analysis[11] that the reaction had gone to 56% completion after 2 min. and 97% completion after 13 min.

Reaction of I and Diethyl Phosphate with Triethylamine in Ether.—A solution of 13.8 g. (0.10 mole) of diethyl phosphite and 20.10 g. (0.10 mole) of I in 150 ml. of ether was cooled in an ice bath. A solution of 10.12 g. (0.10 mole) of triethylamine in 50 ml. of ether was added to the solution over a 4-hr. period. The solution was allowed to warm and was stirred for 18 hr. at room temperature. Filtration afforded 8.0 g. (53%) of triethylamine hydrochloride. Vacuum distillation afforded 11.20 g. (67%) of a material, b.p. 53–58° (4.5 mm.), that exhibited one peak in the v.p.c. which had the same retention time as authentic 3-methyl-5-dichloromethyl-1,2,4-oxadiazole.[9] The infrared spectrum of the material was identical with that of an authentic sample of II.

The pot residue gave two peaks in the v.p.c., which had retention times identical with those of an authentic mixture of tetraethyl pyrophosphate and tetraethyl hypophosphate.[5] The infrared spectra of the two materials were identical. Attempted distillation of the pot residue resulted in considerable decomposition. However, a small amount of impure tetraethyl hypophosphate, b.p. 109–117° (1.0 mm.), n^{25}_{D} 1.4305 (lit.[12] b.p. 116–117°, n^{20}_{D} 1.4284), and a small amount of tetraethyl pyrophosphate, b.p. 132–140° (1.0 mm.), n^{25}_{D} 1.4196 [lit.[13] b.p. 135–138° (1.0 mm.), n^{25}_{D} 1.4180] were isolated. In a similar experiment analysis by v.p.c.[11] indicated that a 69% yield of II was obtained. Also isolated was a 51% yield of triethylamine hydrochloride.

Reaction of I with Triethylamine and an Excess of Diethyl Phosphite in Ether.—The reaction was carried out as above except that 2 equiv. of diethyl phosphite was used instead of 1. A 44.3% yield, based on triethylamine, of triethylamine hydrochloride was isolated. A v.p.c. analysis[11] indicated that a 94% yield of II was formed.

Reaction of I with Triethyl Phosphite in Benzene.—To a solution of 40.30 g. (0.20 mole) of I in 100 ml. of benzene was added 67.20 g. (0.40 mole) of triethyl phosphite over a 1-hr. period. After standing overnight at ambient temperature the benzene was removed at the water pump without heating. Vacuum distillation afforded 8.8 g. (13%) of triethyl phosphite, b.p. 35–40° (15 mm.). Another fraction was collected, b.p. 80–86° (0.1 mm.) (26.51 g.), which was shown to contain III, triethyl phosphate, and one other compound by v.p.c. analysis. Attempted redistillation of this fraction on a 24-in. stainless steel spinning-band column afforded no separation. The distillates were combined and separated by preparative v.p.c. using a 10 ft. × $^3/_8$ in. column packed with 20% SE30 on 60–80 Chromosorb W. The operating temperature was 130° with a flow rate of 200 cc. of helium/min. Considerable decomposition occurred and only small amounts of two peaks could be collected. The first fraction was shown to be triethyl phosphate by comparison of its n.m.r. spectra and its retention time on v.p.c. with an authentic sample. That the second fraction was 3-methyl-5-(α,α-dichloropropyl)-1,2,4-oxadiazole is supported by the following data. The n.m.r. spectra showed resonances at δ 1.25, triplet (J = 7 c.p.s.) ($\mathrm{CH_2C}H_3$, three protons); δ 2.75, quartet (J = 7 c.p.s.) ($\mathrm{C}H_2\mathrm{CH_3}$); and at δ 2.48, singlet (ring methyl). The resonances at δ 2.75 and 2.48 had a combined integration of 4.65 protons. *Anal.* Calcd. for $C_6H_8Cl_2N_2O$: C, 37.80; H, 4.13; Cl, 36.35; N, 14.36. Found: C, 38.09; H, 4.51; Cl, 36.12; N, 14.08.

The high-boiling residue from the first distillation was molecularly distilled at 83° and 12 μ. Four fractions were collected whose refractive indices ranged from 1.4613 to 1.4633; however, v.p.c. and thin layer chromatography indicated that one major product and at least two minor products were present. The products were not positively identified. A similar experiment was performed at ice-bath temperature in which the presence of diethyl chlorophosphate was determined by v.p.c. analysis. It was observed that the amount of diethyl chlorophosphate would increase while the reaction was kept cold; however, after 18 hr. at room temperature, only a small amount of diethyl chlorophosphate could be detected. No diethyl chlorophosphate could be isolated from the reaction mixture by distillation or preparative v.p.c.

Reaction of 3-Methyl-5-trichloromethyl-1,2,4-oxadiazole with Triethyl Phosphite in Ethanol.—A 20.0-g. (0.10-mole) sample of II was dissolved in 100 ml. of ethanol. Triethyl phosphite (33.60 g., 0.20 mole) was added to the solution with stirring over a 1-hr. period. After 18 hr. at ambient temperature, the solvent was removed and the residue was analyzed qualitatively by v.p.c. Triethyl phosphite, triethyl phosphate, and II were shown to be present by comparison of their v.p.c. retention times with those of authentic samples. Diethyl chlorophosphate, I, and III were shown to be absent. Vacuum distillation on a 24-in stainless steel spinning-band column afforded 12.69 g. (36%) of triethyl phosphite, b.p. 45–50° (25 mm.), n^{25}_{D} 1.4114; 16.35 g. (44%) of triethyl phosphate, b.p. 105–108° (25 mm.), n^{25}_{D} 1.4081; 10.07 g. (62%) of II, b.p. 95–105° (25 mm.). The infrared spectra of the different fractions were identical with those of authentic samples as were their retention times on v.p.c.

Acknowledgment.—We wish to thank Dr. Donald L. Heywood and Dr. John Durden, Union Carbide Chemicals Corporation, South Charleston, West Virginia, for helpful discussions. This work was supported by the Union Carbide Chemicals Corporation, South Charleston, West Virginia.

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The Acylation of Phosphine–Methylene Derivatives. The Preparation and Properties of Mixed Phosphorane–Phosphonium Salts

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The reaction of triphenylphosphine and chloroacetyl chloride does not lead to chlorocarbonylmethylene triphenylphosphorane, $Ph_3P{=}CH{-}COA$ (**1d**, A = Cl), but to **2**, which is a mixed phosphorane–phosphonium salt (actually, a formal dimer of **1d**). This reaction is probably analogous to the acylation of the stable phosphoranes **1** (A = OAlk) by the esters of carboxylic acids. The reactions of **2** show its potential synthetic utility in the fields of acetylenic and olefinic ketones, esters, amides, and related compounds.

Phosphine–methylene derivatives (Wittig reagents) have been acylated with acid halides,[1] anhydrides,[2] and certain amide derivatives[1]; only the most reactive ones have been reported to react with esters[1] or thio esters.[1]

We find that esters formed from some strong carboxylic acids can be used to acylate the stable phosphoranes **1** as shown in eq. 1, Scheme I.

The scope of this reaction and its limitations have not been explored; however, it is potentially useful since the diketophosphoranes **4** are intermediates in the preparation of acetylenic esters and ketones.[2–4]

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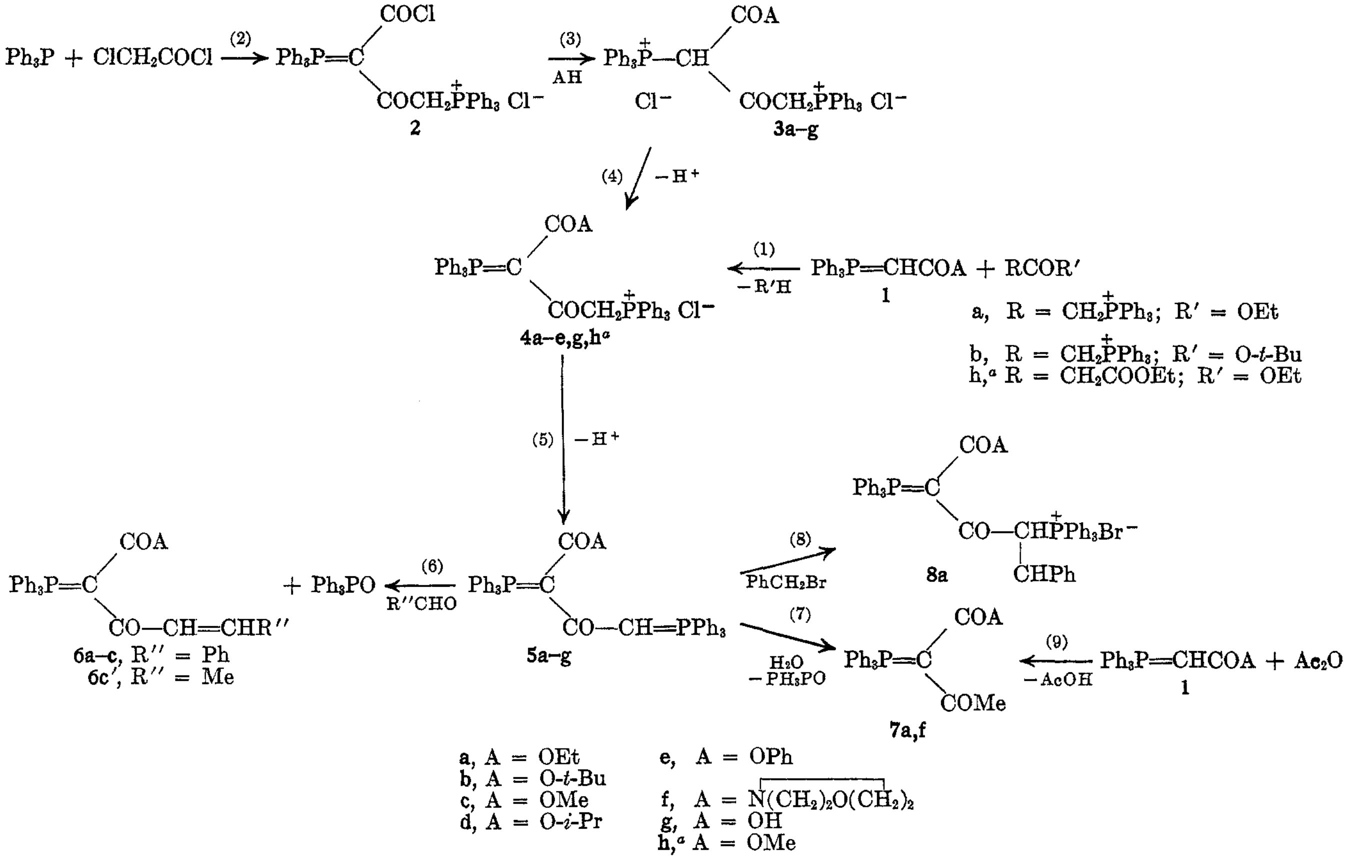
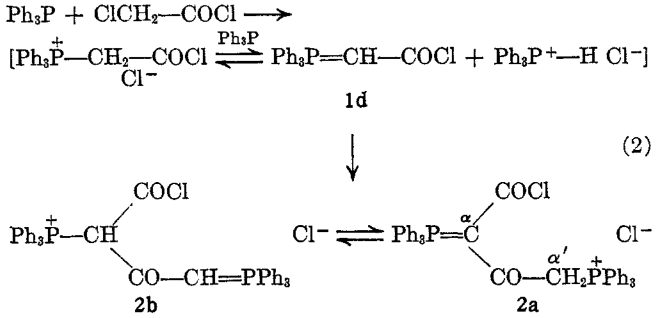
SCHEME I

THE REACTIONS OF α-CHLOROCARBONYL α-TRIPHENYLPHOSPHONIOACETYLMETHYLENE TRIPHENYLPHOSPHORANE CHLORIDE 2



[a] With R = CH_2COOEt (see eq. 1), the corresponding compound **4h** is $Ph_3P{=}C(COOMe)CO_2CHCOOEt$.

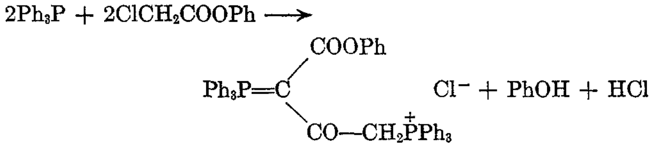
Compounds **4a** to **4d** (mixed phosphorane–phosphonium salts) were also prepared by the alcoholysis of the corresponding acid chloride **2**, an actual dimer of chlorocarbonylmethylenephosphorane **1d** (*vide infra*). It is the main purpose of this article to report some aspects of the chemistry of **2**, a novel intermediate which results from the action of triphenylphosphine on chloracetyl chloride, *viz.*, eq. 2.



(2)

In the presence of an excess of chloroacetyl chloride the above reaction gave a 50% yield of **2** (based on phosphine); however, when stoichiometric quantities of reactants, *i.e.*, 2 moles of Ph_3P for 1 mole of $ClCH_2COCl$ were used, unreacted phosphine could be recovered from the mixture after separation of **2**; this is not surprising in view of the instability of $Ph_3\overset{+}{P}\text{–}H\ Cl^-$. (For example, Ph_3P precipitates readily by dilution from its solution in concentrated HCl.) Although neither phosphorane **1d** nor its parent phosphonium salt were isolated, it is probable that **2** is formed as shown in eq. 2 by the acylation of **1d** in a manner similar to that postulated in eq. 1.

The corresponding reaction of triphenyl phosphine and phenyl chloroacetate, which gave **4e** plus phenol, probably proceeds also in a similar way, *viz.*



4e

Because of its insolubility in all common solvents, the exact structure of **2** was not determined. In principle, it could exist in either of the two forms **2a** and **2b** which differ only by the respective positions of the phosphorane and phosphonium centers. However, it is probable that the proton affinity for the α-carbon is less than for the α′-carbon and structure **2b** is unlikely; this is supported by the following observations. (a) The diketophosphoranes of general structure $Ph_3P{=}C(COA)COB$ (where A and B are alkyl, aryl, or O-alkyl) are very weakly basic because of the high degree of conjugation involved.[2] For example, when the dicarbethoxymethylene phosphorane, $Ph_3P{=}C(COOEt)_2$, is dissolved in aqueous HCl, the resulting hydrochloride spontaneously loses HCl upon evaporation of the solution. (b) The structure of the ester derivative **4c** (see below). As a matter of fact, when compound **2** was treated with alcohols (as stated above), water, and amines, it gave the double phosphonium salts **3**; these, on partial neutralization, gave in turn the phosphorane–phosphonium salts **4** (see reaction 3 and 4), the structure of which is supported by the p.m.r. spectrum of the corresponding methyl ester **4c**; this spectrum actually showed the presence of two equivalent alkyl protons.

In alkaline solution, compounds **4** gave the double phosphoranes **5** (Scheme I) which were stable and nearly colorless in the crystalline form; **5g** is an exception: it is bright yellow and decomposes on standing (see discussion below and also in the Experimental Section). Alkylation of **5** (reaction 8) or the reaction with aldehydes (eq. 6) gave, respectively, a phosphonium salt for which structure **8** is proposed in analogy to previous work[5] and olefins **5**, showing that the active carbanion is in position α' as expected. In hydroxylic solvents (reaction 7), **5** solvolyzes to the acetylphosphoranes **7**; these were also prepared by direct acylation of **1** (reaction 9).

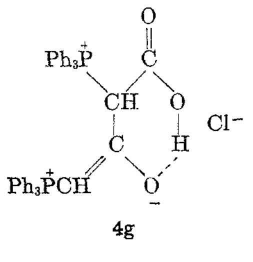
Compound **4f**, mentioned above, was actually not obtained as such but only as its derivative **7f**.

The acid **4g** esterified quickly with alcohols but was stable in the crystalline form and could be kept for an indefinite length of time; all attempts to decarboxylate it in this form were unsuccessful. This contrasts with the properties of other α-carboxymethylphosphonium salts which decompose readily with alkali[6,7]; for example, $\overset{+}{P}Ph_3CH_2COO^- \rightarrow Ph_3P{=}CH_2 + CO_2$, which shows that, unlike the ester group, the carboxylic function has no stabilizing effect on the phosphorane. Similarly, we find that this phosphonium salt is also relatively unstable and cannot be recrystallized under usual conditions,[8] *viz.*

$$Ph_3\overset{+}{P}CH_2COOH \longrightarrow Ph_3\overset{+}{P}CH_3 + CO_2 \qquad (10)$$

The reduced tendency of **4g** to decarboxylate must be due to the conjugation that exists between the phosphorane carbanion and the ketocarbonyl group. Examination of the p.m.r. spectrum showed the presence of two nonequivalent protons, both split by phosphorus; a third proton appears as a singlet at an unusually high field for a carboxylic proton. This indicates that the correct structure for **4g** must be $Ph_3\overset{+}{P}CH(COOH)COCH{=}PPh_3Cl^-$, in contrast to those postulated above for **4a–f**.

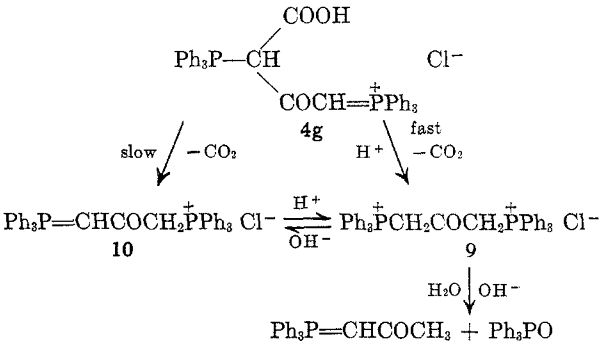
Evidently, several tautomeric structures showing the importance of conjugation and the possibility of enol and hydrogen-bond formation can then be constructed and might explain the peculiar chemical and spectral properties of **4g** (see Experimental Section); one of these structures is shown below.



4g

If this concept is correct, the removal of a proton from **4g** should produce a carbanion for which no possibility of additional stabilization by conjugation is available (except with the phosphorus atom). Actually, as mentioned above, the treatment of **4g** by an aqueous alkaline solution gives the carboxylic double phosphorane **5g**, the properties of which contrast sharply with those of the corresponding esters **5a–e** (see Experimental Section).

In neutral aqueous solution, **4g** slowly decarboxylated giving the phosphorane–phosphonium salt **10**, whereas, under acidic conditions, it rapidly gave the diphosphonium salt **9**; this is not surprising since the addition of a proton will destroy the resonance-stabilizing effect present in **4g** and promote decarboxylation in conditions similar to those discussed for reaction 10. The preparation of **9** has already been reported by another method[9]; when neutralized carefully, we find that it also gives **10**, while in excess aqueous alkali it has been reported to split to triphenylphosphine oxide and acetylmethylene triphenylphosphorane,[9] *vide infra.*



Betaine **10** is a potentially useful intermediate since it leads to asymmetric divinyl ketones, $RCH{=}CHCOCH{=}CHR'$, by the consecutive action of two different aldehydes; this is being investigated.

Experimental Section

Reaction of Triphenylphosphine with Chloroacetyl Chloride.—A solution of triphenylphosphine (50 g., 0.19 mole) in dry tetrahydrofuran (THF) (100 ml.) was added slowly at −40° to a solution of chloroacetyl chloride (10.8 g., 0.095 mole) in THF (100 ml.). The mixture was left for 3 hr. at room temperature after which about 75% of the solvent was removed under reduced pressure. Filtration gave 10.5 g. of compound **2**, m.p. 195–200° dec. (*Anal.* Calcd. for $C_{40}H_{32}Cl_2O_2P_2$: C, 70.95; H, 4.80; Cl, 10.50; P, 9.15. Found: C, 70.98; H, 4.70; Cl, 10.66; P, 8.90.) In Nujol, the infrared carbonyl absorptions were at 1770 and 1650 cm.$^{-1}$. Evaporation of the filtrate under reduced pressure gave triphenylphosphine (38 g.), m.p. 78–81°. The over-all yield based on the phosphine used was 78%; however, in practice, the following procedure which consistently gave 50% yield was preferred. Triphenylphosphine (50 g., 0.19 mole) was dissolved slowly in chloroacetyl chloride (50 ml.), the temperature being kept between 20 and 30° by means of external cooling. After 2–3 hr. standing at room temperature, THF (50 ml.) was added. Compound **2** (32 g.) crystallized out. It was insoluble in all usual inert solvents except dimethyl sulfoxide and was used without further purification.

Reactions of Acid Chloride 2. With Water. A.—Chloride **2** (10 g., 0.0148 mole) was suspended in acetone (50 ml.) and water (5–10 ml.) was added. The solution was rapidly neutralized to pH 6.5–7.0 with 1 *N* sodium hydroxide solution (15 ml.)

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[5] H. J. Bestmann and H. Schulz, *Tetrahedron Letters*, **No. 4**, 7 (1960).

[6] D. B. Denney and L. C. Smith, *J. Org. Chem.*, **27**, 3404 (1962).

[7] R. F. Hudson and P. A. Chopard, *Helv. Chim. Acta*, **46**, 2178 (1963).

[8] Denney has, however, reported the preparation of the carboxymethyltriphenyl phosphonium chloride, m.p. 221–223°.[6] The material we obtained under similar conditions, although analytical and spectral data fitted acceptably, melted at a much lower temperature with evolution of carbon dioxide and formation of the corresponding methylphosphonium salt (see Experimental Section).

[9] J. A. Ford and C. V. Wilson, *J. Org. Chem.*, **26**, 1433 (1961).

and the acetone was removed under reduced pressure. The **carboxylic acid 4g** (9 g., 90%) was collected as the **monohydrate**, m.p. 140° (with gas evolution, resolidification, and remelting at 205–210° dec.). (*Anal.* Calcd. for $C_{40}H_{35}ClO_4P_2$: C, 70.9; H, 5.17; Cl, 5.25; P, 9.16. Found: C, 71.6; H, 5.19; Cl, 5.30; P, 9.25.) The **anhydrous product** was obtained by the recrystallization of the hydrate from a mixture of methylene chloride–monoglyme or by heating it at 120–130° for 24 hr. under a high vacuum: m.p. 205–210° dec. (*Anal.* Calcd. for $C_{40}H_{33}ClO_3P_2$: C, 73.0; H, 5.02; Cl, 5.40; P, 9.40. Found: C, 73.19; H, 5.04; Cl, 5.42; P, 9.73.) The infrared spectrum showed peaks at 2800 (–OH, hydrogen bonded), 1775, 1650 (C═O) and 1320 cm.$^{-1}$ (COO^-). The p.m.r. spectrum showed in addition to the 30 aromatic protons (multiplet at τ = 2.35 p.p.m.), two protons, both split, at τ = 3.90 and 6.60 p.p.m. respectively (separation 9 c.p.s.), and a singlet proton at τ = 7.79 p.p.m.

B.—Chloride **2** (10 g., 0.0148 mole) was dissolved in a mixture of acetone (50 ml.) and water (10 ml.). The solution was heated for a few minutes at the boil; on cooling, **acetone** α,α'**-bis-(triphenylphosphonium chloride)** (**9**,[9] 9.2 g., 88%) separated in the form of a **hydrate**, m.p. 274–276°. (*Anal.* Calcd. for $C_{39}H_{36}Cl_2O_2P_2$: C, 70.0; H, 5.38; Cl, 10.6; P, 9.27. Found: C, 69.7; H, 5.36; Cl, 10.7; P, 9.10.) The compound was identified also by its conversion to acetylmethylene triphenylphosphorane and triphenylphosphine oxide[9] in aqueous alkaline solution. The water of crystallization of the monohydrate was removed by repeated crystallization from mixtures of methylene chloride–ethyl acetate. The rate of C–Cl hydrolysis of **2** was estimated by titrating the chloride ion in the above aqueous acetone solution. It was found that at room temperature 50% hydrolysis occurred in 5 min. Decarboxylation, however, was comparatively slow, and, when the above solution was rapidly evaporated (without neutralization), the acid **4g** was obtained (40–50% yield).

C. With Alcohols (or Phenol). Preparation of the Diphosphonium Salts 3.—Chloride **2** (50 g., 0.074 mole) was dissolved in methanol (150 ml.). After 2 hr. at room temperature, the solvent was removed nearly completely. On the addition of cyclohexane, α**-carbomethoxy acetone** α,α'**-bis(triphenylphosphonium chloride)** (**3c**, 49.2 g., 94%) crystallized out: m.p. 167–168°, from monoglyme–cyclohexane. (*Anal.* Calcd. for $C_{41}H_{36}Cl_2O_3P_2$: C, 69.3; H, 5.08; Cl, 10.00; P, 8.75. Found: C, 69.2; H, 5.16; Cl, 9.60; P, 8.74.) Corresponding derivatives were obtained in comparable yields from other alcohols; for example, ethanol gave **3a**, m.p. 162–164°, from methylene chloride–ethyl acetate. (*Anal.* Calcd. for $C_{42}H_{38}Cl_2O_3P_2$: C, 69.7; H, 5.26; Cl, 9.83; P, 8.56. Found: C, 70.1; H, 5.22; Cl, 9.60; P, 8.32.) Isopropyl alcohol gave **3d**, m.p. 178–180°, from monoglyme–cyclohexane; it was not analyzed but its conversion to **5d** (see below) confirmed its nature.

With *t*-butyl alcohol, the mixture was boiled for 2 hr.; the product which crystallized on cooling had lost 1 mole of HCl and was in the form of the **monophosphonium salt 4b**, m.p. 218–219°, yield 90% (see below for analysis).

Chloride **2** (5 g., 0.0074 mole) was dissolved in 10 molar equiv. of phenol (6.9 g., 0.07 mole) that were freshly recrystallized from petroleum ether (b.p. 65–80°). The solution was maintained for 2 hr. at 70–80°, after which it was allowed to cool to room temperature. The phenol was removed with ether and the crude phosphonium salt (5.2 g., 91%), m.p. 125–130°, was collected. Upon crystallization from mixtures of methylene chloride–ethyl acetate, it lost 1 mole of hydrogen chloride and gave the **monophosphonium salt 4e**, m.p. 185–187° (see below for analysis).

D. With Morpholine.—Chloride **2** (10 g., 0.0148 mole) was dissolved in morpholine (30 ml.). After 1 hr. at room temperature, ethyl acetate containing some ethanol (100 ml.) was added; morpholine hydrochloride was filtered off and petroleum ether was added to the filtrate. α**-Morpholido-**α**-acetylmethylenetriphenylphosphorane** (**7f**, 3.8 g., 58%) crystallized out: m.p. 208–209° from benzene. (*Anal.* Calcd. for $C_{26}H_{26}NO_3P$: C, 72.50; H, 6.04; N, 3.26; P, 7.20. Found: C, 72.36; H, 6.07; N, 3.33; P, 7.32.) This compound was also prepared directly from triphenylphosphine and chloroacetylmorpholide (see below).

Preparation of the Phosphorane–Phosphonium Salts 4. A. By Acylation of Ester Phosphorane 1 (A = O-Alkyl).—Carbethoxymethylenetriphenylphosphorane (50 g., 0.144 mole) and carbethoxymethyltriphenylphosphonium chloride (55 g., 0.144 mole) were suspended in diglyme (300 ml.) and the mixture was stirred for 5 hr. at 120–130°. After cooling, α**-carbethoxy-**β**-keto-**γ**-methyl triphenylphosphoniummethylenetriphenylphosphorane chloride** (**4a**, 53 g., 53%) was collected: m.p. 214–215°, from methylene chloride-ethyl acetate. (*Anal.* Calcd. for $C_{42}H_{37}ClO_3P_2$: C, 73.50; H, 5.40; Cl, 5.17; P, 9.03. Found: C, 73.42; H, 5.54; Cl, 5.16[10]; P, 8.89.) **4a** easily gave a **hydrate**, m.p. 110° with resolidification and remelting at 210–215°. This method was also applied successfully for the preparation of the corresponding *t*-butyl ester **4b**, which was obtained in 82% yield and was identical with the corresponding material described above. (*Anal.* Calcd. for $C_{44}H_{41}ClO_3P_2$: C, 74.0; H, 5.74; Cl, 4.97; P, 8.69. Found: C, 73.6; H, 5.82; Cl, 5.08; P, 8.32.) The two infrared CO absorptions of **4a–e** were all very close to 1750 and 1650 cm.$^{-1}$.

B. By Neutralization of 3.—An ethanolic solution of the double phosphonium salt **3a** (as described above) was treated with 1 equiv. of sodium ethoxide in ethanol. After removing the sodium chloride, the ethanol was evaporated and the residue was crystallized from methylene chloride–ethyl acetate; this gave **4a**, m.p. 210–212°, in 94% yield.

When **3a** was heated for 24 hr. at 140° under high vacuum, hydrogen chloride was slowly eliminated and **4a** was formed.

C. Reaction of Triphenylphosphine with Phenyl Chloroacetate.—Triphenylphosphine (26.3 g., 0.1 mole) and phenyl chloroacetate (17.05 g., 0.1 mole) were dissolved in THF (200 ml.). After 48 hr. standing at room temperature, the solvent was removed and the residue was dissolved in chloroform (70 ml.). The addition of ethyl acetate (500 ml.) produced the crystallization of **4e** (14 g., 38%), m.p. 185–187° from chloroform ethyl acetate, identical with the product prepared above. (*Anal.* Calcd. for $C_{46}H_{37}ClO_3P_2$: C, 75.0; H, 5.04; Cl, 4.84; P, 8.44. Found: C, 74.7; H, 5.25; Cl, 5.07; P, 8.04.) Distillation of the filtrate gave phenol (3.4 g., 36%), b.p. 36–40° (0.01 mm.)

Preparation of the Double Phosphoranes 5.—When either **3** or **4** were treated in aqueous or acetone–water solutions with an excess of normal sodium hydroxide solution, the corresponding betaines **5** were precipitated in nearly theoretical yield. The diphosphoranes were collected and rapidly dried under vacuum with phosphorus pentoxide. The analytical samples were purified from monoglyme–cyclohexane or ethyl acetate–petroleum-ether solutions. Melting points and analyses are recorded in Table I. Only one CO absorption around 1620–1630 cm.$^{-1}$ was visible in the infrared spectrum taken in Nujol.

When the phosphoranes described in Table I were dissolved in dilute HCl and the solvent was removed they reverted to **4**.

Preparation of α**-Morpholido-**α**-acetylmethylenetriphenylphosphorane (7f).**—Triphenylphosphine (52.4 g., 0.2 mole) and chloroacetylmorpholide (32.7 g., 0.2 mole) were dissolved in THF (400 ml.). The solution was heated overnight to reflux and then cooled, and **morpholidomethyltriphenylphosphonium chloride** (49 g., 57%) was collected: m.p. 228–230°, from methylene chloride–ethyl acetate. This salt (10 g.) was dissolved in water and an excess of 2 *N* sodium hydroxide solution was added, giving **morpholidomethylenetriphenylphosphorane** (6 g., 65%), m.p. 215–216°, from methylene chloride–ethyl acetate. (*Anal.* Calcd. for $C_{24}H_{24}NO_2P$: C, 74.0; H, 6.17; N, 4.85; P, 7.95. Found: C, 73.8; H, 6.13; N, 4.90; P, 7.72.)

The above phosphorane (10 g., 0.025 mole) was dissolved in acetic anhydride (40 g.). The solution was heated to 50–60° for 5 hr. after which α**-morpholido-**α**-acetylmethyltriphenylphosphonium acetate** (9.7 g., 75%) crystallized out on cooling: m.p. 178–180°. The infrared spectrum of this substance showed carbonyl peaks at 1600 and 1700 cm.$^{-1}$. It was not purified but was directly converted to the corresponding phosphorane; thus, the above salt (5 g., 0.012 mole) was dissolved in water (150 ml.) and a product identical with **7f** described above (3.6 g., 82%) was formed by the addition of 2 *N* sodium hydroxide solution.

Reaction of Carmebothoxymethylenetriphenylphosphorane with Diethyl Malonate.—Carbmethoxymethylenetriphenylphosphorane **1** (A = OMe) (10 g., 0.03 mole) was dissolved in diethyl malonate (30 ml.) and the solution was heated for 6 hr. at 100°. After cooling the mixture, the addition of petroleum ether gave triphenylphosphine oxide (2 g.), which was removed, then α**-carbomethoxy-**α**-carbethoxyacetylmethylenetriphenylphospho-**

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[10] This value is for ionic chlorine as obtained by titration with silver nitrate; compounds **4** retained chlorinated solvents tenaciously so that total chlorine analysis was generally too high.

TABLE I

Compd.	M.p., °C.	Formula	Calcd., % C	Calcd., % H	Calcd., % P	Calcd., % Mol. wt.	Found, % C	Found, % H	Found, % P	Found, % Mol. wt.[a]
5a	236–237	$C_{42}H_{36}O_3P_2$	77.5	5.54	9.54	650	77.6	5.20	9.26	675
5b	224–226	$C_{44}H_{40}O_3P_2$	77.9	5.90	9.10		77.7	5.90	8.92	
5c	247–249	$C_{41}H_{34}O_3P_2$	77.3	5.35	9.75		77.1	5.32	9.38	
5d	256–257	$C_{43}H_{38}O_3P_2$	77.7	5.72	9.32		77.5	5.48	9.11	
5e	258–261	$C_{46}H_{36}O_3P_2$	79.0	5.15	8.87	698	78.7	5.23	8.62	670

[a] Measured in benzene with a Mechrolab osmometer.

phorane (**4h**, 2.3 g., 17%) as an oil which slowly crystallized on standing, giving yellow crystals, m.p. 143–145° after three crystallizations from ethyl acetate–cyclohexane. (*Anal.* Calcd. for $C_{26}H_{25}O_5P$: C, 69.5; H, 5.60; P, 6.9. Found: C, 69.7; H, 5.85; P, 6.7.) The infrared spectrum showed carbonyl absorptions at 1740, 1680, and 1650 cm.$^{-1}$ and a strongly shifted one at 1540 cm.$^{-1}$.

Reactions of the Carboxylic Phosphorane–Phosphonium Salt 4g. A. With Alcohols.—In a typical experiment, acid **4g** in its dehydrated form, m.p. 205–210° (2.6 g., 0.004 mole), was dissolved in ethanol (50 ml.); the solution was heated to reflux temperature for 15 min., the solvent was removed under reduced pressure, and monoglyme (20 ml.) was added. Ester **4a** (2.3 g., 85%) crystallized out; when **4g** in its hydrated form (m.p. 140°) was used, the corresponding hydrate of **4a** (m.p. 110°) was obtained. With methanol, the corresponding methyl ester **4c** was obtained in 54% yield: m.p. 220–222° from CH_2Cl_2–monoglyme. (*Anal.* Calcd. for $C_{41}H_{35}ClO_3P_2$: C, 73.2; H, 5.21; Cl, 5.31; P, 9.22. Found: C, 73.1; H, 5.15 Cl, 5.42; P, 9.08.) The p.m.r. spectrum showed 30 phenyl protons as a multiplet centered at τ = 2.46 p.p.m., two methyl protons as a doublet (separation 12 c.p.s.) at τ = 4.70 p.p.m., and the three protons of the methyl ester group at τ = 6.91 p.p.m.

B. With Aqueous Alkali.—A water–acetone solution of **4g** (10 g., 0.015 mole) was treated with 2 *N* sodium hydroxide solution until the pH was approximately 13; this resulted in the precipitation of a bright yellow material for which the structure **5g** is proposed. The substance was microcrystalline and difficult to collect. For this reason, the yields were variable, only about 40% in the experiment while with smaller quantities the product could be filtered more rapidly and suffered less decomposition from the presence of water; the melting point was 220–230° after drying over phosphorus pentoxide. It was insoluble or reacted with common solvents and consequently could not be crystallized; for example, with chloroform or methylene chloride it gave deep red solutions which then turned dark slowly. However, the formation of **5g** was reversible; when freshly prepared it dissolved immediately in the calculated amount of dilute hydrochloric acid and evaporation of the solution gave a nearly quantitative yield of **4g**. It was analyzed in crude form. (*Anal.* Calcd. for $C_{40}H_{32}O_3P_2$: C, 77.2; H, 5.14; Cl, 0.00; P, 10.0. Found: C, 74.9; H, 5.06; Cl, 0.05; P, 9.80.) The infrared spectrum showed a shifted carbonyl absorption at 1590 cm.$^{-1}$ and a very strong and broad peak at 1250 cm.$^{-1}$ which probably indicated tightly bonded carboxylic -OH. When the product was allowed to stand in dry air, this peak disappeared and was replaced by a P=O absorption at 1180 cm.$^{-1}$; simultaneously, the substance lost its yellow color and the melting point rose considerably. With water and alcohols, **5g** decomposed and triphenylphosphine oxide was formed, together with compounds which were not identified.

C. With Water.—Acid **4g** (6.5 g., 0.01 mole) was dissolved in aqueous acetone (80 ml.) and heated to the reflux temperature until treatment of a sample with alkali gave no more yellow betaine **5g** but only a white precipitate. This required 1 hr. The solvent was removed under reduced pressure and the residue was crystallized from methylene chloride–monoglyme; this gave **10** (5 g., 80%), m.p. 135–140°, with resolidification and melting at 220–222°. The material retained the solvent of crystallization with tenacity and had to be dried at 100–120° under high vacuum for extended periods before satisfactory analyses could be obtained. (*Anal.* Calcd. for $C_{33}H_{33}ClOP_2$: C, 76.10; H, 5.36; Cl, 5.78. Found: C, 75.67; H, 5.36; Cl, 5.75.[11]) The infrared carbonyl stretching frequency was at 1550 cm.$^{-1}$.

The same compound **10** was obtained in comparable yields when a water solution of the double phosphonium salt **9** (10 g. in 150 ml. of water) was treated with normal sodium hydroxide (15.4 ml.) and extracted with chloroform, the extract was evaporated, and the residue was purified as described above.

Reactions of the Double Phosphoranes 5. A. With Aqueous Ethanol.—Compound **5a** (2 g., 0.003 mole) was dissolved in 95% aqueous ethanol and kept a few minutes at reflux temperature. After cooling, the addition of water gave **α-carbethoxy-α-acetylmethylenetriphenylphosphorane** (**7a**, 0.9 g., 76%), m.p. 168–170°, identical with an authentic sample prepared by acetylation of carbethoxymethylenetriphenylphosphorane.[2]

B. With Alkyl Halide.—Benzyl bromide (1.21 g., 0.0076 mole) was added to a solution of **5a** (5 g., 0.0075 mole) in a mixture of monoglyme (50 ml.) and chloroform (30 ml.). After 2 hr. at room temperature, the solvents were removed; crystallization of the residue in a mixture of chloroform–monoglyme gave **α-carbethoxy-β-keto-γ-(benzyl)methyltriphenylphosphoniummethylenetriphenylphosphorane bromide** (**8a**, 2.9 g., 48%), m.p. 160–165°. (*Anal.* Calcd. for $C_{49}H_{43}BrO_3P_2$: C, 71.7; H, 5.25; Br, 9.74; P, 7.55. Found: C, 71.6; H, 5.20; Br, 10.10; P, 7.25.)

C. With Aldehydes.—Compound **5c** (10 g., 0.0157 mole) was dissolved in benzaldehyde (16.6 g., 0.157 mole); the reaction was exothermic. The mixture was heated at 80° for 7 hr., cooled, and diluted with ethyl ether; this gave **α-cinnamoyl-α-carbomethoxymethylenetriphenylphosphorane** (**6c**, A = Me; R = Ph) (4.1 g., 56%), m.p. 185–186° (from methanol). (*Anal.* Calcd. for $C_{30}H_{25}O_3P$: C, 77.6; H, 5.40; P, 7.70. Found: C, 77.4; H, 5.34; P, 6.74.) The same compound was prepared in 55% yield by direct acylation of carbomethoxymethylenetriphenylphosphorane **1** (A = OMe) with cinnamic anhydride according to a method already described.[2] In the same conditions, **5b** gave **6b** (60%), m.p. 169–171°. (*Anal.* Calcd. for $C_{32}H_{31}PO$: C, 77.0; H, 6.3; P, 6.3. Found: C, 77.3; H, 6.1; P, 6.6.) The same reaction with **5a** gave a compound **6a** in comparable yield, m.p. 147–148°, which analyzed as follows. (*Anal.* Calcd. for $C_{31}H_{27}O_3P$: C, 77.8; H, 5.70; P, 6.45. Found: C, 78.2; H, 5.77; P, 6.37.) However, this compound was not identical with the corresponding one obtained by acylation of **1** (A = OEt),[2] as shown by differences in melting points and absorption spectra; this is probably a question of geometrical isomerism and is being investigated.

With acetaldehyde, **5c** gave in similar conditions the corresponding olefin **6c′** (25%), m.p. 132–134°. (*Anal.* Calcd. for $C_{25}H_{23}O_3P$: C, 74.6; H, 5.8. Found: C, 74.7; H, 5.5.)

Reaction of Triphenylphosphine with Chloroacetic Acid.—Triphenylphosphine (26.2 g., 0.1 mole) and chloroacetic acid (11.3 g., 0.12 mole) were dissolved in dry ether (150 ml.); the solution was heated to 30–35° for 3 days. Colorless crystals (3 g.) were collected and washed with acetone, m.p. 128–130° dec. The infrared spectrum showed peaks at 2600 (carboxylic OH), 1740 (C=O), and a complex band at 1350 cm.$^{-1}$, indicative of a carboxylic acid. (*Anal.* Calcd. for $C_{20}H_{18}ClO_2P$: C, 67.3; H, 5.05; Cl, 9.95; P, 8.70. Found (crude): C, 67.8; H, 5.37; Cl, 10.3; P, 8.60.) Crystallization from mixtures of ethanol and acetone gave a product, m.p. 221–223°, the infrared spectrum of which was identical with that of triphenylmethylphosphonium chloride.

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(11) Value determined for ionic chlorine.