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ACID ESTERS OF ACYL-PHOSPHOROUS ACIDS
AND METHOD OF MAKING THE SAME

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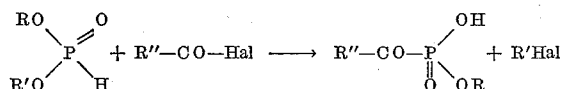
This invention relates to acid esters of acyl-phos-
phorous acids and their salts and to a method of pre-
paring the same from halides of monobasic or polybasic
carboxylic acids and di-substituted phosphites.

It is known that the ethyl ester of acetyl-phosphorous
acid or benzoyl-phosphorous acid may be obtained by a
reaction between acetyl chloride or benzoyl chloride and
triethyl phosphite. The neutral esters thus obtained de-
compose upon saponification either into the correspond-
ing carboxylic acid and phosphorous acid or into the
corresponding aldehyde and phosphoric acid. It is there-
fore not possible to produce acid esters of acyl-phos-
phorous acids or their salts by this method.

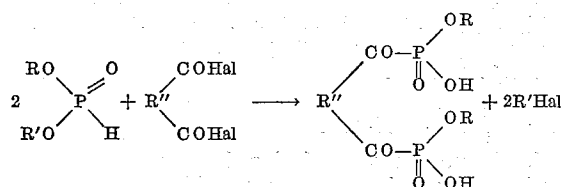
It is an object of the present invention to provide a
process for the production of new and useful acid esters
of acyl-phosphorous acids or their salts from readily
accessible starting materials.

Other objects and advantages of our invention will be-
come apparent as the description proceeds.

We have discovered that acid esters of acyl-phos-
phorous acids may be produced in a very simple fashion
by reacting halides of monobasic or polybasic carboxy-
lic acids with di-substituted phosphites at elevated tem-
peratures. When a monocarboxylic acid halide is used,
the reaction in accordance with the present invention
probably proceeds in accordance with the following gen-
eral equation.



In this equation R and R' represent identical or different
aliphatic or cycloaliphatic hydrocarbon radicals with pre-
ferably less than 8 carbon atoms, and R'' represents an ali-
phatic, cycloaliphatic or aromatic hydrocarbon radical.
The radicals R, R' and R'' may be straight-chain hydro-
carbon radicals or also branched-chain hydrocarbon radi-
cals. They may also be substituted, for example halogen-
substituted. The radical R'' may in addition be inter-
rupted by heteroatoms; that is, by oxygen, sulfur or
nitrogen atoms. If the halide of a dibasic or polybasic
carboxylic acid is used as the starting material for the
process in accordance with the invention, dibasic or poly-
basic acid esters are formed in analogous fashion, for
example, in accordance with the following equation:



Accordingly, the halides, preferably the chlorides or
bromides, of aliphatic, cycloaliphatic or aromatic mono-
carboxylic, dicarboxylic or polycarboxylic acids, the hy-
drocarbon radicals of which carry various substituents or

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are also interrupted by heteroatoms or heteroatom groups,
may be used as starting materials for the process ac-
cording to the present invention; such acids are, for ex-
ample, acetic acid, butyric acid, isobutyric acid, lauric
acid and higher fatty acids, mono-, di- and trichloro-
acetic acid, as well as other halogenated carboxylic acids,
ether-carboxylic acids, thioether-carboxylic acids, amino-
carboxylic acids, cyclohexane-carboxylic acid, benzoic
acid and other substituted or unsubstituted aromatic car-
boxylic acids, as well as di- and poly-carboxylic acids,
such as adipic acid, sebacic acid, tricarballic acid, phthalic
acid, tetrachlorophthalic acid, terephthalic acid,
trimesic acid, and the like.

Di-substituted phosphites which may be reacted with
the carboxylic acid halides in accordance with the in-
vention are, for example, diethyl phosphite, di-isopropyl
phosphite, dibutyl phosphite, dioctyl phosphite, di-(2-
chloroethyl)-phosphite, and the like.

The two reaction components are preferably used in
quantitative ratios such that about one mol of di-substi-
tuted phosphite is present for each -CO-Hal group. The
presence of an excess of one or the other reaction com-
ponents, however, is not detrimental.

The reaction takes place at elevated temperatures, pref-
erably between 50 and 150° C. In some cases, especial-
ly when a particularly reactive carboxylic acid halide is
used, it is advantageous to carry out the reaction in the
presence of an inert organic solvent or diluent, such as
carbon tetrachloride or benzene.

As indicated by the above equations, the reaction
proceeds with the formation of an aliphatic or cyclo-
aliphatic halide. If a low-molecular aliphatic alcohol is
used for the production of the di-substituted phosphite,
this hydrocarbon halide continuously distills out of the
reaction mixture during the reaction. If a high-molecu-
lar aliphatic or cycloaliphatic alcohol is used to produce
di-substituted phosphite, the hydrocarbon halide may be
distilled off in vacuo during or after the reaction.

The acid esters of acyl-phosphorous acids obtained by
reaction in accordance with the invention are useful as
capillary-active agents for various purposes, for example
as cleaning agents or washing agents. The acid ester of
acyl-phosphorous acid as described above may be trans-
formed into their salts, for example their alkali metal
salts in a very simple fashion. These salts are likewise
useful as capillary-active agents and may be used alone
or with usual substances, for example phosphates, alka-
line carbonates and silicates as washing agents, cleaning
agents or as textile-finishing agents.

The acid esters may also be transformed into other
acid esters by ester-radical exchange or into neutral esters
by heating them, preferably with high-molecular alcohols
and, if necessary, in the presence of suitable esterification
catalysts.

The polybasic esters of acyl-phosphorous acids pro-
duced from the halides of di- and polycarboxylic acids
in accordance with the present invention may also be
reacted with polyvalent alcohols to form acid or also
neutral polyesters of varying molecular size.

The following examples will further illustrate the pres-
ent invention and enable others skilled in the art to un-
derstand the invention more completely. However, it
is understood that our invention is not limited to the
embodiments illustrated in these examples.

Example I

A mixture of 55.2 gm. diethyl-phosphite and 87.4 gm.
lauroyl chloride was stirred at a temperature between
85 and 95° C. for 8 hours; 16 gm. ethyl chloride dis-
tilled off during that time. The residue was a clear,
colorless, moderately viscous liquid.

29.2 gm. of the residue were stirred with a solution of

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4 gm. sodium hydroxide in 1.4 liters water. A strongly foaming, turbid solution, similar to a soap solution, was formed. From this solution the pure sodium salt of the monoethyl ester of lauroyl phosphorous acid was obtained in a solid form by salting out with sodium chloride.

Example II

A mixture of 61 gm. adipic acid dichloride and 92 gm. diethyl-phosphite was stirred for 8 hours at 90–95° C.; 40 gm. ethyl chloride distilled off during that time. The reaction product, the di-monoethyl ester of adipoyl phosphorous acid, was a colorless, viscous liquid which dissolved in water to form a clear solution having an acid reaction.

Example III

A mixture of 55.2 gm. diethyl-phosphite and 56.2 gm. benzoyl chloride was heated for 20 hours at a temperature between 85 and 95° C., accompanied by stirring; 25 gm. ethyl chloride distilled off during that time. The reaction product, the monoethyl ester of benzoyl phosphorus acid, was a viscous, colorless, clear liquid which readily dissolved in dilute sodium hydroxide upon being shaken therewith.

Example IV

A mixture of 19 gm. capric acid chloride and 14.5 gm. diethyl-phosphite was stirred for 8 hours at a temperature between 85 and 95° C.; 6 gm. ethyl chloride distilled off during that time. The residue, the monoethyl ester of caproyl phosphorous acid, was a clear, colorless, moderately viscous oil which was readily soluble in dilute sodium hydroxide.

Example V

A mixture of 81 gm. 2-ethylhexanoic acid chloride and 69 gm. diethyl phosphite was stirred for about 6 hours at a temperature between 90 and 95° C. until no more ethyl chloride distilled off. 102 gm. of the moderately viscous residue formed thereby were heated in admixture with 112 gm. 2-ethylhexanol at 100° C. while passing a slow stream of nitrogen therethrough until a reduction in weight of 17 gm. occurred. Thereafter, the excess 2-ethylhexanol was distilled off at a vacuum of 2.5 mm. Hg. The residue had an acid number of 142 and a saponification value of 273 (calculated values for $C_7H_{15}-CO-PO(OH)-OC_8H_{17}$: 143 and 286, respectively). The acid ester dissolved in dilute sodium hydroxide. The solution foamed and exhibited excellent wetting properties.

Example VI

A mixture of 109.3 gm. lauroyl chloride and 97 gm. dibutyl phosphite was heated to 95° C. while passing nitrogen therethrough; the butyl chloride formed thereby was trapped in a condenser. After about 20 hours no more butyl chloride split off. The reduction in weight of the reaction mixture was 43.5 gm. The residue was a viscous, almost colorless oil. The phosphorus and carbon content of the reaction product corresponded to the formula



The chlorine content was smaller than 0.1%. The acid number was 182–186 (calculated 175) and the saponification value was 355–363 (calculated 350).

Example VII

For the cleaning of foodstuff containers, preferably of metal there is excellently suited a product of the following composition:

30% by weight trisodium phosphate ($12 H_2O$).
55% by weight sodium silicate solution 40° Bé.
5% by weight monoethyl ester of lauroyl phosphoric acid obtained as described in Example I, paragraph 1
Water, balance.

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This composition was used after dilution in water (about 10 grams per liter). The solution has good cleaning properties.

Example VIII

50 parts trisodium phosphate
20 parts sodium tripolyphosphate
10 parts sodium sulfate
20 parts acid ester, obtained as described in Example I, paragraph 1

are mixed. The product obtained in this manner after dissolving in water (about 10 grams per liter) is an excellent dishwashing composition.

Example IX

A cleaning agent of similar quality is obtained, if in the above (Example VIII) indicated combination, the acid ester is replaced by 20 parts of the sodium salt of the acid ester, which is described in Example I, paragraph 2.

Example X

An excellent metal cleaning agent is obtained by preparing a 2% aqueous solution of a mixture of the following composition:

25 parts di-monoethyl ester of adipoyl phosphorous acid, obtained as described in Example II
50 parts sodium sulfate
24 parts sodium pyrophosphate ($Na_2H_2P_2O_7$)
1 part 2-mercaptobenzthiazol.

While we have illustrated a few specific embodiments of the present invention, it will be readily apparent to those skilled in the art that the invention is not limited to these embodiments and that various changes and modifications may be made without departing from the spirit of the invention or the scope of the appended claims.

We claim:

1. The process of producing acid esters of acyl-phosphorous acid, which comprises heating a mixture of an organic carboxylic acid halide and a di-lower alkyl phosphite in a ratio of 1 mol di-lower alkyl phosphite per —CO-halide group in the carboxylic acid halide to a temperature between 50 and 150° C., and removing the lower alkyl halide from the reaction mixture.

2. The process of producing the monoethyl ester of lauroyl phosphorous acid, which comprises heating a mixture of equimolar amounts of diethyl-phosphite and lauroyl chloride to a temperature between 85 and 95° C., and removing the ethyl chloride formed thereby from the reaction mixture.

3. The process of producing the di-monoethyl-ester of adipoyl phosphorous acid, which comprises heating a mixture of 1 mol adipic acid dichloride and 2 mols diethyl-phosphite to a temperature between 90 and 95° C., and removing the ethyl chloride formed thereby from the reaction mixture.

4. The process of producing the monoethyl ester of benzoyl phosphorous acid, which comprises heating a mixture of equimolar amounts of diethyl-phosphite and benzoyl chloride to a temperature between 85 and 95° C., and removing the ethyl chloride formed thereby from the reaction mixture.

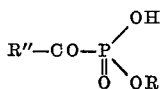
5. The process of producing the monoethyl ester of caproyl phosphorous acid, which comprises heating a mixture of equimolar amounts of capric acid chloride and diethyl-phosphite to a temperature between 85 and 95° C., and removing the ethyl chloride formed thereby from the reaction mixture.

6. The process of producing the monoethyl ester of 2-ethylhexanoyl phosphorous acid, which comprises heating a mixture of equimolar amounts of 2-ethylhexanoic acid chloride and diethyl-phosphite to a temperature between 90 and 95° C., and removing the ethyl chloride formed thereby from the reaction mixture.

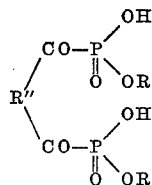
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7. The process of producing the monobutyl ester of lauroyl phosphorous acid, which comprises heating a mixture of equimolar amounts of lauroyl chloride and dibutylphosphite to a temperature of about 95° C., and removing the butyl chloride formed thereby from the reaction mixture.

8. Acid esters of acyl-phosphorous acids having a structural formula selected from the group consisting of



and



wherein R is an alkyl radical, and R'' is selected from the group consisting of mono- and di-valent saturated aliphatic and aromatic hydrocarbon radicals containing 1 to 7 carbon atoms and the radicals of saturated monovalent higher fatty acids, and the alkali metal salts thereof.

9. The monoethyl ester of lauroyl phosphorous acid.

10. The di-monoethyl ester of adipoyl phosphorous acid.

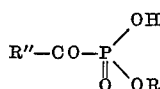
11. The monoethyl ester of benzoyl phosphorous acid.

12. The monoethyl ester of caproyl phosphorous acid.

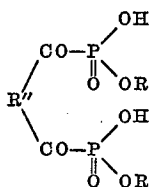
13. The monoethyl ester of 2-ethylhexanoyl phosphorous acid.

14. The monobutyl ester of lauroyl phosphorous acid.

15. Acid esters of acyl-phosphorous acids having a structural formula selected from the group consisting of



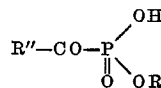
and



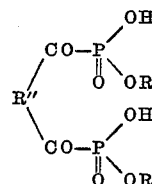
wherein R is selected from the group consisting of lower alkyl radicals with less than eight carbon atoms, and R'' is selected from the group consisting of mono- and di-valent saturated aliphatic and aromatic hydrocarbon radicals containing 1 to 7 carbon atoms and the radicals of saturated monovalent higher fatty acids.

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16. The process of producing acid esters of acyl-phosphorous acid having a structural formula selected from the group consisting of



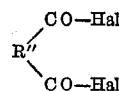
and



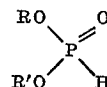
wherein R is selected from the group consisting of lower alkyl radicals with less than eight carbon atoms, and R'' is selected from the group consisting of mono- and di-valent aliphatic, cycloaliphatic and aromatic radicals containing from 1 to 18 carbon atoms, which comprises heating a mixture of a carboxylic acid halide having a structural formula selected from the group consisting of



and



wherein R'' has the meaning above indicated and Hal is a halogen atom, and a di-substituted phosphite having the structural formula



wherein R has the meaning above indicated and R' is selected from the group consisting of lower alkyl radicals with less than 8 carbon atoms, in a ratio of 1 mol di-substituted phosphite per CO-halide group in the carboxylic acid halide to a temperature between 50 and 150° C., and removing the lower alkyl halide formed by the reaction from the reaction mixture.

17. The mono-2-ethylhexyl ester of 2-ethylhexanoyl phosphorous acid.

18. The sodium salt of the mono-ethyl ester of lauroyl phosphorous acid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,491,920	Ernsberger	Dec. 20, 1949
2,629,731	Harman	Feb. 24, 1953
2,719,167	Schmidt	Sept. 27, 1955

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,900,408

August 18, 1959

Bruno Blaser et al

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 29, for "tetrachlorodie" read -- tetrachloride --;
column 6, lines 21 and 22, for "aliphatic cycloaliphatic and aromatic radicals containing from 1 to 18 carbon atoms" read -- saturated aliphatic and aromatic hydrocarbon radicals containing 1 to 7 carbon atoms and the radicals of saturated monovalent higher fatty acids --.

Signed and sealed this 29th day of March 1960.

(SEAL)

Attest:

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