Anion Radicals Derived from the Metallic Reduction of Phenylbiphenylenephosphine[1]

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The reaction of phenylbiphenylenephosphine with alkali metals leads first to phenyl cleavage, with formation of metal biphenylenephosphine and metal phenide. An equilibrium is then established between metal biphenylenephosphine and the diphosphine obtained by the coupling of two biphenylenephosphine groups. Further reaction with alkali metals produces the anion radicals of both the metal biphenylenephosphine and the diphosphine.

The reaction of triphenylphosphine (Ph_3P) with alkali metals (M) in tetrahydrofuran (THF) has recently been reinvestigated in this laboratory and was observed to proceed in two detectable discrete steps.[3] The first reaction was found to be phenyl cleavage, with formation of metal diphenylphosphine and metal phenide. Free-radical production occurred in a second step through reduction of the metal diphenylphosphine to its corresponding negative ion.

We now wish to report the results of similar investigations with phenylbiphenylenephosphine (PBP). PBP was chosen as a suitable compound for study because of its close similarity to Ph_3P, thus allowing some utilization of previous information. On the other hand PBP differs from Ph_3P in two important respects. First, carbon–phosphorus bond cleavage of Ph_3P leads to only one phosphorus-containing product (Ph_2PM); however, carbon–phosphorus bond cleavage of PBP may lead to two different phosphorus-containing products depending upon whether the bond linking the phosphorus to the phenyl group is broken or one of the two equivalent bonds linking the phosphorus to the biphenylene group is broken. Second, the equilibrium between metal diphenylphosphine and tetraphenyldiphosphine (plus free metal) is known to lie greatly in favor of metal diphenylphosphine.[4] In the PBP system, however, there exists indirect evidence that the comparable equilibrium between metal biphenylenephosphine and its corresponding diphosphine may lie somewhat more in favor of the diphosphine.[5] The marked stability of this diphosphine, which is presumably responsible for the equilibrium shift, has been attributed to steric protection of the phosphorus atoms by the biphenylene groups.[5]

Experimental Section

Materials.—Phenylbiphenylenephosphine (PBP) was synthesized from freshly prepared 2,2′-dibromobiphenyl,[6] using the reported procedure[7] (m.p. 89–90°, lit.[7] m.p. 92–94°). The solvent and metals were purified and the solutions were prepared in the usual way.[8]

Procedure.—Approximately 100 mg. of PBP was dissolved in 6 ml. of THF and treated at room temperature with each of the following alkali metals—Li, Na, K, and Cs. The reaction was allowed to proceed until weak free-radical signals were barely detectable by electron spin resonance (e.s.r.). A 3-ml. aliquot was then removed for analysis. The remaining 3 ml. of solution was cooled to −50° and further treated for e.s.r. studies.

Analyses. A. Unreacted Starting Material.—The 3-ml. aliquot was opened at room temperature and then cooled to 0°; 2 ml. of cold water was added dropwise with stirring, followed by the dropwise addition of 2 ml. of cold 3% aqueous H_2O_2. The resulting solution was allowed to warm to 25° and then filtered. The basic filtrate was saturated with NaCl and ether extracted. The starting material (PBP), which is converted to the oxide by this treatment, was then recovered from the ether layer upon concentration and chilling. The yield of PBP oxide ranged from 80–90%, m.p. 161–163° (lit.[5] m.p. 164–165°).

B. Phosphafluorinic Acid.—The water layer was concentrated, acidified, and cooled to 0°. Small amounts of a crystalline white solid were precipitated and recrystallized from 95% ethanol. The white solid was identified as phosphafluorinic acid, m.p. 248–258° dec. (lit.[5,9] m.p. 252–257° dec. The benzylthiouronium salt of the phosphafluorinic acid was also prepared and purified by recrystallization from an ethanol–ether mixture, m.p. 210–212° dec. (lit.[5] m.p. 214–215° dec.).

This procedure is a modification of the reported procedure for the preparation of diphenylphosphinic acid from alkali metal cleavage products of triphenylphosphine.[10]

C. 9,9′-Bi-(9-phosphafluorenyl).—Upon opening to air, the 3-ml. aliquots would fade to a pale yellow color which persisted until H_2O_2 was added. If the H_2O_2 added was insufficient to produce a colorless solution, then minute amounts of a yellow crystalline solid were separated with the phosphafluorinic acid. The mixture of the two solids was physically separated as much as possible, and the resulting impure yellow solid melted at *ca.* 230°. This compound may be the crude diphosphine, 9,9′-bi(9-phosphafluorenyl).

Since the diphosphine reacts with H_2O_2 to form phosphafluorinic acid, a different procedure was employed for its separation. One milliliter of the 3-ml. THF aliquot was concentrated to a few drops. An equal volume of pyridine was then added and the resulting solution was cooled to −15°. A few milligrams of the diphosphine was thereby obtained, m.p. 232–238° (lit.[5] m.p. 242–243°). Further purification was not attempted owing to the small amount of material.

D. Biphenyl.—The procedure for the determination of biphenyl has been reported previously.[3]

Results and Discussion

Under equivalent conditions, the reaction of PBP with alkali metals proceeds much slower and in lower yields than has been observed for the corresponding reaction of Ph_3P. This suggests that the phosphorus is one of the important centers of attack by the metal.

As with the Ph_3P system, the reaction of PBP with alkali metals occurs in two distinct steps, with radical production occurring in the second step. The first detectable reaction is phenyl cleavage (eq. 1). I is yellow in solution and produces the observed phosphafluorinic acid upon treatment with H_2O_2. If the reaction is stopped at this stage by removing the solution from the metal, no free radicals may be observed by altering either temperature or concentration,

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(1) Grateful acknowledgement is made to the donors of the Petroleum Research Fund for support of this research.

(2) To whom inquiries should be addressed.

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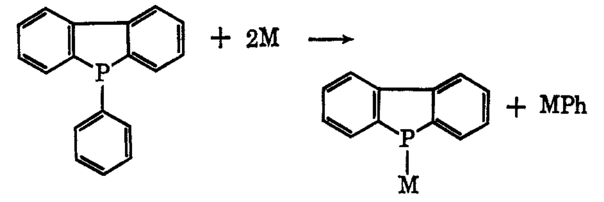


(1)

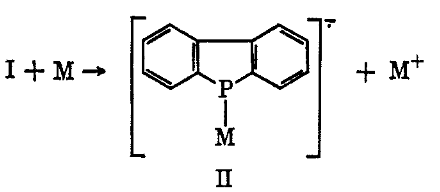
I

nor can free radicals be produced by adding unreacted PBP. The free-radical precursor is therefore not PBP but rather a phenyl cleavage product.

Further treatment with alkali metal initiates a second reaction which produces a red-brown color in solution and a free radical. The products of the second reaction are quite sensitive to temperature, and decomposition to black materials occurs rapidly at room temperature. For this reason, the second reaction was conducted at −50° and e.s.r. measurements were then taken at −65°.

Attempts to analyze the products of the second reaction by dilute H_2O_2 oxidation gave PBP oxide in 80–90% yield; a small (and variable) amount of a clear plastic-like film which retained weak e.s.r. signals with time; and small amounts of phosphafluorinic acid. It is therefore clear that I is involved in free-radical production and/or subsequent decomposition.

On the basis of this established similarity of reactions between PBP and Ph_3P, we may postulate the radical production to occur as shown in eq. 2.[3]



(2)

II

There are several ways to test the nature of the radical and the validity of eq. 2. The tests which were chosen are listed below. (A) The e.s.r. spectrum should be consistent with the structure II. (B) Use of different alkali metals should cause changes in any metal splittings observed by e.s.r. (C) It should be possible to prepare the radical from I directly, with complete exclusion of PBP.

According to the first test then, the e.s.r. spectra should be consistent with one P atom per radical; one metal atom per radical; and an electron distribution pattern from the eight protons in the biphenylene group.

The primary feature of the e.s.r. spectra is the appearance of two broad lines of equal intensity, separated by 8.5 ± 0.1 gauss and attributed to one P atom per radical. (The P splitting in $Ph_2PM^{\cdot}$ is 8.4 gauss.[3]) With increased resolution, each of these two broad lines is seen to be composed of a set of three lines, separated by 2.4 ± 0.1 gauss with intensity ratio 1:2:1. Attempts to analyze additional splittings were complicated by effects which will be discussed in the section dealing with variation of the alkali metals.

The three-line set split by 2.4 ± 0.1 gauss may be attributed to the biphenylene group by consideration of the probable electron distribution pattern. The eight protons are distributed as four groups of two protons each in such radicals as fluorenone ketyl[11] and in the anion radicals of all three oxidation states of dibenzothiophene.[12] It is reasonable to expect that this pattern would be preserved in structure II, though the magnitude of each of the four types of hyperfine splitting cannot be predicted. Any one of these pairs of protons could be responsible for the set of three lines with intensity ratio 1:2:1. Resolution of the splittings from the other three pairs of protons could not be attained.

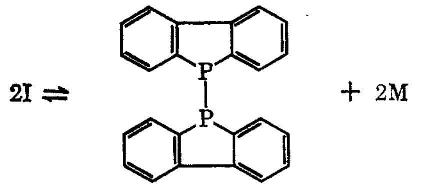
Since only the largest splittings could be analyzed, the results of this first test offer no convincing proof of structure II. It may be stated, however, that the splittings which could be analyzed were consistent with structure II.

According to the second test, variation of the alkali metal should cause changes in any observed metal splittings. For this test, Li, Na, K, and Cs were employed. Each free-radical product showed the e.s.r. spectrum which is described above, and the errors assigned to the two coupling constants represents the range for all four derivatives rather than the error associated with an individual measurement. Attempts to resolve the e.s.r. spectra in order to observe metal splittings were complicated by two additional effects which were a function of the alkali metal.

The first of these effects has been described previously, namely a nonuniform broadening of the individual resonance lines.[3] This effect is independent of concentration and temperature (over the small range of temperature stability of the radical), is reproducible for a given metal, and is distinguishably different among the metals. The magnitude of this effect decreases in the following order: Li > Na > K > Cs. The effect decreases sufficiently for the spectra of the K and Cs derivatives to show 20–30 additional lines, as well as the largest splittings. However, it is not possible to ascribe these additional lines to structure II, owing to a second complication.

This second complication was the presence of another free radical which was formed in increasing concentration through the metal series: Li < Na < K < Cs. The K and Cs free-radical solutions were mixtures of the two free radicals and only the major splittings of each radical could be clearly assigned.

This second free radical was not sensitive to temperature and showed an e.s.r. spectrum of three main lines (intensity ratio 1:2:1) centered on $g = 2$ and split by 8.8 ± 0.1 gauss. This suggests the presence of two P atoms per radical. A possible interpretation of the formation of this second free radical is shown (eq. 3, 4). To check this possibility, the solutions were analyzed for III in addition to the analysis for I. Indeed, III



(3)

III

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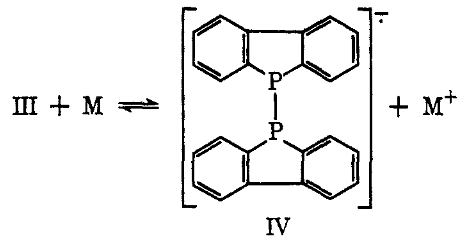
[11] N. Hirota, Ph.D. Thesis, Washington University, St. Louis, Mo. 1963.

[12] D. H. Eargle and E. T. Kaiser, *Proc. Chem. Soc.*, 22 (1964).



(4)

IV

was present and the amount increased in the series Li < Na < K < Cs. The principal result of the alkali metal variation test was then to establish the presence of a second free radical (postulated as being structure IV). However, with the presently available evidence the structure of this second radical cannot be said to be unequivocally established.

Concerning structure II, the presence of a metal atom in the radical could not be established on the usual basis of metal splittings. However, the preservation of the major splittings throughout the alkali metal derivatives implies a basic common structure. Also, the nonuniform line broadening, which apparently was a function of the alkali metal alone, certainly suggests the presence of metal atoms in the radical.

An alternative or possibly complementary scheme for the formation of IV is described in reaction 5.

$$\mathrm{I} + \mathrm{II} \rightleftharpoons \mathrm{IV} + 2\mathrm{M} \qquad (5)$$

A critical examination of the steps postulated in reactions 2–5 is afforded by a detailed study of the e.s.r. spectra and products obtained from the reduction of III.

For this third test, a sample of the diphosphine (III) was obtained and treated with alkali metal. At low concentrations of III no apparent reaction occurred, and it was necessary to employ concentrated solutions of the diphosphine. The pale yellow solution then slowly reacted with alkali metal to form an intensely yellow solution, which gave no e.s.r. signals. The solution was cooled to −50° and further treated. A second reaction then occurred, leading to the formation of a red-brown solution and free radicals. The second reaction was followed stepwise with e.s.r. The first radical to be observed was temperature sensitive and the e.s.r. spectra at −65° showed the same major splittings attributed to structure II. As the second reaction proceeded, an additional free radical was observed. This second free radical was stable to temperature and showed the same three-line P splittings attributed to IV, with the lines being uniformly broadened. Dilution of the concentrated diphosphine–radical mixture sharply decreased the width of the lines attributed to structure IV. The e.s.r. spectra of the resulting dilute mixtures of the two radicals showed good agreement with the corresponding spectra of the radical mixtures from PBP. This agreement was not confined to the major splittings but extended to the 20–30 additional lines as well.

From the results of these various tests and measurements, certain conclusions may be drawn concerning reactions 2–5 and structures II and IV. First, the diphosphine is slowly cleaved in low yield to I, confirming the backward step of reaction 3 as written. Second, the temperature-sensitive radical can be produced only after I is formed, regardless of other species. This supports reaction 2 and, together with other results, supports structure II as the probable structure of the temperature-sensitive radical. Third, the temperature-stable radical is formed only after II is formed. This does not support reaction 4 but does support reaction 5. Fourth, the temperature-stable radical is produced from the PBP system in amounts which correlate with the amounts of analyzed III from the various alkali metal experiments. A comparison of the e.s.r. spectra of the radical mixtures derived from PBP and III shows that the temperature-stable radical is produced in the diphosphine system and undergoes electron-exchange with the diphosphine. Structure IV is therefore taken to be the probable structure of the temperature-stable radical.

Finally, since the formation of biphenyl from the reaction of $\mathrm{Ph}_n\mathrm{X}_m$ species (where X is a heteroatom) with alkali metals is a fairly common occurrence and can cause complications in the interpretation of e.s.r. spectra, it was considered of interest to analyze several of the radical-containing solutions for biphenyl. An estimate of the maximum concentration of biphenyl which might be present was obtained. It had the range $1\text{–}2 \times 10^{-5}\ M$ for the various metal radical solutions. Therefore, the effect of biphenyl was considered to be negligible.

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