

6-1940

The preparation of symmetrical tri aryl phosphines

George Brandes

Union College - Schenectady, NY

Follow this and additional works at: <https://digitalworks.union.edu/theses>



Part of the [Chemistry Commons](#)

Recommended Citation

Brandes, George, "The preparation of symmetrical tri aryl phosphines" (1940). *Honors Theses*. 1709.
<https://digitalworks.union.edu/theses/1709>

This Open Access is brought to you for free and open access by the Student Work at Union | Digital Works. It has been accepted for inclusion in Honors Theses by an authorized administrator of Union | Digital Works. For more information, please contact digitalworks@union.edu.

THE PREPARATION OF SYMMETRICAL
TRI ARYL PHOSPHINES

George Brandes

1940

UNION COLLEGE
LIBRARY

A Thesis presented to the Department of Chemistry
of Union College, in partial fulfillment of the require-
ments for the Degree of Bachelor of Science in
Chemistry by

.....
George Brandes.....

Approved by

.....

Date

.....
May 21, 1940.....

UN92
B81
c.2

INTRODUCTION:

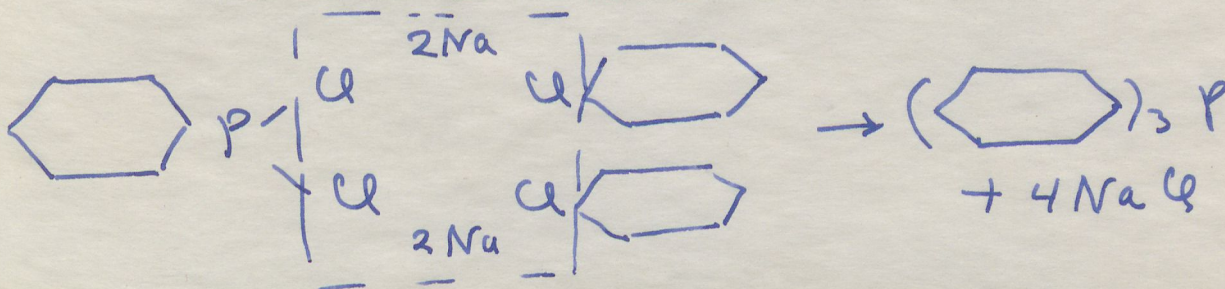
The purpose of this research project was the preparation of pure, symmetrical aromatic phosphines. These were to be used in dipole moment measurements for the calculation of the spatial arrangement of the carbon-phosphorus valence bond in the phosphines.¹

Tri phenyl phosphine and tri biphenyl phosphine were prepared and purified. The preparation of tri para toluyl phosphine was attempted but not completed.

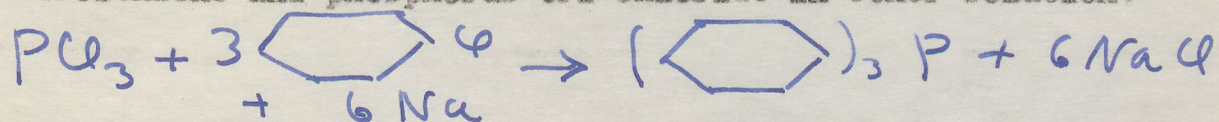
As one would expect from the position of phosphorus in the table of the elements, the phosphines show considerable similarity in chemical and physical properties to the corresponding nitrogen compounds, the amines. Thus tri phenyl amine and tri phenyl phosphine are both solids insoluble in water, having high boiling points and weak basic properties.

The method of preparation of the phosphines differs from that of the amines because the phosphorus tri halide is invariably used whereas the nitrogen halides are too explosive and dangerous to work with.

Tri phenyl phosphine was first prepared in 1882 by Michaelis and Gleichmann by the reaction of phenyl phosphenyl chloride with sodium and chlorobenzene.²



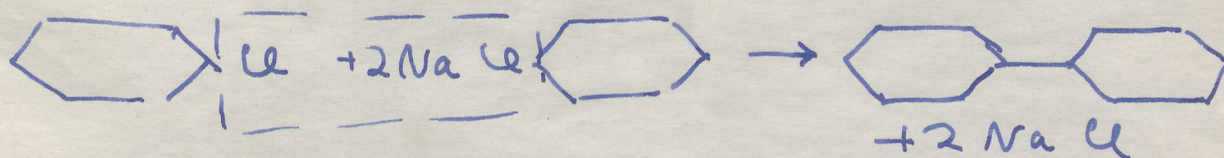
Later Michaelis prepared it by the reaction of sodium, chlorobenzene and phosphorus tri chloride in ether solution.³



He also investigated derivatives of tri phenyl phosphine such as the sulfide and the oxide and later prepared other aromatic phosphines. While Michaelis (with various co-workers) did the pioneer research on this class of compounds, the aliphatic phosphines were investigated at a much earlier period.

Benzene is a more satisfactory solvent for this reaction than is ether for a number of reasons. The violent, very exothermic reaction makes it difficult to keep the temperature below the boiling point of so volatile a solvent as ether. Worrall, in reporting on the preparation of tri biphenyl phosphine⁴ reports a considerable decrease in yield when ether instead of benzene is used as a solvent and suggests that the phosphorus tri chloride may attack the ether.

The reaction is essentially a Wurtz synthesis but the rate of reaction is greater than that of the ordinary Wurtz synthesis because a comparatively small amount of biphenyl is formed by the competing reaction,

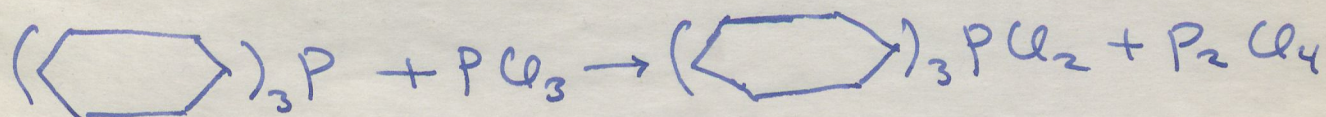


This is the ordinary Wurtz reaction.

The tri aryl phosphines are also made by the usual method of synthesis of organo metallic compounds, the addition of a Grignard reagent to a halogen compound. This method gives higher yields than the reaction using sodium but is less easy to carry out owing to the large number of steps involved and it cannot be readily adapted to the preparation of large quantities of phosphine.

While pure tri aryl phosphines are colorless and odorless, their synthesis is always accompanied by the formation of by-products which impart a yellow or reddish color to the reaction mixture and which have a characteristic fishlike odor. If there is insufficient cooling when PCl_3 is added to a Grignard solution, a vile smelling yellowish brown mass separates out of the ether solution and no tri aryl phosphine is isolated.¹ This took place in the first run in the preparation of tri phenyl phosphine.

The investigations of Challenger and Pritchard⁵ explain the formation of at least part of these by-products as the result of a reaction between the phosphine and excess of PCl_3 ,



The tri phenyl phosphine di chloride formed is hydro-
lyzed after the reaction is over to tri phenyl phosphine
oxide, which frequently is formed as a by-product and indeed
sometimes forms the principle product¹, while P_2Cl_4 and
its decomposition products give rise to the color and odor.

This reaction was found by Challenger and Pritchard
to take place with the corresponding stibines, arsines, etc.
and the halides of these elements.

When a few grams of tri phenyl phosphine was mixed
with phosphorus trichloride it first dissolved but upon
refluxing gently for a few minutes a flocculent yellow
solid separated.

EXPERIMENTAL

Preparation of Tri Phenyl Phosphine

Procedure I:

61 grams (40 cc) of PCl_3 , 157 grams of chlorobenzene and 70 grams of granulated sodium are added to 200 cc of dry benzene in a 2 liter round bottom flask. The reaction mixture is refluxed to start the reaction. The surface of the sodium metal blackens and a violent reaction ensues, which runs for about an hour. The flask is cooled by immersion in an ice bath.

After the reaction has stopped the solution is refluxed for two hours. The hot mixture is then filtered by suction and the residue is washed with warm benzene. The benzene and any biphenyl formed are removed by distilling off in vacuum the fraction boiling below 100° at 20 mm pressure.

The yellow, viscous oil remaining is allowed to stand. Large transparent crystals of tri phenyl phosphine slowly formed. These are purified by several recrystallizations from ether-alcohol. The melting point is given as 79°C . The product obtained in these experiments melted two degrees below this. Yield: 80 grams of crude product.

Tri phenyl phosphine forms very regular crystals belonging to the monoclinic system. It is readily soluble in non-polar solvents such as benzene. It has weakly basic properties, dissolving in concentrated hydrochloric acid but is precipitated out as a white colloidal sol upon the addition of water.

Procedure II: (Grignard Synthesis)¹

85 grams of phenyl magnesium bromide are prepared in a Grignard flask provided with a mechanical stirrer and under dry hydrogen. The solution is cooled with ice and PCl_3 (10.5g in 50cc of dry ether) is added dropwise in the course of one-half hour with stirring and continuous passing through of hydrogen gas. Immediately after the last drop of PCl_3 has been added the Grignard mixture is hydrolyzed by pouring onto crushed ice. 100cc of 6 normal HCl is added with stirring, the mixture is filtered and the ether layer is separated. The aqueous layer is extracted twice with ether, the ether extracts are combined and allowed to stand over dry CaCl_2 . The ether and biphenyl are distilled off in vacuum and the tri phenyl phosphine obtained is purified as in Procedure I.

Procedure III:

Preparation of Tri Biphenyl Phosphine⁴

The same procedure is followed as in I. A crystal of antimony trichloride is used however, as a catalyst to start the reaction.

9 grams of granulated sodium, 25 grams of para chlor biphenyl and 6.1 grams of PCl_3 are reacted in 200 cc of dry benzene to give 12 grams of tri biphenyl phosphine, a cream colored powder consisting of microscopic rod-shaped crystals, melting point 172° .

Procedure IV:

Preparation of Para Toluy1 Phosphine

100 grams of para brom toluene were prepared by the Sandmeyer Reaction.⁶ Attempts to form the Grignard reagent from this compound were unsuccessful, possibly due to incomplete drying.

II.

The Preparation of Some Addition Compounds

Two grams of tri phenyl phosphine and two grams of mercuric chloride were mixed in acetone solution. A double compound of the formula $[(\text{C}_6\text{H}_5)_3\text{P}] \cdot (\text{HgCl}_2)_2$ separated out as small colorless crystals.⁷ This is an unusually stable compound, neither melting nor decomposing below 300°C. Tri biphenyl phosphine did not form an addition compound with HgCl_2 .

Cadmium Chloride is an analogue of Zinc chloride and should show to some extent the action of the latter as a condensing agent in organic reactions. While the work done with cadmium chloride has no direct bearing on the subject of this thesis, it was carried out since research was being done this year on organo cadmium compounds and a supply of the anhydrous salt was available.

CdCl_2 was found to form a double compound with quinoline hydrochloride. When 40 grams of CdCl_2 in 50 cc of 2 Normal HCl was added to 20 grams of quinoline in 50 cc of HCl and 20 cc of water, the addition compound forms so rapidly that the solution set to a solid mass. About 80 grams of white powder are obtained.

The double salt consists of microscopic needles which decompose above 250° . On exposure to air the powder acquires pinkish coloration. CdCl_2 does not react with aniline hydrochloride, so it can be used like zinc chloride to separate quinoline from aniline.

While nothing else was done on this subject, further investigation would doubtless reveal other interesting and useful applications of anhydrous cadmium chloride to organic synthesis.

SUMMARY:

Tri phenyl phosphine and tri biphenyl phosphine were prepared and purified.

Some addition compounds of salts with organic compounds were prepared.

BIBLIOGRAPHY:

1. Sunderlin, C.E., Doctorate Thesis:
 - A. Synthesis and Study of Asymmetric Substituted Phosphorus Compounds
 - B. Dipole Moments of Some Organic Phosphorus Compounds
2. Michaelis and Gleichmann, Berichte 15,801 (1882)
3. Michaelis and Soden, Berichte 17,921 (1884)
4. Worrall, Journal American Chem. Soc. 52,2933 (1930)
5. Challenger and Pritchard, Trans. Chem. Soc.
125,864 (1924)
6. Gilman, Organic Synthesis, P.131
7. For Collected Information on Organo Phosphorus Compounds See Goddard, Textbook of Inorganic Chemistry, Vol. XI, Part III pp. 3-165