Acetylene-Allene Rearrangements. Reactions of Trivalent Phosphorus Chlorides with α-Acetylenic Alcohols and Glycols

A. P. BOISSELLE AND N. A. MEINHARDT

Chemical Research Laboratories, The Lubrizol Corp., Cleveland 17, Ohio

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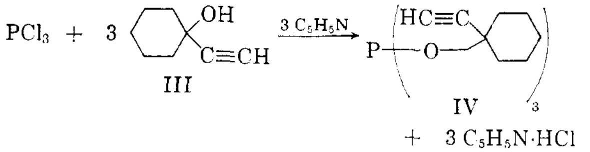
The reaction of trivalent phosphorus chlorides with α-acetylenic alcohols in the presence of an organic base produced allenic, pentavalent phosphine oxides. A mechanism by which this may occur is proposed. A number of phosphinates and phosphonates containing both the allenic and acetylenic structures are also described for the first time. Infrared spectra of compounds of this type indicate intermolecular hydrogen bonding between the ethynyl hydrogen and the phosphoryl oxygen.

It has been reported in the patent literature that the reaction of phosphorus trichloride with 3-methyl-1-butyn-3-ol[1] (I) and 1-ethynylcyclohexanol[2] (III) in the presence of pyridine gave tri(3-methyl-1-butyn-3-yl) phosphite (II) and tris(1-ethynyl-cyclohexyl) phosphite (IV), respectively.

$$\underset{\text{I}}{PCl_3 + 3(CH_3)C(OH)C\equiv CH} \xrightarrow{3C_5H_5N} \underset{\text{II}}{P(OC(CH_3)_2C\equiv CH)_3} + 3C_5H_5N{\cdot}HCl$$



A number of *t*-acetylenic triphosphite esters of the general structure R′ [OP(OR″)OR‴]$_n$ where R″ may be joined to R‴ to form a ring (1,3,2-dioxaphospholanes) and where at least one of the hydrocarbon radicals contains an acetylenic triple bond have also been reported.[3]

Propargyl esters of alkylphosphonous acids have been prepared by the reaction of alkylphosphonous dichlorides, $RPCl_2$ ($R = C_2H_5, C_3H_7, C_4H_9$), with propargyl alcohol in the presence of pyridine in a carbon dioxide atmosphere.[4]

$$RPCl_2 + 2HOCH_2C\equiv CH \xrightarrow[CO_2]{2C_5H_5N} RP(OCH_2C\equiv CH)_2 + 2C_5H_5N{\cdot}HCl$$

The formation of allenic containing phosphorus compounds by the reaction of phosphorus chlorides with α-acetylenic alcohols has not been described in the literature.[5] In fact only two papers on the preparation of allenic containing phosphorus compounds are found in the literature. Allenyl phosphonates have been prepared in low yield by heating 3-chloro-3-methyl-1-butyne with trialkyl phosphites as follows.[6]

$$(CH_3)_2C(Cl)C\equiv CH + P(OR)_3 \xrightarrow{\Delta}$$
$$R = CH_3,\ C_2H_5,\ C_4H_9$$
$$(CH_3)_2C{=}C{=}CH{-}P(O)(OR)_2$$

The reaction of vinylalkylacetylenes with lithium dialkyl phosphides was recently reported[7] to produce allenes as follows:

$$R_2PLi + R'C\equiv C{-}CH{=}CH_2 \longrightarrow R'CH{=}C{=}CH{-}CH_2PR_2$$
$$R = C_2H_5,\ C_4H_9;\ R' = CH_3,\ C_2H_5$$

It has now been found that the reactions of trivalent phosphorus monochlorides, $R'''R^{IV}PCl$, (R''', R^{IV} = aryl), with α-acetylenic alcohols, $R'R''C(OH)C\equiv CH$, in the presence of an organic base such as pyridine or triethylamine produce allenic phosphine oxides, $R'''R^{IV}P(O)CH{=}C{=}CR'R''$, and not acetylenic phosphinites, $R'''R^{IV}P{-}OCR'R''C\equiv CH$, as anticipated in view of the patent literature previously cited. The infrared spectrum of the reaction product from diphenyl phosphinous chloride with 3-methyl-1-butyn-3-ol in the presence of pyridine showed no bands for the ethynyl group or P—O—C. There were, however, definite absorption bands for allene and P→O. This product was assigned the structure $(C_6H_5)_2P(O)CH{=}C{=}C(CH_3)_2$ on the basis of its spectrum, determination of bromine number (one mole of bromine per mole of phosphine oxide), and its catalytic reduction to the known diphenyl isoamylphosphine oxide.[8]

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(1) D. C. Rowlands, U. S. Patent 2,728,791 December 27, 1955.

(2) F. J. Lowes and R. F. Monroe, U. S. Patent 2,809,982, October 15, 1957.

(3) R. C. Morris and J. L. VanWinkle, U. S. Patent 2,728,789 December 27, 1955.

(4) G. Kamai and E. A. Gerasimova, *Trudy Kazan. Khim. Teknol. Inst. im. S. M. Kirova*, **23**, 138 (1957); *Chem. Abstr.*, **52**, 9946 (1958).

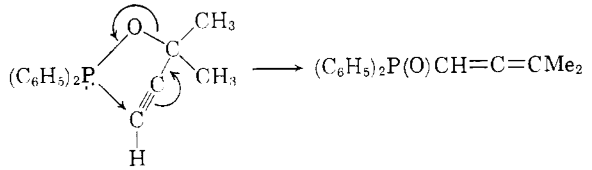
(5) Shortly after the work was completed, the formation of disubstituted phosphinyl allenes, $R_2P(O)CH{=}C{=}CH_2$, by the reaction of R_2PCl with propargyl alcohol was reported. [R. C. Miller, Meeting of the American Chemical Society, Chicago, Ill., September, 1961; Abstracts (Organic Division,] p. 43Q.] The phosphinous halides were also reported to react with 1,4-butynediol to form adducts containing two phosphinyl groups per molecule of glycol used. The isolated products were presumably 1,4-bis(disubstituted phosphinyl) butadienes.

(6) A. N. Pudovik, *J. Gen. Chem.*, **20**, 97 (1950). (English translation.)

(7) A. A. Petrov and V. A. Kormer, *Doklady Akad. Nauk, S.S.S.R.*, **132**, 1095 (1960.)

(8) G. M. Kosolapoff, "Organophosphorus Compounds," J. Wiley and Sons, Inc., New York, 1950, p. 116.

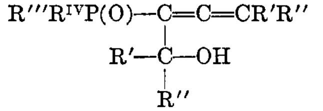
There are two novel features associated with this reaction: (1) Trivalent phosphorus was converted to the pentavalent state at temperatures of less than 25°. (2) Complete conversion to an allenic product was obtained under these mild conditions. Most acetylene-allene rearrangements reported in the literature require more vigorous reaction conditions and result in mixtures of allene, acetylene, and conjugate diene.[9] The absence of any ethynyl product in the present work suggests that the ethynyl phosphinite which is the expected product and which is isolated in certain reactions rearranges by a cyclic mechanism *via* an attack of the two unshared electrons of phosphorus on the ethynyl carbon atom to form a new P—C bond with simultaneous scission of the C—O bond as follows:



Alternatively, the rearrangement may be intermolecular (two molecules of phosphinite) resulting in a ten atom cyclic transition state.

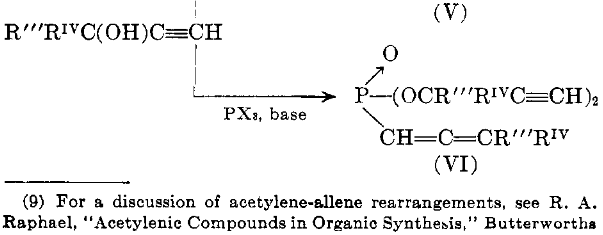
A carbonium ion type mechanism is ruled out since the carbonium ion formed by the cleavage of the C—O bond in the ethynyl phosphinite intermediate, $(HC{\equiv}C-\overset{\oplus}{C}(CH_3) \leftrightarrow H\overset{\oplus}{C}{=}C{=}C(CH_3)_2$, would lead to the formation of a substantial amount of ethynyl phosphine oxide, $(C_6H_5)_2P(O)C(CH_3)_2C{\equiv}CH$.

Trivalent phosphorus monochlorides reacted with α-acetylenic glycols, $R'R''C(OH)C{\equiv}C-C(OH)R'R''$, in a 1:1 ratio to produce hydroxy compounds of the following type:



$$R'''R^{IV}P(O)-\underset{\substack{|\\ R'-C-OH\\ |\\ R''}}{C}{=}C{=}CR'R''$$

The reaction of trivalent phosphorus dichlorides and trichlorides with α-acetylenic alcohols produced phosphinates V and phosphonates VI, rather than the phosphonites and phosphites reported previously.[1-4]



The reaction of phenyl phosphonous dichloride with 3-methyl-1-butyn-3-ol gave a product containing both the allenic and ethynyl groups (V. $R' = C_6H_5$; $R'''R^{IV} = CH_3$). This structure is now the expected one since one acetylene-allene rearrangement results in the formation of a pentavalent phosphorus atom and no further rearrangement is possible. Structures of type V were proved by infrared (discussed in detail later), per cent ethynyl (one C≡CH per molecule), and by bromine number. Bromine numbers correspond to 3 moles of bromine per mole of phosphinate, 2 moles for the acetylene moiety, and one mole for the allene.

The reaction of phosphorus trichloride with 3-methyl-1-butyn-3-ol in the presence of pyridine gave a phosphonate containing both the allene and ethynyl groups. This product was shown to have structure VI by the methods cited above. Phosphorus trichloride also reacted with 1-ethynylcyclohexanol and gave a crystalline product, m.p. 78–79° (reported,[2] m.p. 80–81°). Although the same procedure was followed and the crystalline product appeared to be similar, the structure was also shown to be of type VI and not a *tris*-ethynyl phosphite. As a further check on the literature, the reaction of phosphorus trichloride with propargyl alcohol was carried out as described.[3] As reported, the product was a clear yellow liquid, n^{20}_D 1.4935 but its infrared spectrum had bands at 1960 cm.⁻¹ (allene) and 1270 cm.⁻¹ (P→O) which would not be present if tripropargyl phosphite were the product. This product must also have a structure similar to VI.

The reaction of trivalent phosphorus monochlorides, $\overline{O\text{-}(CH_2)_n\text{-}CHCH_3\text{-}O\text{-}P}\text{-}Cl$ (VII), where $n = 1$ or 2 (dioxaphospholane or dioxaphosphorinane) with α-acetylenic alcohols gave allenic phosphonates rather than the ethynyl phosphites reported.[3] The reaction of 2-chloro-4-methyl-1,3,2-dioxaphospholane with 3-methyl-1-butyn-3-ol or 1-ethynylcyclohexanol in the presence of triethylamine gave products shown by infrared to contain allene and P→O as well as P—O—C. These products reacted readily with water resulting in ring opening and formation of viscous, water-soluble products having infrared absorption bands for POOH, OH, and allene. An anomaly was observed in the reaction involving chlorides of type VII. On warming the reaction mixture to room temperature, the mixture suddenly became quite exothermic and cooling was necessary to maintain temperatures between 25–30°. It was subsequently discovered that the acetylene-allene rearrangement was not complete at the reaction temperature (0–5°) but on warming to 25°, the rearrangement was rapid and exothermic. This was shown by filtering the reaction mixture and stripping the volatile materials while maintaining a temperature below 5°. The product isolated in this manner had only the ethynyl phosphite structure which on standing

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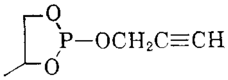
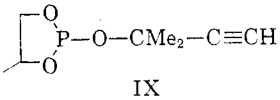
[9] For a discussion of acetylene-allene rearrangements, see R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," Butterworths Scientific Publications, London, 1955, pp. 134–139.

rearranged to the allenyl phosphonate as shown by infrared analysis. Propargyl alcohol and 3-methyl-1-butyn-3-ol reacted with 2-chloro-4-methyl-1,3,2-dioxaphospholane similarly, and the product was isolated as above. A qualitative difference in the rate of rearrangement was observed by following the increase in intensity of the allenic band in the infrared spectra of the products on standing at the ambient temperature of the salt plates. Intermediate VIII rearranged much more slowly than intermediate IX.[10]


VIII


IX

This rate difference is in agreement with the proposed mechanism involving a cyclic intermediate since alkyl groups on the P—O—C carbon atom should facilitate the electron shift required for such a rearrangement to a greater extent than hydrogen (by an inductive effect), and weaken the O—C bond. A similar rate dependence has been observed in the Claisen rearrangement where introduction of alkyl groups in the α or γ positions of the allyl group of allyl phenyl ethers increased the rate of the rearrangement to *ortho* alkylated phenols.[11]

Infrared Spectra. The assignment of the major absorption bands for the compounds is summarized in Table I. All the compounds exhibit a sharp absorption in the 1950-cm.$^{-1}$ region which is characteristic of the allenic structure.[12a] It is re-emphasized that the spectra of the allenic phosphine oxides of Table II indicated the presence of only allene and that the bands characteristic of the ethynyl group (3000 cm.$^{-1}$, 2100–2200 cm.$^{-1}$) were not present in these spectra.

Terminal allenes substituted by an electron-attracting group show a characteristic doublet at 1950–1925 cm.$^{-1}$ and a strong band at 840 cm.$^{-1}$.[13]

The spectrum of allenyldiphenylphosphine oxide (compound 1) exhibits these characteristic absorptions as do the spectra of the allenyl phosphinates and allenyl phosphonates. The spectra of the compounds prepared from acetylenic alcohols and phenyl phosphonous dichloride (compounds 8 and 9) and phosphorus trichloride (compounds 10 and 11) show the characteristic absorptions of both the allenic and the ethynyl structures.

It has been reported that the frequency of the band assigned to P→O absorptions is affected directly by the number of electronegative groups attached to the phosphorus atom.[14] This effect is apparent in the variation of the frequencies of the P→O band shown in Table I, in which the absorptions vary from 1170–1270 cm.$^{-1}$. The allenyldiphenylphosphine oxides, *e.g.*, compound 1, show a P→O absorption at 1170–1200 cm.$^{-1}$ while the allenyl ethynyl phenylphosphonates, *e.g.*, compound 11, show a P→O absorption at approximately 1270 cm.$^{-1}$.

Normally, the ethynyl hydrogen stretching absorption is a strong band at 3300 cm.$^{-1}$.[12a] The neat film spectra of compounds 8, 9 and 10 show a second sharp absorption at 3200 cm.$^{-1}$ in addition to the band at 3300 cm.$^{-1}$. The second band at 3200 cm.$^{-1}$ in these compounds undoubtedly arises from partial intermolecular hydrogen bonding between the ethynyl hydrogen of one molecule and the oxygen of a P→O group from a second molecule since the band was not present in a carbon tetrachloride solution of the compound while the band at 3300 cm.$^{-1}$ was stronger in the solution. A Nujol mull of the crystalline product from the reaction of phosphorus trichloride and 1-ethynylcyclohexanol (compound 11) gave a spectrum which had only the band at 3200 cm.$^{-1}$ while the carbon tetrachloride solution of this compound gave a spectrum which had only the 3300-cm.$^{-1}$ absorption. Only one observation of such a hydrogen bond could be found in the literature. The ethynyl hydrogen absorption frequency of phenylacetylene was shifted from 3333 cm.$^{-1}$ to 3289 cm.$^{-1}$ when dissolved in triethyl phosphate.[15]

Several investigators have shown that terminal acetylenes form intermolecular hydrogen bonds with ethers and amines.[16–18] Intermolecular hydrogen bonding of phenol to the acetylenic triple bond has also been reported.[19] More recently, this effect was used to determine the relative Lewis acidities of a number of acetylenes by measuring the shift of the ethynyl hydrogen absorption frequency on mixing with several bases.[20]

The relative basicity of carbonyl oxygen atoms has been measured by the shift of the ethynyl hydrogen absorption band due to hydrogen bonding.[21,22] A doublet in the 3300–3200-cm.$^{-1}$ region with the intensity of the second band increasing in strongly basic compounds such as dimethylformamide was ascribed to the formation of strong hydrogen bonds.[22]

Intermolecular hydrogen bonding in terminal

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(10) Caution: a mixture of VIII with its rearranged isomer detonated when contacted with air at 50°.

(11) See D. S. Tarbell, *Org. Reactions*, **II**, 25 (1944).

(12) (a) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., J. Wiley and Sons, Inc., New York, 1958, p. 58; (b) L. J. Bellamy, *ibid.*, p. 314 and references therein.

(13) J. H. Wotiz and D. M. Mancuso, *J. Org. Chem.*, **22**, 207 (1957).

(14) L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

(15) S. C. Stanford and W. Gordy, *J. Am. Chem. Soc.*, **63**, 1094 (1941).

(16) E. V. Shuvalova, *Optika i Spectroskopiya*, **6**, 696 (1959); *Chem. Abstr.*, **53**, 19840 (1959).

(17) D. N. Shigorin, M. M. Shemyakin, and M. N. Kolosov, *Izvest. Akad. Nauk, S.S.S.R. Otdel. Khim. Nauk*, 1133 (1958); *Chem. Abtsr.*, **53**, 2067 (1959).

(18) J. C. D. Brand, G. Eglinton, and J. F. Morman, *J. Chem. Soc.*, 2526 (1960).

(19) R. West, *J. Am. Chem. Soc.*, **81**, 1614 (1959).

(20) R. West and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **83**, 765 (1961).

(21) D. Cook, *J. Am. Chem. Soc.*, **80**, 49 (1958).

(22) A. W. Baker and G. H. Harris, *J. Am. Chem. Soc.*, **82**, 1923 (1960).

TABLE I

INFRARED SPECTRA[a] (CM.$^{-1}$)

Compound[b]	—OH	—C≡CH	—C≡C—	C=C=C	Aromatic C=C	C_6H_5—P	P → O	P—O—C
1	..	....	..	1950, 1925	1590, 1450	1430	1200	....
2	..	....	..	1950	1600, 1450	1430	1170	....
3	..	....	..	1950	1590, 1450	1430	1190	....
4	..	....	..	1930	1590, 1460	1430	1210–1170	....
5	..	....	..	1950	1590, 1460	1430	1185	....
6	3420	....	..	1950	1590, 1450	1430	1190–1160	....
7	3400	....	..	1950	1570, 1475	1445	1180–1160	....
8	..	3285, 3200(s)	2110	1950	1590, 1440	1430	1240–1220	980–970
8[c]	..	3300, 3175(w)	2110	1950	1590, 1440	1430	1250	990–980
9	..	3250, 3150	2100	1940	1590, 1460	1440	1230–1245	995–980
10	..	3300, 3200	2110	1950	....	..	1250–1245	1030–960
10[c]	..	3300	2110	1950	....	..	1260	1030–960
11	..	3200	2110	1950	....	..	1250, 1238	1000–970
11[d]	..	3333	2110	1950	....	..	1260, 1250	1000–980
12	..	....	..	1950	....	..	1270–1260	1025–1010
13	..	....	..	1950	....	..	1270–1260	1025–1000
14	..	....	..	1960	....	..	1270	1025–1010
15	..	....	..	1950	....	..	1270–1260	1025–1010

[a] Spectra were taken with either the Perkin-Elmer Infracord, Model 137 or the Perkin-Elmer Model 221 recording spectrophotometer equipped with sodium chloride prism. Unless otherwise noted, the spectra were taken as neat films on sodium chloride plates. [b] Numbers refer to compounds described in Tables II, III, and IV. [c] In carbon tetrachloride solution. [d] In carbon disulfide solution.

TABLE II

PHOSPHINE OXIDES [$R_2R'P(O)$]

No.	R	R′	Formula	Yield,[a] %	M.P.[b]	$n^{20}D$	% P Calcd.	% P Found	Bromine No.[c] Calcd.	Bromine No.[c] Found
1	C_6H_5	$CH{=}C{=}CH_2$	$C_{15}H_{13}OP$	60	96–99	....	12.41	12.4	66.7	69.7
2	C_6H_5	$CH{=}C{=}C(CH_3)_2$	$C_{17}H_{17}OP$	75	70–73	....	11.56	11.3	59.6	57.0
3	C_6H_5	$CH{=}C{=}C(CH_3)C_2H_5$	$C_{18}H_{19}OP$	80	69–71	....	10.97	10.73	56.6	56.1
4	C_6H_5	$CH{=}C{=}CHC_3H_7$	$C_{18}H_{19}OP$	95	43–46	....	10.97	10.9	56.6	62.4
5	C_6H_5	$CH{=}C{=}\overline{C{-}(CH_2)_4{-}CH_2}$	$C_{20}H_{21}OP$	90	107–109	....	10.04	9.89	51.8	56.7
6	C_6H_5	$C[C(OH)(CH_3)C_2H_5]{=}C{=}C(CH_3)C_2H_5$	$C_{22}H_{27}O_2P$	90	.....	1.5711	8.74	8.55	45.1	60.0
7	ClC_6H_4	$C[C(OH)(CH_3)C_2H_5]{=}C{=}C(CH_3)C_2H_5$	$C_{22}H_{25}O_2PCl_2$	99	.....	1.5840	7.34	7.08[d]	47.1	49.5

[a] Yields are based on residue after stripping. [b] Recrystallized from petroleum ether (b.p. 30–60° or 60–90°). [c] Although the results vary from the theoretical values, the bromine numbers are quite satisfactory since the corresponding ethynyl isomers would have theoretical bromine numbers three times the calculated values, *cf.* Tables III and IV. [d] % Cl: Calcd. 16.75. Found: 16.5, 16.4.

TABLE III

PHOSPINATES [$(C_6H_5)P(O)(OR)R'$]

No.	R	R′	Formula	Yield,[a] %	$n^{20}D$	% P Calcd.	% P Found	% Ethynyl Calcd.	% Ethynyl Found	Bromine No. Calcd.	Bromine No. Found
8	$C(CH_3)_2C{\equiv}CH$	$CH{=}C{=}C(CH_3)_2$	$C_{16}H_{19}O_2P$	60	1.5344	11.3	11.5	9.13	9.46	175	182
9	$CHC_3H_7C{\equiv}CH$	$CH{=}C{=}CHC_3H_7$	$C_{18}H_{23}O_2P$	95	1.5325	10.3	10.0	..	..	159	169

[a] Yields based on residue after stripping.

acetylenes such as 1-hexyne has been postulated to occur between the ethynyl hydrogen of one molecule and the pi electrons of the triple bond of the other.[20] Bonding of this type resulted in ≡C—H frequency shifts of only 12–14 cm.$^{-1}$.

Intramolecular hydrogen bonding between O—H and the acetylenic triple bond in *o*-ethynylphenol[23] and aliphatic acetylenic alcohols[24] was observed by the shift in O—H absorption frequencies. No change in the —C≡C— absorption band was reported.

The phosphoryl (P→O) absorption frequency was reported to be shifted as much as 80 cm.$^{-1}$ when the molecule contained OH or NH groups available for hydrogen bond formation.[12b]

In the present work hydrogen bonding between P→O and ethynyl hydrogen was observed to result in a shift of the P→O absorption frequency of 10–15 cm.$^{-1}$. This was determined by comparison of the neat film spectra with those of solutions in carbon tetrachloride or carbon disulfide (Table I). Such small shifts of the P→O frequency due to hydrogen bonding have been reported previously. Phosphoryl frequency shifts of 2–8 cm.$^{-1}$ have been observed when phosphates and phosphine

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(23) V. Prey and H. Berbalk, *Monatsh.*, **82**, 990 (1951); *Chem. Abstr.*, **46**, 11138 (1952).

(24) P. v. R. Schleyer, D. S. Trifan, and R. Baeskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958).

TABLE IV

PHOSPHONATES $[(RO)_2P(O)R']$

Compound	R	R′	Formula	Yield,[a] %	M.P.[b]	$n^{20}D$	% P Calcd.	% P Found	% Ethynyl Calcd.	% Ethynyl Found	Bromine No. Calcd.	Bromine No. Found
10	$C(CH_3)_2C{\equiv}CH$	$CH{=}C{=}C(CH_3)_2$	$C_{15}H_{21}O_3P$	78	...	1.4859	11.05	10.9	17.85	18.84	286	247
11	$\overline{CH_2{-}(CH_2)_4{-}C}(C{\equiv}CH){-}$	$CH{=}C{=}\overline{C({-}CH_2)_4{-}CH_2}$	$C_{24}H_{33}O_3P$	88	78–79	....	7.73	7.65	12.48	12.42	200	223
12	$CH_2{-}CHCH_3{-}$	$CH{=}C{=}C(CH_3)_2$	$C_8H_{13}O_3P$	91	...	1.4917	16.4	16.2	...	...	84.6	80.5
13	$CH_2{-}CHCH_3{-}$	$CH{=}C{=}CHC_3H_7$	$C_9H_{15}O_3P$	95	...	1.4910	15.3	15.1	...	...	79	88
14	$CH_2{-}CHCH_3$	$CH{=}C{=}\overline{C({-}CH_2)_4{-}CH_2}$	$C_{11}H_{17}O_3P$	85	89–91	....	13.5	13.2	...	...	70	69.8
15	$CH_2{-}CH_2{-}CHCH_3$	$CH{=}C{=}C(CH_3)C_2H_5$	$C_{10}H_{16}O_3P$	94.5	...	1.4950	14.3	14.2	...	...	74	74

[a] Yield based on residue after stripping. [b] Recrystallized from petroleum ether (b.p. 30–60° or 60–90°).

oxides were dissolved in solvents such as chloroform.[25,26] However, the shift of the phosphoryl frequency due to hydrogen bonding with acetylenic hydrogen has not been reported previously.

Experimental[27]

The acetylenic alcohols and glycol were provided (one exception) by the Air Reduction Chemical Co., New York, and were used as received. Propargyl alcohol was provided by Antara Chemicals, New York, and was also used as received.

Diphenylphosphinous chloride was prepared by a previously described method.[28]

Di(chlorophenyl)phosphinous chloride was also prepared by the above method; b.p. 144–150°/0.3–0.4 mm., $n^{20}D$ 1.5900.

Anal. Calcd. for $C_{12}H_8PCl_3$: P, 10.7; Cl, 36.8. Found: P, 10.6; Cl, 36.2.

2-Chloro-4-methyl-1,3,2-dioxaphospholane was prepared in 88% yield by the previously described method[29] which was modified in that the hydrogen chloride was removed as it was formed; b.p. 46–48°/18 mm., $n^{20}D$ 1.4752.

Anal. Calcd. for $C_3H_6O_2PCl$: P, 22.0; Cl, 25.2. Found P, 21.8; Cl, 24.5.

2-Chloro-4-methyl-1,3,2-dioxaphosphorinane was prepared by the above method in 70% yield; b.p. 39–41°/2–3 mm., $n^{20}D$ 1.4794; reported,[30] b.p. 65°/12 mm., $n^{20}D$ 1.4765.

General Procedure for the Reaction of Phosphorus Monochlorides with α-Acetylenic Alcohols and Glycols (Phosphine Oxides).—A solution of 1 mole of the phosphorus monochloride in 100 ml. of diethyl ether was added dropwise to a stirred solution of 1 mole of acetylenic alcohol in 1.2 moles of pyridine and 400 ml. of diethyl ether. The addition was carried out in a nitrogen atmosphere over a period of 3–4 hr. at 0–5°. Upon completion of the addition, the mixture was stirred 1 hr. at 0–5° and then warmed slowly to room temperature overnight. Water (400 ml.) was added to dissolve the pyridine hydrochloride and the lower aqueous layer was extracted with two 100-ml. portions of ether. The ether extracts were combined, washed with two 100-ml. portions of dilute hydrochloric acid, and two 100-ml. portions of 10% aqueous potassium carbonate. After drying over anhydrous potassium carbonate, the ether was removed by distillation under reduced pressure and the products recovered as the residue.[31]

Liquid products were filtered while solid products were recrystallized before analysis. Yields, physical properties, and analytical data of the phosphine oxides prepared in this manner are given in Table II. The major absorption bands observed in the infrared spectra are given in Table I.

General Procedure for the Reaction of Phenylphosphonous Dichloride with α-Acetylenic Alcohols (Phosphinates).—The above procedure was followed using 0.5 mole of phenylphosphonous dichloride, 1 mole of acetylenic alcohol, 1.2 moles of pyridine, and 400 ml. of ether. Yields, physical

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(31) All of the allenic-containing phosphorus compounds were found to be thermally sensitive. Heating of the solid residues resulted in the formation of highly colored resinous materials which resisted crystallization. Attempts to distil liquid products under reduced pressures resulted in decomposition with the evolution of a gas.

properties, and analytical data of the phosphinates prepared in this manner are given in Table III and the major infrared absorption bands are listed in Table I.

General Procedure for the Reaction of Phosphorus Trichloride with α-Acetylenic Alcohols (Phosphonates).—The general procedure for the preparation of phosphine oxides given above was followed using 0.33 mole of phosphorus trichloride, 1 mole of acetylenic alcohol, 1.2 moles of pyridine, and 400 ml. of ether as solvent. The phosphonates prepared in this manner are described in Table IV (compounds 10 and 11), and the major infrared absorption bands are listed in Table I.

General Procedure for the Reaction of 2-Chloro-4-methyl-1,3,2-dioxaphospholane (and Phosphorinane) with α-Acetylenic Alcohols (Phosphonates).—Addition of the chloride (1 mole) in 100 ml. ether to the solution of acetylenic alcohol (1 mole), base (1.2 moles), and ether (400 ml.) was carried out in the usual manner. On warming the reaction mixture to room temperature, an exothermic reaction occurred when the temperature reached 20° and cooling was necessary to maintain a temperature below 30°. Since the products of this reaction were susceptible to hydrolysis, triethylamine was used as the base and the hydrochloride was separated by filtration. The filtrate was stripped of ether and unchanged triethylamine by heating to 50° at 5 mm. The residue was refiltered with suction and the product recovered as the filtrate. Yields, physical properties, and analytical data are given in Table IV and the major infrared absorption bands are given in Table I.

Hydrogenation of Diphenyl(3-methyl-1,2-butadien-1-yl)-phosphine Oxide.—A solution of 3.1 g. (0.012 mole) of diphenyl(3-methyl-1,2-butadien-1-yl)phosphine oxide in 60 ml. of absolute ethanol containing 1 g. of platinum oxide was hydrogenated at room temperature (4 hr.) under an initial pressure of 48 p.s.i.g. The catalyst was removed by filtration. Water (100 ml.) was added to the filtrate and this solution was extracted with three 50-ml. portions of ether. The ether extracts were combined, washed with two 100-ml. portions of water and dried over anhydrous potassium carbonate. The ether was removed by distillation leaving a white solid residue (3.0 g., 95% yield) which was recrystallized from petroleum ether (b.p. 60–90°), m.p. 95–96° (reported,[7] m.p. 96–97°). The infrared spectrum exhibited no absorption bands usually assigned to carbon-carbon unsaturation (allene or olefin).

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A New Phosphorylation Reaction of Olefins. II. A Novel Synthesis of a Four-Membered Phosphorus-Containing Ring Compound[1,2]

J. J. McBride, Jr., Eric Jungermann,[3] J. V. Killheffer,[4] and R. J. Clutter

Armour Industrial Chemical Co., Research Laboratories, McCook, Ill.

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Reaction of 2,4,4-trimethyl-2-pentene with phosphorus trichloride and aluminum chloride in methylene chloride at 0–5° followed by decomposition of the product with water gives 1,1,2,3,3-pentamethyltrimethylenephosphinic acid chloride in good yield. The conversions: acid chloride → acid → ester are readily accomplished by conventional reactions. Structure assignment is based on proton-NMR spectra, absence of unsaturation in the products, and evidence for the existence of *cis-trans* isomers in the esters. This four-membered ring is stable to several powerful reagents such as hot concentrated nitric acid, hot concentrated sulfuric acid, and refluxing concentrated aqueous sodium hydroxide.

The reaction of olefins with phosphorus trichloride and aluminum chloride is a new method for forming carbon-phosphorus bonds.[1,2,5] This paper reports the first detailed structural study of a product of this reaction.

Addition of 2,4,4-trimethyl-2-pentene (hereafter referred to as TMP) to a cold suspension of equimolar amounts of phosphorus trichloride and aluminum chloride in methylene chloride followed by partial hydrolysis with water or aqueous methanol gives a product (I) which contains phosphorus and chlorine in a 1:1 ratio. Further hydrolysis of I gives a chlorine-free acidic material (II). I also reacts with sodium methoxide in methanol to give a neutral phosphorus - containing material (III). Saponification of III followed by acidification regenerates the acid (II) and treatment of II with thionyl chloride gives I.

These interconversions are those to be expected of an acid chloride and the corresponding acid and methyl ester.

Neither I, II, nor III decolorizes bromine water or permanganate. This stability suggests the absence of unsaturation and of P—H bonds. II is recovered unchanged after treatment with boiling concentrated nitric acid and prolonged refluxing with concentrated aqueous sodium hydroxide; this confirms the absence of P—O—C bonds in this compound. Infrared spectra support these conclusions; a band near 8 μ in all three compounds indicates P → O to be present.

Potentiometric titration indicates II to be a strong monobasic acid. Elemental analyses agree best with the formulas $C_8H_{16}PO_2H$, $C_8H_{16}POCl$, and

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[3] Present address: Armour Soap Division, 1355 West 31st Street, Chicago 31, Ill., to whom inquiries should be addressed.

[4] Present address: Dept. of Chemistry, Northwestern University, Evanston, Ill.

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