

## **BOOK REVIEW**

### **The Development of Organic Phosphorus Chemistry: Discoveries of the Nineteenth Century**

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This treatise is an excellent review of the birth of organophosphorus chemistry with respect to the generation of C-P bonds. Dr. Quin has done a superb job in ferreting out the facts concerning the early work in this field in the 19<sup>th</sup> century. Four chapters compose the book with each chapter focusing mainly on work done by specific chemists. The publication in 1950 by G. M. Kosolapoff is cited often and is the first text in English which addresses nearly the entire area of organophosphorus chemistry prior to that time. References from early times and a few modern citations make this present work of value to all who have an interest in the historical development of C-P bond formation.

#### **Preface and Chapter 1**

Experimental work by Paul Thenard in 1845 involved heating calcium phosphide with methyl chloride in sealed tubes at elevated temperatures (250-300 °C). These dangerous conditions generated trimethylphosphine whose structure was proven only by elemental analysis. This result appears to be the first example of C-P bond formation. Another 10 years occurred before triethylphosphine was synthesized. August W. Hofmann became the champion of the emerging field of organophosphorus chemistry and published many works from 1855-1873 and which involved a variety of phosphine oxides, phosphonic acids, and several other types of compounds. A reference to the work of F. Berle indicated that he utilized sodium phosphide and ethyl iodide in a stream of carbon dioxide to obtain triethylphosphine which he proceeded to heat with ethyl iodide and proposed formation of tetraethylphosphonium iodide whose structure is probably correct although only an analysis for the iodide content was given. This chapter also contains an overview of the early conditions (many being dangerous) employed by the pioneers in organophosphorus chemistry to produce C-P compounds. The naming of many common organic phosphorus functional groups is presented along with some early notations of structural designations.

#### **Chapter 2**

August W. Hofmann made many contributions to organophosphorus chemistry which are described in this chapter. His discoveries of a large number of stable C-P containing compounds make him the major figure in this field in the mid 19<sup>th</sup> century. His work is the basis of considerable value in the area even today. A photo and brief biography are provided in the chapter including his birth in 1818 in Giessen, Germany, and death in 1892 in Berlin. He was Director of the Royal College of Chemistry in London (1845-1864) after which he returned to Bonn, Germany, in 1864 and finally to the University of Berlin where he remained for the rest of his life. Hofmann worked on other areas including the coal tar and dye industries. His work also resulted in the first description of primary, secondary, and tertiary amines and included his famous Hofmann degradation of amides to amines and the elimination process with quaternary ammonium hydroxides to alkenes. He was a founding member for the Deutsche Chemische Gesellschaft and the journal "Berichte".

Hofmann used dialkylzincs in reactions with  $\text{PCl}_3$  to obtain trialkylphosphines. His finding that  $\text{ZnCl}_2$  was "bound" to these phosphines is indicative of the Lewis base characteristics of phosphines and ligands as are known today. Interestingly, he utilized an atmosphere of  $\text{CO}_2$  to prevent oxidation of the phosphines which is related to the common technique of using an inert gas to blanket a reaction. He prepared triethylphosphine oxide, triethylphosphine sulfide, trialkylphosphine selenide, and a crystalline product evolved from reaction of  $\text{Et}_3\text{P}$  with  $\text{PtCl}_2$ . A novel discovery was that  $\text{Me}_3\text{P}^+\text{-CH}_2\text{CO}_2^-$  could be prepared as the counterpart of betaine. His synthesis of primary and secondary phosphines using alkyl halides with  $\text{PH}_4\text{I}$  and zinc oxide introduced a direct avenue to such systems. Passing methylphosphine into boiling nitric acid generated methylphosphonic acid  $[\text{MeP}(\text{O})(\text{OH})_2]$  which was converted to certain salts. A bis(phosphonium) salt  $[\text{Et}_3\text{P}^+\text{-CH}_2\text{CH}_2\text{-P}^+\text{Et}_3, 2 \text{ Br}^-]$  was the first of this family to be obtained as was  $\text{H}_2\text{C}=\text{CH-P}^+\text{Et}_3, \text{ Br}^-$ . Certain secondary phosphines and

elemental sulfur reacted to yield what is now known as  $R_2P(S)SH$  systems. They were characterized as salts which were later confirmed. Because of his wide interest in some many different functional groups in the organophosphorus family, it is stated that Hofmann should be ascribed at the "Founding Father" of organophosphorus chemistry, a statement with which this reviewer agrees.

### Chapter 3

The central theme of this chapter follows the work of Karl Arnold August Michaelis. A photo and brief biography are included, his birth being in Bierbergen, Hannover, Germany, in 1847 and his death in 1916. His training was at Gottingen and Jena Universities followed by an appointment at the Technical Hochschule of Karlsruhe where he became Professor in 1876. In 1880 he accepted a position at the University of Aachen until 1890 after which he became a Professor at the University of Rostock where he remained until his death. He used the name of August Michaelis in most papers. The enormity of his contributions to organophosphorus chemistry is staggering. A list of his accomplishments are given on page 29. The first synthesis of several families of C-P containing compounds include  $PhPH_2$ ,  $PhP(OR)_2$ ,  $ArPX_2$ ,  $Ar_2P(O)-OH$ ,  $Ar_3P$ ,  $ArP(O)(OH)_2$ ,  $ArP(S)(OR)_2$ ,  $HP(O)(OR)_2$ ,  $RP(O)(OH)_2$ ,  $RPCl_2$ ,  $RPH(O)(OH)_2$ , and many other systems. He was most known for his preparations of triarylphosphines via reaction of  $ArPCl_2$  and  $Ar-Br$  in the presence of sodium metal at room temperature over several days. An unusual reaction of  $Ph_2POPh$  with  $MeX$  (or  $PhCH_2X$ ) resulted in alkylation of  $Ph_2P^+(Me)OPh$ ,  $X^-$  which, in turn, underwent hydrolysis to yield  $Ph_2P(O)-Me$ . Synthesis and reactions of alkylphosphonous dichlorides are summarized as is the synthesis of phosphines from chlorophosphorus compounds. Early work with a variety of P-aryl phosphorus acids are also outlined with many examples commonly known today. Arylphosphonic acids led to an enormous number of derivatives. The same can be said regarding the utility of  $Ar_2P(O)OH$  molecules which are precursors for many phosphinates and related systems. Michaelis was quick to recognize the versatility of such acids early in his career. He expanded his studies to include the synthesis of phosphonous acids [ $ArPH(O)OH$ ] and phosphinous acids [ $Ar_2POH$ ]. Some emphasis was directed towards obtaining P-alkyl phosphonic and phosphinic acids, with esters being primary targets. The Michaelis-Arbuzov reaction is of major importance today since many trialkyl phosphites exist and react easily with alkyl halides to generate phosphonates. Some mention is made of a few reactions which lead to phosphorus compounds containing a P=S bond. As modern theory for carbon valence began to develop in the late 19<sup>th</sup> century, Michaelis recognized in 1872 that phosphorus could possess a valence of 3 or 5. He began to draft structures with a P=O bond, but, of course, the exact nature of such bonding is still being evaluated. Michaelis was a giant for phosphorus chemistry during his lifetime, and his work is still the basis for much chemistry involving phosphorus atoms in today's chemical arena. The chapter is very well written.

### Chapter 4

This chapter deals with contributions to phosphorus chemistry by other chemists during the period of 1870-1900. A variety of organophosphorus compounds were obtained by many scientists especially from Germany and France. Phosphonic acids, phosphines, phosphonium salts, phosphine oxides, phosphine sulfides, and several phosphorus halides were described. Some overlap of results cited in prior chapters occurs, but the descriptions make for consistency in the overall discussion.

In summation, the book is an excellent source for the early chemistry of C-P bond formation. Indeed, there are a few reactions which are tempting to explore with modern technology for the potential generation of C-P compounds in straight-chain systems as well as in novel heterocycles. Chemistry history buffs will find this an attractive addition to their collection.

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