

[A COMMUNICATION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL CO.]

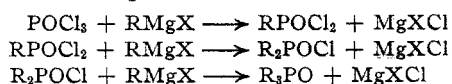
An Improved Method of Preparation of *bis*-Arylphosphonic Acids

BY GENNADY M. KOSOLAPOFF

The usual method of preparation of phosphonic acids, $\text{RPO}(\text{OH})_2$ and R_2POH , involves the preparation of the corresponding halophosphines by the Friedel-Crafts reaction of the corresponding hydrocarbon with phosphorus trichloride, followed by oxidation and hydrolysis. Generally, the preparation of the halophosphines is quite unsatisfactory because of meager yields. At the same time, the odor and the vapor toxicity of the halophosphines frequently make them rather inconvenient to handle. Particularly unsatisfactory are the methods of preparation of the *bis*-arylphosphonic acids. The necessary halophosphines form only as by-products in the usual Friedel-Crafts reaction of the hydrocarbons with phosphorus trichloride, with the consequently very low yields. Some improvement in this respect was introduced by Pletz¹ who obtained fair yields of R_2PCl by the thermal decomposition of *tris*-arylphosphine dichlorides. However, this method of preparation of the phosphonic acids involves at least four steps, with the consequently lowered over-all yields and necessitates operations with the objectionable halophosphines.

It is felt that a direct, preferably one-step, method of preparation of *bis*-arylphosphonic acids was needed as a stimulus for investigations of this relatively little studied class of organic compounds of phosphorus. The elimination of the actual operations with the halophosphines was also highly desirable.

The most convenient method of attack appeared to be the Grignard reaction, which has been used with success in the preparation in good yields of tertiary phosphine oxides by the addition of phosphorus oxychloride into an excess of the desired Grignard reagent.² The reaction probably occurs in three stages, *i. e.*



the high order of reactivity of the intermediate halophosphines making the over-all reaction very rapid.

It was felt that it should be possible to separate

(1) V. M. Pletz, "Secondary Chlorophosphines," Dissertation, Kazan (1938).

(2) Grignard and Savard. *Compt. rend.*, **192**, 592 (1931)

the component reactions and to obtain the intermediate products by the proper choice of conditions. In the usual procedure for the preparation of R_3PO , the reaction is run with the phosphorus oxychloride always in position to react with an excess of the Grignard reagent. By reversing the addition order, it was thought to be possible to arrest the reaction at the desired stage of having the Grignard reagent always in position to react with an excess of the phosphorus oxychloride. The utilization of as dilute a solution as practicable and the employment of low temperatures were the remaining factors.

In preliminary experiments, solutions of Grignard reagents were added slowly to ether solutions of phosphorus oxychloride with vigorous stirring, with or without cooling. The drops of the Grignard reagent produced an immediate turbidity of the solution and as the reaction proceeded there was a gradual deposition of a white, or pale-yellow, solid on the flask walls. On working up the ether solutions they were found to be essentially free of magnesium compounds and to contain only the normal amounts of R-R and R-X , with very small amounts of the tertiary phosphine oxides. The solid precipitate, on hydrolysis, gave satisfactory yields (usually over 50%) of *bis*-arylphosphonic acids. No appreciable amounts of the mono-arylphosphonic acids were detected in the temperature range studied: 0° to the reflux temperature of the ether solution. A slight improvement of the yield of the phosphonic acid was found at the higher temperature, while dilution of the reagents also had a beneficial effect for dilutions up to approximately one liter total volume for 0.2-mole runs, which was regarded as a practical limit for dilution. The maximum molar ratio of phosphorus oxychloride to RMgX used was 1:1.

The above results indicate that the halophosphines, as formed, combine with MgXCl forming an ether-insoluble addition complex, probably of the type $\text{R}_2\text{POCl} \cdot \text{MgXCl}$. Generally, this is a crystalline solid, although in some cases gummy solids are formed.

The procedure probably can be extended to the aliphatic series.

Experimental

Diphenylphosphonic Acid.—Phenylmagnesium bromide (from 31.4 g. of bromobenzene and 4.86 g. of magnesium in 200 cc. of absolute ether) solution was diluted to 500 cc. by absolute ether, filtered with exclusion of air and added slowly (three and one-half hours) to a gently refluxing stirred solution of 30.6 g. of phosphorus oxychloride in 500 cc. of absolute ether; after standing overnight the ether solution was decanted from the solid precipitate and the latter treated with 200–300 g. of ice-water. The white solid which was insoluble in water was washed with water and triturated with 1 l. of warm dilute sodium hydroxide solution, filtered and filtrate acidified with dilute hydrochloric acid. The precipitated diphenylphosphonic acid was filtered, dried and recrystallized from dilute alcohol; m. p. 190–192°; yield 12 g., 55%. The sodium hydroxide-insoluble solid on repeated recrystallization yielded 4 g. of triphenylphosphine oxide, m. p. 152–153° (from dilute alcohol).

bis-*p*-Chlorophenylphosphonic Acid.—The Grignard reagent from 39 g. of *p*-chlorobromobenzene was diluted to 400 cc. with absolute ether and added in the course of one and one-half hours to a gently refluxing stirred solution of 30.6 g. of phosphorus oxychloride in 500 cc. of absolute ether. After standing overnight, the reaction mixture was worked up as above, yielding 15 g. (51%) of bis-*p*-chlorophenylphosphonic acid, m. p. 133–135° (from dilute alcohol) and 4.5 g. of *tris-p*-chlorophenylphosphine oxide, m. p. 171–2.5° (from dil. alcohol).

Anal. Calcd. for $C_{12}H_9O_3PCl_2$: eq. wt., 287; Cl, 24.7. Found: eq. wt., 283; Cl, 24.58.

Summary

An improved method for the preparation of bis-arylphosphonic acids has been devised in which phosphorus oxychloride is treated with Grignard reagents in dilute solution.

DAYTON, OHIO

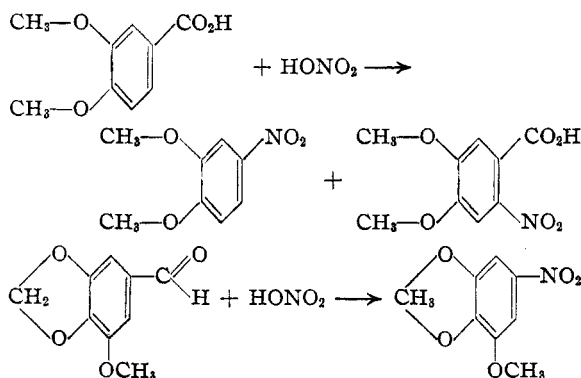
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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Studies in the Veratrole and Methyleneedioxybenzene Series

BY RICHARD T. ARNOLD AND FREDERICK BORDWELL¹

Interest in the veratrole (*o*-dimethoxybenzene) and methylenedioxybenzene (1,3-benzodioxole) compounds has been aroused largely for two reasons. First, these nuclei frequently make up important component parts of well known naturally occurring substances (opium alkaloids, apioles, etc.); and, second, the parent substances have exceedingly reactive benzenoid rings which orient incoming substituents in a unique and (according to the classical orientation rules) unpredictable manner. Two typical examples may be cited to illustrate the latter point.^{2,3}



The remarkable susceptibility of these aromatic

(1) Abstracted from a Ph.D. thesis submitted to the Graduate School in July, 1941.

(2) Tiemann and Matsumoto, *Ber.*, **9**, 937 (1876).

(3) Salway, *J. Chem. Soc.*, **95**, 1155 (1909).

rings to attack by electrophilic reagents at the positions para to the oxygen atoms can be accounted for by resonance contributing structures of the type A and B.



In spite of the easily recognizable similarities, it is well established that the benzenoid ring of methylenedioxybenzene is more reactive than that of veratrole.⁴

To enable us to make a comparative study of the aromatic bond types in these two series we have prepared a number of substituted phenols (I–IX below) and have measured their *pK* values under identical circumstances. These values were determined by measuring the *pH* of half-

<chem>COc1cc(OC)ccc1O</chem>	<chem>COc1cc(OC)ccc1O</chem>	<chem>COc1cc(OC)ccc1O</chem>	<chem>COc1cc(OC)ccc1O</chem>
I, X = —CHO	II, X = —CN	V, X = —CHO	VII, X = —NO ₂
III, X = —NO ₂	IV, X = —CO ₂ H	VI, X = —CN	VIII, X = —CO ₂ H
<i>pK</i>		<i>pK</i>	
9.12	8.69	8.90	8.41
8.33	4.60	8.17	4.58

(4) Hudson and Robinson, *J. Chem. Soc.*, 715 (1941).