Phosphonic Acids and Esters. IX. Thermal Reactions of Trialkyl Phosphites with Nonactivated Acetylenes[1]

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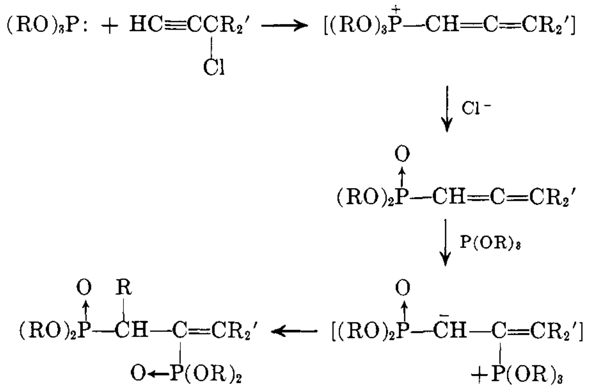
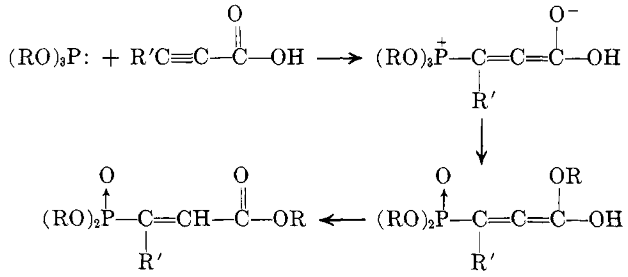
Received January 27, 1965

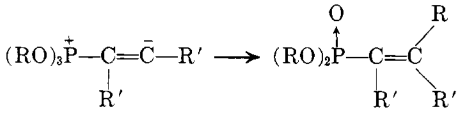
The noncatalyzed reaction of triethyl phosphite with phenylacetylene at 150° has been shown to proceed through a dipolar adduct which collapses by a *cis*-β-elimination process to yield ethylene and diethyl β-styrylphosphonate. In the presence of large excesses of triethyl phosphite, the styrylphosphonate undergoes further attack to yield 1,2-bis(diethylphosphono)-1-phenylethane. The use of trimethyl phosphite at 120° led to formation of the styrylphosphonate; the bisphosphonate was not formed at 120° even in the presence of large excesses of phosphite. Nonterminal and alkyl acetylenes are less reactive. Methylphenylacetylene gave results analogous to those obtained with phenylacetylene, but at significantly lower rates. Diphenylacetylene, hexyne-1, nonyne-1, and *t*-butylacetylene failed to give significant reaction with trialkyl phosphites at 150°. At higher temperatures (190°), both diphenylacetylene and nonyne-1 reacted with tri-*n*-butyl phosphite to yield the bisphosphonates; the initially formed vinylphosphonates are not isolated and are completely converted to the bisphosphonates at this temperature.

The nucleophilic attack of trialkyl phosphites on electrophilic olefins has been investigated in detail and a number of synthetic applications of these reactions have been demonstrated.[3] However, relatively little attention has been directed to the corresponding reactions with acetylenes. In 1950, Pudovik showed that tertiary acetylenic chlorides underwent an Arbuzov reaction by an SN2′ attack of trialkyl phosphites to yield dialkyl allenylphosphonates.[4] The allenylphosphonates underwent further attack by phosphite to yield bisphosphonates as ultimate products; collapse of the dipolar intermediate by an oxygen to carbon alkyl migration was postulated. A closely related internal rearrangement of dialkyl propargyl phosphites has been reported recently by Mark,[5a] Boisselle and Meinhardt,[5b] and Pudovik.[5c,d] These workers showed that dialkyl propargyl phosphites underwent a rapid SNi′ rearrangement to produce dialkyl allenylphosphonates. The postulation of an SNi′ mechanism was supported by studies of the rates of rearrangement of substituted propargyl phosphites.[5a] Addition of trialkyl phosphites to an activated acetylene in an intermolecular process has been reported by Kirillova, Kukhtin, and Sudakova.[6] Trialkyl phosphites were shown to add to acetylenic acids by a 1,4 process to produce dialkyl β-carboalkoxyvinylphosphonates. The initial adduct is postulated to undergo an internal oxygen to oxygen transalkylation[7] to yield an enolic allene which tautomerizes to the observed product.





The striking ease and facility of these reactions and the lack of activation of the triple bond in the propargyl phosphites suggested that an intermolecular attack of trialkyl phosphites on unactivated acetylenes incapable of yielding allenes might be a feasible process. The initial adduct (**1**) resulting from such an attack could potentially undergo an oxygen to carbon alkyl transfer to produce a vinylphosphonate (**2**) in analogy to the internal transalkylations cited above.[4,6,7] Such a reaction, if successful, would constitute a new synthetic entry to vinylphosphonates and a study of the reaction could provide information regarding the mode of collapse of quasi-phosphonium salts (**1**) in the absence of external nucleophiles.[8]



1 **2**

Reaction of a 2:1 molar ratio of triethyl phosphite (**3**) and phenylacetylene (**4**) at 150° under an inert atmosphere was conveniently followed by infrared spectroscopy. After 36 hr., the terminal acetylenic band (3300 cm.$^{-1}$) had disappeared and bands at 1610

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[1] Part VIII: C. E. Griffin, R. P. Peller, and J. A. Peters, *J. Org. Chem.*, **30**, 91 (1965).

[2] Taken in part from the M.S. Thesis of T. D. M., University of Pittsburgh, 1964.

[3] R. G. Harvey and E. R. DeSombre, "Topics in Phosphorus Chemistry," Vol. 1, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp. 92–96.

[4] A. N. Pudovik, *Zh. Obshch. Khim.*, **20**, 92 (1950).

[5] (a) V. Mark, *Tetrahedron Letters*, 281 (1962); (b) A. P. Boisselle and N. A. Meinhardt, *J. Org. Chem.*, **27**, 1828 (1962); (c) A. N. Pudovik and I. M. Aladzheva, *J. Gen. Chem. USSR*, **33**, 700, 702 (1963); (d) A. N. Pudovik, I. M. Aladzheva, and L. M. Yakovenki, *ibid.*, **33**, 3373 (1963).

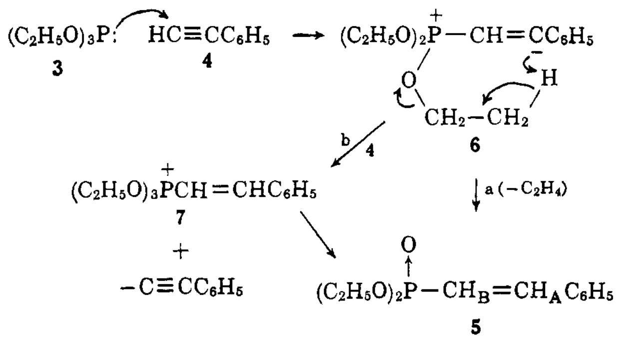
[6] K. M. Kirillova, V. A. Kukhtin, and T. M. Sudakova, *Proc. Acad. Sci. USSR, Chem. Sect.*, **149**, 209 (1963).

[7] G. Kamai and V. A. Kukhtin, *Zh. Obshch. Khim.*, **27**, 2372, 2376 (1957).

[8] The attack of halide ion and other nucleophiles on quasi-phosphonium salts is well known and constitutes the second stage of the Arbuzov reaction; *cf.* ref. 3.

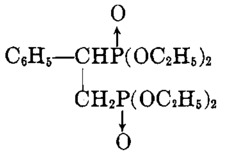
(C=C) and 1242 cm.$^{-1}$ (P→O) had developed. Diethyl β-styrylphosphonate (**5**), identified by its absorption spectra and by comparison with an authentic sample, was isolated in 6% yield. In addition to **5**, a large amount of intractable tar was formed. Krasouskii and Kiprianov[9] have shown that **4** is readily converted to tarry materials by heating with ammonia, amines, water, and other bases and it is probable that the basic action of **3** is producing a similar polymerization in this instance. Reaction in diglyme at 150° increased the yield of **5** to 15.2%, but substantial amounts of tars were still produced. No other materials, particularly products resulting from the postulated oxygen to carbon alkyl transfer, could be isolated from the reaction mixture.

In view of the structure of the product, two mechanisms for the formation of **5** appeared to be feasible. Nucleophilic attack by **3** on the terminal carbon of **4** would produce the dipolar intermediate **6** which may undergo (a) an internal proton transfer by a cyclic *cis*-β-elimination process[10] to yield **5** and ethylene, or (b) protonation by **4**, the only reasonable external proton donor in the system, to yield a quasi-phosphonium cation (**7**) and phenylacetylide. Nucleophilic dealkylation of **7** by the attack of either **3** or phenylacetylide would yield **5**.



Evidence in support of the *cis*-β-elimination mechanism (a) was provided by the isolation of ethylene in 68% yield from the reaction of **3** and **4**. Additional evidence was provided by the stereochemistry of the isolated product (**5**). The *cis*-β-elimination process requires the formation of a *trans*-styrylphosphonate. The proton magnetic resonance (p.m.r.) spectrum of **5** shows a 1H vinyl proton signal at τ 3.70 p.p.m. assignable as H_B of **5**. This signal is split into an apparent 1:2:1 triplet with distinct broadening of the center peak and a line separation of 17 c.p.s. This signal (H_B of a typical ABX system) should be split into a doublet of doublets by coupling with H_A and phosphorus (X). The apparent triplet arises from the near equivalence of J_{HH} and J_{PH}, producing near coincidence of the center peaks in the predicted doublet of doublets.[11] The observed coupling of 17 c.p.s. lies in the range normally observed for *trans*-vinylic couplings (11–18 c.p.s.); *cis*-vinylic couplings fall in the lower range of 6–14 c.p.s.[12] If **5** possessed *cis* stereochemistry, the doublet of doublets should be observable cleanly since J_{HH} and J_{PH} should be nonequivalent (6–14 and 17 c.p.s.).[13] Consequently, **5** possesses a *trans* configuration and most probably arises by the *cis*-β-elimination process.[14]

In an attempt to minimize side reactions and increase the yield of **5**, the reaction was repeated using a 12:1 molar ratio of **3** to **4** at 150°; **5** was isolated in lower yield (10.6%). In addition, 16.7% of a product identified as 1,2-bis(diethylphosphono)-1-phenylethane (**8**) was obtained. In a separate experiment, it was shown that the thermal reaction of triethyl phosphite with **5** led to the formation of **8**. Thus, in the presence of a large excess of triethyl phosphite, the initial product (**5**) of the reaction undergoes a nucleophilic attack to yield **8**, probably by the *cis*-β-elimination process. The tendency of vinylphosphonates[4,15] to undergo attack by nucleophiles and of electrophilic olefins to undergo attack by phosphites[3] is well documented.



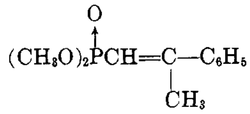
$$C_6H_5-\underset{|\;CH_2\overset{\downarrow}{P}(OC_2H_5)_2 \;\to\; O}{CH}\overset{O\uparrow}{P}(OC_2H_5)_2$$

8

In a further effort to realize the internal oxygen to carbon alkyl transfer (**1** → **2**), the reaction of trimethyl phosphite (**9**) with **4** was examined. In the anticipated intermediate (**10**), the *cis*-β-elimination process is much less likely than in **6**; internal alkyl transfer would be expected to lead to the formation of dimethyl β-(α-methylstyryl)phosphonate (**11**). Reaction of a 2:1 molar ratio of **9** and **4** at 120° led to complete disappearance of terminal acetylenic absorption after 92 hr.; the corresponding reaction stage was reached with triethyl phosphite in 36 hr. The lower reaction rate

$(CH_3O)_3\overset{+}{P}CH=\overset{-}{C}C_6H_5$

10



$$(CH_3O)_2\overset{O\uparrow}{P}CH=\underset{|\;CH_3}{C}-C_6H_5$$

11

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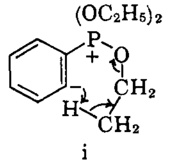
[9] K. Krasouskii and A. Kiprianov, *Zh. Russ. Fiz.-Khim. Obshchestva*, **56**, 1 (1925).

[10] Evidence for similar processes has recently been obtained. (a) The dipolar intermediate i from the reaction of benzyne and triethyl phosphite collapses with the formation of ethylene and diethyl phenylphosphonate: V. A. Notaro, Ph.D. Thesis, University of Pittsburgh, 1965. (b)



i

The analogous zwitterion from the reaction of benzyne and diethyl sulfide has been shown to collapse with the formation of ethylene and ethyl phenyl sulfide: V. Franzen, H. I. Joschek, and C. Mertz, *Ann.*, **654**, 82 (1962).

[11] For a report of similar observations in the p.m.r. spectra of β-styrylphosphonic acid and its monoalkyl esters, see J. A. Maynard and J. M. Swan, *Australian J. Chem.*, **16**, 609 (1963).

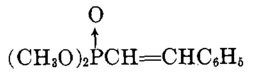
[12] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p. 85.

[13] This assignment of stereochemistry is supported by other studies of the p.m.r. spectra of styrylphosphonates carried out in this laboratory. In the *p*-nitro analog of **5**, J_{PH} and the *trans* J_{HH} for H_B are nonequivalent and the predicted doublet of doublets is observed at τ = 3.68 p.p.m., *J* = 16.2, 17.2 c.p.s.

[14] The mechanistic conclusion drawn from the *trans* configuration of **5** presupposes that *cis* **5** is not the product of kinetic control and is not being isomerized under the conditions of reaction or isolation to *trans* **5**. This supposition is supported by the observation that only the vinyl signal cited above is observed when the progress of the reaction is followed by p.m.r. spectroscopy and by the observation that *cis*-β-chlorovinylphosphonate possesses a high degree of configurational stability at 150° (W. M. Daniewski, unpublished observations).

[15] A. N. Pudovik and O. N. Grishina, *Zh. Obshch. Khim.*, **23**, 267 (1953).

probably is a reflection of the difference (30°) in reaction temperatures for the two processes. The only product isolated from this reaction was dimethyl β-styrylphosphonate (**12**) in 12.5% yield; as in the cor-

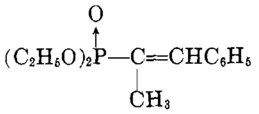


$(CH_3O)_2\overset{\overset{O}{\uparrow}}{P}CH{=}CHC_6H_5$

12

responding reaction with triethyl phosphite, a large amount of intractable tar was formed. No evidence for the formation of **11** could be obtained by p.m.r. examination of the reaction product, mixture, or distillation residues; in no case was a C-methyl signal observed. No explanation for the formation of **12** rather than **11** in this reaction is immediately obvious. Collapse of **10** to **12** requires both protonation and dealkylation steps and probably occurs by mechanism b cited in the reaction of **4** with triethyl phosphite. The large amount of tars formed in the reaction precluded further mechanistic investigations. P.m.r. studies indicated that **12** possessed *trans* stereochemistry.[16]

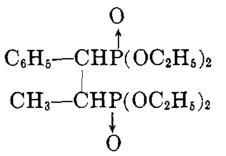
In contrast to the results obtained in the reaction of **5** and triethyl phosphite, the dimethyl ester **12** does not apparently undergo further attack by trimethyl phosphite. Reaction of 4–13:1 molar ratios of phenylacetylene and trimethyl phosphite at 109–113° for 4–6 days produced only **12** (10–29%) and intractable tars. No evidence for the formation of the tetramethyl analog of **8** could be obtained. Since the relative reactivities in the methyl and ethyl ester systems should be comparable, the lack of reaction of trimethyl phosphite with **12** must be attributed to the lower reaction temperature. In an extension of the reaction to a nonterminal acetylene, methylphenylacetylene (**13**) and triethyl phosphite (**3**) were allowed to react at 150° for 4 days. A 24% yield of diethyl β-(β-methylstyryl)-phosphonate (**14**) was isolated. In contrast to the



$(C_2H_5O)_2\overset{\overset{O}{\uparrow}}{P}-\underset{\underset{CH_3}{|}}{C}{=}CHC_6H_5$

14

results obtained in reactions with phenylacetylene, negligible amounts of tars were formed. Extension of the reaction time to 9 days gave **14** (22.8%) and 1,2-bis(diethylphosphono)-1-phenylpropane (**15**, 10.6%).



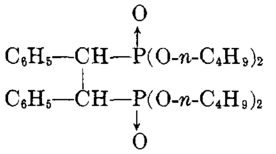
$$\begin{array}{l} C_6H_5-CH\overset{\overset{O}{\uparrow}}{P}(OC_2H_5)_2 \\ \qquad\quad | \\ CH_3-CH\underset{\underset{O}{\downarrow}}{P}(OC_2H_5)_2 \end{array}$$

15

The structures of **14** and **15** were fully substantiated by analysis and their p.m.r. and infrared spectra. Thus, **14** showed the following proton resonances: 5.9H multiplet centered at τ 2.77 p.p.m. [aromatic + vinyl proton (H_A)]; 4.0H quintet centered at τ 6.00 p.p.m. ($—O—CH_2—CH_3$, $J_{HH} = J_{PH} = 7.1$ c.p.s.); 3.0H doublet of doublets, τ 8.02 p.p.m. ($=C—CH_3$, $J_{PH} = 14.7$ c.p.s., $J_{HH_A} = 1.6$ c.p.s.); 5.9H triplet, τ 8.70 ($—O—CH_2—CH_3$, $J_{HH} = 7.1$ c.p.s.). Since the vinylic proton (H_A) is obscured by aromatic proton absorptions, J_{PH_A} could not be determined and no assignment of stereochemistry can be made for **14**; on the basis of the analogous **5**, it is assumed that **14** exists as the isomer with methyl and phenyl in a *cis* relationship.

The results of these reactions are completely analogous to the results obtained with phenylacetylene, although the order of reactivity of the nonterminal alkyne is lower. Trimethyl phosphite and **13** failed to react at 120° (8 days); the acetylene was recovered in near quantitative amounts.

The reaction of diphenylacetylene (**16**) with triethyl phosphite at 150° for 5 days led to a 90% recovery of **16**. Since the preceding studies had indicated reaction temperature to be a critical variable, a higher reaction temperature was obtained by the use of tri-*n*-butyl phosphite (**17**). Reaction of **17** and **16** (2:1 molar ratio) at 190° for 8 days led to the isolation of 1,2-bis(di-*n*-butylphosphono)-1,2-diphenylethane (**18**) in 12% yield. Although the corresponding stilbenylphosphonate is most probably the precursor of **18**, no evidence for its formation could be obtained.



$$\begin{array}{l} C_6H_5-CH-\overset{\overset{O}{\uparrow}}{P}(O\text{-}n\text{-}C_4H_9)_2 \\ \qquad\quad | \\ C_6H_5-CH-\underset{\underset{O}{\downarrow}}{P}(O\text{-}n\text{-}C_4H_9)_2 \end{array}$$

18

The attempted reaction of trialkyl phosphites with a number of aliphatic acetylenes was also investigated. The reaction of hexyne-1 and triethyl phosphite at 110–160° for 1–3 days led to recovery of the alkyne (90%). Diethyl ethylphosphonate, the thermal isomerization product of triethyl phosphite,[3,17] was the only product isolated. Similar results were obtained in the attempted reaction of *t*-butylacetylene and triethyl phosphite.

A higher reaction temperature was obtained by the use of nonyne-1 (**19**). Reaction of a 2:1 molar ratio of triethyl phosphite and **19** at 150° for 8 days led to the recovery of **19** (89%) and a high-boiling material. Infrared and p.m.r. spectra indicated the material to be a mixture of the vinylphosphonate and alkylenebisphosphonate corresponding to **5** and **8**. This material could not be purified further by fractional distillation. The use of tri-*n*-butyl phosphite (**17**) in reaction with **19** (2:1 molar ratio) gave a reaction temperature of 190°. After 5 days, 51% of **19** was recovered and a 17.8% yield of 1,2-bis(di-*n*-butylphosphono)nonane (**20**) was obtained. Examination of the p.m.r. spectra of the reaction mixture at varying time periods showed the presence of weak complex vinyl absorptions, indicating that the vinylphosphonate, the presumed precursor of **20**, was most probably present.

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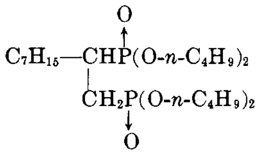
(16) The *trans* configuration of **12** could arise mechanistically by a *cis-α*-elimination process; collapse of intermediate **10** in this manner would yield *trans* **12** and carbene. Although the formation of carbene would not be favored energetically, a similar process is suggested by the work of Franzen[10b] who showed that the zwitterion formed by the nucleophilic attack of dimethyl sulfide on benzyne collapses to yield methyl phenyl sulfide and polymethylene. The latter product is presumably formed from carbene, but attempted interception of the intermediate was unsuccessful. The extensive tar formation in reactions leading to **12** made the attempted isolation of polymethylene unfeasible.

(17) A. Simon and W. Schulze, *Chem. Ber.*, **94**, 3251 (1961).



$$C_7H_{15}\text{—}\underset{\underset{\underset{\displaystyle O}{\downarrow}}{CH_2P(O\text{-}n\text{-}C_4H_9)_2}}{|}}{CH}\overset{\overset{\displaystyle O}{\uparrow}}{P}(O\text{-}n\text{-}C_4H_9)_2$$

20

The volatile products from the reactions leading to the formation of **14**, **15**, **18**, and **20** were collected and were identified (infrared and mass spectra) as the appropriate olefins, ethylene and 1-butene. Thus it is probable that the *cis*-β-elimination process is general in the reactions of trialkyl phosphites with acetylenes.

The reaction of triethyl phosphite with three α-hydroxyacetylenes (ethynylcyclohexanol, 3-methyl-3-hydroxybutyne-1, and 3,5-dimethyl-3-hydroxyhexyne-1) proceeded readily at 150°. In each case, triethyl phosphate was isolated (>40%) along with high-boiling fractions. All of these fractions possessed infrared and p.m.r. absorptions characteristic of trisubstituted olefins and diethyl phosphonates, but spectra indicated the absence of the hydroxy group. Gas–liquid chromatographic analysis of the high-boiling fraction from the reaction with ethynylcyclohexanol indicated four major components. Attempted fractionation of these mixtures was unsuccessful and the reaction was not further investigated.

The results of this study show the feasibility of obtaining an intermolecular nucleophilic attack by trialkyl phosphites on simple unactivated acetylenes, but the reaction would appear to possess synthetic potential only in the case of monoarylacetylenes. The observed order of reactivity of the acetylenes studied is consistent with expectation.[18] In the more reactive phenylacetylenes, stabilization of the negative charge in the initial adducts (**1**) provides a driving force for reaction not present in the alkylacetylenes. The lower order of reactivity observed for nonterminal acetylenes is probably a steric effect, possibly a disruption of the planar transition state necessary for the *cis*-β-elimination process.

Experimental[19]

Reaction of Triethyl Phosphite with Phenylacetylene. A. Formation of Diethyl β-Styrylphosphonate (5).—A mixture of 10.2 g. (0.10 mole) of phenylacetylene and 33.2 g. (0.20 mole) of triethyl phosphite was refluxed (150°) with constant stirring for 48 hr. After removal of unreacted phosphite by distillation at reduced pressure, the residual dark oil was distilled to give 1.38 g. (5.75%) of **5**, b.p. 125–126° (0.3 mm.). Anisimov and Nesmeyanov report b.p. 138° (2 mm.) for **5**.[20] The infrared spectrum of **5** showed characteristic bands at 1608 (C=C), 1242 ($P\rightarrow O$), 1157 (P–O–ethyl), 740, and 690 cm.$^{-1}$ (monosubstituted phenyl). The p.m.r. spectrum showed the following signals: τ = 2.23–2.72, multiplet, 5.8H[21] (aromatic + $C_6H_5CH_A$=); 3.70 (1.0H vinyl signal described in text); 5.95 quintet, 3.9H (-O-CH_2-, $J_{PH} \cong J_{HH} \cong 7$ c.p.s.); and 8.88 p.p.m., triplet, 6.0 H(-C-CH_3, $J_{HH} \cong 7$ c.p.s.). The infrared and p.m.r. spectra of this compound were identical in all respects with an authentic sample of **5** prepared by the esterification[20] of β-styrylphosphonic dichloride.[22]

In a repetition of the above reaction, the volatile products were swept from the reaction mixture by a stream of nitrogen and collected at liquid nitrogen temperatures. The volatile products were distilled in a vacuum line through a −78° trap to remove entrained triethyl phosphite. The product was identified as ethylene by comparison of its infrared and mass spectra with those of an authentic sample; no peaks of m/e >28 were observed.

A similar reaction of triethyl phosphite (0.20 mole) and phenylacetylene (0.10 mole) in 50 ml. of diglyme at 150° for 72 hr. gave 3.64 g. (15.2%) of **5**.

B. Formation of 1,2-Bis(diethylphosphono)-1-phenylethane (8).—A solution of 10.2 g. (0.10 mole) of phenylacetylene in 50 ml. of triethyl phosphite was added dropwise with stirring to 150 ml. of refluxing triethyl phosphite. After addition was completed, the reaction mixture was allowed to reflux for 48 hr. After removal of excess phosphite by distillation at atmospheric pressure, the residual oil was distilled to give 2.55 g. (10.6%) of **5** and 6.21 g. (16.7%) of **8**, b.p. 184–186° (1.0 mm.) [lit.[23] b.p. 181° (1.0 mm.)]. The infrared spectrum of **8** showed the same diagnostic bands as that of **5** with the expected absence of a C=C stretching absorption. The p.m.r. spectrum showed the following signals: τ = 2.80, multiplet, 5.0H (aromatic); 5.9–6.8, multiplet, 8.8H (methine + -O-CH_2-); 7.78, multiplet, 2.0H (-C-CH_2-P); and 8.72, 8.99, 9.02, and 9.05 p.p.m., triplets, 12.0H (-C-CH_3, J_{HH} = 7.0–7.1 c.p.s.). The nonequivalence of the four methyl signals (equal intensities) is probably the result of rotational restriction. The compound was identical in all repects with an authentic sample of **8** prepared from β-bromostyrene and sodium diethylphosphonate by the method of Arbuzov and Lugovkin.[23]

The bisphosphonate (**8**) was also prepared by heating (160°) a mixture of 26.6 g. (0.111 mole) of **5** and 38.4 g. (0.230 mole) of triethyl phosphite for 16 days. Distillation of the reaction mixture gave 31.9 g. of a mixture of diethyl ethylphosphonate and triethyl phosphate,[24] 18.7 g. of **5** (70% recovery), and 8.7 g. (68.8% based on unrecovered **5**) of **8**. No triethyl phosphite was recovered.

Reaction of Trimethyl Phosphite with Phenylacetylene.—A mixture of 10.2 g. (0.10 mole) of phenylacetylene and 33.2 g. (0.20 mole) of trimethyl phosphite was refluxed (120°) for 92 hr. After excess phosphite was removed by atmospheric distillation, the residue was distilled to give 2.65 g. (12.5%) of **dimethyl β-styrylphosphonate** (**12**), b.p. 138.5–139° (1 mm.) [lit.[20] b.p. 129° (2 mm.)]. The infrared spectrum of **12** was essentially identical with that of **5** with the replacement of the P-O-ethyl absorption at 1157 by P-O-methyl absorption at 1178 cm.$^{-1}$. The p.m.r. spectrum of **12** showed a similar correspondence with that of **5**. The following signals were observed: τ = 2.25–2.90, multiplet, 5.9H (aromatic + H_A); 3.75, triplet, 0.9H (H_B, $J_{HH} = J_{PH}$ = 17 c.p.s.); and 6.59 p.p.m., doublet, 6.0H(-O-CH_3, J_{POCH} = 11.0 c.p.s.). This compound was identical in all respects with an authentic sample of **12** prepared by the methanolic esterification of β-styrylphosphonic dichloride following established procedures.[18]

Reaction of trimethyl phosphite and phenylacetylene in 4.4:1 and 12.8:1 molar ratios at 109–113° for 4 and 6 days, respectively, led to the isolation of **12** (29.2 and 10%, respectively). Large amounts of intractable tars were formed in this reaction and in the reactions with triethyl phosphite.

A mixture of 2.0 g. of **12** isolated from the trimethyl phosphite reaction and 10 ml. of 1:1 hydrochloric acid was refluxed overnight and reduced in volume on a steam bath to give a residue which solidified on cooling. This solid was washed with chloroform, filtered, and dried over phosphorus pentoxide to give 1.0 g. (57.7%) of **β-styrylphosphonic acid**, m.p. 142–142.5° (lit.[25] m.p.

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[18] R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," Academic Press Inc., New York, N. Y., 1955, pp. 37–40; J. F. Arens, *Advan. Org. Chem.*, **2**, 179 (1960).

[19] All reactions were carried out under an atmosphere of dry nitrogen. Infrared spectra were determined on a Beckman IR-8 spectrophotometer in carbon tetrachloride solutions or as films. P.m.r. spectra were determined with a Varian Associates A-60 spectrometer on 20–30% solutions in carbon tetrachloride using tetramethylsilane as an internal standard. Microanalyses were performed by Galbraith Microanalytical Laboratories.

[20] K. N. Anisimov and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1003 (1955).

[21] Relative integrated intensity. Chemical shift values are cited as the centers of the indicated multiplets.

[22] K. N. Anisimov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 803 (1954).

[23] B. A. Arbuzov and B. D. Lugovkin, *Zh. Obshch. Khim.*, **21**, 99 (1951).

[24] These compounds were identified by a comparison of their g.l.c. behavior with that of authentic samples. The g.l.c. analysis employed essentially the conditions which have been described previously: J. B. Plumb and C. E. Griffin, *J. Org. Chem.*, **28**, 2908 (1963).

[25] G. M. Kosolapoff and F. Huber, *J. Am. Chem. Soc.*, **68**, 2540 (1946).

140–144°). β-(α-Methylstyryl)phosphonic acid is reported to melt at 95°.[26]

Reaction of Triethyl Phosphite wth Methylphenylacetylene. A. Formation of Diethyl β-(β-Methylstyryl)phosphonate (14).—A mixture of 11.6 g. (0.10 mole) of methylphenylacetylene and 33.2 g. (0.20 mole) of triethyl phosphite was refluxed (150°) for 4 days. Distillation under reduced pressure gave triethyl phosphite, 9.6 g. of methylphenylacetylene (83.5% recovery), 10.2 g. of a mixture of triethyl phosphate and diethyl ethylphosphonate,[24] and 1.1 g. (24% based on unrecovered acetylene) of **14**, b.p. 128° (0.5 mm.), 144–145° (1.0 mm.).

Anal. Calcd. for $C_{13}H_{19}O_3P$: C, 61.41; H, 7.53; P, 12.18. Found: C, 61.18, 61.27; H, 7.74, 7.68; P, 12.00, 11.91.

The infrared spectrum was quite similar to that of **5**; the p.m.r. spectral data have been reported in the text.

B. Formation of 1,2-Bis(diethylphosphono)-1-phenylpropane (15).—A repetition of the above reaction with an increase in reaction time to 9 days led to the recovery (65.5%) of the acetylene and the isolation of **14** (22.8% based on unrecovered acetylene) and 1.43 g. of **15**, b.p. 195–196° (1.0 mm.). The p.m.r. spectrum of this fraction indicated slight contamination by **14**. This was purified by chromatography through a silicic acid column (70 g., 2.5-cm. diameter); elution with chloroform gave **15**, 1.17 g.

Anal. Calcd. for $C_{17}H_{30}O_6P_2$: C, 52.03; H, 7.70; P, 15.80; mol. wt., 392. Found: C, 51.86, 52.09; H, 7.63, 7.81; P, 15.97, 16.13; mol. wt., 407, 411.[27]

The infrared spectrum of **15** confirmed the presence of diethylphosphono and monosubstituted benzene functions. The p.m.r. spectrum of **15** showed a group of four broad complex multiplets centered at τ = 2.47 (5.0H aromatic), 4.00 (7.9H, $-O-CH_2-$), 7.75 (1.8H, methine), and 8.85 p.p.m. (15.3H, methyl).

Reaction of Tri-*n*-butyl Phosphite with Diphenylacetylene.—A mixture of 17.8 g. (0.10 mole) of diphenylacetylene and 50.0 g. (0.20 mole) of tri-*n*-butyl phosphite was refluxed at 190° for 8 days. Distillation of the reaction mixture gave a low-boiling fraction consisting of tri-*n*-butyl phosphate, di-*n*-butyl *n*-butylphosphonate, and unreacted acetylene[24] and 6.82 g. of **1,2-bis(di-*n*-butylphosphono)-1,2-diphenylethane (18)**, b.p. 152–154° (0.2 mm.). G.l.c. analysis indicated this fraction to be contaminated with tri-*n*-butyl phosphate. A solution of 2.0 g. of this material was chromatographed through a silicic acid column (100 g., 2.5-cm. diameter); elution with chloroform gave 1.57 g. of **18**.

Anal. Calcd. for $C_{30}H_{58}O_6P_2$: C, 63.59; H, 8.54; P, 10.93; mol. wt., 577. Found: C, 63.24, 63.30; H, 8.38, 8.35; P, 11.17, 11.10; mol. wt., 553, 557.[27]

The infrared spectrum showed bands at 1241 ($P\rightarrow O$) and 754 and 698 cm.$^{-1}$ (monosubstituted phenyl) and the absence of olefinic absorption. The p.m.r. spectrum showed signals at τ = 2.8, multiplet, 10.2H (aromatic); 6.15, multiplet, 10.1H ($-O-CH_2-$ + methine); 8.5, multiplet, 14.9H (methylene); and 9.07 p.p.m., triplet, 12.7H (methyl, $J_{HH} \cong 7.0$ c.p.s.). The p.m.r. spectrum is consistent in all respects with the postulated structure.

Reaction of Tri-*n*-butyl Phosphite with Nonyne-1.—A mixture of 16.2 g. (0.10 mole) of nonyne-1 and 50.0 g. (0.20 mole) of tri-*n*-butyl phosphite was refluxed at 190° for 5 days. Distillation of the reaction mixture gave a series of low-boiling fractions identified as nonyne-1 (51.2% recovery), tri-*n*-butyl phosphite, di-*n*-butyl *n*-butylphosphonate (37.3%), and tri-*n*-butyl phosphate (17.3%),[24] and 5.8 g. of material with b.p. 175–176° (0.5 mm.). G.l.c. analysis of the material indicated contamination by both tri-*n*-butyl phosphate and di-*n*-butyl *n*-butylphosphonate. A 2.0-g. sample of this material was chromatographed on silicic acid (100 g., 2.5-cm. diameter column); elution with chloroform gave 1.48 g. of **1,2-bis(di-*n*-butylphosphono)nonane (20)**.

Anal. Calcd. for $C_{25}H_{54}O_6P_2$: C, 58.78; H, 10.60; P, 12.09; mol. wt., 512. Found: C, 58.81, 58.74; H, 10.79, 10.88; P, 12.13, 12.27; mol. wt., 493, 497, 504.[27]

The compound showed a strong phosphoryl absorption at 1242 cm.$^{-1}$. The p.m.r. spectrum of **20** showed multiplets centered at τ = 6.0 (8.0H, $-O-CH_2-$) and 8.3 (33.5H, methylene + mehtine) and a triplet at 9.07 p.p.m. (14.9H, methyl, J_{HH} = 7.0–7.2 c.p.s.).

Acknowledgment.—The authors are indebted to the Victor Chemical Division, Stauffer Chemical Company, for generous gifts of starting materials.

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[26] E. Bergmann and A. Bondi, *Ber.*, **63**, 1158 (1930).

[27] Molecular weight determinations were carried out with a Mechrolab Model 301A vapor pressure osmometer, using dilute solutions in benzene at 37°. We are indebted to Mr. M. Bollinger for carrying out these determinations.

3d-Orbital Resonance in Trivalent Organophosphines. I. Metalation of Methylphosphines

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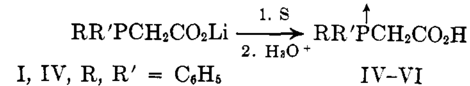
Received December 3, 1964

Alkyllithium compounds selectively metalate methyldiphenylphosphine, dimethylphenylphosphine, and di-*n*-hexylmethylphosphine on a methyl carbon atom to give the corresponding phosphino carbanions in yields ranging from 14–54%. The relative rates of metalation of dimethyldodecylphosphine to dimethyldodecylamine have been found to be *ca.* 15:1. The enhanced rates of metalation of the methylphosphines provide evidence for 3d-orbital resonance stabilization of the incipient α-phosphino carbanion by trivalent phosphorus.

Although the hydrogen–metal interchange reaction (metalation) has been used extensively as a method for the preparation of heteroatom-substituted organometallic compounds,[1] little is known about the metalation of tertiary organophosphines. In 1945 Gilman and Brown reported[2] that triphenylphosphine was metalated in the *meta* position by *n*-butyllithium to the extent of 6%. More recently, Aguiar and coworkers[3] have demonstrated that benzyldiphenylphosphine is metalated at the benzyl position by phenyllithium.

We now wish to report the results of a study of the metalation of some methylphosphines. We find that *t*-butyllithium selectively metalates methyldiphenylphosphine (I), dimethylphenylphosphine (II), and di-*n*-hexylmethylphosphine (III) on a methyl carbon atom. The yields of the phosphino carbanions, based on the weights of the derivatives obtained from carbonation and subsequent sulfurization, vary from 14 to 54% (see Table I).



$$\underset{\text{I–III}}{RR'PCH_3} + t\text{-}C_4H_9Li \longrightarrow RR'PCH_2Li + t\text{-}C_4H_{10} \xrightarrow{CO_2}$$

$$RR'PCH_2CO_2Li \xrightarrow[2.\ H_3O^+]{1.\ S} \underset{\text{IV–VI}}{RR'\overset{\overset{S}{\uparrow}}{P}CH_2CO_2H}$$

I, IV, R, R′ = C_6H_5
II, IV, R = C_6H_5, R′ = CH_3
III, VI,[4] R, R′ = *n*-C_6H_{13}

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[1] H. Gilman and J. W. Morton, Jr., *Org. Reactions*, **8**, 258 (1954).

[2] H. Gilman and G. E. Brown, *J. Am. Chem. Soc.*, **67**, 824 (1945).

[3] A. M. Aguiar, J. Giacin, and A. Mills, *J. Org. Chem.* **27**, 674 (1962).