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Part I

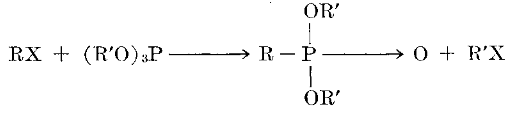
Phosphorus Derivatives of Fatty Acids

RICHARD SASIN, Drexel Institute of Technology

This paper deals with those phosphorus derivatives of fatty acids that contain a carbon-phosphorus bond, which as a class are known as alkylphosphonates. Much of this work was done under a fellowship sponsored by the Fatty Acid Producers' Council at the Eastern Regional Research Laboratory. This research on the preparation of pure derivatives from fats was directed mainly toward the correlation of structure with important physical properties desired in plasticizers and also in synthetic lubricants.

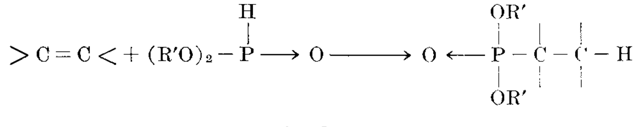
There are two principal methods by which the phosphorus atom may be incorporated into the fatty acid chain.

1) By the Michaelis-Arbuzov "isomerization" reaction of trialkyl phosphites with alkyl halides (1).



$$RX + (R'O)_3P \longrightarrow R-\overset{\overset{\displaystyle OR'}{|}}{\underset{\underset{\displaystyle OR'}{|}}{P}} \longrightarrow O + R'X$$

2) By the radical catalyzed addition of dialkyl phosphonates to olefins.



$$>C=C< + (R'O)_2-\overset{\overset{\displaystyle H}{|}}{P} \longrightarrow O \longrightarrow O \longleftarrow \overset{\overset{\displaystyle OR'}{|}}{\underset{\underset{\displaystyle OR'}{|}}{P}} - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} - H$$

An alkylphosphonate is obtained in each case. Since alkyl halides are rather expensive, the second method generally is the more economical one.

Synthesis

1. Diethyl acylphosphonates

The first systematic study of diethyl acylphosphonates was made by Ackerman and co-workers (2). These were prepared by the reaction of acyl chlorides with triethyl phosphite. The compounds prepared in 45–60% yield were derived from the even-numbered C_4-C_{18} saturated fatty acids and oleic acid. The acylphosphonate structure was confirmed by molecular refraction, infrared spectroscopy, and polarographic studies. As might be expected, the acylphosphonates are quite unstable to moisture with the rate of hydrolysis decreasing with increase in the size of acyl chain.

2. Diethyl 2-Acyloxyethylphosphonates

The diethyl 2-acyloxyethylphosphonates derived from long-chain fatty acids were prepared by the reaction of the 2-bromoethyl esters with triethyl phosphite (3). Hydrolysis studies on these compounds led to the following conclusions:

(a) Hydrolysis of the carboxyl ester occurs much more rapidly than that of the phosphonic esters.
(b) Rate of hydrolysis is not affected by length of acyl chain or size of phosphonic ester groups.
(c) Rate of hydrolysis is approximately the same as that of the ethyl ester of the corresponding fatty acid.

Dialkyl 2-acyloxyethylphosphonates were also prepared in 45–65% yield by the addition of dialkyl phosphonates to vinyl esters under free radical conditions (4).

Most of these phosphonates are colorless liquids at room temp except those derived from myristic, palmitic, and stearic acids which are low melting solids.

3. Trialkyl α-Phosphonates

Trialkyl α-phosphonates of long-chain fatty acids were prepared in 30–90% yield from the appropriate trialkyl phosphite and alkyl ester of the α-bromocarboxylic acid (5).

The α-phosphonates are colorless, odorless, thermally stable liquids, insoluble in water and soluble in organic solvents. These compounds were found to be resistant to hydrolysis with 0.1 N hydrochloric acid. When refluxed for 18–24 hr with 20–35% hydrochloric

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acid they are converted to the tribasic α-phosphonocarboxylic acids. With dilute base in ethanol, the carboxylic ester group is preferentially hydrolyzed yielding α-dialkylphosphonocarboxylic acids.

4. Vinyl α-Diethylphosphonates

A series of vinyl α-bromo esters was prepared from α-bromocarboxylic acids and vinyl acetate by acidolysis in the presence of mercuric sulfate. By heating the vinyl α-bromo esters with triethyl phosphite, the corresponding vinyl α-diethylphosphonates were prepared in 35–75% yield (6).

The vinyl α-phosphonates are colorless, odorless liquids which are insoluble in water and soluble in organic solvents. Under prolonged heating with benzoyl peroxide, they form polymers with a low degree of polymerization.

5. ω-Dialkyl Phosphonoundecanoates

This series of compounds was prepared in 53-87% yield by heating a series of ω-bromoundecanoates with trialkyl phosphites (7).

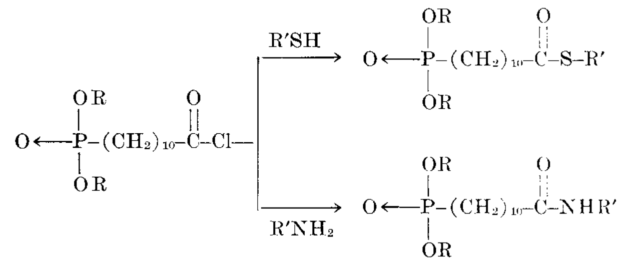
These compounds were also prepared in 53–66% yield by the addition of dialkyl phosphonates to alkyl undecenoates (4).

This reaction was catalyzed by decomposing peroxides and also by ultraviolet radiation. Symmetrical trialkyl ω-phosphonoundecanoates as well as mixed ω-phosphoundecanoates were prepared.

The indices of refraction and infrared spectra of the compounds prepared by the addition reaction were identical to those prepared by the Michaelis-Arbuzov reaction.

The addition of dialkyl phosphonates to undecenoic acid yielded a series of ω-dialkyl phosphonoundecanoic acids (8).

Reaction with oxalyl chloride yielded the corresponding acyl chlorides, which on treatment with mercaptans and amines yielded the corresponding thiol esters and substituted amides, respectively.



The thiol esters are all colorless high-boiling liquids while the amides are white crystalline solids.

6. Trialkyl 9(10)-Phosphonostearates

Addition of dialkyl phosphonates to alkyl oleates in the presence of decomposing *t*-butyl perbenzoate yielded trialkyl 9(10)-phosphonostearates in 66-77% yield (4).

Attempts to catalyze the reaction with ultraviolet radiation yielded only unchanged reactants. The 9(10)-phosphonostearates are colorless, high-boiling, thermally stable liquids, insoluble in water and soluble in organic solvents.

7. Bis(3-Dialkylphosphonopropyl) Esters

The addition of dialkyl phosphonates to diallyl esters of aliphatic dibasic acids under free radical conditions yielded bis(3-dialkylphosphonopropyl) esters in 30–99% yield (9).

This reaction provides a process whereby compounds containing two phosphorus atoms are readily obtained in good yields. The parent dibasic acids ranged from oxalic to sebacic. All of these compounds are colorless, high-boiling thermally stable liquids.

8. Phosphonated Oils and Phosphonated Esters

The addition of dialkyl phosphonates to unsaturated compounds has been extended to include alkyl and glyceryl esters of polyunsaturated acids or mixtures containing them (10). Some typical natural triglycerides to which dialkyl phosphonates have been added are soybean, cottonseed, safflower, corn, sunflower, tung, and linseed oils, fish oils, tallow, lard, lard oil, and oleo oil. These triglycerides are mixed glyceryl esters of saturated, monounsaturated, and polyunsaturated fatty acids. It is readily apparent that products with a wide range of phosphorus content may be made from triglycerides.

Properties and Uses

1. Lubricity Additives

Several of the alkyl phosphonates were examined as lubricity additives in bis(2-ethylhexyl) sebacate and mineral oil (10). It was found that the lubricity properties of some of these long-chain phosphorus additives compare favorably with the values determined on presently used hypoid gear oils. Some were effective anti-wear and extreme pressure agents.

2. Viscosity Characteristics

The viscosity, viscosity index, and the pour or freezing point of these phosphorus derivatives of fatty acids were determined (12). The viscosity index of the ω-dialkyl phosphonoundecanoates was found to be generally high, equaling or exceeding that of the conventional diesters in most cases. In addition, some of these compounds have rather low pour points, in the range of −65C.

The trialkyl 9(10)-phosphonostearates are characterized by low pour points in the narrow range of −52 to −64C.

3. Plasticizers for Vinyl Chloride Polymers

Long-chain phosphorus compounds have been found to be efficient, primary plasticizers imparting good low temperature flexibility to poly(vinyl chloride) compositions containing them. The dialkyl 9(10)-phosphonostearates are of particular interest. All of these compounds are outstanding in having low migration losses in addition to imparting low stiffening temp to poly(vinyl chloride). Some of the dialkyl ω-phosphonoundecanoates also have these characteristics.

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