The Reaction of Stable Phosphoranes with Acid Anhydrides. A New Synthesis of Acetylenic Ketones

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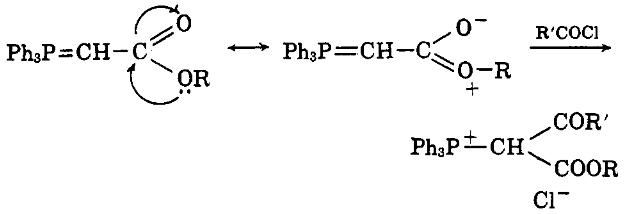
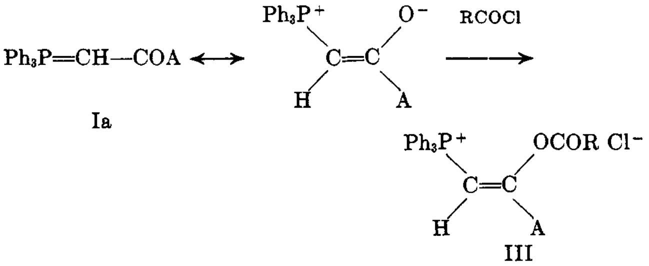
The stable phosphoranes, $Ph_3P{=}CH{\cdot}COR$, have been C-acylated by acid anhydrides to give products which undergo C-C bond cleavage with alcoholic mineral acid. When R is alkyl or aryl, pyrolysis of the acylated phosphoranes gives acetylenic ketones. In contrast to the behavior of anhydrides, acetyl chloride has been shown to give O-acylated phosphonium chlorides. The mechanism of the anhydride acylation is discussed.

Reactive phosphinemethylene derivatives, *e.g.*, $Ph_3P{=}CH_2$, are acylated by esters, [1,2] thio esters,[3] acid halides,[2,3] and N-acylimidazoles.[4,5] When the phosphinemethylene derivative (or phosphorane) has one substituent allowing stabilization by delocalization of the charge on the carbanion, its reactivity is markedly decreased. This is the case when R in I is CN, C=N—A, —NO—A, SO_2—A, and —CO—A. Phosphoranes of this type can generally be isolated and stored under normal conditions and have been alkylated with alkyl halides[6,7] and acylated with acid chlorides.[3,8,9] The results obtained have depended on the nature of the stabilizing group and especially on A since the phosphoranes I (R = COA) can function as ambident anions. When A opposes, to some extent, the delocalization of the negative charge, *i.e.*, A = OR or NR_2, the acylation or alkylation takes place on the α-carbon as shown.[3,7–9]

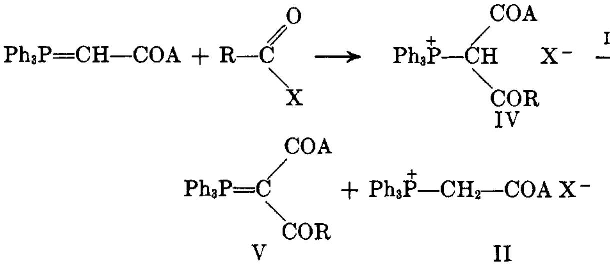
$$\underset{\text{I}}{Ph_3P{=}CH{\cdot}R} \qquad \underset{\text{II}}{Ph_3P^+{-}CH_2CO{\cdot}A\ Cl^-}$$



If this effect is decreased, A = alkyl or aryl, alkylation or acylation with aromatic acid chlorides (R = Ar) takes place on oxygen as shown,[6,9] whereas aliphatic acid chlorides produce the phosphonium salt II corresponding to the original phosphorane[9] (*vide infra*).

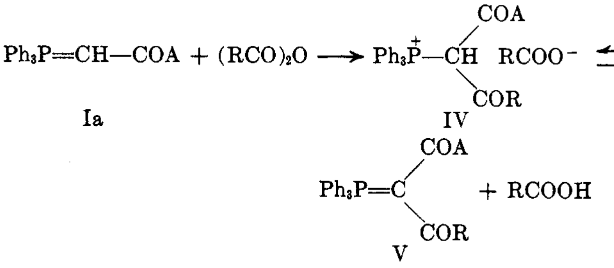


When stabilized phosphoranes (A = OAlk) are acylated by acid halides (X = Cl), the initially produced phosphonium salt IV is dehydrohalogenated by the starting phosphorane Ia, it being a stronger base than chloride ion under the condition used,[10] to give a mixture of acylated phosphorane V and phosphonium salt II (reaction 1). This mixture can be difficult to separate and 2 moles of Ia gives only 1 mole of V.[8,9]



(1)

We now find that, in acylation with acid anhydrides (reaction 2), no salt corresponding to II was formed and a 1:1 reaction took place. The product gave an elemental analysis corresponding to IV (A = OAlk), a labile adduct, from which the acylated phosphorane V could easily be obtained by treatment with aqueous bases or by heating under vacuum (when R—COOH is volatile). In some cases IV was not isolated and V was obtained directly from the reaction mixture.



(2)

Table I shows a series of IV and V obtained by this method. The absence of salt II resulting normally from the abstraction by Ia of the labile proton of IV throws some suspicion on the ionic structure shown above for IV. Comparison of the Nujol infrared spectra of IV and V gives the following information. The carbonyl absorptions of IV fall in the 1650–1750-cm.$^{-1}$ region, whereas, for V, they are shifted roughly 100–150 cm.$^{-1}$ lower (see Table I). This is consistent with the figures found generally for the α-ketophosphonium salts II and the corresponding phosphoranes I (R = COA).[11] However, IV also shows a broad peak in the 2500–2700-cm.$^{-1}$ region (a characteristic of

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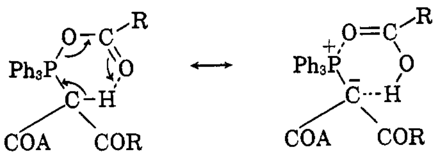
TABLE I

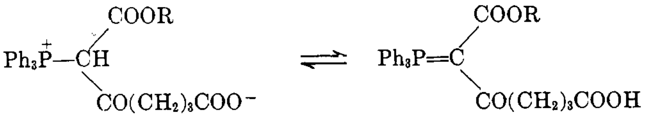
THE ACYLATION OF PHOSPHORANES Ia (A = OALK) WITH CARBOXYLIC ACID ANHYDRIDES [$(RCOO)_2O$]

			Acylated adduct IV*x*, $Ph_3P{=}C{<}^{COA}_{COR}\cdot RCOOH$			Acylated phosphorane V*x*, $Ph_3P{=}{<}^{CCOA}_{COR}$		
x	A	R	Yield % based on I	M.p., °C.	$\nu_{C=O}$, cm.$^{-1}$	Yield %[a] based on Ia	M.p. °C.	$\nu_{C=O}$, cm.$^{-1}$
a	OEt	Me	75	99	1670, 1725	...	172–174[b]	1540, 1640
b	OEt	Ph	88	111–112	1690, 1730	...	139–140[c]	1530, 1675
c	OEt	$ClCH_2$	96	84–86	1660, 1700, 1740	...	137–138	1590, 1660
d	OEt	Et		Not isolated		50	123–125	1550, 1650
e	OEt	*n*-Pr		Not isolated		54	132–133[d]	1540, 1650
f	OEt	$Ph{-}CH{=}CH_2$		Not isolated		72	118–120	1670, 1680
g	OEt	Cl_3C		Not isolated		54	161–162	1550, 1640, 1670
h	OMe	$ClCH_2$		Not isolated		24[e]	138–139	1610, 1670
i	OMe	Me	84	128–129	1670, 1720		153–155[f]	1550, 1670

[a] Yields of V from IV are practically quantitative. [b] L. Horner and H. Oediger[*Chem. Ber.*, 91 437(1958)] reported m.p. 170°. [c] Lit.[9] m.p. 142–143°. [d] Lit.[9] m.p. 130–131°. [e] No attempt was made to improve the yield (see Experimental). [f] Lit.[7] m.p. 152–154°.

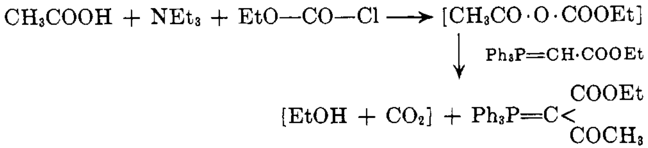
carboxylic acids) and a sharp one around 1150–1160 cm.$^{-1}$ (P–O–C region)[12]; both of these absorptions are absent in V. Hence, there is some reason to believe that IV is actually an adduct of V and the carboxylic acid, in which pentacovalent phosphorous may be a stabilizing factor, as follows. Although chloroacetic anhydride gives an acylated product, a side reaction, probably involving displacement of halogen, was also observed. This is being investigated. The product resulting from the action of glutaric anhydide on Ia (A = OEt) can have the structures VIa and VIb; on the basis of its infrared carbonyl absorption frequencies, we consider that VIa is the probable form (see Experimental).





VIa VIb

Since symmetrical anhydrides of carboxylic acids are not always readily available, the use of mixed anhydrides derived from chloroformates was also investigated. This method, which has been applied to the acylation of various nucleophiles,[13–15] is known to proceed with the liberation of CO_2, produced presumably by the decomposition of the alkoxycarbonyl anion. Thus the phosphorane Va was prepared as follows. In this case, no compound corresponding to IV in reaction 1 (A = OEt, R = Me, X = EtO—COO) was detected.



$$CH_3COOH + NEt_3 + EtO{-}CO{-}Cl \longrightarrow [CH_3CO\cdot O\cdot COOEt] \xrightarrow{Ph_3P=CH\cdot COOEt} [EtOH + CO_2] + Ph_3P{=}C{<}^{COOEt}_{COCH_3}$$

Va

We find also that phosphoranes of type Ia (A = alkyl, aryl), where acid chlorides give O-acylated or other products, give directly with anhydrides the desired C-acylated phosphoranes V (A = alkyl, aryl) previously unobtainable by other methods.[9] Both alkyl and aryl anhydrides can be used and the phosphoranes V obtained are listed below in Table II.

TABLE II

THE ACYLATION OF PHOSPHORANES Ia (A = ALKYL, ARYL) WITH CARBOXYLIC ACID ANHYDRIDES [$(RCOO)_2O$]

Acylated phosphorane V*x*, $Ph_3P{=}C{<}^{COA}_{COR}$					
x	A	R	Yield, %	M.p., °C.	$\nu_{C=O}$, cm.$^{-1}$
j	Me	Me	83	167–169	1545, 1580
k	Me	Ph	97	172–173	1530, 1560
l	Me	p-$MeOC_6H_4$	96	193–195	1525, 1550
m	Me	p-$O_2NC_6H_4$	42	190–191	1530, 1570
n	Ph	Ph	89	191–192	1520

The above compounds have been characterized by their elemental analyses, molecular weights, infrared spectra and also by some of their reactions. Table II shows that the carbonyl stretching frequencies of compounds Vj to Vm are less separated than those of compounds Va to Vi listed in Table I. This is not surprising since one might expect less delocalization of the carbanion charge toward the carbalkoxy group than toward the keto group.[11]

In contrast to the phosphoranes Ia which normally cleave to triphenylphosphine oxide and hydrocarbon in neutral or alkaline solutions,[6,16] the new phosphoranes are very stable to aqueous bases, even to hot 30% sodium hydroxide solution for 24 hr. They are readily cleaved, however, by hydrogen chloride in methanol-water solution. For example, with α,α-diacetylmethylenetriphenylphosphorane Vj the product isolated is acetylmethyltriphenylphosphonium chloride (II, A = CH_3).

This novel acid cleavage of a phosphorane (reaction 3) probably proceeds by areversible proton ation followed by nucleophilic attack of water on carbonyl carbon.

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(13) R. A. Boissonnas, *Helv. Chim. Acta*, **34**, 874 (1951).

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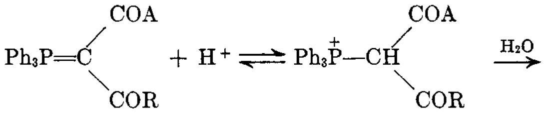
TABLE III

PREPARATION OF ACETYLENIC KETONES

Phosphorane	Product	Yield, %[a]	$\nu_{C\equiv C}$, cm.$^{-1}$ [b] Found	$\nu_{C\equiv C}$, cm.$^{-1}$ [b] Lit.[c]	$\nu_{C=O}$, cm.$^{-1}$ [b] Found	$\nu_{C=O}$, cm.$^{-1}$ [b] Lit.[c]
Vj	$CH_3C\equiv CCOCH_3$	88	2290 m 2220 s	2283 m 2222 s	1675 s	1678 s
Vn	$PhC\equiv CCOPh$	67	2208 s	2203 s	1631 s	1634 s
Vk	Mixture of $PhC\equiv CCOCH_3$ and $CH_3C\equiv CCOPh$	90	2137 m 2217 s 2247 s	2128 s 2212 s 2242 s	1672 s 1645 s	1675 s 1645 s

[a] Crude yield. [b] s = strong, m = medium. [c] M. Fontaine, J. Chauvelier, and P. Barchewitz, *Bull. soc. chim. France*, 2145 (1962).



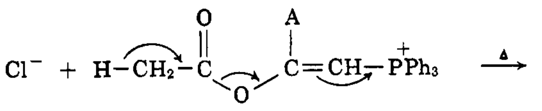
$$Ph_3P{=}C(COA)(COR) + H^+ \rightleftharpoons Ph_3\overset{+}{P}{-}CH(COA)(COR) \xrightarrow{H_2O}$$

$$Ph_3P{=}CH{-}COA + RCOOH + H^+ \longrightarrow Ph_3P^+{-}CH_2COA \quad (3)$$

This latter stage is obviously irreversible and is energetically favorable because of the stabilization by conjugation of the phosphorane produced. As expected from the above scheme, the conditions necessary to effect the hydrolysis were dependent on the amount of stabilization by conjugation in the products; for example, where phosphonium salts like II (R = alkyl or aryl) were formed, heating a few minutes at 50–60° was sufficient, while, when the degree of stabilization by delocalization of the carbanion charge is decreased, *i.e.*, when $Ph_3P{=}CH{-}COOR$ is formed, more vigorous conditions were required (see Experimental). In the extreme case, when a stabilized phosphorane such as Ia is treated with aqueous acid, only the phosphonium salt II is produced and no cleavage to $Ph_3P{=}CH_2$ is observed.

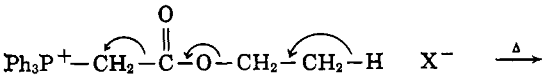
In a similar reaction to that already used to prepare acetylenic esters,[8,9] the new phosphoranes V (R = alkyl, aryl) gave good yields of acetylenic ketones and the results of the three pyrolyses undertaken are shown in Table III. The method would appear to be quite general and capable of extension to many other acetylenic ketones, with the understanding that a mixture of two products results where A ≠ R.

In view of the C-acylation of the phosphoranes Ia, (A = alkyl, aryl) with acid anhydrides we have reinvestigated their reaction with acetyl chloride in benzene at room temperature. Contrary to a previous report,[9] the O-acetylated phosphonium chlorides III (R = CH_3) can be isolated as hygroscopic solids which decompose on heating to give the phosphonium salts II, probably as follows. This mechanism is very



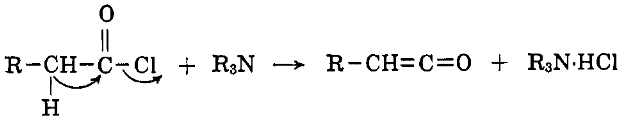
$$Ph_3P{=}CH{\cdot}COA + HCl + CH_2{=}C{=}O \quad (4)$$

similar to that proposed for the decomposition of carbethoxymethyl triphenylphosphonium halides[17] with evolution of ethylene and carbon dioxide, as follows,



$$Ph_3P^+{-}CH_3\ X^- + CH_2{=}CH_2 + CO_2$$

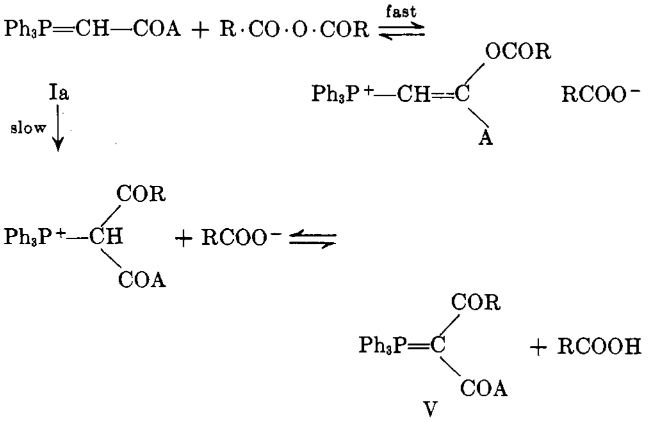
or to the reaction of tertiary amines on aliphatic acid chlorides which produces ketenes.[18,19]



$$R{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}Cl + R_3N \longrightarrow R{-}CH{=}C{=}O + R_3N{\cdot}HCl$$

In reaction 4, the fate of the acetoxy group is unknown, although it may produce ketene; this would be in accord with the reported reaction[20] of benzoylmethylenetriphenylphosphorane (Ia, R = Ph) with phenylacetyl chloride which gives the corresponding phosphonium salt and a product probably derived from phenyl ketene. The fluoroborate salt corresponding to III is quite stable to heat.

The different results obtained using different acylating agents with phosphoranes Ia (A = alkyl, aryl) require some kind of explanation. It is difficult to visualize why Ia which normally gives O-alkyl and O-acyl phosphonium salts with, respectively, alkyl and acyl halides should react differently with anhydrides unless some large difference in the stability of the products is involved. It is therefore highly probable that O-acylation of Ia (A = alkyl, aryl) does actually occur but that the products rapidly reverse to reactants owing to the high reactivity of carboxylate ions toward carbonyl centers; C-acylation can then take place according to the following scheme. A mechanism



of this kind would provide another example of thermodynamic *vs*. kinetic control in ambident action.[21,22] As would be expected from the above scheme treating

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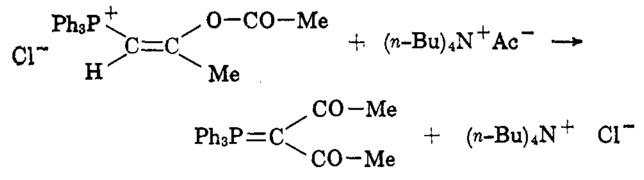
[22] R. Gompper, *ibid.*, **76**, 412 (1964).



Vj

O-acetoxypropenyltriphenylphosphonium chloride (III, A = R = Me) with tetrabutylammonium acetate gives the C-acylated product Vj.

Experimental

Acylation of Carbethoxymethylenetriphenylphosphorane (Ia, A = OEt) **with Acid Anhydrides. Method A.**—A 1:1 mixture of the phosphorane and the anhydride was heated without solvent at 100–120° for 2 hr. Treating the cold reaction mixture with ethyl acetate gave the intermediates IV. These were converted to the phosphoranes V by aqueous sodium carbonate, methanolic sodium hydroxide, or by heating at 140° (0.01 mm.) for 5 hr. Both the adducts and the phosphoranes were crystallized from ethyl acetate unless otherwise stated.

The reaction mixture produced from the phosphorane and propionic anhydride was treated with acetone–cyclohexane to give directly **α-carbethoxy-α-propionylmethylenetriphenylphosphorane** (Vd).

Method B.—A 1:1 mixture of the reactants was refluxed in dry monoglyme (50 ml./0.3 mole of reactant) for 7–15 hr. The reaction solution was concentrated to about one-third of its volume and the phosphoranes V were precipitated by the addition of petroleum ether (b.p. 60–80°) or cyclohexane. The products were recrystallized from ethyl acetate. Glutaric anhydride gave the **product VI**, m.p. 158–160°, in 65% yield.

Anal. Calcd. for $C_{27}H_{27}O_5P$: C, 70.10; H, 5.85; P, 6.70. Found: C, 69.70; H, 5.60; P, 6.40.

The infrared spectrum of this compound has peaks at 2750 (very small), 1750, and 1680 cm.$^{-1}$.

Using method A or B, carbmethoxymethylenetriphenylphosphorane (Ia, A = OMe) gave **α-acetyl-α-carbmethoxytriphenylphosphonium acetate (IVi)**. When heated at 140° (0.01 mm.) for 15 hr. the salt IVi gave the corresponding **phosphorane Vi**. Analytical data concerning the compounds prepared according to methods A and B are recorded in Table IV.

Acylations with Chloroacetic Anhydride.—Carbethoxymethylenetriphenylphosphorane (10 g., 0.0285 mole) and chloroacetic anhydride (4.88 g., 0.0285 mole) were dissolved in a mixture of dry ether (50 ml.) and methylene chloride (10 ml.), and the solution was stirred at 40° overnight. Concentration of the solution to half its volume and the addition of petroleum ether (b.p. 60–80°) gave the **acylated phosphonium chloroacetate IVc**. This salt, when treated with 2 *N* aqueous sodium hydroxide, gave **α-carbethoxy-α-chloroacetylmethylenetriphenylphosphorane** (Vc). The p.m.r. spectrum showed a multiplet accounting for 15 aromatic protons at τ = 2.50, a singlet at 5.20, a quadruplet centered at 6.27, and a triplet centered at 9.37 p.p.m. representing, respectively, 2 protons from the $ClCH_3$ group, 2 methylenic protons, and 3 protons from the methyl group. This is in agreement with the proposed structure. When the above reaction was performed according to method A, without solvent, at 110–120° for 1 hr., a product Y, different from IVc and Vc, was isolated. This was crystallized from ethanol and had m.p. 188–189°.

Anal. Calcd. for $C_{46}H_{39}ClO_6P_2$: C, 70.40; H, 4.97; Cl, 4.53. Found: C, 70.50; H, 4.93; Cl, 4.50.

If method B were used for the acylation, a mixture of Vc and Y was obtained; longer reaction times increased the relative yield of Y. Similar results were obtained with carbmethoxymethylenetriphenylphosphorane and chloroacetic anhydride. The product of unknown structure corresponding to Y had m.p. 190–191° and was analyzed for an empirical formula $C_{45}H_{37}ClO_6P_2$, a methyl analog of Y.

Anal. Calcd. for $C_{45}H_{37}ClO_6P_2$: C, 70.00; H, 4.67; Cl, 4.62; P, 8.10. Found: C, 69.70; H, 4.73; Cl, 4.81; P, 8.26.

Other analytical data are found in Table IV.

Acylation with Acetic–Ethylcarbonic Anhydride.—To a stirred solution of acetic acid (3.1 g., 0.05 mole) and triethylamine (5.05 g., 0.05 mole) in monoglyme (35 ml.) at 0° was added dropwise

TABLE IV

	Adduct IVx							Phosphorane Vx								
		Calcd., %			Found, %				Calcd., %				Found, %			
x	Formula	C	H	P	C	H	P	Formula	C	H	Cl	P	C	H	Cl	P
a[a]	$C_{26}H_{27}O_5P$	69.40	6.00	6.89	68.80	6.03	6.50	...	...	...	...	...	...	...	...	...
b[b]	$C_{36}H_{31}O_5P$	75.30	5.41	5.40	75.40	5.40	5.00	$C_{29}H_{26}O_5P$	77.00	5.50		6.90	77.60	5.50		6.40
c[c]	...	...	...	...	...	...	...	$C_{24}H_{22}ClO_3P$[d]	68.00	5.20	8.31	7.30	67.10	5.00	8.20	7.00
d[e]	...	...	...	...	...	...	...	$C_{25}H_{25}O_3P$	74.30	6.20		7.70	74.50	6.20		7.30
e[e]	...	...	...	...	...	...	...	$C_{26}H_{27}O_3P$	74.70	6.50		7.40	74.90	6.50		6.90
f[e]	...	...	...	...	...	...	...	$C_{31}H_{27}O_3P$	77.80	5.70			77.90	5.60		
g[e]	...	...	...	...	...	...	...	$C_{24}H_{20}Cl_3O_3P$	58.50	4.10			59.30	4.21		
h[c]	...	...	...	...	...	...	...	$C_{23}H_{20}ClO_3P$	67.30	4.90	8.60	7.50	67.50	4.90	8.50	7.10
i[a,e]	$C_{25}H_{25}O_5P$	68.80	5.70	7.10	69.30	5.50	6.80	...	...	...	...	...	...	...	...	...

[a] Prepared by method A. [b] Recrystallized from acetone. [c] Prepared in a mixture of ether and methylene chloride (see text). [d] Mol. wt.: calcd., 424; found, 426. Molecular weights were determined with a Mechrolab vapor pressure osmometer, Model 301-A, and were measured in chloroform. [e] Prepared by method B.

TABLE V

PHOSPHORANE V*x*

x	Formula	Calcd., % C	H	P	Mol. wt.[a]	Found, % C	H	P	Mol. wt.[a]
j	$C_{23}H_{21}O_2P$	76.60	5.90	8.60	360	76.30	5.90	8.90	369[b]
k	$C_{28}H_{23}O_2P$	79.60	5.50	7.30	422	79.30	5.50	7.60	424[c]
l	$C_{29}H_{25}O_3P$	77.00	5.60	6.90	452	76.50	5.40	7.10	441[c]
m	$C_{28}H_{22}NO_4P$	71.90	4.70	6.60	467	71.80	4.90	6.80	460[b]
n	$C_{33}H_{25}O_2P$	81.80	5.20	6.40	484	82.00	5.10	6.70	486[c]

[a] Molecular weights were determined in a Mechrolab vapor pressure osmometer, Model 301-A. [b] Measured in benzene. [c] Measured in chloroform.

ethyl chloroformate (5.46 g., 0.05 mole). Immediate precipitation of triethylamine hydrochloride occurred. After 1 hr. at 0° carbethoxymethylenetriphenylphosphorane (Ia, A = OEt) (17.4 g., 0.05 mole) was added, and the volume of the solution was increased to 100 ml. by the addition of more monoglyme. The mixture was stirred for 6–8 hr. and allowed to come to room temperature and then filtered. The filtrate was treated with petroleum ether to precipitate unreacted phosphorane (3.1 g.) which was removed and the filtrate was evaporated to give 8.7 g. (40%) of α-acetyl-α-carbethoxymethylenetriphenylphosphorane (Va) which had m.p. and m.m.p. 172–174° after one recrystallization from ethyl acetate.

Acylation of Phosphoranes. Ia (A = Alkyl, Aryl) with Acid Anhydrides. With Acetic Anhydride.—A mixture of phosphorane (0.03 mole) and acetic anhydride (0.3 mole) in dry chloroform (10–20 ml.) was stirred at 60° for 2–8 hr. The resulting dark solution was evaporated at 80° (12 mm.) to give a glue which was triturated with ether and the precipitated product was filtered and recrystallized from ethyl acetate–ether or ethyl acetate–petroleum ether.

With Benzoic Anhydride.—A mixture of phosphorane, benzoic anhydride, and chloroform in the same proportions as for acetylation was stirred and refluxed for 3–5 hr. The solvent was evaporated, and the residue was extracted several times with petroleum ether (b.p. 60–80°) to remove the excess benzoic anhydride. Addition of ether then gave the crude product.

By this procedure acetylmethylenetriphenylphosphorane gave 67% of **α-acetyl-α-benzoylmethylenetriphenylphosphorane (Vk)**, m.p. and m.m.p. 172–173°.

Analytical data concerning the acylation of Ia (A = alkyl, aryl) are recorded in Table V.

Reaction of the Phosphoranes V with Acid.—In a typical experiment the phosphorane (1.5 g.) was dissolved in 5 ml. of methanol and 5 drops of concentrated hydrochloric acid was added. The solution was warmed for a few minutes and then evaporated at 60° (12 mm.) to give a glue which was crystallized from chloroform–ethyl acetate to give the phosphonium salt II. When formation of II (A = OAlk) was concerned, 2-5-hr. refluxing periods were required. In this way phosphorane Vj gave acetylmethylphosphonium chloride (II, A = CH_3), m.p. and m.m.p. 242–244°. Phosphorane Vk gave II (A = Ph), m.p. and m.m.p. 267°. Phosphorane Va gave II (A = OEt) which was isolated as the corresponding phosphorane Ia (A = OEt), m.p. and m.m.p. 125–127°, by treating the evaporated reaction mixture with aqueous sodium carbonate.

Pyrolysis of the Phosphoranes V.—The phosphoranes were heated at 250–280° (0.01 mm.) for 1 hr. and the distillates were collected in a liquid air cooled receiver. In this way Vj gave 88% of almost pure pent-2-yn-3-one (n^{21}_D 1.443, lit.[23] $n^{22.5}_D$ 1.438). The 2,4-dinitrophenylhydrazone crystallized from ethanol had m.p. 149.5–150° (lit.[23] m.p. 149°). Similarly, Vn gave 67% of crude 3-phenylpropiolophenone, m.p. 46–48° (lit.[24] m.p. 54°), the 2,4-dinitrophenylhydrazone of which had m.p. 224° (lit.[24] m.p. 224°). Pyrolysis of Vk gave a mixture of **tetrolophenone** and **4-phenylbut-3-yn-2-one** in a total yield of 90%. This mixture was not separated, but from its infrared spectrum, refractive index, and melting point of the mixture of isomeric 2,4-dinitrophenylhydrazones it was concluded that 4-phenylbut-3-yn-2-one was the major constituent.

The mixture of 2,4-dinitrophenylhydrazones had m.p. 175–180° (lit.[25,26] m.p. 242° for tetrolophenone derivative and m.p. 190° for 4-phenylbut-3-yn-2-one derivative).

Anal. Calcd. for $C_{16}H_{12}N_4O_4$: C, 59.30; H, 3.73; N, 17.30. Found: C, 59.50; H, 3.90; N, 17.20.

Reaction of the Phosphoranes Ia (A = Alkyl, Aryl) with Acetyl Chloride.—The phosphorane (0.01 mole) and acetyl chloride (0.012 mole) were stirred in dry benzene (20 ml.) at room temperature overnight. The product was filtered and washed with ether and ethyl acetate to give quantitative yields of the O-acetylated phosphonium chlorides III (R = CH_3; A = alkyl, aryl) as hygroscopic white solids. They were dissolved in dry acetonitrile and treated with silver tetrafluoroborate to give the phosphonium fluoroborates which could be crystallized from ethyl acetate. By the above procedure the following compounds were prepared.

O-Acetoxypropenyltriphenylphosphonium tetrafluoroborate had m.p. 150–153°.

Anal. Calcd. for $C_{23}H_{22}BF_4O_2P$: C, 61.60; H, 4.95. Found: C, 61.60; H, 4.89.

O-Acetoxystyryltriphenylphosphonium tetrafluoroborate had m.p. 163–165°.

Anal. Calcd. for $C_{28}H_{24}BF_4O_2P$: C, 65.90; H, 4.74. Found: C, 65.70; H, 4.54.

O-Acetoxy-*p*-nitrostyryltriphenylphosphonium tetrafluoroborate had m.p. 180–182°.

Anal. Calcd. for $C_{28}H_{23}BF_4NO_4P$: C, 60.50; H, 4.08. Found: C, 60.20; H, 4.14.

Action of Heat on O-Acetoxypropenyltriphenylphosphonium Chloride (III, A = R = Me).—Heating the chloride (1 g.) gently in a bunsen flame for 1–2 min., cooling the mixture, and adding dry ethyl acetate gave a white solid, m.p. 240–242°, identified as acetylmethyltriphenylphosphonium chloride by comparison of the infrared spectra.

In another experiment an attempt was made to trap ketene. The freshly prepared, dry chloride was heated at 200° for 3 hr. in a stream of dry nitrogen, and the effluent gases passed into aniline. No acetanilide could be isolated at the end of the experiment. The residue in the reaction vessel was acetylmethyltriphenylphosphonium chloride.

Conversion of III (A = CH_3) into Vj.—A 1:1 mixture of freshly prepared O-acetoxypropenyltriphenylphosphonium chloride and tetrabutylammonium acetate in dry chloroform was stirred at 50° overnight. The solution was evaporated, and the residue was treated with water and filtered to give 40% of Vj, m.p. and m.m.p. 167–169° after one recrystallization from ethyl acetate–ether.

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