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The Reaction of Diphenyl Cadmium

with Phosphorus Trichloride

Any study of the stereochemistry of tricovalent atoms would necessarily involve members of the third and fifth periodic groups. Tertiary phosphines with heavy groups would be most valuable for this work.

A thesis presented to the Department of Chemistry of Union College, in partial fulfillment of the requirements for the Degree of Bachelor of Science in Chemistry, by Alfred W. Case and make possible the resolution of the optical isomers.

However, this work has been retarded by the lack of a convenient means of preparing asymmetrical substituted triaryl phosphines. The usual method of preparing triaryl phosphines is by the reaction of the appropriate phosphorus trichloride with a Grignard reagent. However, the magnesium compound is reactive enough to replace both available chlorine atoms and the resulting compound is not completely asymmetrical.

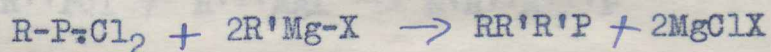
Approved by _____

June, 1940

Historical

Any study of the stereochemistry of tricovalent atoms would necessarily involve members of the third and fifth periodic groups. Tertiary phosphines with heavy groups would be most valuable for this work since phosphorus seems to be better suited to exhibit asymmetry than any other element of the fifth group.⁽²⁴⁾ It is believed that the heavy groups would slow down the oscillations of the phosphorus atom and make possible the resolution of the optical isomers.

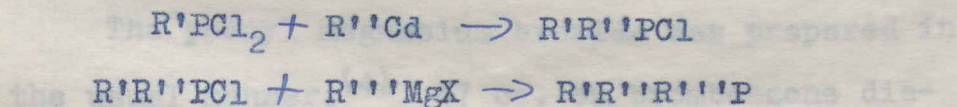
However, this work has been retarded by the lack of a convenient means of preparing asymmetrical substituted triaryl phosphines. The usual method of preparing triaryl phosphines is by the reaction of the appropriate phosphenyl chloride with a Grignard reagent. However, the magnesium compound is reactive enough to replace both available chlorine atoms and the resulting compound is not completely asymmetrical.



The problem is to find a reagent to take the place of the Grignard which will replace only one of the chlorines. Sunderlin attempted to prepare the phosphine with sodium diphenyl and subsequent hydrolysis of the product.

desired compounds by the reaction of phosphenyl chlorides with the less reactive organo-mercury compounds. ⁽²⁴⁾ Although this method did work, it required a temperature of about 300° and the yields were so poor as to make the reaction of little value.

Through the extensive studies of organo-metallic compounds by Gilman, ^(6,7,8,9) it has been found that, in the matter of reactivity, cadmium compounds lie between those of magnesium and mercury. This suggests that it may be possible, through the medium of organo-cadmium compounds to replace one chlorine atom of phosphenyl chlorides by an aryl group, leaving the other chlorine intact. Then by the use of a suitable Grignard reagent, the other chlorine could be replaced, giving a completely asymmetrical triaryl phosphine.



That this is apparently true was found by Sunderlin ⁽²⁴⁾ when he succeeded in preparing diphenyl phosphinic acid by the reaction of phenyl dichlorophosphine with cadmium diphenyl and subsequent hydrolysis of the product.

The purpose of this investigation was a further study of this possibility, particularly the reaction of organo-cadmium compounds with phosphorus trichloride. In this case two of the chlorine atoms should be replaced, leaving one intact. It was originally intended to investigate the generality of the reaction, with phosphenyl chlorides in general, but time did not permit.

Experimental

The experimental method used was as follows. A mixture of diphenyl cadmium and phenyl cadmium bromide was formed,⁽⁹⁾ and the phosphorus trichloride was added to this. The reaction mixture was then hydrolyzed and an attempt made to separate the phosphinic acid which would result from the hydrolysis of the diaryl phosphorus trichloride.

The phenyl magnesium bromide was prepared in the usual manner.⁽⁴⁾ 47 cc. of brombenzene dissolved in 200 cc. of anhydrous ether was slowly added to 7 g. of magnesium turnings in a Grignard flask equipped with a reflux condenser and a mechanical stirrer. The oil became very thick and a white solid formed in the condensing tube. This was identified as diphenyl. No phosphorus compound was found.

The main product of this reaction should be

All reactions after the Grignard were carried out under an atmosphere of dry hydrogen and at temperatures below 10° .

In the next step, Krause recommends the use of cadmium bromide and reports that the chloride causes a precipitate of magnesium chloride which hinders the reaction.⁽¹⁶⁾ However, Gilman has been successful in using cadmium chloride.

In this work, 20 g. of cadmium chloride was used and was added directly to the Grignard solution. 30 cc. of phosphorus trichloride dissolved in 100 cc. of anhydrous ether was then added slowly. As soon as this hit the solution in the flask, a white precipitate was formed, indicating that some reaction did take place. After this addition the reaction mixture was poured, with stirring, into a mixture of ice and water, made slightly acid with hydrochloric acid. After the hydrolysis and evaporation of the ether, the remaining aqueous solution separated into two layers, one a clear liquid, the other a yellow oil.

The oil was subjected to distillation and below 115° the distillate consisted of water and brombenzene. At 115° the oil became very thick and a white solid formed in the condensing tube. This was identified as biphenyl. No phosphorus compound was found.

The main product of this reaction should be phenyl phosphinic acid, $\text{C}_6\text{H}_5\text{PO}(\text{OH})_2$, diphenyl phosphinic acid, $(\text{C}_6\text{H}_5)_2\text{PO}(\text{OH})$, or triphenyl phosphine, $(\text{C}_6\text{H}_5)_3\text{P}$. It was hoped that the diphenyl compound would be obtained.

The entire reaction was run seven times and different methods tried for the extraction of the product. Extraction was first tried with ether. However, evaporation of the ether left no solid residue whatever. Several other solvents, including toluene and petroleum ether, were tried with the same negative results.

Another method of separation was tried, following a suggestion from Friend's Textbook of Inorganic Chemistry.⁽⁵⁾ The hydrolysis was carried out in a mixture of 100cc. of concentrated hydrochloric acid and 100 cc. of water. 120 cc. of concentrated nitric acid were then added and the solution boiled. When the solution was cooled, white needle crystals separated which were soluble in water and insoluble in ether. After being washed with ether several times, these crystals were tested qualitatively for phosphorus. A small amount of the substance was added to a few drops of a mixture of concentrated nitric and sulfuric acids and boiled. This was then diluted

with water and about 4 cc. of ammonium molybdate solution was added. No precipitate of ammonium phosphomolybdate formed, showing that no phosphorus was present in the original compound. Addition of ammonium sulfide to a basic solution of the crystals gave a yellow precipitate of cadmium sulfide and addition of silver nitrate solution gave a positive test for halogen. These facts indicate that the crystals were of either cadmium chloride or cadmium bromide.

Some interesting color changes in the solution were observed after the addition of the nitric acid. The solution changed from colorless, through yellow, brown, and deep red to a light reddish color. It seems strange that the organic reaction which this seems to indicate should cause the precipitation of an inorganic salt. Possibly the cadmium salt was present in an addition compound with an organic group and was released in some way by the acid.

Although the characteristic odor of organic phosphorus compounds could be detected during each run, no solid phosphorus compound could be separated.

On one run, the solution after hydrolysis was evaporated to dryness on a steam bath. Ether was then added to the solid salts left and mixed thorough-

ly with them. The ether was then decanted off and evaporated but left no solid residue. This seems to indicate that no diphenylphosphinic acid was formed in the reaction since the compound is very soluble in ether. (5)

An interesting substance was encountered at one time in this work, during an attempt to prepare p-chlordiphenyldichlorophosphine by a Friedel-Craft reaction between p-chlordiphenyl and phosphorus trichloride. (24) When the reaction was complete, a solid, white substance was present in the ether solution. After being filtered off and dried, and allowed to stand in air for a few minutes, it decomposed spontaneously with apphosphorescent glow, leaving a yellow residue. Time did not permit a further investigation of this compound.

Organo-Cadmium Compounds.

Considerable progress has been made in the last few years on the study of organo-cadmium compounds, particularly in regard to their preparation and physical properties. However, a survey of the literature shows a definite lack of information on their chemical properties and reactions.

The most successful methods of preparing organo-

cadmium compounds make use of other organo-metallic compounds. Both cadmium dialkyls and diaryls are best prepared by adding finely powdered cadmium bromide to the appropriate Grignard reagent in ether solution and vacuum distilling the resulting mixture. (9,16)

Cadmium diphenyl has also been prepared by the reaction of the metal itself with mercury diphenyl. (13) However, in this case the product was always found to contain considerable quantities of mercury diphenyl which could not be separated.

Another method, not involving other metals, has been used by Lohr. (2,17,18,25) This consists in heating together an alkyl iodide and metallic cadmium. In this way he succeeded in preparing the very pure methyl and ethyl compounds, although the yields were poor due to the coupling of the alkyl groups forming higher hydrocarbons.

Krause has made an extensive study of cadmium dialkyls and reports that in general they are colorless, highly refractive liquids, having very irritating vapors. They are stable if stored in the dark under nitrogen, but ignite spontaneously in air. In water they decompose with a crackling noise which may last for hours. (16)

An extensive review of the physical properties

of these compounds, including boiling points, densities, and refractive indices, has been compiled by Jones. (15)

Their molecular volumes have been found to decrease with increasing molecular weight of the organic group. (12)

Cadmium dialkyls are salts and undergo dissociation to a considerable extent when dissolved in certain solvents. Hein and Pauling have found that solutions of these compounds in tetralkyl ammonium halides will conduct electric current. (11)

The diaryl compounds of cadmium are similar in many respects to the dialkyl compounds except that they are crystalline solids, (13) colorless when pure. They too are spontaneously combustible in air and must be kept in an inert atmosphere.

The literature shows only meager knowledge of the general reactions of both of these types of compound. However, it is apparent that they are similar to Grignards and differ from them in degree rather than type of reaction. This would indicate reactions with active hydrogen atoms, alkyl halides, carbonyl group, cyanide group, etc. An investigation of these possible reactions should yield some valuable information.

The relative reactivity of cadmium compounds, as compared with other organo-metallic compounds, has been

investigated by at least two different methods, with excellent agreement. Nelson attacked the problem through the reactions of organo-metallic compounds with active hydrogen atoms attached to O, S, or N, or C attached to a negative element.⁽¹⁹⁾ He found that the order of increasing reactivity in metals near cadmium was Hg, Cd, Zn, Mg. Gilman found the same order in a study of the reactions of these compounds with Michler's ketone.⁽⁸⁾

Besides these simple organic compounds, cadmium also forms many complex addition and coordination compounds. Burrows and Lench have prepared the coordination compounds $\text{Cd}(\text{PhMe}_2\text{As})\text{Cl}_2$ and $\text{Cd}(\text{PhMe}_2\text{As})\text{Br}_2$ by treating hot, alcoholic solutions of the inorganic cadmium salt with the appropriate tertiary arsine,⁽³⁾ Similarly, Rosenheim and Meyer have prepared $\text{Cd}(\text{CH}_4\text{N}_2\text{S})_2\text{Cl}_2$ and $\text{Cd}(\text{CH}_4\text{N}_2\text{S})_2(\text{SCN})_2$ from thiocarbamide and the inorganic salts.⁽²³⁾ These compounds, as expected, are crystalline solids with fairly high melting points. Grossman and Schuck have succeeded in getting triethylenediamine cadmium thiocyanate from the reaction of ethylenediamine with cadmium thiocyanate.⁽¹⁰⁾

Other complex compounds of the metal have been formed with phthalocyanine,⁽¹⁾ aa' dipyridyl,⁽¹⁴⁾

Literature Cited

propylenediamine,⁽²⁰⁾ and substituted pyridines.⁽²¹⁾

One use for these complex compounds has been found by Porter in his studies of the stereochemistry of the cadmium derivatives of pyrromethenes.⁽²²⁾

There is still much work to be done on organo-cadmium compounds. It is very probable that in the future they will become valuable in many syntheses where the very important Grignard reagent is too reactive.

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