 1500 ml of hot acetonitrile followed by addition of 2 l. of ethyl acetate. The resultant white solid was dried at 40° (<1 mm) for 45 min to give 125 g of solid, mp 190° dec. The nmr spectrum revealed the solid to be pure *trans* salt (no *cis* detected), with no solvent present: ir (CHCl₃) 1710 (s), 1645 cm⁻¹ (m); nmr (CDCl₃) τ 2.27 (m, 15, ArH), 4.18 (dd, 1, *J*_{PH} = 4.8 Hz, *J*_{HH} = 1.2 Hz, C=CH), 4.93 (d, 2, *J*_{PH} = 16 Hz, CH₂P), 5.93 (q, 2, *J* = 7 Hz, OCH₂CH₃), 7.97 (dd, 3, *J*_{PH} = 3.0 Hz, *J*_{HH} = 1.2 Hz, CH₃), 8.82 (t, 3, *J* = 7 Hz, OCH₂CH₃).

Anal. Calcd for C₂₅H₂₆BrO₂P: C, 63.97; H, 5.58; Br, 17.03. Found: C, 63.99; H, 5.66; Br, 17.20.

Ethyl 3-Methyl-5-phenyl-2,4-pentadienoate from **4.** After 0.92 g (0.040 mol) of sodium had reacted completely in 15 ml of ethanol at reflux under N₂, the solution was cooled to 25° and 50 ml of THF was added. Then 19.7 g (0.042 mol) of pure *trans*-phosphonium salt **4** was added with stirring under N₂. To the stirred yellow

(21) See ref 8, pp 88–92, for a discussion of the mechanism of phosphorus ylide hydrolysis.

(22) Obviously, the use of lower temperatures for the reaction of **9** with aromatic aldehydes will result in higher proportions of *cis*-2 products.

(23) (a) Reference 8, pp 152–189; (b) L. D. Bergelson, L. I. Barsukov, and M. M. Shemyakin, *Tetrahedron*, **23**, 2709 (1967); (c) L. D. Bergelson and M. M. Shemyakin in "Newer Methods of Preparative Organic Chemistry," Vol. V, W. Foerst, Ed., Academic Press, New York, N. Y., 1968, pp 154–175.

solution was added 4.24 g (0.040 mol) of redistilled benzaldehyde; the temperature rose to 45°. After 1.5 hr, the light yellow reaction mixture was held at reflux for 1.5 hr. The mixture was concentrated under vacuum, and the residue was triturated with hexane; gc analysis of the residual solid triphenylphosphine oxide and NaBr showed the ester extraction to be complete. The hexane solution was concentrated under vacuum to 8.3 g of oil (95% yield). The nmr spectrum (CDCl₃ solution) was taken (no triphenylphosphine oxide detected); analysis for the isomers was performed by integration over the vinyl methyl signals. The 3-methyl groups of the trans-2,trans-4 isomer, the trans-2,cis-4 isomer, the cis-2,trans-4 isomer, and the cis-2,cis-4 isomer appeared at τ 7.60, 7.84, 7.90, and 8.18, respectively (lit.² values for methyl esters in CCl₄ are 7.67, 7.88, 8.00, and 8.27). The composition of the oil is given in Scheme I.

A 200-ml ether solution of the 8.3 g of oil and 8 ml of a 0.5% I₂ in benzene solution was held 1 ft from a 100-W incandescent light bulb for 6 hr and then was washed twice with sodium thiosulfate solution, dried (Na₂SO₄), and concentrated under vacuum to give 7.9 g of oil that consisted of 1.6% trans-2,cis-4 ester, 47.6% cis-2,trans-4 ester, and 50.8% trans-2,trans-4 ester. Chromatography of the mixture on a dry column of 800 g of silicic acid with benzene gave 1.4 g of oil that contained 94% cis-2,trans-4 ester, ca. 1% trans-2,trans-4 ester, and ca. 4% unknown (gc assay on a 2-ft 10% XE-60 at 150°). The nmr spectrum (CDCl₃ solvent) was consistent with the cis-2,trans-4 assignment: τ 1.58 (d, 1, J = 16 Hz, ArCH=CH), 2.6 (m, 5, ArH), 3.11 (d, 1, J = 16 Hz, ArCH=CH), 4.25 (q, 1, J = 1.2 Hz, CH₃C=CH), 5.78 (q, 2, J = 7 Hz, OCH₂CH₃), 7.90 (d, 3, J = 1.2 Hz, CH₃), 8.70 (t, 3, J = 7 Hz, OCH₂CH₃); ir (CCl₄) 1700 (s), 1618 (s), 1595 cm⁻¹ (s).

Anal. Calcd for C₁₄H₁₆O₂: C, 77.75; H, 7.46. Found: C, 77.81; H, 7.61.

The next material obtained, 3.8 g, consisted of 51% cis-2,trans-4 ester and 49% trans-2,trans-4 ester. The next material, 1.6 g of oil (88% trans-2,trans-4 ester, 5.5% cis-2,trans-4 ester, and 6.5% unknown) was crystallized once from ethanol at -78° to give a solid that turned to an oil upon warming to room temperature. This sample was 99.1% pure trans-2,trans-4 ester (gc assay); the nmr spectrum (CDCl₃ solvent) was consistent with the trans-2,trans-4 assignment: τ 2.67 (m, 5, ArH), 3.11 (d, 1, J = 16 Hz, HC=CH), 3.23 (d, 1, J = 16 Hz, HC=CH), 4.10 (q, 1, J = 1.2 Hz, CH₃C=CH), 5.80 (q, 2, J = 7 Hz, OCH₂CH₃), 7.60 (d, 3, J = 1.2 Hz, CH₃), 8.72 (t, 3, J = 7 Hz, OCH₂CH₃); ir (CCl₄) 1708 (s), 1607 cm⁻¹ (s).

Anal. Calcd for C₁₄H₁₆O₂: C, 77.75; H, 7.46. Found: C, 77.96; H, 7.66.

Ethyl 3-Methyl-5-phenyl-2,4-pentadienoate from 3. A procedure identical with that above was employed starting with phosphonium salt 3 instead of 4 and was performed on one-half the scale. The product mixture obtained, 3.6 g of oil (83% yield), was 99% pure ester (gc assay). The nmr analysis of the oil indicated the composition given in Scheme I.

(3-Ethoxycarbonyl-2-methylallylidene)triphenylphosphorane. A solution of 10.0 g (0.0213 mol) of phosphonium salts 3 and 4 in 50 ml of chloroform was extracted at 0° with 0.88 g (0.022 mol) of NaOH in 50 ml of water and then with 0.44 g (0.011 mol) of NaOH in 25 ml of water. The chloroform layer was dried at 0° over CaSO₄. The solution was filtered and concentrated under vacuum (CaSO₄ drying tube in vacuum line). From this point on, operations were carried out under N₂ in a glove bag. Dry ethyl acetate was added, and the solution was scratched to induce crystallization. The resultant yellow crystals were collected and washed with ethyl acetate to give 5.7 g (63%) of ylide, mp 165–167°. A portion was recrystallized from ethyl acetate (filtration) for an analytical sample: mp 165–167°; ir (CHCl₃) 1632 (s), 1492 cm⁻¹ (vs).

Anal. Calcd for C₂₃H₂₅O₂P: C, 77.30; H, 6.48. Found: C, 77.58; H, 6.76.

(trans-3-Ethoxycarbonylallyl)triphenylphosphonium Bromide. A solution of 76 g (0.290 mol) of triphenylphosphine and 75 g (75% pure, 0.291 mol) of ethyl 4-bromocrotonate (Aldrich Chemical Co.) in 200 ml of benzene was stirred at 25° for 4 hr. The resultant yellow solid was collected, washed with benzene, and crystallized from 500 ml of acetonitrile to give a white solid, which, after it was dried for several hours at 90° (0.5 mm) to remove solvated CH₃CN, weighed 58.9 g and had mp 189–191° dec, ir (CHCl₃) 1715, 1650 cm⁻¹. The salt was hygroscopic and gave analyses consistent with varying degrees of hydration.

Anal. Calcd for C₂₄H₂₄BrO₂P·0.3H₂O: C, 62.56; H, 5.38. Found: C, 62.56; H, 5.63.

Anal. Calcd for C₂₄H₂₄BrO₂P·0.7H₂O: C, 61.60; H, 5.47. Found: C, 61.59; H, 5.43.

A sample of the salt exposed to air overnight showed strong solvated water absorption at τ 7.5 (CDCl₃ solvent).

Nmr spectra of the salt were determined at 60 MHz with and without proton decoupling and at 100 MHz with and without phosphorus decoupling to determine the coupling constants: nmr (CDCl₃) τ 2.2 (m, 15, ArH), 3.14 (m, 1, J_{PH} = 5 Hz, J_{AB} = 6.5 Hz, J_{BC} = 15 Hz, PCH₂CH=CH₂), 3.56 (dd, 1, J_{PH} = 4 Hz, J_{BC} = 15 Hz, H_C), 4.78 (dd, 2, J_{PH} = 16.5 Hz, J_{AB} = 6.5 Hz, PCH₂), 5.87 (q, 2, J = 7 Hz, OCH₂CH₃), 8.79 (t, 3, J = 7 Hz, OCH₂CH₃).

An additional 32.8 g of white solid, mp 189–191° dec, was obtained from the filtrates.

Ethyl 5-Phenyl-2,4-pentadienoate. After 0.92 g (0.040 mol) of sodium had been allowed to react with 15 ml of ethanol under nitrogen, the solution was cooled to 25°, and 50 ml of THF was added. Then 19.1 g (0.042 mol) of (3-ethoxycarbonylallyl)triphenylphosphonium bromide was added. To the stirred yellow mixture was added 4.24 g (0.040 mol) of benzaldehyde. The mild exothermic reaction raised the temperature to 40°. After 20 min, gc analysis (2-ft 10% SE-30 column) showed ca. 6% benzaldehyde left. The product ester mixture consisted of 1% cis-2,cis-4 ester, 56% trans-2,cis-4 ester, 4% cis-2,trans-4 ester, and 39% trans-2,trans-4 ester. The reaction mixture was stirred an additional 1.4 hr; gc analysis revealed that <1% benzaldehyde remained and that the product ester mixture consisted of 1% cis-2,cis-4 ester, 55% trans-2,cis-4 ester, 5% cis-2,trans-4 ester, and 39% trans-2,trans-4 ester. The reaction mixture was concentrated under vacuum. The residue was extracted with hexane, and the resultant solid was filtered off (the undissolved solid contained no residual esters based on gc analysis). Concentration of the hexane filtrate gave 7.5 g of oil that consisted of 94% esters and 6% triphenylphosphine oxide (87% yield of esters). Pure samples of the trans-2,cis-4 and trans-2,trans-4 esters were collected from the gc for ir and nmr spectra. The trans-2,cis-4 ester has ir (CCl₄) absorptions at 1710 (s), 1630 (s), 990 cm⁻¹ (vw); the trans-2,trans-4 ester has ir (CCl₄) absorptions at 1710 (s), 1630 (s), and 990 cm⁻¹ (m). The trans-2,cis-4 isomer has nmr (CDCl₃) absorptions at τ 2.16 (dd, 1, J = 15 Hz, J = 11 Hz, ArCH=CH₂CH=CH₂CO₂Et), 2.66 (s, 5, ArH), 3.15 (d, 1, J = 11 Hz, H_D), 3.55 (t, 1, J = 11 Hz, H_C), 3.95 (d, 1, J = 15 Hz, H_A), 5.77 (q, 2, J = 7 Hz, OCH₂CH₃), 8.72 (t, 3, J = 7 Hz, OCH₂CH₃). The trans-2,trans-4 ester has nmr (CDCl₃) absorptions at τ 2.65 (m, 6, ArH + ArCH=CH₂CH=CH₂CO₂Et), 3.15 (m, 2, H_C, H_D), 4.01 (d, 1, J = 15 Hz, H_A), 5.75 (q, 2, J = 7 Hz, OCH₂CH₃), 8.70 (t, 3, J = 7 Hz, OCH₂CH₃).

A solution of the 7.5 g of oil in 100 ml of ether and 8 ml of 0.5% iodine in benzene was held 9 in. from a 100-W light bulb for 69 hr. The solution was washed twice with sodium thiosulfate solution and was concentrated under vacuum. The 7.3 g of oil, which consisted of 1% trans-2,cis-4 ester, 6.5% cis-2,trans-4 ester, and 92.5% trans-2,trans-4 ester, was crystallized twice from methanol at low temperature to give 5.0 g of pure trans-2,trans-4 ester, mp 39–40° (lit.²⁴ mp 25–26°).

(3-Ethoxycarbonylallyl)triphenylphosphorane. A slight variation of the procedure used by Buchta and Andreev^{5b} for (3-methoxycarbonylallyl)triphenylphosphorane was employed. A solution of 31.5 g (0.0678 mol) of phosphonium salt 6 in 250 ml of chloroform was extracted at 0° with a 150-ml mixture of ice and water that contained 3.0 g (0.075 mol) of NaOH. The yellow-orange chloroform layer was dried over CaSO₄ at 0° and concentrated under vacuum (CaSO₄ drying tube in vacuum line). The following operations were all carried out under N₂. Dry ethyl acetate was added, and the solution was scratched. The resultant solid was recrystallized from hot ethyl acetate (filtration). There was obtained 12.1 g (48%) of yellow crystals: mp 186–188°; ir (CHCl₃) 1636 (s), 1530 cm⁻¹ (vs).

Anal. Calcd for C₂₄H₂₅O₂P: C, 76.98; H, 6.19. Found: C, 77.10; H, 6.32.

HBr Quench of Ylide 9. A 0.1-g sample of pure cis-phosphonium salt 3 in 0.4 ml of CDCl₃ was shaken with 5 drops of 48% HBr. Nmr examination of the mixture revealed no change in 15 min. A similar experiment with the trans salt 4 also showed no change in the trans salt in 15 min.

A 0.94-g (0.0020 mol) sample of pure trans salt in 10 ml of CDCl₃ was extracted at 0° with 5 ml of water containing 0.08 g (0.0020 mol) of NaOH. After 2 min at 0°, the yellow CDCl₃ layer was

(24) K. V. Awers, *J. Prakt. Chem.*, **105**, 361 (1923).

extracted at 0° with 5 ml of water containing 0.38 g of 48% HBr (0.00225 mol of HBr). The yellow color was discharged. The CDCl_3 layer was dried (Na_2SO_4) and analyzed by nmr. The sample consisted of a mixture of ca. 90% *cis*-phosphonium salt and ca. 10% *trans*-phosphonium salt with ca. 10% by-product signified by a weak vinyl methyl signal at τ 8.08. There was no detectable amount of hydrolysis product, ethyl 3-methyl-3-butenolate, present.

A 0.94-g (0.0020 mol) sample of pure *cis* salt in 10 ml of CDCl_3 was extracted at 0° with 5 ml of water containing 0.088 g (0.0022 mol) of NaOH. A 0.5-ml aliquot was dried and immediately analyzed by nmr; the spectrum was identical with that of the ylide from the *trans* salt. After 5 min at 0°, a 5-ml aliquot of the yellow CDCl_3 solution was extracted at 0° with 3 ml of water containing 0.22 g of 48% HBr (0.0013 mol of HBr). The colorless CDCl_3 solution was dried (Na_2SO_4) and analyzed by nmr. The product mixture consisted of 87% *cis* salt and 13% *trans* salt, with ca. 10% unknown material (vinyl methyl signal at τ 8.08, not ethyl 3-methyl-3-butenolate). After 20 min at 0°, the residual 4.5 ml of yellow ylide solution was extracted at 0° with 3 ml of water containing 0.22 g of 48% HBr. Analysis of the colorless, dried CDCl_3 layer revealed the salt mixture to consist of 88% *cis* salt and 12% *trans* salt.

Hydrolysis of Ylide 9. Solutions of 0.1938 g of decane (internal gc standard) and 0.94 g (0.0020 mol) of pure *trans*-phosphonium salt 4 in 15 ml of CH_2Cl_2 and 0.084 g (0.0021 mol) of NaOH in 5 ml of water were stirred together vigorously under nitrogen at 25°. At various time intervals, a 0.5-ml aliquot of the CH_2Cl_2 layer was withdrawn, dried (CaSO_4), and analyzed by gc (2-ft 10% SE-30) at 80° for the esters and decane internal standard; then the temperature was raised to 250° for the triphenylphosphine (?) and triphenylphosphine oxide. After 15 min, gc assay showed a 58% yield of ethyl 3-methyl-3-butenolate, a 6.4% yield of ethyl 3-methylcrotonate, a 90% yield of triphenylphosphine oxide, and the presence of a material with 0.18 times the area of the oxide peak at the same retention time as triphenylphosphine. After 30 min, there was a 77% yield of ethyl 3-methyl-3-butenolate, a 6.4% yield of ethyl 3-methylcrotonate, a 100% yield of triphenylphosphine oxide, and triphenylphosphine (?) with 0.06 times the area of the oxide. After 3 hr, there was a 90% yield of ethyl 3-methyl-3-butenolate, a 7.3% yield of ethyl 3-methylcrotonate, and a 98.5% yield of triphenylphosphine oxide, with <1% of triphenylphosphine.

A solution of 9.4 g (0.020 mol) of pure *trans*-phosphonium salt in 150 ml of CH_2Cl_2 was stirred with 0.84 g (0.021 mol) of NaOH in 50 ml of water for 30 min. The organic layer was washed with water, dried (Na_2SO_4), and concentrated using an 18-in. Vigreux column. To the residue was added 80 ml of pentane. The resultant solid, 4.63 g (83% yield), was identified as triphenylphosphine oxide from the nmr and ir spectra. The filtrate was

distilled to give 1.71 g (67% yield) of colorless liquid that consisted of 90% ethyl 3-methyl-3-butenolate and 10% ethyl 3-methylcrotonate (gc analysis). Pure samples were collected from the gc for ir spectra and mass spectroscopy. The major component, ethyl 3-methyl-3-butenolate, has ir absorptions (CHCl_3 solution) at 1720 (s), 1645 cm^{-1} (w) and mass spectra parent ion at m/e 128. The minor component had an infrared spectrum which included absorptions at 1695 (s) and 1645 cm^{-1} (m), had a gc retention time identical with that of authentic ethyl 3-methylcrotonate, and had the mass spectra parent ion at m/e 128. The nmr spectrum of the ester mixture (CHCl_3 solution) showed the following signals due to the major component: τ 5.18 (m, 2, $W_{1/2}$ = 6 Hz, $\text{H}_2\text{C}=\text{C}$), 5.88 (q, 2, J = 7 Hz, OCH_2CH_3), 7.01 (s, 2, $\text{CH}_2\text{-CO}_2\text{Et}$), 8.18 (t, 3, $J + J'$ = 2.3 Hz, $\text{H}_2\text{C}=\text{CCH}_3$), 8.75 (t, 3, J = 7 Hz, OCH_2CH_3).

(2-Methylallyl)triphenylphosphonium Chloride. A solution of 200 g (0.764 mol) of triphenylphosphine and 90.6 g (1.0 mol) of 3-chloro-2-methylpropene in 400 ml of acetonitrile was stirred at reflux for 24 hr. The resultant mixture was filtered while still hot; the insoluble solid was washed with 300 ml of acetonitrile. The resultant 189 g (70% yield) of white solid [mp 216–218° (lit.²⁶ mp 218°)] had nmr (CDCl_3) τ 1.9–2.3 (m, 15, ArH), 4.92 (m, 2, $\text{C}=\text{CH}_2$), 5.21 (d, 2, J_{PH} = 16 Hz, PCH_2), 8.33 (m, 3, CH_3). Irradiation at τ 4.92 collapsed the multiplet at 8.33 to a doublet, $J_{\text{P-CH}_3}$ = 2.9 Hz.

(2-Methylpropenyl)triphenylphosphonium Chloride.²⁶ A solution of 5.0 g of (2-methylallyl)triphenylphosphonium chloride in chloroform was passed slowly through a column of 180 g of Woelm Activity 1 basic alumina. The first 500 ml of eluate gave 3.2 g of hygroscopic white solid: mp 219–221°; nmr (CDCl_3) τ 2.0–2.5 (m, 15, ArH), 3.45 (bd, 1, J_{PH} = 22.5 Hz, $\text{CH}=\text{C}$), 7.52 (s, 3, $W_{1/2}$ = 3 Hz, *trans* CH_3), 8.18 (dd, 3, $J_{\text{H-CH}_3}$ = 1.05 Hz, J_{PCH_3} = 3.0 Hz, *cis* CH_3). Upon irradiation at τ 3.45, the signal at τ 7.52 became a singlet, $W_{1/2}$ = 1.7 Hz, and the signal at 8.18 became a doublet, J = 3 Hz. A weak water signal occurred at τ 7.1.

Anal. Calcd for $\text{C}_{25}\text{H}_{23}\text{ClP} \cdot 0.3\text{H}_2\text{O}$: C, 73.76; H, 6.36. Found: C, 73.88; H, 6.12.

Acknowledgment. We are indebted to Dr. Pierre Berger of Monsanto Co. for assistance in obtaining the 100-MHz nmr spectra and the ^{31}P nmr spectra.

(25) H. Plieninger, M. Hoebel, and V. Liede, *Chem. Ber.*, **96**, 1618 (1963).

(26) This compound has been reported but in incomplete detail: H. I. Zelinger, J. P. Snyder, and H. J. Bestmann, *Tetrahedron Lett.*, 3313 (1970).