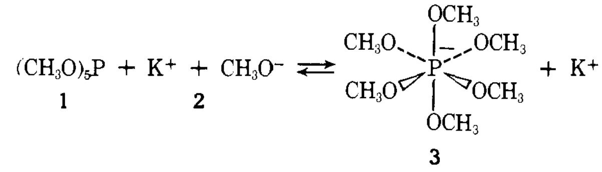
Potassium Hexamethoxyphosphate

Sir:

The number of organic hexacoordinate phosphorus compounds that has been prepared is quite small,[1] and no simple acyclic nonhalogenated derivative has been reported. Recently Ramirez and co-workers[2] have prepared zwitterionic compounds which contain hexacoordinate phosphorus. Archie and Westheimer[3] have found that hydrolysis of pentaphenoxyphosphorane proceeds through a hexacoordinate phosphorus compound.

The ready availability of pentamethoxyphosphorane,[4] **1**, makes it now possible to study its chemistry. It has now been found that **1** reacts with potassium methoxide, **2**, in the presence of 18-crown-6-ether to give a solution of potassium hexamethoxyphosphate, **3**, in which the potassium ion is coordinated to the 18-crown-6-ether.



The structural assignment for **3** is based upon the following evidence. The ^{31}P NMR resonance of **1** at δ +67 ppm relative to 85% phosphoric acid is diminished in intensity when **1** is allowed to react with 1 mol of **2** in the presence of 1 mol of 18-crown-6-ether in benzene. It totally disappears when 2 mol of **2** and 18-crown-6-ether are allowed to react with **1**. In both cases a new resonance appears in the ^{31}P NMR spectrum at δ +145. High field resonances are generally associated with hexacoordinate phosphorus compounds.[1] The proton coupled ^{31}P NMR spectrum reveals that the +145 absorption is a multiplet and 13 lines of the expected 19 can be observed, J_{POCH} = 13 Hz. It is not surprising that all 19 lines were not observed since the relative intensities of the strongest to the weakest absorption is calculated to be 48620:1.[5] The ^{1}H NMR spectrum of the 2:1 reaction mixture shows an absorption for crown ether. The doublet at δ 3.50 (J_{POCH} = 10 Hz) for **1** is no longer present and a new doublet is found at δ 3.76 (J_{POCH} = 13 Hz). Similarly the ^{13}C NMR spectrum reveals that all of **1** has reacted, δ 54.65 (J_{POC} = 11.7 Hz) and a new doublet has arisen at δ 53.21 (J_{POC} = 9.8 Hz).

When **1**, was treated with 2 mol of **2** in hexamethylphosphoramide (HMPA) an entirely similar behavior was noted. The ^{31}P NMR spectrum had a new resonance at δ +144, the ^{1}H NMR spectrum had a doublet at δ 3.33 (J_{POCH} = 13 Hz) and the ^{13}C NMR spectrum, proton decoupled, had a doublet at δ 52.61 (J_{POC} = 10.3 Hz).

The collected NMR data are in total agreement with the formation of **3**. The data require that all of the methoxy groups be equivalent, and this requirement is met if the structure is octahedral. The experiment in which equimolar amounts of **1** and **2** were used indicates that the reaction is an equilibrium reaction. The rate of equilibration on the NMR time scale must be slow, otherwise time averaged spectra without POC and POCH coupling would have been observed. It is also interesting to note that the five-membered ring effect on the ^{31}P NMR chemical shifts which is found with P(III), P(IV), and P(V) compounds is also found with P(VI) compounds. Compound, **3**, δ +144 can be compared to its relative which contains three ethylenedioxy rings and which absorbs at δ +89.[6]

Attempts to isolate **3** have so far been fruitless. When ether is added to an HMPA solution of **3** a precipitate forms; however, this appears to be mainly **2**. It was thought that it might be possible to prepare **3** in methanol and that it would precipitate from solution. Unfortunately addition of **1** to **2** in methanol led to the decomposition of **1**.

Treatment of pentaethoxyphosphorane, **4**, 1 mol with potassium ethoxide, **5**, 1 mol, in HMPA did notlead to any detectable potassium hexaethoxyphosphate, **6**. When the ratio of **4**:**5** was changed to 1:2.5 a reaction occurred and all of the **4** disappeared. An absorption at δ +147 was observed in the ^{31}P NMR spectrum; however, this quickly disappeared and phosphate(s) were produced. Evidently, hexaalkoxyphosphates are congested molecules and it may be that very few of them can be formed.

Acknowledgments. This research has been supported by the National Science Foundation and by the Public Health Service Research Grant No. CA-10737 from the National Cancer Institute. We also wish to thank the Mobil Chemical Foundation for funds which aided in the purchase of NMR equipment.

References and Notes

(1) D. Hellwinkel, "Organic Phosphorus Compounds", G. M. Kosolapoff and L. Maier, Ed., Wiley, New York, N.Y., Chapter 5b, pp 303–308.
(2) F. Ramirez, M. Nowakowski, and J. F. Marecek, *J. Am. Chem. Soc.*, **96**, 7269 (1974).
(3) W. C. Archie, Jr., and F. H. Westheimer, *J. Am. Chem. Soc.*, **95**, 5995 (1973).
(4) Pentamethoxyphosphorane can be prepared by the reaction of trimethyl phosphite and methyl benzenesulfenate. The yield is ca. 55%, and the purity of the product is high. Details of the preparative procedure will be supplied upon request.
(5) H. Kruglak and J. T. Moore, "Basic Mathematics for the Physical Sciences", McGraw-Hill, New York, N.Y., 1963, pp 101–102.
(6) B. C. Chang, D. B. Denney, R. L. Powell, and D. W. White, *Chem. Commun.*, 1070 (1971).

Donald B. Denney,* Dorothy Z. Denney, Chi-Fei Ling
Wright and Rieman Laboratories
Rutgers, The State University of New Jersey
New Brunswick, New Jersey 08903

Received August 5, 1976

In Situ Generation and Intramolecular Trapping of *o*-Xylylenes by Cobalt-Catalyzed Acetylene Cooligomerizations. A One-Step Synthesis of Polycycles

Sir:

Intramolecular cycloadditions to *o*-xylylenes constitute an elegant approach to the synthesis of complex natural products.[1-3] However, the unavailability of appropriately substituted benzocyclobutenes, coupled with the tedious, multistep synthetic procedures associated with their preparation,[3,4] make this route somewhat unattractive as a general method. We wish to report a novel approach to the synthesis of complex systems via the cobalt-catalyzed cooligomerization of appropriately substituted 1,5-hexadiynes and bis(trimethylsilyl)acetylene (BTMSA).[5]

Slow addition of diyne A (Scheme I) over several days to a solution of CpCo(CO)$_2$ (ca. 5 mol%) in refluxing neat BTMSA under N$_2$ using a syringe pump gave good yields of the tri- and tetracyclic products B on column chromatography (Table I). The structure of compounds B was in accord with their analytical, spectral, and chemical characteristics.[6] Further detailed structural information was obtained by a combination of 360-MHz ^{1}H and ^{13}C NMR spectroscopy[6] in conjunction with

Scheme I