Synthesis of some organophosphorus compounds: a study of the electron spin resonance spectra of the free radical anions formed by the reactions of 4,4′-bis(diphenylphosphine)biphenyl with alkali metals

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By the halogen–lithium interconversion method, 4,4′-bis(diphenylphosphine)biphenyl (**1**) was prepared. Under different reaction conditions, mono- and di-oxygenated products were obtained. An attempt to prepare **1** by the Grignard reagent method failed to give the expected product but

$$C_6H_5(OH)(O)PC_6H_4C_6H_4P(O)(OH)C_6H_5$$

was obtained. Bis(diphenylamine)phenylphosphine was also prepared. Tetraphenyldiphosphine monoxide resulted from an attempt to prepare N-diphenylaminodiphenylphosphine. The mechanism of this reaction is discussed. Infrared spectroscopy, elemental analysis, and activation analysis for the determination of oxygen content were performed for the identification of the above compounds.

Reactions of **1** with sodium–potassium alloy in tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) gave a radical anion which was identified by its electron spin resonance spectra at different temperatures.

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Introduction

The utilization of the halogen–lithium interconversion method (1) has been found to be useful for the synthesis of a variety of organometallic compounds. Curtis and Allred (2) have utilized the reaction between *n*-butyl lithium and the corresponding halogenated biphenyl for the preparation of the compounds 4-$(CH_3)_3MC_6H_4C_6H_5$ and 4,4′-$(CH_3)_3MC_6H_4C_6H_4M(CH_3)_3$, where M = Si, Ge, or Sn.

Cowley and Hnoosh (3) reported the preparation of 4,4′-$(CH_3)_2P$—$C_6H_4C_6H_4$—$P(CH_3)_2$. Both investigations also included electron spin resonance (e.s.r.) studies of the free radical anions formed by the reduction of these compounds with alkali metals.

In the present investigation the preparation of the compound 4,4′-$(C_6H_5)_2PC_6H_4C_6H_4P(C_6H_5)_2$ is reported and its reactions with alkali metals in tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) have been studied by e.s.r. spectroscopy. The interest in the e.s.r. study of the latter compound lies in the comparison with that of triphenylphosphine (4) and its oxide (3), where a phenyl group has been shown to cleave from the phosphorus atom in their reactions with alkali metals in the same solvents.

Sisler and Smith (5) reported the preparation of N-diphenylaminodiphenylphosphine by means of the reaction of chlorodiphenylphosphine with sodium diphenylamine produced by the reaction of diphenylamine with NaH in diglyme. In this work a similar approach has been used for the preparation of bis(diphenylamino)phenylphosphine. In addition, an attempt to prepare $[(C_6H_5)_2N](C_6H_5)_2P$ under different conditions from those previously reported (5) resulted in the formation of the unexpected product, tetraphenyldiphosphine monoxide $(C_6H_5)_2P$—$P(O)(C_6H_5)_2$. This reaction appears to be similar to that reported for the production of tetraphenyldiphosphine dioxide by the reaction of diphenylphosphine chloride in the presence of a tertiary amine like diethylaniline (6).

Experimental

Reagents

All the chemical reagents used in this work were obtained from the usual commercial sources. *n*-Butyl lithium was in the form of a hexane solution. It was pumped from the storage container into the reaction vessel under a pressure of dry nitrogen in order to avoid atmospheric contamination. 4,4′-Dibromobiphenyl was used following recrystallization from butanol. Sodium hydride was used in the form of a 50% dispersion in oil. Diethylene glycol dimethyl ether (diglyme) was dried over CaH_2 and distilled prior to its use. THF and DME were purified by distillation after drying over CaH_2 and potassium metal.

The sodium–potassium alloy which was used in the

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reduction of 4,4′-bis(diphenylphosphine)biphenyl was prepared by mixing proper amounts of sodium and potassium metals after they were first cleaned by treatment with benzene and then ether. They were sublimed by heating under vacuum in the reaction apparatus used for free radical generation.

Apparatus

All infrared spectra were recorded on a Beckman Model IR-12 spectrometer using KBr pellets. The e.s.r. spectra were measured using the X-band of a Varian V-4502-15 e.s.r. spectrometer.

Oxygen determinations were performed using the neutron activation and analysis system at the Activation Analysis Research Lab., Texas A&M University. Weighed amounts of dry primary standard grade benzoic acid in polyethylene vials were used as standards. The unknown samples and standards were subjected to the same experimental conditions. The other elemental analyses were performed by the Galbraith Laboratories, Inc., Knoxville, Tennessee.

Preparation of 4,4′-Bis(diphenylphosphine)biphenyl, 4,4′-$(C_6H_5)_2PC_6H_4C_6H_4P(C_6H_5)_2$

To 31.2 g (0.1 mole) of 4,4′-dibromobiphenyl dissolved in 200 ml of anhydrous ether contained in a 1 l three-necked flask, equipped with a mechanical stirrer, a reflux condenser, and dropping funnel, 12.8 g (0.2 mole) of *n*-butyl lithium (in hexane) was added dropwise, with stirring, under an atmosphere of dry nitrogen at room temperature. The lithium exchange reaction was essentially complete after 30 min. Chlorodiphenylphosphine, $(C_6H_5)_2PCl$, (22.05 g, 0.2 mole) was added dropwise to the lithium compound. After 3 min the brown color began to fade and a yellowish precipitate formed The reaction was slightly exothermic. The mixture was stirred for 2 h after completion of the $(C_6H_5)_2PCl$ addition. It was then refluxed for 2 h and allowed to cool under nitrogen. The reaction mixture was hydrolyzed with saturated aqueous ammonium chloride solution. The ether layer plus washings were dried overnight over anhydrous sodium sulfate. The ether solution was then evaporated under reduced pressure, and the brown-yellow product was recrystallized first from ethanol and then from a mixture of ether and petroleum ether. This resulted in a yield of 51.2% of white crystals which melted at 195 °C.

Anal. Calcd. for $(C_6H_5)_2P{-}C_6H_4C_6H_4{-}P(C_6H_5)_2$: C, 82.76; H, 5.37; P, 11.87. Found: C, 82.79; H, 5.52; P, 11.67.

In this reaction it was found that if the conditions were changed slightly, different products were formed. In one run. all steps up to the hydrolysis were carried out in a similar manner. The reaction flasks, while hot, were opened to the air and hydrolyzed with saturated ammonium chloride solution with stirring. Evaporation of the organic layer yielded another quantity of solid product. The solid product from the water layer was recrystallized from ethanol and then *n*-butanol. The white crystals melted at 205–206 °C.

The analysis is in agreement with a stoichiometry which suggests the compound 4,4′-bis(diphenylphosphine)biphenyl monoxide.

Anal. Calcd. for 4,4′-$(C_6H_5)_2PC_6H_4C_6H_4P(O)(C_6H_5)_2$: C, 80.29; H, 5.23; P, 11.62. Found: C, 80.26; H, 5.18; P, 11.62.

A second solid was obtained from the organic layer which was recrystallized first from ethanol and then *n*-butanol; m.p. 265–266 °C. The analysis suggests the compound 4,4′-bis(diphenylphosphine oxide)biphenyl.

Anal. Calcd. for 4,4′-$(C_6H_5)_2(O)PC_6H_4C_6H_4P(O)(C_6H_5)_2$: C, 77.97; H, 5.05; P, 11.30. Found: C, 77.49; H, 5.49; P, 11.01.

Activation analysis for oxygen gave 5.54%, compared with the calculated value of 5.68%.

An attempt to prepare 4,4′-bis(diphenylphosphine)biphenyl by the use of Grignard reagent in THF with I_2 to catalyze the reaction resulted in the formation of 4,4′-bis(diphenylphosphoric acid)biphenyl, 4,4′-$C_6H_5(OH)(O)P{-}C_6H_4C_6H_4{-}P(O)(OH)C_6H_5$, which was identified by chemical analysis, infrared spectrum, and molecular weight determination.

Preparation of Bis(diphenylamino)phenylphosphine $[(C_6H_5)_2N_2]PC_6H_5$

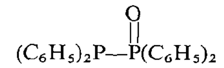
A solution of 33.8 g, (0.2 mole) of diphenylamine in 150 ml of dry (over CaH_2) diethylene glycol dimethyl ether (diglyme) was added to a suspension of 14 g of NaH (50% dispersion in oil) in 300 ml of diglyme. When the evolution of hydrogen was over, 18 g (0.1 mole) of $C_6H_5PCl_2$ was added, with stirring, to the mixture. The solution was warmed to 110 °C and kept at this temperature for 2 h. The solid reaction product (sodium chloride) was filtered hot, and washed with dry ether. The filtrate and the ether washings were combined and the solvents removed under reduced pressure. The residue was recrystallized from ethanol and then ether. The resulting crystals melted at 139–140 °C.

Anal. Calcd. for $[(C_6H_5)_2N]_2PC_6H_5$: C, 81.02; H, 5.67; P, 7.01; N, 6.30. Found: C, 80.27; H, 5.74; P, 7.54; N, 6.25.

This compound was found to be exceedingly sensitive to air and moisture. On standing, even in a desiccator, the crystals turned yellow and then bluish green.

Attempts to prepare diphenylaminodiphenylphosphine $[(C_6H_5)_2N](C_6H_5)_2P$ as reported (5) with slightly different conditions resulted in the formation of tetraphenyldiphosphine monoxide. The diphenylamine was added to the NaH suspension dropwise at room temperature. After the addition of $(C_6H_5)_2PCl$ the mixture was refluxed for about 2 h. Then the precipitate was filtered, while hot, in the atmosphere. The organic solvent was evaporated under reduced pressure and the product was recrystallized from ethanol and then ether. The compound melted at 122 °C and the yield was 17.2%.

The elemental analysis fits the stoichiometry of the compound



$$(C_6H_5)_2P{-}\overset{\overset{\displaystyle O}{\|}}{P}(C_6H_5)_2$$

Determination of the oxygen content by oxygen analysis gave very good results compared with the calculated value.

Anal. Calcd. for $(C_6H_5)_2P{-}PO(C_6H_5)_2$: C, 74.61; H, 5.18; P, 16.06; O, 4.15. Found: C, 74.82; H, 4.96; P, 15.90; O, 4.20.

The Reactions of 4,4′-Bis(diphenylphosphine)biphenyl with Alkali Metals

These reactions with alkali metals were carried out in an apparatus specially designed for this purpose which was connected to a vacuum line of conventional design. The compound was permitted to react in the reaction bulb after the metals were heated and condensed as shiny mirrors on this bulb and after the solvent was distilled under vacuum into the same bulb. Samples were taken after various times and at various temperatures.

Results and Discussion

I. Syntheses and Infrared Spectra

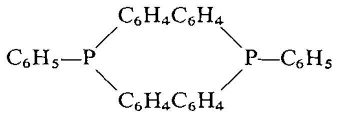
During the synthesis of 4,4′-bis(diphenylphosphine)biphenyl it was noted that two kinds of products, the monoxide and the dioxide, were obtained when the reaction mixture was opened to air and hydrolyzed while hot, immediately following the reflux period. The stability of this compound toward oxidation is not surprising in view of the fact that each phosphorus atom bears three aryl substituents. The formation of a monoxide is quite unusual and further illustrates the oxidative stability of this molecule. The formation and isolation of the stable monoxide suggests that this species may be the first one formed during the atmospheric oxidation process.

A comparison of the infrared spectra of the unoxygenated compound and that of the oxygenated products has been made. The absorption band of principal interest is the fundamental P—O stretching vibration, ν_s(P—O). Zingaro and Hedges reported P—O stretching frequencies of a number of organophosphine oxides (7). These were found over the range 1144–1206 cm^{-1}. Kuchen and Buchwalt (8) reported P—O stretching frequencies for tetraphenyl diphosphine dioxide at 1180 cm^{-1}. In the present study strong bands have been observed at 1196 and 1190 cm^{-1} for the di- and monoxide, respectively. These bands were absent in the infrared spectrum of the unoxygenated compound.

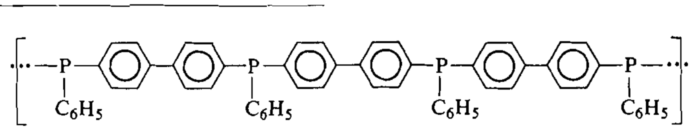
Attempts to prepare 4-diphenylphosphinebiphenyl in the same manner, i.e., by the halogen–lithium interconversion reaction, failed to give the desired product. It appears that the reaction of mono-halogenated biphenyl with *n*-butyl lithium proceeds with difficulty, or not at all. This may be due to the fact that the carbon–bromine bond is much stronger than when there is present another C—Br bond in the opposite position (4′) on the biphenyl. The failure of this reaction may also be due to the extreme sensitivity of the product toward oxygen and water.

In the attempt to prepare the 4,4′-bis(diphenylphosphine)biphenyl via the Grignard reagent using I_2 as a catalyst, the desired product was not formed. As described in the experimental part, 4,4′-bis(phenylphosphonic acid)biphenyl was obtained. This means that the chlorodiphenylphosphine underwent cleavage of one phenyl group and then reacted with 4,4′-dibromobiphenyl. This was followed by hydrolysis and oxidation. However, the mechanism of this unusual reaction remains indefinite. The infrared spectrum also shows the principal absorption bands expected for this molecule, including ν_s(P—O) at 1183 cm^{-1} and ν_s(P—O—H) at 1131 cm^{-1}.

Attempts to prepare the compound



by the reaction of $C_6H_5PCl_2$ with 4,4′-dibromobiphenyl by the halogen–lithium interconversion method resulted in a very low yield of noncrystalline solid which may be a polymer of the following type.



The material was formed in very small quantities and was found to be exceedingly insoluble in the usual organic solvents.

The reaction of diphenylamine with chlorodiphenylphosphine proceeded as expected. The synthesis of diphenylaminodiphenylphosphine $[(C_6H_5)_2N](C_6H_5)_2P$ was accomplished in the manner described (5) by the following reaction sequence.

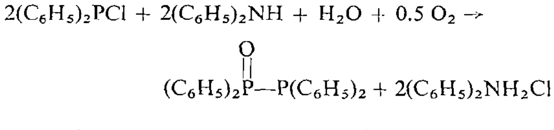
$$(C_6H_5)_2NH + NaH \xrightarrow{\text{Diglyme}} (C_6H_5)_2NNa + H_2$$

$$(C_6H_5)_2NNa + (C_6H_5)_2PCl \longrightarrow [(C_6H_5)_2N](C_6H_5)_2P + NaCl$$

In this reaction the addition of the diphenylamine solution to the NaH suspension was not carried out dropwise, but both reagents were mixed together completely prior to the reaction. When the addition was carried out in a dropwise manner without heat, the expected product was not obtained. The product obtained was tetraphenyldiphosphine monoxide. Comparison of the infrared spectrum of this compound with that for the dioxygenated compound (8) showed that the spectra are essentially superimposible. Both possess a strong absorption band for the P—O stretching frequency in the region of 1180 cm^{-1}.

The manner of the formation of tetraphenyl diphosphine monoxide is similar to that reported by Quin and Anderson (6) who utilized phosphinous chlorides for the formation of the phosphorus–phosphorus bond. They reported a similar case in which they obtained tetraphenyldiphosphine dioxide from the reaction of chlorodiphenylphosphine in the presence of an amine like diethylaniline, a very small amount of water, and air.

In the present case, as in that reported by Quin and Anderson, in order to account for the formation of the diphosphine monoxide it was necessary to assume that both hydrolytic and oxidative reactions are involved



$$2(C_6H_5)_2PCl + 2(C_6H_5)_2NH + H_2O + 0.5\ O_2 \rightarrow (C_6H_5)_2\overset{\overset{\displaystyle O}{\|}}{P}—P(C_6H_5)_2 + 2(C_6H_5)_2NH_2Cl$$

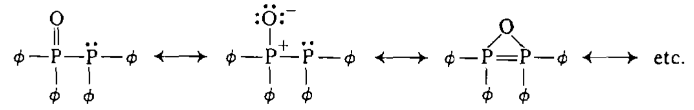
The diphenylamine hydrochloride was isolated and unequivocally characterized.

In the present study, when the amine solution was added dropwise to the sodium hydride without heat, it did not react. When the chlorodiphenylphosphine was added, the amine probably functioned as a catalyst in the formation of the diphosphine. In the case just referred to (6), it was reported that the amine plays a vital role as no coupling occurs in its absence. In this process, phosphorus–phosphorus bond formation precedes the hydrolysis and oxidation steps, and the amine is involved in the coupling reaction, but in a manner different from that of metals when they participate in coupling reactions since the amine cannot function as a reducing agent. It is quite possible that an amine–phosphinous chloride complex, similar to those which have been reported to form between amines and phosphorus trihalides (9) is first formed. The complex is susceptible to attack by a second molecule of phosphinous chloride, with displacement of the amine (10). The intermediate which forms would be of the type

$$[(C_6H_5)_2\ddot{P}—\overset{+}{P}(C_6H_5)_2Cl]Cl^-$$

which is easily hydrolyzed and oxidized. It is to be noted that in this process the same kind of atom is involved, first in electrophilic, and then in nucleophilic behavior.

It is difficult to account for monoxide formation without the formation of any dioxide. The stability of the monoxide may be the most important factor. Resonance among the following structures may explain this stability



The preparation of bis(diphenylamino)phenylphosphine proceeded in the manner expected. This compound is very sensitive to moisture and oxygen. The sensitivity toward oxidation is to be expected because of the availability of unbonded electron pairs on both the nitrogen and phosphorus atoms.

II. Electron Spin Resonance Studies of the Reactions of 4,4′-Bis(diphenylphosphine)biphenyl with Alkali Metals in THF and DME

These reactions proceeded similarly with lithium, sodium, potassium, and sodium–potassium (NaK) alloy in both THF and DME. When each reaction started, a purple color developed. This color intensified as the reaction mixture was permitted to stand for longer times in contact with the alkali metal as the solution warmed to room temperature. At the latter temperature the color became deep violet.

The sample prepared by the reaction of this compound with sodium–potassium alloy in THF gave the best resolved e.s.r. spectrum. This spectrum, Fig. 1, which was recorded at temperatures between −65 and −10 °C consists of 23

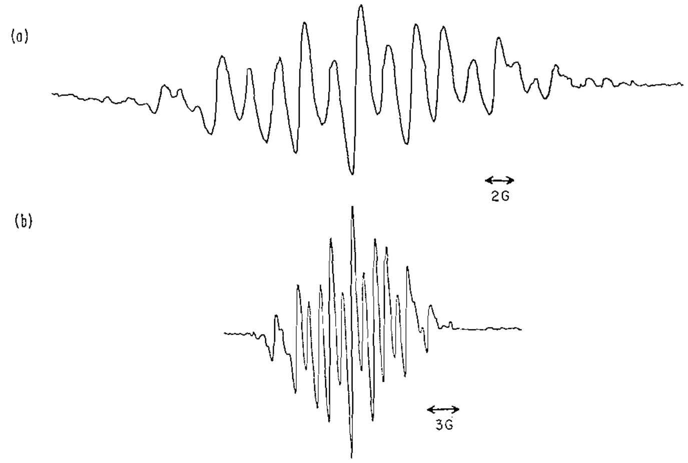
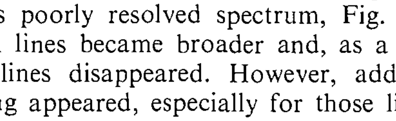


FIG. 1. Electron spin resonance spectrum of the free radical anion formed by the reaction of 4,4′-bis(diphenylphosphine)biphenyl with sodium–potassium alloy in THF: *a*, at −10 °C; *b*, at −65 °C.

lines. The overlap of the lines reduces the number of the lines from the expected 105 to 23. According to the hyperfine splitting constants and relative line intensities, these lines arise from the interaction of the unpaired electron of the radical anion with three different sets of equivalent nuclei. First, there is a triplet with a hyperfine splitting constant of 3.05 G which arises from the interaction with 2 phosphorus nuclei (spin of 1/2). These 3 lines have relative intensities of 1:2:1. Each of these 3 lines splits into 7 as a result of the interaction with a set of 6 equivalent protons. The hyperfine splitting constant of the splitting is 2.05 G and the relative line intensities are 1:6:15:20:15:6:1. The resultant lines each split into 5 lines of relative intensities 1:4:6:4:1, having a hyperfine splitting constant of 1.02 G. This is caused by the interaction with 4 equivalent protons. The 4 lines at both extreme ends of the spectrum almost disappear because of their low intensities.

The 6 equivalent protons are those on 2 phenyl groups. They are the 2 in the ortho position and the 1 in the para position of each phenyl group. The ortho and para positions in the phenyl group usually have very similar electron densities as in triphenylphosphine (4) and its oxide (3). Since each phenyl group should be attached to a separate phosphorus atom, this means that the reaction of this compound with alkali metals resulted in cleavage of 1 phenyl group from each phosphorus atom. The set of 4 equivalent protons which caused the quintet splitting are on the biphenyl part of the molecule, namely, at positions 9, 14, 23, and 26. This analysis suggests the following radical–anion structure



The resolution of the e.s.r. spectrum appeared to be temperature dependent. As the temperature of the sample was raised to room temperature, the resolution of the spectrum decreased, particularly in the middle portion of the spectrum. In this poorly resolved spectrum, Fig. 2, the central lines became broader and, as a result, some lines disappeared. However, additional splitting appeared, especially for those lines at the extreme ends of the spectrum. This additional splitting is in the form of a quintet which is caused by the interaction of a set of four equivalent protons. The hyperfine splitting constant of this quintet is 0.4 G and the relative intensities

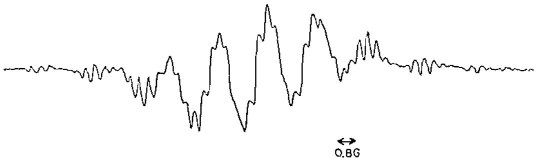


FIG. 2. Electron spin resonance spectrum of the free radical anion formed by the reaction of 4,4′-bis(diphenylphosphine)biphenyl with sodium–potassium alloy in THF at room temperature.

are 1:4:6:4:1. These protons are believed to be in positions 10, 13, 24, and 25. No alkali metal splitting was observed.

Acknowledgments

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