POLYMER COMPONENTS INVOLVING PHOSPHORUS(III)

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The stability of the ring \( \left( \text{R}_2 \text{P} \text{F}_3 \text{H}_2 \right) \), trimers relative to the open-chain \( \left( \text{R}_2 \text{P} \text{F}_3 \text{H}_2 \right)_n \) high-polymers is discussed theoretically in relation to other polymer types. Some stabilization of the trimers by B-H to Pd \( \text{P} \text{F}_3 \text{H}_2 \) bonding is indicated by infrared spectroscopy but not thereby proved. For stabilization of phosphorborine high-polymers it seems best to form more cross-linkages, as in retins made by incorporating \( \text{R}_2 \text{P} \text{F}_3 \text{H}_2 \) units in boron-hydride polymers. Toward the further development of this possibility, new kinds of polyphosphine derivatives have been extensively explored. Some of the new types may be of interest in relation to other kinds of polymers as well.

The strongly bonded multivalence of phosphorus makes it an important connecting atom for polymers; but in its development as a polymer component it has been mostly pentavalent, as in the well-known polyphosphates and polymeric phosphate esters or the \( \left( \text{X}_2 \text{P} \text{F}_3 \text{H}_2 \right)_n \) system. Utilization of trivalent phosphorus for polymers has been slow, perhaps mostly because most substituted phosphines are very reactive, labile, or unstable substances. However, a more thorough study of phosphorus(III) chemistry has brought forth a variety of new types of combination and may yet offer new paths to thermally stable polymers. Especially, the incorporation of new phosphine bases in boron-hydride networks offers considerable promise but should be investigated much further in detailed variety.

Such a more thorough study requires many new organophosphine derivatives, and accordingly much of our recent work has been turned toward the discovery of novel phosphines and polyphosphines which might be applicable to polymer development. The possible value of these new phosphorus(III) compounds need not be limited to P-P-H resins; for example, the C-P-Phosphines point toward interesting new ways to connect or cross-link fluorocarbon polymer chains, or to vulcanize rubber, or to make \( \left( \text{X}_2 \text{P} \text{F}_3 \text{H}_2 \right)_n \) polymers in which \( \text{X} \) is a ring-connecting polynuclear or fluorocarbon or heavy metal salt. Such phosphines even can connect nickel carbonyl units to make a polymer, and may relate even more broadly to coordination polymers of the transition elements. Further relations to polymer chemistry will appear as the properties of the new phosphine types are discussed in more detail. The possible lines of new knowledge in this field are so numerous that this presentation must be regarded only as a start rather than as a mature development.
New Knowledge of Phosphinoborine Polymers

The Stability of [(CH₃)₃P][PH₆]ₙ Polymers. Open-chain polymers of the (H₃)₃PH₆ unit have been made by using a phosphine base or amine to complete the four-coordination of a chain-ending boron atom; but heat converts such polymers to the very stable trimer [(H₃)₃p][PH₆]₃. Various devices may be suggested for preserving the high-polymer chain; one might seek a Lewis acid which would serve to coordinate the chain-ending phosphorus atom without being quite strong enough to remove the base from the other end or the acid might gain some stability if it were employed as a plasticizer incorporated in an otherwise too brittle but thermally stable resin made from B₃H₆ and a phosphine base; or one might place large hydrocarbon units on the phosphorus atom so that the chain-form (PH₆)ₙ ring would be strained by axial-group interference. However, none of these devices would offer much advantage if thermodynamic considerations fail to confer upon the open-chain polymers any special stability of their own, as it seems to do for the trimer form. Thus a thermodynamic argument is needed to decide whether the instability of the open chains can be overcome.

One factor strongly affecting the stability of simple open-chain polymers is the increase of translational entropy when one large polymer molecule is converted to many small rings such as the trimer. Designating the polymer unit as U, we can define for the breakdown an equilibrium constant \[ K = \frac{[U]}{[U]} \], and \[ \Delta F = -\Delta H - \Delta S = -RT \ln K \], so that a positive \[ \Delta S \] means a larger value of \[ K \], favoring the trimer form. Still smaller molecules would be favored even more by the entropy effect, but they often would represent too great a loss of bond energy, which is part of the term \[ \Delta H \].

Favorable to the high polymers would be the entropy of their bond bending and rotation, whereby many distinct configurations are possible, in contrast to the relatively fixed structures of small rings. This effect probably does not ever quite compensate for the complete freedom of separate molecules, but its importance must vary greatly from one polymer system to another. In polymer chains with very small polarity between adjacent chain atoms there would be little chain-to-chain attraction, so that the packing of chains would be fairly random and the entropy high; but when the polarity alters from atom to atom down the chain, the packing tends to become fixed and the entropy is far less. A good example is the base-supported chain \( \text{(Base}^+)\{\text{H}^2 \text{P} \text{Me} \text{Me} \} \), which rapidly and completely breaks down to \( \text{Me} \text{Me} \text{Me} \).

the free base, the monomer \( \text{(CH₃)₃NH₂} \), and the dimer \( \text{(CH₃)₃NHMe₂} \). But even this monomer-dimer mixture is metastable relative to the trimer \( \text{(CH₃)₃NHMe₃} \), even though this has some steric strain because of contact among the axial methyl groups. There must also be some alternating polarity in the \( \text{(Base}^+)\{\text{H}^2 \text{P} \} \) chain, although this \( \text{H} \text{Me} \text{Me} \) charge effect is diminished by the larger volume of the phosphorus atom as well as by some special electronic effects. In sum, the entropy effect probably is a major reason for the low stability of the long-chain \( \text{(CH₃)₃P}[\text{PH₆}] \) polymers relative to the trimer.
Another approach toward stabilization of long-chain polymers would be to choose a bonding situation such as to demand bond angles wider than could occur in small rings. Then the high polymer may be actually stabler than small rings of the same unit, if alternation of polarity in the chain can be minimized at the same time. A good example would be the C-HalSiO (silicate) polymers, in which the normal Si-O-Si bond angle seems to be nearly 135°, while the O-Si-O angle also is definitely wider than the tetrahedral 109.5°. Such wide angles would correlate with the use of two lone electron-pairs on each oxygen for Feeney 2p-3d π'-ative bonding to silicon. This supplementary bonding not only widens the chain-bond angles and lends extra strength, but also overcomes much of the alternating polarity in the chain, so that the high-polymer chain can be fairly free to develop the many attitudes leading to high entropy. In the (XePN)ₙ polymers the N-P π'-ative bonding is even more obvious, and is especially strong when X is Cl or some more electronegative group. Then the wide P-N-P angles and the minimization of chain polarity mean that small rings actually convert to higher polymers on heating.

A somewhat similar bond-widening effect seems to be present also in [(CH₃)₂PB₃]ₙ, for W. C. Hamilton's X-ray study (Acta Cryst. 8, 1964) showed the 3-P-B angle to be near 116° and the P-B-P angle near 112°. But if there is to be any plan to improve this bond-widening effect, in order to maintain a high-polymer form with no loss of bond-strength, the situation needs to be understood from a theoretical viewpoint, supported by experimental facts.

Spectroscopic Evidence of Structure. The relatively wide bond angles in the [(CH₃)₂PB₃]ₙ ring suggest that two P-B bonding, includes some B to P π'-ative bonding; which would be possible only through some delocalization of the B-H bonding electrons for interaction with the appropriate P₂d orbitals. One effect of this would be to widen the H-B-H angle, which Hamilton actually reports as 119.3°, well above the rough prediction of 108°, based on the normal effect of a 112° P-B-P angle. Another effect would be to improve the P to B π'-ative bonding by partially neutralizing the formal charge, normally written as P⁺B⁻. A contrary argument, to the effect that both P to B π'-ative bonds on each boron atom would have relatively low electron-density on boron, and so permit the H atoms to turn toward a linear pattern, would fail to account for the high stability of the trimer ring. However, the whole structural hypothesis rests upon the assumption that the H-B-H bond angle really is as wide as reported. A really dependable placement of hydrogen in a molecule having the scattering power contributed by the three nearby P atoms is so difficult that an independent approach to the subject, as by way of infrared spectroscopy, seems necessary.

Toward this purpose we have recorded the infrared spectra of [(CH₃)₂PB₃]ₙ, [(CH₃)₂PB₃]₉, [(CH₃)₂PB₃]₁₅, [(CH₃)₂PB₃]₂₄, and [(CH₃)₂PB₃]₄₈ in a definite manner, with [(CH₃)₂PB₃]ₙ for comparison and with some data also for the new trimer (CH₃)₂C₅P₃B₃H₅.

Of primary interest in relation to the above theory was the indication that the BH₃ wagging mode increases frequency much more sharply than does the BH₃ rocking mode, with step-wise replacement
of CH₄ by the far more electronegative CF₃ groups. This result may be explained as due to an increase in the H-B-H angle as phosphorus becomes more electronegative. To understand this situation, we must define the BH₂ rocking and wagging vibrations in terms of the following picture of a phosphinoborine trimer with one BH₂ group magnified.

For both the rocking and wagging modes we assume that the BH₂ group retains a fixed shape. Then rocking is an in-plane motion of the pair of H atoms along the dotted circle, while boron performs a small back-lash. Wagging is an out-of-plane motion of the pair of H atoms along a cylindrical surface with the dashed line as the axis, while boron performs a small out-of-plane back-lash. Evidently the radius of gyration will change little with increasing H-B-H angle as far as the rocking mode is concerned, but for wagging the radius of gyration decreases with the cosine of the half-angle, measured at the center of gyration. Now for the same reduced mass, the vibrational frequency increases inversely to the decreasing radius of gyration; hence for a wider H-B-H angle we must expect a higher vibrational frequency for wagging, but little change of rocking frequency.

The actual frequencies for these wagging and rocking modes, as recognized by BH₂-BH₂ comparisons, are shown in the following table. Trimer of (CH₃)₂PHH₂ (CH₃)₂PBD₂ CH₃CF₃PHH₂ (CF₃)₂PHH₂ (CF₃)₂PBD₂ Wagging 310 w 603 ms 903 ms 995 mw 755 w Rocking 665 mw 515 w 695 m 711 ms 535 w

Thus the results agree with the qualitative predictions from the theory, which needs to be developed in a more nearly quantitative manner if it is to be tested rigorously by reference to the observed frequencies. It is apparent that the H-B-H angle is widened by making phosphorus more electronegative, but the exact meaning of this effect can be judged only through rigorous and very difficult wave-mechanical calculations. It does seem that the trifluoromethyl compound (CF₃)₂PHH₂ is far stabler than it could be if there were no B-H to P-B interaction, but the indicated increase in this effect, relative to (CH₃)₂PHH₂, is not enough to compensate for the weaker P-B sigma bonding by the more electronegative phosphorus atom. Then the main problem is still with us: how to improve the action of the P-Bd orbitals toward linearizing the polymer bonding, without at the same time weakening the whole bonding pattern.

In the meantime, the phosphino-polypedorane resins have been well worthy of further development. The possible pattern of invention of such resins is considerably broadened by the discovery of new areas of polyphosphine chemistry, as next described.

Polyphosphine Chains and Rings

Polyphosphines based on P-P bonding have been very rare and little understood; yet their study is important not only on account
of their possible utility for making thermally stable phosphorus-polyborane resins, but also because they raise significant questions concerning the theory of polymer bonding. For example, the slightly volatile ring compounds \((\text{C}_3\text{P}_3)\) and \((\text{C}_3\text{P}_3)\), although interconvertible by a catalyst such as trimethylphosphine, are thermodynamically stabler than any other \((\text{C}_3\text{P}_3)\) polymers; nevertheless these rings are easily opened by alcoholsysis reactions to form the furthest and least stable open-chain \((\text{C}_3\text{P}_3)\) polyphosphines, along with least-studied alkoxy-polyposphines of the types \((\text{C}_3\text{P}_3)\)H and \((\text{C}_3\text{P}_3)\)OR. The initial reaction evidently forms \((\text{C}_3\text{P}_3)\)H and then a second P-F bond cleavage occurs almost at random, forming polyphosphines and alkoxy-polyposphines with groups varying from 1 to 1. The dicydrogen polyphosphines decompose most easily when the \(\text{P}_4\) chain is longest, according to the general equation \(\text{H}(\text{C}_3\text{P}_3)\)H \(\rightarrow\) \((\text{C}_3\text{P}_3)\)H \(+\) \((\text{C}_3\text{P}_3)\)m \(-\) \(\text{H}\) arriving finally at a mixture of \((\text{C}_3\text{P}_3)\), \((\text{C}_3\text{P}_3)\), and \((\text{C}_3\text{P}_3)\).

Other chain polyphosphines can be built up by reactions such as \((\text{C}_3\text{P}_3)\)H \(\rightarrow\) \((\text{C}_3\text{P}_3)\)H \(+\) \((\text{C}_3\text{P}_3)\)H + \(\text{P}_3\) \((\text{C}_3\text{P}_3)\). Again the stability decreases sharply with increasing chain length. Thus the decomposition \((\text{C}_3\text{P}_3)\) \(\rightarrow\) \((\text{C}_3\text{P}_3)\)H \(+\) \((\text{C}_3\text{P}_3)\) requires heating above 350°C, whereas the process \((\text{C}_3\text{P}_3)\) \(\rightarrow\) \((\text{C}_3\text{P}_3)\)H + \(\text{P}_3\) \((\text{C}_3\text{P}_3)\) can be observed at room temperature.

The evident metastability of these open-chain polyphosphines can be ascribed to the greater stability of the \((\text{C}_3\text{P}_3)\) rings. To explain that, one must consider a few contributing causes. First is the increased entropy of the open-chain polyphosphines as decomposition into a larger number of molecules: the general process \(\text{H}(\text{C}_3\text{P}_3)\)H \(\rightarrow\) \((\text{C}_3\text{P}_3)\)H \(+\) \((\text{C}_3\text{P}_3)\)H + \(\text{P}_3\) \((\text{C}_3\text{P}_3)\) increases the translational entropy in accord with m - 1 more molecules per n moles of the chain polyphosphate. However, the entropy of bond rotation and bending in the open chains is higher than in the relatively fixed ring structures, so that the net increase of entropy in the conversion to the monophosphate and the ring compound is less than the increase of translational entropy alone.

Another cause of the special stability of ring polyphosphinates is the behavior of the lone-pair electrons on phosphorus. In any P-F bonding situation we must expect a delocalization of these lone pairs through interaction with the nearest P-F orbitals. In a chain, this effect gives less supplementary bond energy for the end phosphorus atoms than for those in the middle; and in a ring the delocalization contributes the most bond energy per phosphorus atom. But then in \((\text{C}_3\text{P}_3)\) and \((\text{C}_3\text{P}_3)\) there is still another effect: a bonding action by the lone-pair electrons reaching across the ring. This effect is strong enough to distort the \(\text{P}_4\) ring from the expected square form into a bispheonoid pattern, with P-P bond angles of 84.7° instead of 90° (Dohnohe and Palenik, Acta Cryst., in press); and the \(\text{P}_4\) ring has a similar twist in its pattern. All of the factors here cited—entropy and two kinds of P-P bond bonding, serve to make \((\text{C}_3\text{P}_3)\) and \((\text{C}_3\text{P}_3)\) not only stabler than open chains, but also stabler than the higher \((\text{C}_3\text{P}_3)\) ring compounds.

For all their stability, however, \((\text{C}_3\text{P}_3)\) and \((\text{C}_3\text{P}_3)\) can be
depolymerized quite easily by reaction with trimethylphosphine, to make the monomer-complex \((\text{CH}_3)_3\text{P-FCF}_3\). Here we recognize that the sigma-dative \(\text{P}-\text{F}\) bond is supplemented by \(\pi\)-dative bonding in the opposite direction, by the two lone-pairs on the \(\text{FCF}_3\) group; however, there could be no such \(\pi\)-bonding in the similarly stable complex \((\text{CH}_3)_3\text{N-FCF}_3\). Both of these monomer-complexes can be dissociated in vivo, with recovery of the tertiary bases and an equilibrium mixture of \((\text{CF}_3)\text{P}^-\) and \((\text{CF}_3)\text{P}\). Thus a base catalyzes the interconversion of these ring phosphorus; and the same effect accounts for the base-catalysis of the decomposition of the open-chain polyporphosphines. It is also interesting that the dissociation of the \(\text{FCF}_3\) complexes makes this unit available for many chemical reactions which would be far harder to perform by the direct use of the \((\text{CF}_3)\text{P}\) ring compounds.

**Hydrocarbon-Fluorocarbon Phosphines**

It is well established that hydrocarbon substituents on \(\text{P}\) in phosphines greatly enhance the base strength of phosphorus, whereas fluorocarbon groups have the opposite effect, actually causing the phosphorus to behave as an electron-acceptor (Lewis acid) in some compounds. The resulting extreme chemical differences between the \((\text{CH}_3)_3\text{P}\) and \((\text{CF}_3)\text{P}\) groups make it important to know more about the chemistry of the intermediate \(\text{CH}_3\text{CF}_3\text{P}\) group. Another reason for developing syntheses of \(\text{CH}_3\text{CF}_3\text{P}\) compounds is for comparison of methyl with trifluoromethyl in regard to ease of \(\text{P}-\text{C}\) bond cleavage. If the present indications are borne out—to the effect that it is much easier to remove \(\text{CH}_3\) than \(\text{CF}_3\) from its bond to phosphorus—we may expect that the projected hydrocarbon-connected double phosphine \(\text{CH}_3\text{CF}_3\text{PCH}_2\text{CF}_3\text{PCH}_3\text{CF}_3\) could be brought to reaction with \(\text{H}_2\text{B}\) to make phosphine-polyborane resists from which \(\text{H}_2\text{B}\) could be driven out by heat. Thus as the temperature is raised the cross-linking must increase, tending to maintain the mechanical properties of the resin during the rise of temperature. If all of the \(\text{CF}_3\) groups were taken off, the final bonding unit would be \(\text{CH}_3\text{PCH}_2\text{HCH}_3\), which should give resins having mechanical strength quite superior to that of resins incorporating only \((\text{CH}_3)_2\text{P}\) groups in the boron-hydride polymer.

**Synthesis of CH\(_3\)CF\(_3\)-Phosphines.** Fair yields of \(\text{CH}_3\text{CF}_3\text{PFI}\) can be obtained by the addition of methyl iodide to \((\text{CF}_3)\text{P}\), at 150°C. (a process requiring critical control of time and temperature) or by the action of iodine on \(\text{CH}_3\text{P(CF}_3)\) at 200°C. Or one can attach methyl iodide to the monomer-complex \((\text{CH}_3)_3\text{P-FCF}_3\) and treat the solid product with HCl to make a mixture which dimethylamine converts to the aminophosphine \((\text{CH}_3)_3\text{NPFCH}_3\text{CF}_3\). From this it is easy to make a \(\text{CH}_3\text{CF}_3\text{P}-\text{halide} by reaction with the hydrogen halide.

The phosphine \(\text{CH}_3\text{CF}_3\text{P=PH}\) can be made in reasonable yields by the process \(2\text{H}_2\text{PH} + \text{CF}_3\text{I} \rightarrow \text{CH}_3\text{PH}_2\text{I} + \text{CH}_3\text{CF}_3\text{PH}\), during two weeks at \(-78^\circ\text{C}\); or one can use \(\text{PH}_3\) to displace iodine from \(\text{CH}_3\text{CF}_3\text{PFI}\), for a very efficient conversion to \(\text{CH}_3\text{CF}_3\text{PH}\). This use of phosphine is closely related to our synthesis of a new diphosthine and a new triphosphine, as described in the following section.

For the diphosphpine \(\text{CH}_3\text{CF}_3\text{P-PCH}_3\text{CF}_3\) a number of procedures are effective, but the most unusual is the action of HCl on the adduct.
\((\text{CS})_6\)P\(\cdot\text{PO}_{2}\)-2\(\text{CH}_2\)I in liquid sulfur dioxide. The production of the \(\text{R}_2\text{P}-\text{R}_2\) type of compound here must be accompanied by the oxidation of some other component of the mixture, but at present writing it is difficult to conjecture what the oxidation product may be.

The Reaction of \((\text{CF}_3)_2\text{PF}\) with \(\text{CH}_3\text{PH}_2\). The reaction \((\text{CF}_3)_2\text{PF} + 2\text{CH}_3\text{PH}_2 \rightarrow \text{CH}_3\text{PH}_2\text{H}_3 + \text{CH}_3\text{FP}-\text{P}(\text{CF}_3)_2\) was nearly quantitative at -78°C. The resulting new diphenylphosphine (b.p. est. 92°C.) was decomposed by light or heat, quantitatively forming \((\text{CF}_3)_2\text{PH}\) and viscous oily material which might have included \((\text{CH}_3\text{P})_n\) polymers.

The reaction of \(\text{CH}_3\text{H}_2\text{P}(\text{CF}_3)_2\) with more \((\text{CF}_3)_2\text{PF}\) and \((\text{CH}_3)_2\text{N}\) gave a very high yield of the new triphenylphosphine \(\text{CH}_3\text{P}(\text{CF}_3)_2\) (b.p. est. 135°C.), which proved to be stable on heating to 74°C, but decomposed completely during 20 hours at 160°C.

Both the diphenylphosphine and the triphenylphosphine showed ultraviolet absorption, with wide, flat peaks near 2200 Å. and very shallow minima at 2525 and 2100 Å., results suggesting a complex pattern of lone-pair electronic delocalizations from two different phosphorus atoms in each compound. The potential for further syntheses from these new polyphosphines has not been much explored.

Hydrocarbon-connected Polyphosphines. Diphosphines of the type \(\text{R}_2\text{P}-\text{R}_2\) have the pseudohalogen property of adding into carbon-carbon pi bonds, more easily when the R groups are more electronegative. For example, \((\text{CF}_3)_2\text{P}-\text{P}(\text{CF}_3)_2\) reacts with \(\text{H}_2\text{C}=\text{CH}_2\) at room temperature to give 95% yields of \((\text{CF}_3)_2\text{PC}_{2}\text{H}=\text{CH}(\text{CF}_3)_2\) (b.p. est. 135°C.), whereas the similar action of \((\text{CH}_3)_2\text{P}-\text{P}(\text{CH}_3)_2\) to give high yields of the bis-phosphine \((\text{CH}_3)_2\text{PC}_{2}\text{H}_2\text{P}(\text{CH}_3)_2\) (b.p. est. 188°C.) requires heating nearly to 300°C. In both cases the minor side reactions; for example the \(\text{C}_6\text{H}_5\text{CH}_2\text{P}(\text{CF}_3)_2\) reaction at 65°C. gives a 1.5% yield of \((\text{CF}_3)_2\text{P}\), showing that there is some cleavage and new connections of P-CF bonds.

The addition of \(\text{P}_2(\text{CF}_3)_4\), to \(\text{CF}_3\text{P}\) is less spontaneous, but can be promoted by a catalytic trace of iodine. However, one effect of iodine is to form C-I bonds, which add across the CF=CF=CF pi bond, so that larger fluorocarbon units are formed. Thus after a 3-4-hour heating at 160°C., nearly 14% of the consumed CF3P had been converted to cyclo-CF3P and twice as much had gone to form the heterocyclic phosphine CF3PCF3. Even so, the yield of \((\text{CF}_3)_2\text{PC}_{2}\text{H}_2\text{P}(\text{CF}_3)_2\) (b.p. est. 127°C.) represented nearly 60% of the consumed \(\text{P}_2(\text{CF}_3)_4\), about 5% of which went to form \((\text{CF}_3)_2\text{P}\). The non-volatile by-products were assumed to be polymer.

The reaction of \(\text{P}_2(\text{CF}_3)_4\) with acetylene also required catalysts by iodine, and gave a still wider variety of by-products arising from the cleavage of P-CF3 bonds. The nearly equimolar mixture was heated with a trace of iodine for 67 hours at 107°C., giving a 57% yield of \((\text{CF}_3)_2\text{PC}_{2}\text{H}_2\text{P}(\text{CF}_3)_2\) and 7% \((\text{CF}_3)_2\text{P}\), 3% \((\text{CF}_3)_2\text{P}_{2}\text{H}_2\text{P}(\text{CF}_3)_2\), 6% of the triphosphine \(\text{CF}_3\text{P}(\text{CF}_3)_2\text{PC}_{2}\text{H}_2\text{P}(\text{CF}_3)_2\), and smaller yields of polyphosphines slightly less volatile than this last. A non-volatile oil probably represented a polymer-chain principle. The new bis-phosphines \((\text{CF}_3)_2\text{PC}_{2}\text{H}_2\text{P}(\text{CF}_3)_2\) proved to have a trans configuration, probably because the cis form would be sterically unfavorable; and steric

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interference also may be the chief reason that this double tertiary phosphine cannot receive another $P_{2}(CF_{3})_{4}$ into the remaining pi bond.

Yet another bis-phosphine was made by the fairly easy reaction $2(CF_{3})_{2}PCl + 2C_{2}H_{2} + 2(CH_{3})_{2}N \rightarrow 2(CH_{3})_{2}NEC_{2} + (CF_{3})_{2}P-Cac-P(CF_{3})_{2}$. This also failed to add $P_{2}(CF_{3})_{4}$ to the carbon-carbon pi bonds.

**Hydroboration of These Polyphosphines.** Of the above hydrocarbon-connected polyphosphines, those having C-C pi bonds all reacted with diborane at room temperature or even lower, adding one BH$_{2}$ to each such pi bond. Thus the compound $(CF_{3})_{2}P(C_{2}H_{2})_{2}(CF_{3})_{2}$ formed the RBB$_{2}$ and $H_{R}$ molecular weight indicating two forms: the bridged dimer $H_{R}H_{R}$ and a monomer having a P-B dative-bonded four-atom ring. Similarly, $(CF_{3})_{2}P-O=C-P(CF_{3})_{2}$ added two BH$_{2}$ groups to make an R(BH$_{2}$)$_{2}$ type, with some uncertainty whether both boron atoms went to the same carbon atom. Also, $CF_{3}P(C_{2}H_{2})(CF_{3})_{2}$ formed an R(BH$_{2}$)$_{2}$ type with a considerable variety of possible structures.

These hydroboration reactions show the possibility of using C-C pi-bonded polyphosphines for making phosphorus-polyborane resins in which the phosphine-base units not only would be incorporated in the boron hydride polymer, but also would be connected by $P_{2}H_{2}$ units acting at the same time as substituents for hydrogen on boron. For best results, however, it might be well to develop polyphosphines of this type with CH$_{3}$ groups instead of CF$_{3}$. The resulting resins then should have at least as much resistance to elevated temperatures as the monophosphine-polyborane resins, but far better mechanical strength.

**Oxyphosphines**

Possible Polymers. It is interesting to consider high-polymer chains in which trivalent phosphorus alternates with oxygen, not only because they would belong to a new polymer system which would be useful for testing theories of the stability of long open chains, but also because the phosphorus lone-pair electrons could attach oxidizing groups to make useful new polymers of pentavalent phosphorus. For stability, however, the --O-P-O-P-- chains probably must have just the right R groups on phosphorus. For example, our new compound $(CF_{3})_{2}POP(CF_{3})_{2}$ proved to be quite stable, whereas all attempts to make the corresponding methyl derivative $(CH_{3})_{2}POP(CH_{3})_{2}$ led only to equimolar yields of $(CH_{3})_{2}P-O(CH_{3})_{2}$ and $(CH_{3})_{2}O-P(CH_{3})_{2}$. In order to understand this result we may suppose that tetrakisethylphosphoxane would easily rearrange in the Abuzam manner $R_{2}FOR \rightarrow R_{2}PFO$, with one $P(CH_{3})_{2}$ group playing the role of R, for P-O bonding to $P(CH_{3})_{2}$. Then the resulting diphosphine monoxide $(CH_{3})_{2}P-O(P(CH_{3})_{2})$ would very rapidly disproportionate by exchanging a $(CH_{3})_{2}PO$ group for $(CH_{3})_{2}P$ to give the observed result. The initial rearrangement to the diphosphine monoxide would be far more difficult in the case of $(CF_{3})_{2}POP(CF_{3})_{2}$ because here phosphorus lacks the base strength to bond a $(CF_{3})_{2}P^{+}$ group effectively, and the P-O-P bonding should be
greatly strengthened by Osp-Pag pl bonding. For similar reasons, the (CF₃PO)ₙ polymers might well be stable (with a preference for long chains and wide bond angles), whereas the analogous (CH₃PO)ₙ polymers might not exist at all. Actually, a polymer-bonding of CF₃PO units does seem to exist, according to results obtained in the following study of acetoxynophosphines.

The Acetoxynophosphine Approach. It was considered probable that (CF₃PO)ₙ polymers would be formed by loss of AcO from a compound of the type CF₃P(OAc)₂. For the preliminary exploration of this kind of chemistry, the new compound (CF₃)₂P(OCCF₃)₉ (I) was made from AgCO₂CF₃ and (CF₃)₂PI. Its dissociation to (CF₃)₂P(O)PO(CF₃)₂ (II) and (CF₃PO)₂O (III) proved to be fairly fast at room temperature, but limited in extent. An infrared spectroscopic study gave a rough estimate of the dissociation constant as K = [III][II]/[I] = 0.11. The acetoxynophosphine (I) proved to be a readily volatile liquid, but its dissociation was too rapid to permit accurate characterization. Attempts to make the diacetoxynophosphine CF₃P(OOCOCF₃)₉ from AgCO₂CF₃ and CF₃PO₂ gave the anhydride (CF₃PO₂CF₃)₂ as the only volatile product. It seemed probable that a (CF₃PO)ₙ polymer was mixed with the silver iodide, and could not have been proportioned without forming the volatile compounds (CF₃PO)₂ and (CF₃PO)₃.

Next it was argued that the acetoxynophosphine (CF₃)₂P(OCCF₃)₉ would be stabler than the corresponding trifluoroacetoxynophosphine, for a less electronegative oxygen in the C-O-P bond would form a stronger Osp-Pag pl bond, while other differences would cancel out. Accordingly, (CF₃)₂PI was allowed to react with AgCO₂CF₃ to make (CF₃)₂P(OCCCF₃)₉, which proved to be entirely stable and not difficult to characterize: m.p. -58°C; b.p. est. 96°C.

The analogous reaction of CF₃PO₂ with AgCO₂CF₃ produced a major yield of acetic anhydride, along with nearly one-third of the calculated yield of a slightly volatile liquid purporting to be the desired diacetoxynophosphine CF₃P(OOCOCF₃)₉. On standing, this formed more acetic anhydride and a non-volatile white solid. This most probably was a diacetoxypolyphosphoxane embodying a short (CF₃PO)ₙ chain with acetox- end groups. It showed no tendency toward a disproportionation into (CF₃PO)ₙ rings and (CF₃PO₂)ₙ polymers, but on long standing it did form a red-brown gum in which the CF₃ groups seemed to exist in a wide variety of environments, leading to wide banding in its infrared spectrum. Thus the converse of the presumed diacetoxypolyphosphoxanes to a simple open-chain high polymer may be very difficult.

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