## 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.
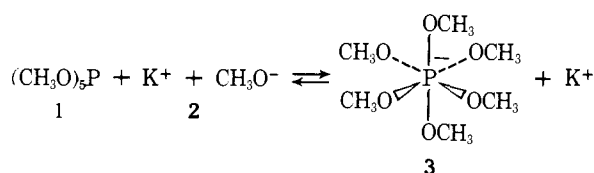
The structural assignment for 3 is based upon the following evidence. The ^{31}P NMR resonance of 1 at δ +67 ppm relative to 85% phosphoric acid is diminished in intensity when 1 is allowed to react with 1 mol of 2 in the presence of 1 mol of 18-crown-6-ether in benzene. It totally disappears when 2 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 meth-

anol 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.

References and Notes

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(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.
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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 N₂ 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
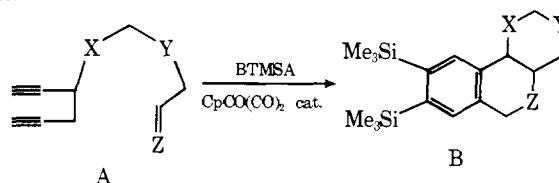
Scheme I

Table I. Polycycles by Cobalt-Catalyzed Acetylene Cyclization

| Starting diyne	Product[6]	Yield, %	J_{trans} Hz
1	2	60	9.5
3	4 + regioisomers (unseparated mixture)	65	
5	6	50	
7	8	45	10
9	10a + cis isomer (ca. 15%) 10b	90	12
11	12a + cis isomer (<5%) 12b	80	11

decoupling and off-resonance decoupling experiments. Spectra calculated on the basis of models agreed well with observed ones.[7] Quantitative protodesilylation ($CF_3COOH-CCl_4$, 1:1, room temp, 2 days) of the mixture 10a/10b gave the corresponding unsubstituted naphthopyran derivatives 13a and 13b,[6] separable by preparative GLC (10 ft × ¼ in. glass 20% UCW98 on Chromosorb W, DMCS-AW 60/80; 180 °C). Similarly, the parent octahydrophenanthrenes 14a/14b[6] could be obtained from 12. The pure authentic cis isomer 14b was

13a, X = O
14a, X = CH₂

13b, X = O
14b, X = CH₂
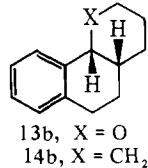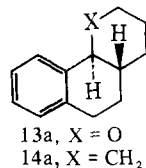
prepared by an alternate route[8] and equilibrated with 14a (10% Pd/C, 230 °C, 10 h), the identity of which was ascertained by GC, 360-MHz ¹H NMR and ¹³C NMR. The synthesis of precursors 1 (56%, not optimized) and 3 (87%) was accomplished by straightforward alkylation of 1,5-hexadiyne-3-ol.[9] Aldehyde 5 (74%, mp 48.5-49.0 °C) could be prepared by reduction with diisobutylaluminum hydride (−78 °C) of the corresponding nitrile, in turn available by alkylation of 1,5-hexadiyne-3-ol with o-cyanobenzyl bromide (64%). Derivatization of 5 with methoxyammonium chloride results in imino ether 7 (80%). A facile new synthetic entry into the series of

3-alkyl-1,5-hexadiynes was found by alkylation of 1,5-hexadiyne trianion [generated with BuLi (3 equiv) -TMEDA (1 equiv) in THF at −40 °C, 3 h]. Thus, reaction of the trianion with ethylene oxide (−40 °C, 1 h, 1 equiv) leads to the precursor alcohol to 9 (65%, bp 95 °C (5 mm)), and with 6-chloro-1-hexene, to 11 (85%, bp 80 °C (5 mm)). Compound 9 is obtained by simple alkylation of the above alcohol with allyl bromide (91%).

Several comments are in order with respect to the products described in Table I. First, the stereochemistry of the new ring junction is almost always exclusively trans. A cobalt-"catalyzed" cis-trans isomerization was ruled out by exposure of pure 14b to the reaction conditions and its quantitative recovery. This observation suggests that, when there are no other constraints on the system,[1] the exo transition state 15 is more favored than its endo counterpart 16.[10] Models indicate that this might be due to lesser eclipsing of the side chain hydrogens in 15 and possible steric interference of the benzene ring in 16.

15

16

17, Y = O
18, Y = CH₂
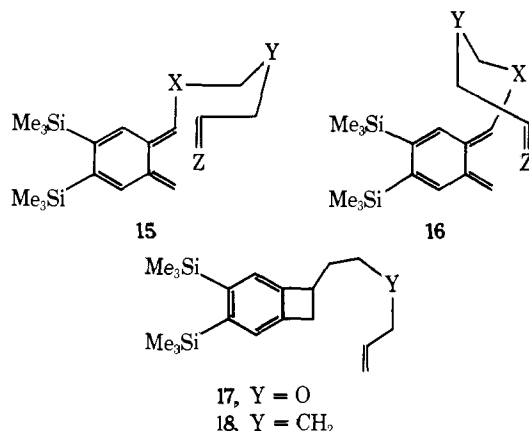
Second, regioisomers of the cycloadducts observed occur when added flexibility in the transition state to o-xylylene cycloaddition is available (cf. 3 → 4) or when electronic effects operate (cf. 5 → 6).

Third, intermediate benzocyclobutenes may be isolated when shorter reaction times are employed, but only in the cases of the more stable, alkylated derivatives 17 and 18. Protodesilylation (CF_3COOH-ether, 1:1, 1% H_2SO_4, room temp, 16 h), followed by pyrolysis (refluxing decane, 30 h), results in 13 and 14, respectively, with no apparent change in the cis-trans isomer ratio, ruling out any unusual contribution of the trimethylsilyl groups to the relative stabilities of 15 and 16.

It is clear that the methodology described here provides a striking simplification of currently available routes to natural products via benzocyclobutenes. The attractive features include simplicity, high yields, control of stereochemistry, and essential control of aromatic ring substitution.[5,11]

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(6) **2**: colorless oil; *m/e* 332 (M⁺, 23%), 73 (Me₃Si, 100%); NMR τ (C₆D₆) 1.71 (br s, 1 H), 2.53 (br s, 1 H), 5.93 (br d, *J* = 11 Hz, 1 H, -OC*HH*), 6.03 (d, *J* = 9.5 Hz, 1 H, ArC*HO*), 6.62 (ddd, *J* = 13, 11, 2 Hz, 1 H, -OCH*H*), 7.33 (ddd, *J* = 17, 11.5, 6 Hz, 1 H, ArC*HH*), 7.43 (ddd, *J* = 17, 6, 1.5 Hz, 1 H, ArCH*H*), 8.36–9.13 (m, 7 H), 9.61 (s, 18 H, Me₃Si); **6**: colorless crystals, mp 115–116 °C; *m/e* 382 (M⁺, 39%), 119 (100%), 73 (Me₃Si, 80%); NMR τ (C₆D₆) 2.34 (s, 1 H, Ar*H*), 2.53 (s, 1 H, Ar*H*), 2.93 (dd, *J* = 8, 7 Hz, 1 H, Ar*H*), 2.99 (dd, *J* = 8, 7 Hz, 1 H, Ar*H*), 3.13 (br dd, *J* = 9, 7 Hz, 2 H, Ar*H*), 4.10 (s, 1 H, ArCH*O*₂), 4.91 (m, 2 H, ArCH₂O), 5.30 (d, 1 H, *J* = 14 Hz, ArC*HO*), 6.96 (d, *J* = 9 Hz, 2 H, ArCH₂), 9.58 (s, 9 H), 9.62 (s, 9 H); **8**: colorless crystals, mp 170–171 °C; *m/e* 411 (M⁺, 14%), 73 (Me₃Si, 100%); NMR τ (C₆D₆) 1.63 (s, 1 H, Ar*H*), 2.00 (d, *J* = 7.5 Hz, 1 H, Ar*H*), 2.55 (s, 1 H, Ar*H*), 2.80 (dd, *J* = 9, 8 Hz, 1 H, Ar*H*), 2.94 (dd, *J* = 10.5, 7 Hz, 1 H, Ar*H*), 3.34 (d, *J* = 7 Hz, 1 H, Ar*H*), 4.59 (d, *J* = 10 Hz, 1 H, ArC*HO*), 5.09 (m, 2 H, ArCH₂O), 5.68 (d, *J* = 18 Hz, 1 H, ArC*HN*), 5.82 (d, *J* = 10 Hz, 1 H, ArCH*N*), 5.87 (d, *J* = 18 Hz, 1 H, ArC*HN*), 6.63 (s, 3 H, MeO), 9.56 (s, 9 H), 9.57 (s, 9 H); **13a**: colorless oil; *m/e* 188 (M⁺, 84%), 129 (100%); NMR τ (C₆D₆) 2.98 (m, 4 H), 5.95 (dd, *J* = 11, 4 Hz, 1 H, C*HO*), 6.15 (dd, *J* = 11.5, 4 Hz, 1 H, C*HO*), 6.68 (ddd, *J* = 13, 12, 2 Hz, 1 H, C*HO*), 7.03 (dd, *J* = 12, 11 Hz, 1 H, C*HO*), 7.38 (m, 2 H, ArCH₂), 7.82 (br dd, *J* = 12, 12 Hz, 1 H, ArC*H*tert), 8.13 (br d, *J* = 13 Hz, 1 H, C*H*HCH₂O), 8.52 (m, 2 H), 8.68 (m, 1 H), 8.95 (m, 1 H); **14a**: colorless oil; *m/e* 186 (M⁺, 100%), 129 (67%); NMR τ (C₆D₆) 2.75 (d, *J* = 7.5 Hz, 1 H), 2.92 (m, 2 H), 3.00 (d, *J* = 6.5 Hz, 1 H), 7.30 (m, 2 H, ArCH₂), 7.68 (br dd, *J* = 12.5, 3 Hz, 1 H, ArCH*tert*C*HH*), 7.87 (br dd, *J* = 12, 12 Hz, 1 H, ArCH*tert*), 8.17–9.08 (m, 10 H).

(7) Spectra were calculated using simple additivity rules. Models consisted of the various isomeric decalins and perhydrophenanthrenes: J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972; D. K. Falling and D. M. Grant, *J. Am. Chem. Soc.*, **96**, 1827 (1974).

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(10) We have assumed predominant conrotatory outward cyclobutene ring opening to give **15**. We cannot, however, rigorously rule out a mechanism which involves a conrotatory inward process to give a reactive o-xylylene undergoing cycloadditions to the observed products via the endo transition state.

(11) Preliminary results indicate useful regioselectivity in electrophilic substitutions of the trimethylsilyl groups.

(12) Fellow of the Alfred P. Sloan Foundation, 1976–1978.

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Structure of Tetrakis(*N,N*-diethylmonothiocarbamato)titanium (IV). A Limitation on Orgel's Rule

Sir:

In 1960, Orgel[1] proposed that the π-bonding capabilities of the ligands in eight-coordinate, dodecahedral MX_4Y_4 complexes could determine the manner in which the ligands sort into A and B sites.[2] More specifically, Orgel postulated that in complexes of d^1 and d^2 ions the π-acceptor ligands should occupy the dodecahedral B sites, since the partially or completely filled metal $d_{x^2-y^2}$ orbital is of appropriate symmetry for $d\pi \to p\pi$ bonding with ligands in the B sites. However, for complexes of d^0 ions π-donor ligands should occupy the B sites so as to facilitate $p\pi \to d\pi$ interaction involving the vacant metal $d_{x^2-y^2}$ orbital.[3]

While the structures of $[(CH_3NC)_4Mo(CN)_4]^4$ and $[Zr(nes)_4]^5$ (nes = *N*-ethylsalicylaldiminate) tend to support Orgel's proposal, a more definitive test of this idea involves structural comparison of the two closely related complexes $[W(QBr)_4]^6$ and $[ZrQ_4]^7$ (QBr = 5-bromoquinolin-8-olate and Q = quinolin-8-olate); the only important difference between these complexes is the electronic configuration of the metal ion. In the former compound, a d^2 complex, the π-acceptor quinolinolate nitrogen atoms occupy the B sites and the π-donor oxygen atoms occupy the A sites; in the latter compound, a d^0 complex, the site occupancies are reversed, as predicted by Orgel's rule.

We report herein the synthesis and x-ray structure of the eight-coordinate MX_4Y_4 complex $[Ti(Et_2mtc)_4]$ (Et₂mtc = *N,N*-diethylmonothiocarbamate), a complex in which the four sulfur or the four oxygen donor atoms might have been expected to sort into the B sites, depending on the relative π-donor ability of sulfur and oxygen. Instead, the sulfur and oxygen atoms cluster on opposite sides of the molecule so as to give a "cis" arrangement of sulfur atoms.

Air-sensitive, red crystals of composition Ti(SOCN-(C₂H₅)₂)₄ were isolated following insertion of carbonyl sulfide into the titanium–nitrogen bonds of tetrakis (*N,N*-diethylamido)titanium(IV).[8] The compound exhibits a methyl resonance at τ 8.83 and a methylene resonance at τ 6.48 in the ¹H NMR spectrum of a dichloromethane solution at 37 °C. It shows the following characteristic infrared bands: $\nu(C\text{---}O)$ and $\nu(C\text{---}N)$, 1547 and 1530; $\nu(C\text{---}S)$, 941; $\nu(Ti\text{-}O)$, 558; and $\nu(Ti\text{-}S)$, 320 cm⁻¹ (Nujol mull).

Crystal data: Ti(C₅H₁₀NOS)₄, mol wt = 576.72; monoclinic, space group $C2/c$ (C_{2h}^6, No. 15); $a = 13.687$ (2), $b = 13.974$ (3), $c = 16.990$ (4) Å; $\beta = 111.39$ (2)°; $d_{measd} = 1.267$ g cm⁻³, $Z = 4$, $d_{calcd} = 1.266$ g cm⁻³. The structure was solved by straightforward application of the heavy-atom method and was refined to a final R_1 value of 0.086 and an R_2 value of 0.087 using 3899 observed reflections having $2\theta_{MoK\alpha} < 65°$ (the equivalent of 1.6 limiting Cu Kα spheres) and $|F_o| > 2\sigma(|F_o|)$ measured with a Picker FACS-I automated diffractometer.
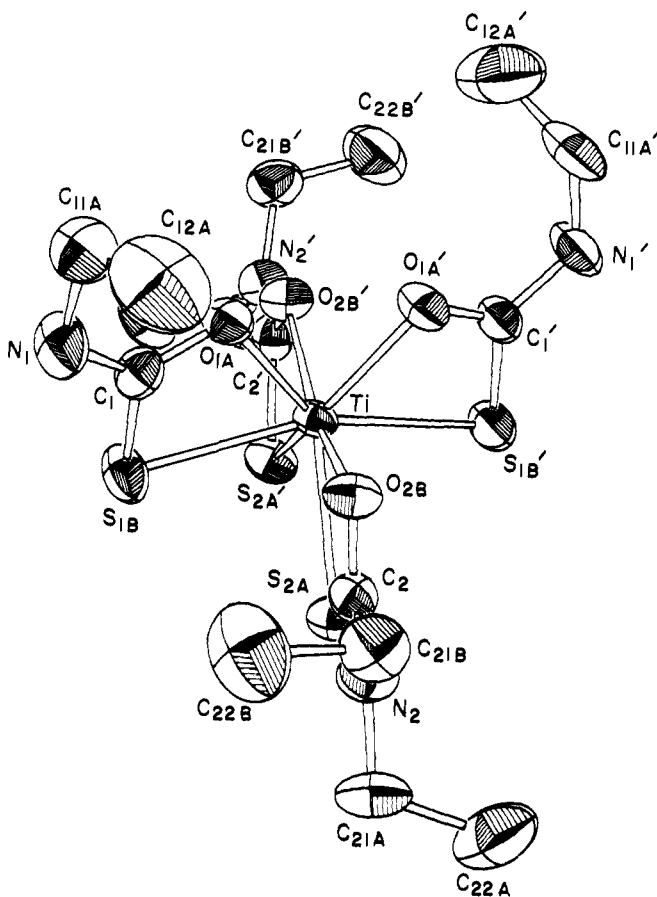

Figure 1. A perspective view of the [Ti(Et₂mtc)₄] molecule. The primed atoms are related to the unprimed atoms by a crystallographic twofold axis. A disordered ethyl group on ligand 1 has been omitted for clarity.