Synthesis and Deprotection of [1-(Ethoxycarbonyl)-4-[(diphenylmethoxy)carbonyl]-1-methyl-2-oxobutyl]-triphenylphosphonium Chloride: A Key Intermediate in the Wittig Reaction between a Cyclic Anhydride and a Stabilized Ylide

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[1-(Ethoxycarbonyl)-4-[(diphenylmethoxy)carbonyl]-1-methyl-2-oxobutyl]triphenylphosphonium chloride (**16**) has been synthesized as an unstable oil. Removal of the (diphenylmethoxy)carbonyl group gave *E* enol lactone **5** stereoselectively and without evidence of phosphonium salt **8**. When enol lactone formation is not favored as with phosphonium salt **27**, loss of triphenylphosphine oxide occurs to yield an allene. Phosphonium salts **16**, **17**, **18**, **20**, and **35** have also been shown to yield an allene on treatment with base. The chemistry of these derivatives and the mechanism of enol lactone and allene formation is discussed. Phosphonium salts such as **8** and **27** are postulated as key intermediates in the Wittig reaction between a cyclic anhydride and a stabilized ylide.

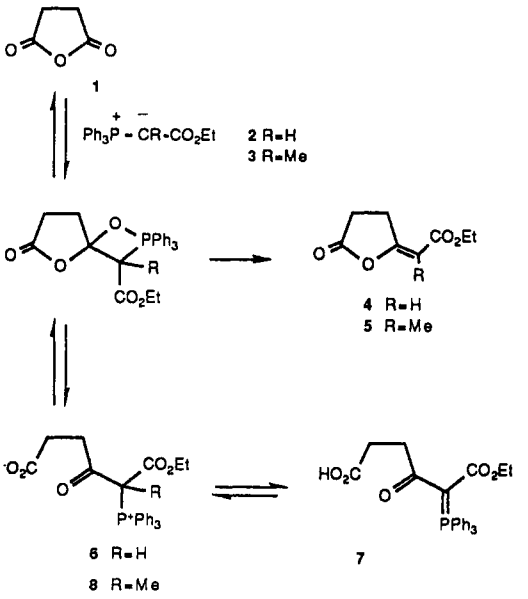
Introduction

Acyl phosphoranes, produced from the reaction of an acid chloride or acid anhydride with a phosphorus ylide, e.g. **2**, continue to find use in organic synthesis.[1-8] The related acyl phosphonium salts, produced by using a substituted ylide such as **3** or by using low temperatures to suppress transylidation, have received less attention due to relative instability and increased difficulty of preparation.[4,9]

The reaction of ylide **2** with a cyclic anhydride from the succinic, phthalic, and glutaric series is an important method for the preparation of acyl phosphoranes[7-9] of the type **7**. Phosphorane **7** can be isolated and shown to be a precursor to the expected enol lactone **4** (Scheme I) The initially formed, but undetected, phosphonium salt **6** must undergo a reversible rearrangement to the presumably more stable phosphorane **7**.

The reaction between ylide **3** and five- and six-membered cyclic anhydrides has received less attention, but it is known that phosphonium salts such as **8** are not observed (Scheme I). Rather, an enol lactone is produced stereoselectively without evidence of an acyclic intermediate.[10,11] Some work[11] has also been carried out on the reaction of large-ring anhydrides and **3**. Here, an allene rather than an enol lactone is produced and again there is no evidence of an acyclic intermediate. Phosphonium salts are not observed in these reactions because either they are not formed or else they are unstable and rapidly rearrange to a stable product. The formation of an acyclic intermediate would only appear to be observed when the phosphonium salt, e.g. **6**, formed from initial ring cleavage can be stabilized by rearrangement to a phosphorane, e.g.

Scheme I



7. To our knowledge phosphonium salts of the type **6** and **8** have not been previously reported. An earlier report[7] on the phosphonium salt **6** has recently been revised.[10] In this paper we present studies on the preparation of this novel class of compound and subsequent conversion to enol lactones and allenes.

Results and Discussion

An independent synthesis of the previously unknown phosphonium salt **8** was undertaken to determine whether or not these compounds could account for the formation of enol lactones and allenes in the Wittig reaction between a cyclic anhydride and a stabilized ylide.

Benzhydryl phosphorane **15** (Scheme II) was initially prepared to establish the conditions for the preparation and deprotection of the benzhydryl phosphonium salt **16**. It was anticipated that both **16** and the corresponding deprotected form **8** would be labile while **15** and **7** would be stable and easily handled. Extended reflux of succinic anhydride with benzhydrol gave the half ester **9**, which was converted into the corresponding acid chloride **12** with oxalyl chloride and *N*,*N*-dimethylformamide. Reaction of **12** with 2 equiv of ylide **2** then gave the benzhydryl phosphorane **15**. Removal of the benzhydryl protecting

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(11) Tsuboi, S.; Fukumoto, H.; Wada, H.; Takeda, A.; Fukuyama, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 689.

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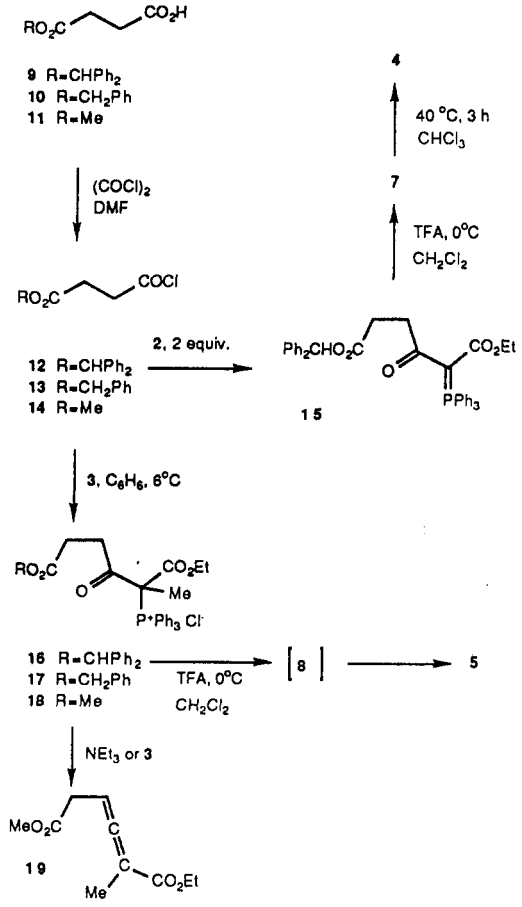
Scheme II



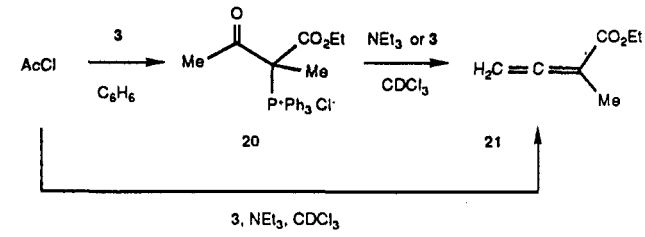
group was achieved by treatment with trifluoroacetic acid in CH_2Cl_2. The ^1H NMR spectrum of the product is consistent with the acyl phosphorane **7** previously isolated from the reaction between succinic anhydride and ylide **2**. Heating this sample at 40 °C for 1 h gave rise to the expected *E* enol lactone **4**. The benzhydryl group of **15** could also be removed by catalytic hydrogenation with palladium on carbon. Again heating the resultant oil at 40 °C gave the expected *E* enol lactone. The TFA deprotection was chosen for subsequent deprotections as it was readily followed by TLC or ^1H NMR spectroscopy.

The reaction between the acid chloride **12** and ylide **3** in benzene at 6–7 °C gave the benzhydryl phosphonium salt **16** as a benzene insoluable unstable oil, which could not be purified further (Scheme II). Phosphonium salts **17**, **18**, **20**, and **35** were also successfully prepared from the corresponding acid chlorides. The phosphonium salts were labile and co-precipitated with protonated ylide **3**.

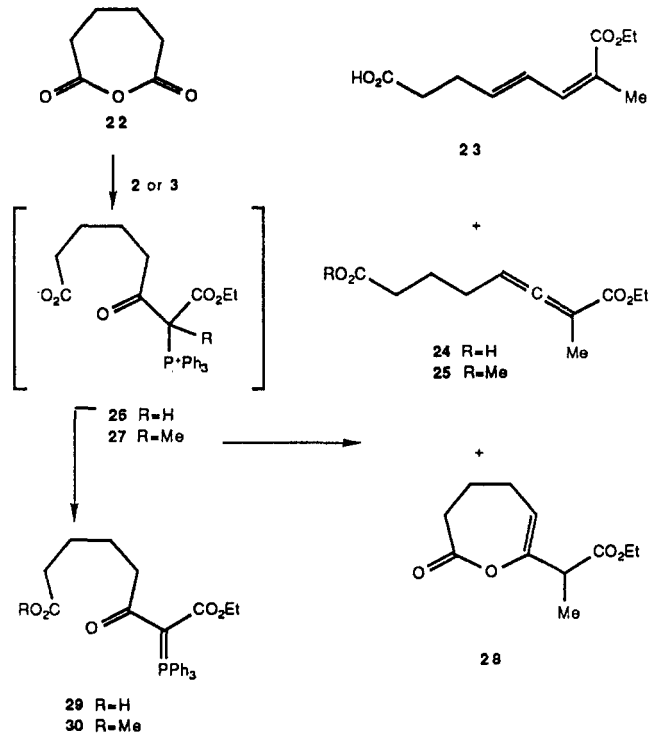
The benzhydryl group of **16** was removed with TFA and the product gave identical ^1H NMR spectral data with authentic *E* enol lactone **5**. The initially formed phosphonium salt **8** must rapidly cyclize to give the *E* enol lactone. This represents the first evidence for the cyclization of a phosphonium salt to give an enol lactone. Hence, a phosphonium salt, although undetected in the Wittig anhydride olefination reaction, can give rise to an enol lactone of the expected configuration.

Tsuboi et al.[11] reported that the reaction of adipic anhydride (**22**) with **3** at reflux for 13 h gave the endo enol lactone **28** (13%) accompanied by the formation of ring-opened products, allenic ester **24** (4%) and its isomer **23** (6%), and hydrogen ethyl adipate (Scheme IV). Similarly, azelic anhydride gave the corresponding allenic ester (9%) after 12 h of reflux. Under milder conditions (7 days at

Scheme III



Scheme IV



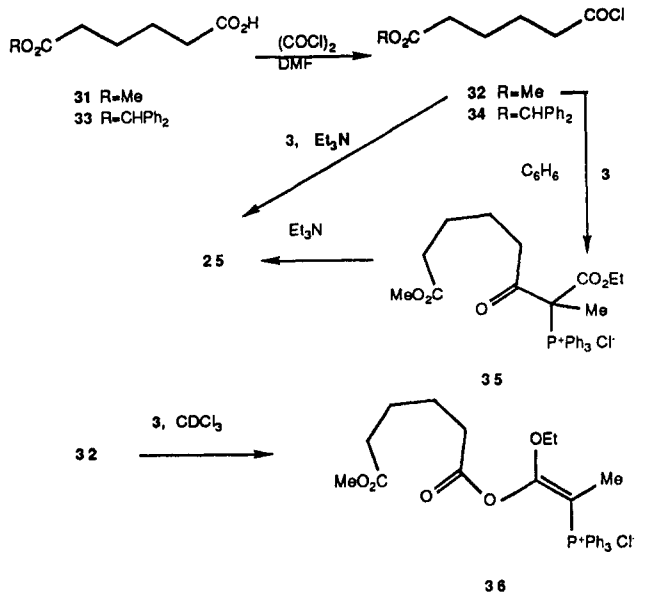
15 °C), we found that the reaction of adipic anhydride with **3** gave the allene **24** as the sole product, which was isolated in 56% yield after methylation with diazomethane. We suggest that formation of **24** occurs via an acylphosphonium salt, **27** (Scheme IV), rather than via enol lactone isomerization as previously proposed.[11] In this instance cyclization of **27** to yield enol lactone is less favorable than conversion to allene. Two areas must be addressed to support this proposition. Firstly, the possibility of allene formation directly from the enol lactone needs to be eliminated. Secondly, phosphonium salts of the type **8** and **27** need to be established as feasible structures likely to give rise to allenes and under favorable conditions to cyclize to an enol lactone (discussed earlier).

Separate samples of the *E* enol lactone **5**[12] and the endo enol lactone **28**[11] were dissolved in $CDCl_3$, and to each was added an equivalent of ylide **3**. ^1H NMR spectral analysis after 24 h at 15 °C revealed that no rearrangement to the allene had taken place in either sample such that the enol lactones would appear unlikely precursors to the allenes.

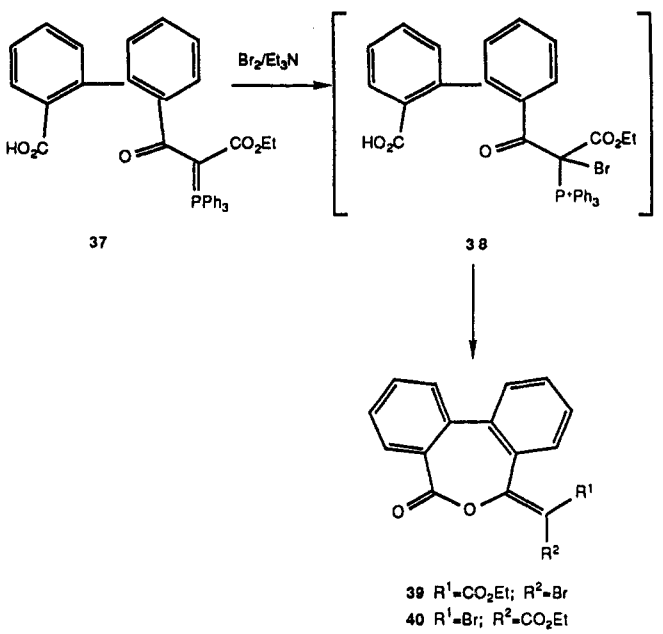
Phosphonium salts prepared from acid chlorides are known to give rise to allenes upon treatment with a base, either 1 equiv of triethylamine[9] or a second equivalent of ylide.[4] Two parallel experiments were set up (Scheme III), experiment 1 consisted of a solution of acetyl chloride and 1 equiv of ylide **3** in benzene. Experiment 2 in $CDCl_3$ contained acetyl chloride, 1 equiv of ylide **3** and 1 equiv

(12) Ingham, C. F.; Massy-Westropp, R. A.; Reynolds, G. D.; Thorpe, W. D. *Aust. J. Chem.* **1975**, *28*, 2499.

Scheme V



Scheme VI



of triethylamine (or a second equivalent of **3**). After stirring at 15 °C for 2 h, both samples were analyzed by ^{1}H NMR spectroscopy. Experiment 1 revealed the presence of the phosphonium salt **20** (70%), the protonated form of ylide **3** (22%), and allene **21** (8%). To this sample was added a drop of triethylamine (or a second equivalent of **3**). Reanalysis by ^{1}H NMR showed that the phosphonium salt **20** had given the allene **21** as the sole product. Examination of experiment 2 by ^{1}H NMR showed that the allene **21** had also been formed as the sole product. Similarly, the phosphonium salts **18** and **35** gave the allenes **19** and **25**, respectively, when treated with either triethylamine or an equivalent of ylide **3**. The allene **25** gave identical spectroscopic data with the sample previously isolated from the adipic anhydride reaction. Unfortunately, the acid chloride **34** (Scheme V) derived from the monobenzhydryl esters of adipic acid failed to give rise to the corresponding phosphonium salt and gave only protonated ylide **3**. It was hoped that removal of the benzhydryl protecting group in the phosphonium salt would lead to the allene **24** isolated from the adipic anhydride reaction with ylide **3**.

^{1}H NMR monitoring of the formation of the phosphonium salt **35** in $CDCl_3$ indicated that the *O*-acyl phosphonium salt **36** was initially formed at 0 °C. Warming to 15 °C gave the expected *C*-acyl phosphonium salt **35**. The *O*-acyl intermediate gave characteristic ^{1}H NMR spectral data.[13] The ^{13}C NMR spectral data obtained for phosphonium salts **17**, **18**, **20**, and **35** were also characteristic and quite distinctive from that of a phosphorane.[7,13,14] The ^{13}C NMR signal for the carbon directly bonded to phosphorus in the phosphonium salts (C2) gave rise to a doublet at approximately δ 66 (J = 49–50). The equivalent signal for the phosphorane **15** occured downfield (δ 70.7) and with a larger coupling constant (J = 111), consistent with previous reports. The phenyl carbon bonded directly to phosphorus of the phosphonium salt gave a doublet at approximately δ 117 (J = 85–86). Again the corresponding signal in the phosphorane was downfield with a larger coupling constant, δ 126.4 (J = 94). The diastereotopic methylene ethyl ester hydrogens (OCH_2CH_3) of **16**, **17**, **18**, **20**, and **35** gave rise to complex multiplets by ^{1}H NMR with resonances centered at δ 3.3. The ^{31}P NMR resonance for the phosphonium salts occurred characteristically[13] at δ 36 while phosphorane **15** gave a resonance at δ 17.4.

The ^{1}H NMR spectra of the allene **24** and the methylated derivative **25** reveal that all the methylene hydrogens are diastereotopic. A total assignment of the ^{1}H NMR spectra of **24** and **25** was achieved by using homonuclear decoupling.

Adipic anhydride did not give enol lactone on reaction with the ylide **3** but rather gave acyclic products via an alternative breakdown of the phosphonium salt intermediate (Scheme IV). For comparison, the reaction of ylide **2** with adipic anhydride was carried out. The phosphorane **29** was isolated as the only product and was further characterized by methylation with diazomethane. The phosphorane **29** failed to cyclize to the corresponding enol lactone on extended reflux in $CDCl_3$. Therefore, when enol lactone formation is not favorable, as in this case, the initially formed phosphonium salt **26** can be stabilized by formation of the corresponding phosphorane rather then by allene formation as was observed with ylide **3**. Interestingly, the bromo phosphonium salt **38**, prepared from **37** by treatment with Br_2/Et_3N, yielded the corresponding seven-membered *Z* and *E* bromo enol lactones **39** and **40**, respectively[15] (Scheme VI). **38** is unable to form an allene, and consequently the cyclization pathway is followed.

In conclusion (Scheme VII), it would appear that the phosphonium salts can react in three ways to afford either a phosphorane, an enol lactone, or an allene. We postulate that in the reactions of ylide **3** with a cyclic anhydride ring opening can occur to produce a phosphonium salt, which is unable to undergo rearrangement to the more stable phosphorane (Scheme VII, pathway a) and therefore rapidly undergoes cyclization to give an enol lactone (Scheme VII, pathway b) or, when cyclization is disfavored, rearrangement to give an allene (Scheme VII, pathway c). The formation of a stable acyclic intermediate is only observed when the phosphonium salt formed from initial ring cleavage can be stabilized by rearrangement to a phos-

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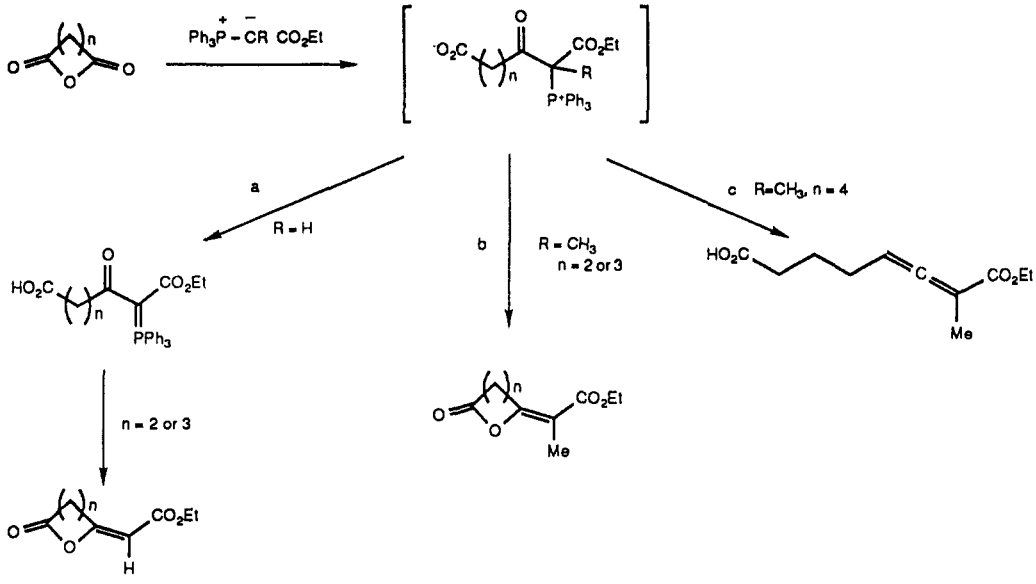
(15) Unpublished results.

Scheme VII



phorane (Scheme VII, pathway a). The fact that an intermediate was not observed does not necessarily imply that phosphonium salt intermediates are not formed in the reactions of **3** with cyclic anhydrides. Rather, it could simply be a consequence of the fact that salts such as **8** (Scheme I) cannot be stabilized by the presumably rapid phosphonium salt–phosphorane rearrangement or perhaps oxaphosphetane formation and fragmentation is faster with **8** than with, for example, **7**.

Experimental Section

Melting points were obtained by using a Hot Stage Microscope and are uncorrected. NMR spectra were obtained at 300 MHz for ^1H NMR, 75.5 MHz for ^{13}C NMR, and 121.5 MHz for ^{31}P NMR spectra. J values are in hertz. Preparative chromatography was carried out on a Chromatotron (Harrison Research Inc.) using glass plates coated with silica gel (P.F. 254 60) of 2-mm thickness. All chemicals were reagent grade unless otherwise stated. The monomethyl ester of adipic anhydride and 3-carbomethoxypropionyl chloride were purchased from the Aldrich Chemical Company.

Succinic Acid, Monobenzhydryl Ester (9). The monobenzhydryl ester of succinic acid (**9**) was prepared by modification of the literature procedure.[16] Succinic anhydride (2.1 g, 0.02 mol) and benzhydrol (4 g, 0.02 mol) were heated under N_2 at 180–190 °C for 6 h. After cooling, the solid product was dissolved in CH_2Cl_2 (150 mL) and washed with saturated aqueous sodium bicarbonate (200 mL). The aqueous layer was acidified with concentrated HCl and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic fractions were dried ($MgSO_4$) and evaporated under reduced pressure to yield an oil. Crystallization from petroleum ether gave **9** as colorless crystals: 1.56 g (26%); mp 72–75 °C (lit.[16] mp 78 °C); ^1H NMR ($CDCl_3$) δ 2.72 (m, 4 H), 6.90 (s, 1 H), 7.31 (m, 10 H, ph_2).

Acid Chlorides 12, 13, and 32. A solution of monobenzhydryl ester of succinic acid (**9**) (1.0 g, 3.4 mmol) and DMF (1 drop) in CH_2Cl_2 (50 mL) was cooled to 0 °C, and oxalyl chloride (2.36 g, 19.0 mmol, 1.6 mL) was slowly added. After 30 min at 15 °C, the solvent was removed under reduced pressure. Benzene (20 mL) was added to the resultant oil and again the solvent was removed to yield the acid chloride **12** as an unstable oil that was not purified further (essentially pure by ^1H NMR): 770 mg (75%); ^1H NMR ($CDCl_3$) δ 2.81 (t, J = 6.4, 2 H), 3.22 (t, J = 6.4, 2 H), 6.88 (s, 1 H), 7.32 (m, Ph_2).

Acid chlorides **13** and **32** were similarly prepared from monobenzyl succinate (**10**)[17] and monomethyl adipate (**31**), respectively. **13**: ^1H NMR ($CDCl_3$) δ 2.73 (t, J = 6.5, 2 H), 3.23 (t, J = 6.5, 2 H), 5.15 (s, 2 H, CH_2Ph), 7.36 (m, Ph). **32**: ^1H NMR ($CDCl_3$) δ 1.66 (m, 4 H, $(H3)_2$, $(H4)_2$), 2.35 (t, J = 7.0, 2 H, $(H5)_2$), 2.92 (t, J = 7.0, 2 H, $(H2)_2$), 3.68 (s, 3 H, Me).

[1-(Ethoxycarbonyl)-4-[(diphenylmethoxy)carbonyl]-2-oxobutylidene]triphenylphosphorane (15). A solution of the acid chloride **12** (513 mg, 1.7 mmol) in benzene (25 mL) was cooled in an ice bath, and the ylide **2** (1.77 g, 3.4 mmol) was added. The mixture was stirred at 15 °C or a further 16 h under N_2. After filtration the filtrate was evaporated under reduced pressure and the resultant oil was chromatographed on a 2-mm silica chromatotron plate (19:1 chloroform–ethyl acetate). Crystallization from ether gave **15** as colorless crystals: 0.498 g (48%); mp 109–110 °C; ^1H NMR ($CDCl_3$) δ 0.69 (t, J = 7.2, 3 H, OCH_2CH_3), 2.76 (t, J = 7.0, 2 H, $(H4)_2$), 3.32 (t, J = 7.0, 2 H, $(H5)_2$), 3.74 (q, J = 7.2, 2 H, OCH_2CH_3), 6.84 (s, 1 H, $CHPh_2$), 7.2–7.6 (m, Ph); ^{13}C NMR ($CDCl_3$) δ 13.8, 29.8, 35.0 (d, J = 7.3), 58.5, 70.8 (d, J = 110.6), 76.5, 126.5 (d, J = 93.6), 127.1, 127.5, 128.3, 128.4, (d, J = 12.5), 131.6, 133.1 (d, J = 10.1, 140.6, 167.7 (d, J = 14.6), 172.7, 194.8 (d, J = 3.7); IR (KBr) 1740, 1670 cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 17.4. Anal. Calcd for $C_{39}H_{35}O_5P$: C, 76.20; H, 5.74. Found: C, 76.34; H, 5.71.

Phosphonium Salts 16, 17, 18, 20, and 35. A solution of the acid chloride **12** in benzene (20 mL), prepared from monobenzhydryl succinate (**9**) (320 mg, 1.2 mmol) as previously described, was added to an ice-cooled solution of ylide **3** (400 mg, 1.1 mmol) in dry benzene (15 mL). After 18 h at 7 °C the benzene and precipitated protonated ylide **3** were decanted and the residual oil was pumped to dryness under reduced pressure (1 mm, 1 h). The ^1H NMR spectrum revealed a mixture of the unstable phosphonium salt **16** and protonated ylide **3** (2:5) that could not be purified further: 132 mg; ^1H NMR ($CDCl_3$) δ 1.02 (t, J = 7.1, 3 H, OCH_2CH_3), 2.16 (d, J = 17, 3 H, CH_3), 2.71 (m, 2 H, $(H4)_2$), 3.28 and 3.47 (each 1 H m, $(H3)_2$), 4.15 (m, 2 H, $OHCH_2CH_3$), 6.79 (s, 1 H, $CHPh_2$), 7.40–8.20 (m, Ar); ^{31}P NMR ($CDCl_3$) δ 36.5.

In the following experiments, the acid chloride (weight, mmol), reaction time, and phosphonium salt/protonated ylide **3** ratio are given in abbreviated format.

13 (65 mg, 0.3 mmol), reaction time 12 h under N_2. 1:1 mixture of the phosphonium salt **17** and protonated ylide **3**. **17**: ^1H NMR ($CDCl_3$) δ (t, J = 7.1, 3 H, OCH_2CH_3), 2.11 (d, J = 16.2, 3 H, CH_3), 2.72 (m, 2 H, $(H4)_2$), 3.22 and 3.40 (each 1 H m, $(H3)_2$), 4.15 (m, 2 H, OCH_2CH_3), 5.06 and 5.09 (AB q, J = 12.6, 2 H, CH_2Ph), 7.6–8.0 (m, Ar); ^{13}C NMR ($CDCl_3$) δ 13.2, 21.6, 27.5, 35.2 (d, J = 2.1), 64.9, 66.1 (d, J = 50.0), 66.3, 117.7 (d, J = 85.6), 127.7, 128.0, 128.3, 130,3 (d, J = 13.0), 134.0 (d, J = 10.0), 135.3, 135.4,

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165.9, 171.5, 202.2 (d, J = 4.1); ^{31}P NMR ($CDCl_3$) δ 36.2.

14 (0.15 g, 1.0 mmol), reaction time 12 h under N_2. 3:2 mixture of the phosphonium salt **18** and protonated ylide **3**. **18**: ^{1}H NMR ($CDCl_3$) δ 1.11 (t, J = 7.2, 3 H, OCH_2CH_3), 2.20 (d, J = 18.0, 3 H, CH_3), 2.66 (m, 2 H, $(H4)_2$), 3.25 and 3.46 (each 1 H, m, $(H3)_2$), 3.66 (s, 3 H, OCH_3), 4.15 (m, 2 H, OCH_2CH_3), 7.6–8.2 (m, 15 H, PPh_3); ^{13}C NMR ($CDCl_3$) δ 12.1, 20.5, 26.3, 34.2 (d, J = 1.5), 50.6, 63.8, 64.8 (d, J = 50), 116.5 (d, J = 86.0), 129.3 (d, J = 13.2), 139.2 (d, J = 10.8), 134.3, 164.7, 171.0, 201.2 (d, J = 4.2); ^{31}P NMR ($CDCl_3$) δ 36.0.

Acetyl chloride (22 mg, 0.3 mmol), reaction time 72 h under N_2. 3:1 mixture of the phosphonium salt **20** and protonated ylide **3** (8% **21** was also observed). **20**: ^{1}H NMR ($CDCl_3$) δ 1.10 (t, J = 7.1, 3 H, OCH_2CH_3), 2.20 (d, J = 17.7, 3 H, CH_3), 2.66 (s, 3 H, $COCH_3$), 4.15 (m, 2 H, OCH_2CH_3), 7.6–8.0 (m, 15 H, PPh_3); ^{13}C NMR ($CDCl_3$) δ 13.3, 21.6, 28.7 (d, J = 2.0), 64.8, 66.3 (d, J = 50.4), 117.7 (d, J = 86.6), 130.4 (d, J = 12.8), 134.6 (d, J = 10.2), 135.3 (d, J = 3.0), 166.5, 201.2 (d, J = 4.3); ^{31}P NMR ($CDCl_3$) δ 36.3.

32 (416 mg, 2.3 mmol), reaction time 17 h under H_2. 2:3 mixture of the phosphonium salt **35** and protonated ylide **3**. **35**: ^{1}H NMR ($CDCl_3$) δ 1.10 (t, J = 7.1, 3 H, OCH_2CH_3), 1.58 (m, 4 H, $(H4)_2$), $(H5)_2$, 2.19 (d, J = 18.0, 3 H, CH_3), 2.30 (m, 2 H, $(H6)_2$), 2.85 and 3.28 (each 1 H, m, $(H3)_2$), 3.65 (s, 3 H, OCH_3), 4.12 (m, 2 H, OCH_2CH_3), 7.9–8.2 (m, 15 H, PPh_3); ^{13}C NMR ($CDCl_3$) δ 13.1, 21.3, 22.3, 23.3, 33.3, 39.8, 51.1, 64.6, 66.0 (d, J = 49), 116.6 (d, J = 84.8), 130.2 (d, J = 13.1), 131.6 (d, J = 9.5), 134.3, 166.3, 173.1, 203.0 (d, J = 3.6); a HETCOR showed correlation between (H 1.1 and C 13.1), (H 1.58 and C 22.3, 23.3), (H 2.2 and C 21.3), (H 2.3 and C 33.2), (H 2.9 and C 39.8), (H 3.6 and C 51.1), (H 4.12 and C 64.06); ^{31}P NMR ($CDCl_3$) δ 36.5.

Removal of the Benzhydryl Group from the Phosphorane 15. Method A. A solution of **15** (50 mg, 0.08 mmol) in CH_2Cl_2 (2 mL) was cooled to 0 °C. TFA (1 mL) was added and the solution stirred for 5 min. The mixture was diluted to 15 mL with CH_2Cl_2, washed with H_2O (4 × 15 mL), and dried ($MgSO_4$). Evaporation under reduced pressure gave the phosphorane **7**, which was not purified further but gave identical ^{1}H NMR and ^{13}C NMR spectra with an authentic sample prepared from succinic anhydride and ylide **2**.[7]

Method B. To a solution of **15** (50 mg, 0.08 mmol) in dry ethanol (5 mL) was added sodium carbonate (50 mg) and 10% Pd on charcoal (10 mg). The solution was filtered through a small Celite column (ethyl acetate) after being stirred under a hydrogen atmosphere for 1 h. The filtrate was evaporated under reduced pressure to give the phosphorane **7** which was not purified further.

The above phosphorane samples were separately dissolved in $CHCl_3$ (1.0 mL) and heated at 40 °C for 3 h. The resultant solution was chromatographed on a 2-mm silica chromatotron plate (17:3 ethyl acetate–petroleum ether) to give the E enol–lactone **4** in 65% yield as the sole product: mp, 92–94 °C (lit.[12] mp 94–96 °C); ^{1}H NMR spectrum identical with that reported.[12]

Removal of the Benzhydryl Group from the Phosphonium Salt 16. A solution of the crude benzhydryl phosphonium salt **16** (130 mg) in CH_2Cl_2 (4 mL) was cooled to 0 °C. TFA (2 mL) was slowly added and the solution was stirred for 5 min at 0 °C under N_2. Workup as described above gave an oil that was chromatographed on a 2-mm silica chromatotron plate (1:9 ethyl acetate–petroleum ether). The E enol–lactone **5** was obtained as an oil, which crystallized on standing (23 mg); mp 55–57 °C (lit.[10] mp 56–57 °C). The phosphonium salt **8** was not detected in the crude sample by ^{1}H NMR spectroscopy.

2-Methyl-2,3-octadienedioic Acid, 1-Ethyl Ester (24) and 8-Methyl Ester (25). A solution of adipic anhydride (**22**) (50 mg, 0.4 mmol) and ylide **3** (0.257 g, 0.7 mmol) in CH_2Cl_2 (10 mL) was stirred at 15 °C for 7 days under a N_2 atmosphere. Evaporation under reduced pressure gave the allene **24** as an oil, which was difficult to purify: ^{1}H NMR ($CDCl_3$) δ 1.25 (t, J = 7, 3 H, OCH_2CH_3), 1.79 (m, 2 H, $(H3)_2$), 1.84 (d, J = 3, 3 H, $(H9)_3$), 2.14 (m, 2 H, $(H4)_2$), 2.39 (m, 2 H, $(H2)_2$), 4.17 (m, 2 H, OCH_2CH_3), 5.44 (m, 1 H, H5).

A solution of the allene **24** (83 mg) in THF (5 mL) was methylated with an excess of diazomethane. Evaporation under reduced pressure gave an oil, which was chromatographed on a 2-mm silica chromatotron plate (19:1 chloroform–ethyl acetate). The allene **25**[11] was obtained as an oil, 49 mg (58%): ^{1}H NMR ($CDCl_3$) δ 1.27 (t, J = 7.1, 3 H, OCH_2CH_3), 1.78 (m, 2 H, $(H3)_2$), 1.86 (d, J = 3.0, 3 H, $(H9)_3$), 2.16 (q, J = 7.0, 2 H, $(H4)_2$), 2.40 (m, 2 H, $(H2)_2$), 3.67 (s, 3 H, OCH_3), 4.19 (m, 2 H, OCH_2CH_3), 5.43 (m, $(H5)_1$); ^{13}C NMR ($CDCl_3$) δ 14.2, 15.1, 23.8, 27,3, 32.9, 51.4, 60.8, 92.7, 167.7, 173.8, 210.1.

Attempted Isomerism of the Enol Lactones 5[10] and 28.[11] The following general procedure was used: To a sample of the enol lactone (5 mg) in $CDCl_3$ (0.5 mL) was added a further equivalent of ylide **3**. After standing at 15 °C for 24 h, the samples were examined by ^{1}H NMR and in all cases there was no evidence of the corresponding allene.

Conversion of the Phosphonium Salts to Allenes. A separate solution of the phosphonium salts **18**, **20**, and **35** (5 mg) in $CDCl_3$ (0.5 mL) was treated with Et_3N (one drop) or an equivalent of the ylide **3**. The ^{1}H NMR after 5 min was consistent with those of allene **19**,[9] **21**,[9] and **25**,[11] respectively. Similarly, the allenes were prepared directly from the corresponding acid chloride in $CDCl_3$ by reaction with either ylide **3** (1 equiv)/Et_3N (1 equiv) or ylide **3** (2 equiv).

***O*-Acyl Phosphonium Salt 36.** To a solution of the acid chloride **32** (10 mg, 0.06 mmol) in $CDCl_3$ (0.5 mL) was added ylide **3** (20.3 mg, 0.06 mmol): **36** ^{1}H NMR ($CDCl_3$) δ 0.52 (t, J = 7.1, 2 H, OCH_2CH_3), 1.64 (d, J = 14.4, 3 H, CH_3), 1.73 (m, 4 H), 2.39 (t, J = 6.8, 2 H), 2.78 (t, J = 6.9, 2 H), 3.67 (s, 3 H, OCH_3), 3.72 (q, J = 7.1, 2 H, OCH_2CH_3). The solution was allowed to warm to 15 °C and after 1 h the ^{1}H NMR indicated C-acyl phosphonium salt **35** (90%) and allene **25** (10%).

[1-(Ethoxycarbonyl)-6-carboxy-2-oxohexylidene]triphenylphosphorane (29). A solution of ylide **2** (1.36 g, 4 mmol) and adipic anhydride (**22**) (0.5 g, 4 mmol) in CH_2Cl_2 (25 mL) was stirred at 15 °C for 18 h under a N_2 atmosphere. The solution was poured into dry petroleum ether to give an oil. Crystallization from ethyl acetate and petroleum ether gave the phosphorane **29** as a white crystalline solid: 0.53 g (29%); mp 134–135 °C; ^{1}H NMR ($CDCl_3$) δ 0.64 (t, J = 7.1, 3 H, OCH_2CH_3), 1.61 (q, J = 6.5, 4 H, $(H_5)_2$, $H_6)_2$), 2.17 (t, J = 6.9, 2 H, $(H4)_2$), 2.91 (t, J = 6.8, $(H7)_2$), 3.70 (q, 2 H, J = 7.1, 2 H, OCH_2CH_3), 7.53 (m, 15 H), 10.27 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.7, 24.3, 25.0, 34.0, 39.5 (d, J = 6.5), 58.5, 71.9 (d, J = 109.5), 126.4 (d, J = 93.7), 128.5 (d, J = 12.7), 131.7 (d, J = 3.0), 133.0 (d, J = 9.9), 167.8 (d, J = 14.8), 177.1, 197.7 (d, J = 3.1); ^{31}P NMR ($CDCl_3$) δ 18.21; IR (KBr) 2950, 2650 (b), 1720, 1680 cm^{-1}. Anal. Calcd for $C_{28}H_{29}O_5P$: C, 70.58; H, 6.13. Found: C, 70.74; H, 6.60.

[1-(Ethoxycarbonyl)-6-(methoxycarbonyl)-2-oxohexylidene]triphenylphosphorane (30). Method A. A solution of the adipic acylated phosphorane **29** (51.3 mg, 0.11 mmol) in the THF (5 mL) was methylated with an excess of diazomethane. Crystallization from ethyl acetate and petroleum ether gave **30**: 30 mg (58%); mp 88–89 °C; ^{1}H NMR ($CDCl_3$) δ 0.65 (t, J = 7.2, 3 H, OCH_2CH_3), 1.64 (t, J = 3.7, 4 H, $(H_5)_2$, $(H_6)_2$, 2.31 (t, J = 7.2, 2 H, $(H4)_2$), 2.91 (t, J = 7.1, 2 H, $(H7)_2$), 3.64 (s, 3 H, CO_2CH_3), 3.71 (q, J = 7.3, 2 H, OCH_2CH_3), 7.4–7.7 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 13.6, 24.9, 25.1, 34.0, 39.7 (d, J = 6.3), 51.2, 58.2, 70.7 (d, J = 110.8), 126.9 (d, J = 93.6), 128.4 (d, J = 12.7)8 131.4 (d, J = 2.9), 133.0 (d, J = 90.6), 167., (d, J = 15.3), 174.2, 197.3 (d, J = 3.3); a HETCOR showed correlation between (H 3.6 and C 51.2); H 3.7 and C 58.2); (H 2.9 and C 39.7); (H 2.3 and C 34.0); (H 1.6 and C 25.1); (H 0.65 and C 13.6); ^{31}P NMR δ ($CDCl_3$) 18.06; IR (KBr) 1750, 1660 cm^{-1}. Anal. Calcd for $C_{29}H_{31}O_5P$: C, 71.00; H, 6.37. Found: C, 71.24; H, 6.35.

Method B. Ylide **2** (2.17 g, 6.2 mmol) was added to a solution of the acid chloride **32** (prepared from adipic acid monomethyl ester **31** (0.5 g, 3.12 mmol) as previously described) in benzene (50 mL). The solution was stirred under a N_2 atmosphere for 12 h and filtered, and the filtrate was evaporated to give an amber oil. Crystallization from ethyl acetate and petroleum ether gave **30**: 1.42 g (93%); NMR spectra identical with that above.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra for phosphonium salts **16**, **17**, **18**, **20**, and **35** (13 pages). Ordering information is given on any current masthead page.