

## POLYMER COMPONENTS INVOLVING PHOSPHORUS(III)

Anton B. Burg

Department of Chemistry  
University of Southern California

The stability of the ring  $(R_2PBH_2)_3$  trimers relative to the open-chain  $(R_2PBH_2)_n$  high-polymers is discussed theoretically in relation to other polymer types. Some stabilization of the trimers by B-H to  $P_{3d}$  pi-dative bonding is indicated by infrared spectroscopy but not thereby proved. For stabilization of phosphinoborine high-polymers it seems best to form more cross-linkages, as in resins made by incorporating  $R_2P$  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  $(X_2PN)_n$  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-B-H resins; for example, the  $CF_3$ -phosphines point toward interesting new ways to connect or cross-link fluorocarbon polymer chains, or to vulcanize rubber, or to make  $(X_2PN)_n$  polymers in which X is a ring-connecting polyfunctional fluorocarbon or hydrocarbon moiety. 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  $[(CH_3)_2PBH_2]_n$  Polymers. Open-chain polymers of the  $(CH_3)_2PBH_2$  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  $[(CH_3)_2PBH_2]_3$ . 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 chain might gain some stability if it were employed as a plasticizer incorporated in an otherwise too brittle but thermally stable resin made from  $B_5H_9$  and a phosphine base; or one might place large hydrocarbon units on the phosphorus atom so that the chair-form  $(PB)_3$  ring would be strained by axial-group interference. However, none of these devices would offer much advantage if thermodynamics should 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  $K = (U_3)^n / (U_{3n})$ , and  $\Delta F = \Delta H - T\Delta S = -RT \ln K$ , 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  $(Base^+):(B^-N:)_n$ , which rapidly and completely breaks down to

$$\begin{array}{c} H_2 \quad Me_2 \\ | \quad | \\ B^- - N: \end{array}$$

the free base, the monomer  $(CH_3)_2NBH_2$ , and the dimer  $[(CH_3)_2NBH_2]_2$ . But even this monomer-dimer mixture is metastable relative to the trimer  $[(CH_3)_2NBH_2]_3$ , even though this has some steric strain because of contact among the axial methyl groups. There must also be some alternating polarity in the  $(Base^+):(B^-P:)_n$  chain, although this

$$\begin{array}{c} H_2 \quad Me_2 \\ | \quad | \\ B^- - P: \end{array}$$

charge effect is diminished by the larger volume of the phosphorus atom as well as some special electronic effects. In sum, the entropy effect probably is a major reason for the low stability of the long-chain  $(CH_3)_2PBH_2$  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  $(\text{CH}_3)_2\text{SiO}$  (silicone) polymers, in which the normal Si-O-Si bond angle seems to be nearly  $145^\circ$ , while the O-Si-O angle also is definitely wider than the tetrahedral  $109.5^\circ$ . Such wide angles would correlate with the use of two lone electron-pairs on each oxygen for two-way 2p-3d pi-dative 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  $(\text{X}_2\text{PN})_n$  polymers the N-P pi dative 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.

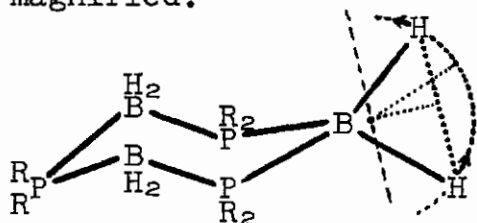
A somewhat similar bond-widening effect seems to be present also in  $[(\text{CH}_3)_2\text{PBH}_2]_3$ , for W.C. Hamilton's X-ray study (Acta Cryst. 8, 199 -- 1955) showed the B-P-B angle to be near  $118^\circ$  and the P-B-P angle near  $112^\circ$ . But if there is to be any plan to improve this 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  $[(\text{CH}_3)_2\text{PBH}_2]_3$  ring suggest that the B-P bonding includes some B to P pi bonding effect, which would be possible only through some delocalization of the B-H bonding electrons for interaction with the appropriate  $\text{P}_{3d}$  orbitals. One effect of this would be to widen the H-B-H angle, which Hamilton actually reports as  $119.3^\circ$ — well above the rough prediction of  $108^\circ$ , based upon the normal effect of a  $112^\circ$  P-B-P angle. Another effect would be to improve the P to B sigma dative bonding by partially neutralizing the formal charge, normally written as  $\text{P}^+\text{B}^-$ . A contrary argument, to the effect that both P to B dative 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  $[(\text{CH}_3)_2\text{PBH}_2]_3$ ,  $[(\text{CH}_3)_2\text{PBD}_2]_3$ ,  $[(\text{CF}_3)_2\text{PBH}_2]_3$ , and  $[(\text{CF}_3)_2\text{PBD}_2]_3$  in a definitive manner, with  $[(\text{CH}_3)_2\text{NBH}_2]_3$  for comparison and with some data also for the new trimer  $(\text{CH}_3\text{CF}_3\text{PBH}_2)_3$ .

Of primary interest in relation to the above theory was the indication that the  $\text{BH}_2$  wagging mode increases frequency much more sharply than does the  $\text{BH}_2$  rocking mode, with step-wise replacement

of  $\text{CH}_3$  by the far more electronegative  $\text{CF}_3$  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  $\text{BH}_2$  rocking and wagging vibrations in terms of the following picture of a phosphinoborane trimer with one  $\text{BH}_2$  group magnified.



For both the rocking and wagging modes we assume that the  $\text{BH}_2$  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  $\text{BH}_2\text{-BD}_2$  comparisons, are shown in the following table.

Trimer of	$(\text{CH}_3)_2\text{PBH}_2$	$(\text{CH}_3)_2\text{PBD}_2$	$\text{CH}_3\text{CF}_3\text{PBH}_2$	$(\text{CF}_3)_2\text{PBH}_2$	$(\text{CF}_3)_2\text{PBD}_2$
Wagging	810 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  $[(\text{CF}_3)_2\text{PBH}_2]_3$  is far stabler than it could be if there were no B-H to  $\text{P}_{3d}$  interaction, but the indicated increase in this effect, relative to  $[(\text{CH}_3)_2\text{PBH}_2]_3$ , 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  $\text{P}_{3d}$  orbitals toward linearizing the polymer bonding, without at the same time weakening the whole bonding pattern.

In the meantime, the phosphino-polyborane resins seem 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 upon 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  $(CF_3P)_4$  and  $(CF_3P)_5$ , although interconvertible by a catalyst such as trimethylphosphine, are thermodynamically stabler than any other  $(CF_3P)_n$  polymers; nevertheless these rings are easily opened by alcoholysis reactions to form the far less stable open-chain  $H(CF_3P)_mH$  polyphosphines, along with less-studied alkoxy-polyphosphines of the types  $H(CF_3P)_mOR$  and  $RO(CF_3P)_mOR$ . The initial reaction evidently forms  $H(CF_3P)_nOR$ ; and then a second P-P bond cleavage occurs almost at random, forming polyphosphines and alkoxy-polyphosphines with  $m$  varying from 1 to  $n - 1$ . The dihydrogen polyphosphines decompose most easily when the  $P_m$  chain is longest, according to the general equation  $H(CF_3P)_mH \rightarrow \frac{1}{n}(CF_3P)_n + H(CF_3P)_{m-1}H$ , arriving finally at a mixture of  $(CF_3P)_4$ ,  $(CF_3P)_5$ , and  $CF_3PH_2$ .

Other chain polyphosphines can be built up by reactions such as  $CF_3PH_2 + 2(CF_3)_2PI + (CH_3)_3N \rightarrow 2(CH_3)_3NHI + P_3(CF_3)_5$ . Again the stability decreases sharply with increasing chain length. Thus the decomposition  $P_2(CF_3)_4 \rightarrow \frac{1}{n}(CF_3P)_n + (CF_3)_3P$  requires heating above  $300^\circ C.$ , whereas the process  $P_3(CF_3)_5 \rightarrow \frac{1}{n}(CF_3P)_n + P_2(CF_3)_4$  can be observed at room temperature.

The evident metastability of these open-chain polyphosphines can be ascribed to the greater stability of the  $(CF_3P)_n$  rings. To explain that, one must consider several contributing causes. First is the increased entropy as the open-chain polyphosphines decompose to form a larger number of molecules: the general process  $nH(CF_3P)_mH \rightarrow nCF_3PH_2 + (m-1)(CF_3P)_n$  increases the translational entropy in accord with  $m-1$  more molecules per  $n$  moles of the chain polyphosphine. 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 monophosphine and the ring compounds is less than the increase of translational entropy alone.

Another cause of the special stability of ring polyphosphines is the behavior of the lone-pair electrons on phosphorus. In any  $\overset{\cdot\cdot}{P}-\overset{\cdot\cdot}{P}$ -bonding situation we must expect a delocalization of these lone pairs through interaction with the nearest  $P_{3d}$  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  $(CF_3P)_4$  and  $(CF_3P)_5$  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  $P_4$  ring from the expected square form into a bisphenoid pattern, with P-P-P bond angles of  $84.7^\circ$  instead of  $90^\circ$  (Donohue and Palenik, *Acta Cryst.*, in press); and the  $P_5$  ring has a similar twist in its pattern. All of the factors here cited—entropy and two kinds of  $P_{3p}-P_{3d}$  bonding, serve to make  $(CF_3P)_4$  and  $(CF_3P)_5$  not only stabler than open chains, but also stabler than the higher  $(CF_3P)_n$  ring compounds.

For all their stability, however,  $(CF_3P)_4$  and  $(CF_3P)_5$  can be

depolymerized quite easily by reaction with trimethylphosphine, to make the monomer-complex  $(\text{CH}_3)_3\text{P-PCF}_3$ . Here we recognize that the sigma-dative P-P bond is supplemented by pi-dative bonding in the opposite direction, by the two lone-pairs on the  $\text{PCF}_3$  group; however, there could be no such pi-bonding in the similarly stable complex  $(\text{CH}_3)_3\text{N-PCF}_3$ . Both of these monomer-complexes can be dissociated in vacuo, with recovery of the tertiary bases and an equilibrium mixture of  $(\text{CF}_3\text{P})_4$  and  $(\text{CF}_3\text{P})_5$ . Thus a base catalyzes the interconversion of these ring polymers; and the same effect accounts for the base-catalysis of the decomposition of the open-chain polyphosphines. It is also interesting that the dissociation of the  $\text{PCF}_3$  complexes makes this unit available for many chemical reactions which would be far harder to perform by the direct use of the  $(\text{CF}_3\text{P})_n$  ring compounds.

### Hydrocarbon-Fluorocarbon Phosphines

It is well established that hydrocarbon substituents on 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  $(\text{CH}_3)_2\text{P}$  and  $(\text{CF}_3)_2\text{P}$  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 P-C bond cleavage. If the present indications are borne out—to the effect that it is much easier to remove  $\text{CF}_3$  than  $\text{CH}_3$  from its bond to phosphorus—we may expect that the projected hydrocarbon-connected double phosphine  $\text{CH}_3\text{CF}_3\text{PC}_2\text{H}_4\text{PCH}_3\text{CF}_3$  could be brought to reaction with  $\text{B}_5\text{H}_9$  to make phosphino-polyborane resins from which  $\text{HCF}_3$  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  $\text{CH}_3\text{P}(\text{C}_2\text{H}_4)\text{PCH}_3$ , 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  $\text{CH}_3\text{CF}_3$ -Phosphines. Fair yields of  $\text{CH}_3\text{CF}_3\text{PI}$  can be obtained by the addition of methyl iodide to  $(\text{CF}_3\text{P})_4$  at  $150^\circ\text{C}$ . (a process requiring critical control of time and temperature) or by the action of iodine on  $\text{CH}_3\text{P}(\text{CF}_3)_2$  at  $200^\circ\text{C}$ . Or one can attach methyl iodide to the monomer-complex  $(\text{CH}_3)_3\text{P-PCF}_3$  and treat the solid product with  $\text{HCl}$  to make a mixture which dimethylamine converts to the aminophosphine  $(\text{CH}_3)_2\text{NPCH}_3\text{CF}_3$ . From this it is easy to make a  $\text{CH}_3\text{CF}_3\text{P-halide}$  by reaction with the hydrogen halide.

The phosphine  $\text{CH}_3\text{CF}_3\text{PH}$  can be made in reasonable yields by the process  $2\text{CH}_3\text{PH}_2 + \text{CF}_3\text{I} \rightarrow \text{CH}_3\text{PH}_3\text{I} + \text{CH}_3\text{CF}_3\text{PH}$ , during two weeks at  $-78^\circ\text{C}$ .; or one can use  $\text{PH}_3$  to displace iodine from  $\text{CH}_3\text{CF}_3\text{PI}$ , 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 diphosphine and a new triphosphine, as described in the following section.

For the diphosphine  $\text{CH}_3\text{CF}_3\text{P-PCH}_3\text{CF}_3$  a number of procedures are effective, but the most unusual is the action of  $\text{HCl}$  on the adduct

$(\text{CH}_3)_3\text{P}\cdot\text{PCF}_3\cdot\text{CH}_3\text{I}$  in liquid sulfur dioxide. The production of the  $\text{R}_2\text{P}-\text{PR}_2$  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  $(\text{CF}_3)_2\text{PI}$  with  $\text{CH}_3\text{PH}_2$ . The reaction  $(\text{CF}_3)_2\text{PI} + 2\text{CH}_3\text{PH}_2 \rightarrow \text{CH}_3\text{PH}_3\text{I} + \text{CH}_3\text{HP}-\text{P}(\text{CF}_3)_2$  was nearly quantitative at  $-78^\circ\text{C}$ . The resulting new diphosphine (b.p. est.  $92^\circ\text{C}$ .) 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  $\text{CH}_3\text{HP}-\text{P}(\text{CF}_3)_2$  with more  $(\text{CF}_3)_2\text{PI}$  and  $(\text{CH}_3)_3\text{N}$  gave a very high yield of the new triphosphine  $\text{CH}_3\text{P}[\text{P}(\text{CF}_3)_2]_2$  (b.p. est.  $136^\circ\text{C}$ .), which proved to be stable on heating to  $74^\circ\text{C}$ . but decomposed completely during 20 hours at  $160^\circ\text{C}$ .

Both the diphosphine and the triphosphine showed ultraviolet absorption, with wide, flat peaks near  $2200 \text{ \AA}$ . and very shallow minima at  $2025$  and  $2100 \text{ \AA}$ .— results suggesting a complex pattern of lone-pair electronic delocalizations from two different phosphorus-atom situations in each compound. The potential for further syntheses from these new polyphosphines has not been much explored.

Hydrocarbon-Connected Polyphosphines. Diphosphines of the type  $\text{R}_2\text{P}-\text{PR}_2$  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  $(\text{CF}_3)_2\text{PC}_2\text{H}_4\text{P}(\text{CF}_3)_2$  (b.p. est.  $135^\circ\text{C}$ .), 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  $(\text{CH}_3)_2\text{PC}_2\text{H}_4\text{P}(\text{CH}_3)_2$  (b.p. est.  $188^\circ\text{C}$ .) requires heating nearly to  $300^\circ\text{C}$ . In both cases there are minor side reactions; for example the  $\text{C}_2\text{H}_4-\text{P}_2(\text{CF}_3)_4$  reaction at  $65^\circ\text{C}$ . gives a 1.5% yield of  $(\text{CF}_3)_3\text{P}$ , showing that there is some cleavage and new connections of P- $\text{CF}_3$  bonds.

The addition of  $\text{P}_2(\text{CF}_3)_4$  to  $\text{C}_2\text{F}_4$  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  $\text{F}_2\text{C}=\text{CF}_2$  pi bond, so that larger fluorocarbon units are formed. Thus after a 34-hour heating at  $165^\circ\text{C}$ ., nearly 14% of the consumed  $\text{C}_2\text{F}_4$  had been converted to cyclo- $\text{C}_4\text{F}_8$ ; and twice as much had gone to form the heterocyclic phosphine  $\text{CF}_3\text{PC}_4\text{F}_8$ . Even so, the yield of  $(\text{CF}_3)_2\text{PC}_2\text{F}_4\text{P}(\text{CF}_3)_2$  (b.p. est.  $127^\circ\text{C}$ .) represented nearly 60% of the consumed  $\text{P}_2(\text{CF}_3)_4$ , about 8% of which went to form  $(\text{CF}_3)_3\text{P}$ . The non-volatile by-products were assumed to be polymeric.

The reaction of  $\text{P}_2(\text{CF}_3)_4$  with acetylene also required catalysis by iodine, and gave a still wider variety of by-products arising from the cleavage of P- $\text{CF}_3$  bonds. The nearly equimolar mixture was heated with a trace of iodine for 67 hours at  $100^\circ\text{C}$ ., giving a 57% yield of  $(\text{CF}_3)_2\text{PC}_2\text{H}_2\text{P}(\text{CF}_3)_2$ , 7%  $(\text{CF}_3)_3\text{P}$ , 3%  $(\text{CF}_3)_2\text{PC}_2\text{H}_2\text{CF}_3$ , 6% of the triphosphine  $\text{CF}_3\text{P}[\text{C}_2\text{H}_2\text{P}(\text{CF}_3)_2]_2$ , and smaller yields of polyphosphines slightly less volatile than this last. A non-volatile oil probably represented a polymer-chain principle. The new bis-phosphine  $(\text{CF}_3)_2\text{PC}_2\text{H}_2\text{P}(\text{CF}_3)_2$  proved to have a trans configuration, probably because the cis form would be sterically unfavorable; and steric

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  $2(CF_3)_2PCl + C_2H_2 + 2(CH_3)_3N \rightarrow 2(CH_3)_3NHCl + (CF_3)_2P-C\equiv C-P(CF_3)_2$ . 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  $BH_3$  to each such pi bond. Thus the compound  $(CF_3)_2PC_2H_2P(CF_3)_2$  formed the  $RBH_2$  type  $(CF_3)_2P-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{BH_2}{C}}-P(CF_3)_2$ , having an infrared spectrum and average molecular weight indicating two forms: the bridged dimer  $\begin{matrix} H & H & H \\ | & | & | \\ B & - & B \\ | & & | \\ R & & R \end{matrix}$  and a monomer having a P-B dative-bonded four-atom ring. Similarly,  $(CF_3)_2P-C\equiv C-P(CF_3)_2$  added two  $BH_3$  groups to make an  $R(BH_2)_2$  type, with some uncertainty whether both boron atoms went to the same carbon atom. Also,  $CF_3P[C_2H_2P(CF_3)_2]_2$  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  $C_2H_n$  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  $--O-\overset{R}{\underset{R}{P}}-O-\overset{R}{\underset{R}{P}}--$  chains probably must have just the right R groups on phosphorus. For example, our new compound  $(CF_3)_2POP(CF_3)_2$  proved to be quite stable, whereas all attempts to make the corresponding methyl derivative  $(CH_3)_2POP(CH_3)_2$  led only to equimolar yields of  $(CH_3)_2P-P(CH_3)_2$  and  $(CH_3)_2P-P(CH_3)_2$ . In order to understand this result we may suppose that tetramethyldiphosphoxane would easily rearrange in the Arbuzov manner  $R_2POR' \rightarrow R_2R'PO$ , with one  $P(CH_3)_2$  group playing the role of  $R'$ , for P-P bonding to  $(CH_3)_2PO$ . Then the resulting diphosphine monoxide  $(CH_3)_2P-P(CH_3)_2$  would very rapidly disproportionate by exchanging a  $(CH_3)_2PO$  group for  $(CH_3)_2P$  to give the observed result. The initial rearrangement to the diphosphine monoxide would be far more difficult in the case of  $(CF_3)_2POP(CF_3)_2$  because here phosphorus lacks the base strength to bond a  $(CF_3)_2P^+$  group effectively, and the P-O-P bonding should be



greatly strengthened by  $O_{2p}-P_{3d}$  pi bonding. For similar reasons, the  $(CF_3PO)_n$  polymers might well be stable (with a preference for long chains and wide bond angles), whereas the analogous  $(CH_3PO)_n$  polymers might not exist at all. Actually, a polymer-bonding of  $CF_3PO$  units does seem to exist, according to results obtained in the following study of acetoxyphosphines

The Acetoxyphosphine Approach. It was considered probable that  $(CF_3PO)_n$  polymers would be formed by loss of  $Ac_2O$  from a compound of the type  $CF_3P(OAc)_2$ . For the preliminary exploration of this kind of chemistry, the new compound  $(CF_3)_2POOCCF_3$  (I) was made from  $AgCO_2CF_3$  and  $(CF_3)_2PI$ . Its dissociation to  $(CF_3)_2POP(CF_3)_2$  (II) and  $(CF_3CO)_2O$  (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  $K = [II][III]/[I]^2 = 0.11$ . The acetoxyphosphine (I) proved to be a readily volatile liquid, but its dissociation was too rapid to permit accurate characterization. Attempts to make the diacetoxyphosphine  $CF_3P(OOCCF_3)_2$  from  $AgCO_2CF_3$  and  $CF_3PI_2$  gave the anhydride  $(CF_3CO)_2O$  as the only volatile product. It seemed probable that a  $(CF_3PO)_n$  polymer was mixed with the silver iodide, and could not have disproportionated without forming the volatile compounds  $(CF_3P)_4$  and  $(CF_3P)_5$ .

Next it was argued that the acetoxyphosphine  $(CF_3)_2POOCCCH_3$  would be stabler than the corresponding trifluoroacetoxyphosphine, for a less electronegative oxygen in the C-O-P bond would form a stronger  $O_{2p}P_{3d}$  pi bond, while other differences would cancel out. Accordingly,  $(CF_3)_2PI$  was allowed to react with  $AgCO_2CH_3$  to make  $(CF_3)_2POOCCCH_3$ , which proved to be entirely stable and not difficult to characterize: m.p.  $-58^\circ C$ .; b.p. est.  $96^\circ C$ .

The analogous reaction of  $CF_3PCl_2$  with  $AgCO_2CH_3$  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 diacetoxyphosphine  $CF_3P(OOCCCH_3)_2$ . On standing, this formed more acetic anhydride and a non-volatile white solid. This most probably was a diacetoxy-polyphosphoxane embodying a short  $(CF_3PO)_n$  chain with acetoxy- end groups. It showed no tendency toward a disproportionation into  $(CF_3P)_n$  rings and  $(CF_3PO_2)_n$  polymers, but on long standing it did form a red-brown gum in which the  $CF_3$  groups seemed to exist in a wide variety of environments, leading to wide bands in the infrared spectrum. Thus the conversion of the presumed diacetoxy-polyphosphoxane to a simple open-chain high polymer may be very difficult.

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