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-workers² have prepared zwitterionic compounds which contain hexacoordinate phosphorus. Archie and Westheimer³ 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.

 $(CH_{3}O)_{5}P + K^{+} + CH_{3}O^{-} \rightleftharpoons CH_{3}O \xrightarrow{V}_{CH_{3}O} \xrightarrow{V}_{CH_{3}O} + K^{+}$

The structural assignment for 3 is based upon the following evidence. The ³¹P 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 ³¹P NMR spectrum at δ +145. High field resonances are generally associated with hexacoordinate phosphorus compounds.1 The proton coupled ³¹P 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 ¹H NMR spectrum of the 2:1 reaction mixture shows an absorption for crown ether. The doublet at δ 3.50 ($J_{POCH} = 10 \text{ Hz}$) 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 ³¹P NMR spectrum had a new resonance at δ +144, the ¹H NMR spectrum had a doublet at δ 3.33 (J_{POCH} = 13 Hz) and the ¹³C NMR spectrum, proton decoupled, had a doublet at δ 52.61 ($J_{POC} = 10.3 \text{ Hz}$).

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 ³¹P 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 $\delta + 89.6$

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 ³¹P 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.

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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 ¹H and ¹³C NMR spectroscopy⁶ in conjunction with Scheme I



Communications to the Editor

Table I. Polycycles by Cobalt-Catalyzed Acetylene Cyclization



decoupling and off-resonance decoupling experiments. Spectra calculated on the basis of models agreed well with observed ones.⁷ Quantitative protodesilylation (CF₃COOH-CCl₄, 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 $\times \frac{1}{4}$ 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



prepared by an alternate route⁸ 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 6chloro-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.



Second, regioisomers of the cycloadducts observed occur when added flexibility in the transition state to o-xylylene cycloaddition is available (cf. $3 \rightarrow 4$) or when electronic effects operate (cf. $5 \rightarrow 6$).

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 (CF₃COOH-ether, 1:1, 1% H₂SO₄, 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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- (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, Orgel¹ proposed that the π -bonding capabilities of the ligands in eight-coordinate, dodecahedral MX₄Y₄ 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 $d\pi \rightarrow p\pi$ 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 $p\pi \rightarrow d\pi$ 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 be-



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.

tween these complexes is the electronic configuration of the metal ion. In the former compound, a d² 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 $[Ti(Et_2mtc)_4]$ ($Et_2mtc =$ 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- $(C_2H_5)_2)_4$ 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: $\nu(C \cdots O)$ and v(C=N), 1547 and 1530; v(C=S), 941; v(Ti-O), 558; and ν (Ti-S), 320 cm⁻¹ (Nujol mull).

Crystal data: $Ti(C_5H_{10}NOS)_4$, 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)°; $d_{\text{measd}} = 1.267$ $g \text{ cm}^{-3}$, Z = 4, $d_{calcd} = 1.266 \text{ g cm}^{-3}$. 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 $2\theta_{MoK\alpha} < 65^{\circ}$ (the equivalent of 1.6 limiting Cu K $\tilde{\alpha}$ spheres) and $|F_o| >$ $2\sigma(|F_0|)$ measured with a Picker FACS-I automated diffractometer.