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(54) Title: PROCESS FOR THE PREPARATION OF PHOSPHORUS ACID CARBOXYLIC ACID MIXED ANHYDRIDES AND ANHYDROUS PHOSPHOROUS ACID

(57) Abstract

A process for the preparation of phosphorus compounds by the reaction of phosphorus trichloride with a volatile carboxylic acid (e.g., acetic acid or propionic acid), wherein an excess of the carboxylic acid is employed at a temperature maintained below the boiling point of the reactant mixture, followed by removal of chlorine containing compounds is disclosed. The resulting mixture, which comprises phosphorus acid, the anhydride of said carboxylic acid, and mixed anhydrides of said carboxylic acid and phosphorus acid can be converted to anhydrous phosphorus acid or used to prepare aminomethylphosphonic acid.


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TITLE
PROCESS FOR THE PREPARATION OF
PHOSPHOROUS ACID/CARBOXYLIC ACID MIXED ANHYDRIDES
AND ANHYDROUS PHOSPHOROUS ACID

BACKGROUND OF THE INVENTION

1. Field of the Invention:

This invention relates to a process for the preparation of phosphorus compounds from phosphorus trichloride. More specifically, the invention relates to a process that involves the reaction of phosphorus trichloride with a volatile carboxylic acid followed by removal of chlorine containing compounds.

2. Description of the Related Art:

Phosphorous acid (H₃PO₃) is produced industrially by the reaction of phosphorus trichloride (PCl₃) with water. As disclosed by Cremer, U.S. Patents 3,859,419 and 3,937,616, phosphorus trichloride is sprayed with steam at a temperature between 150⁰ to 200⁰ C into a hot reaction zone. The excess water and hydrogen chloride formed in the reaction are evaporated off by passing an inert gas through the reaction product in a separate evaporation zone.

Production of phosphorous acid by this process is costly due to high capital and operating costs. To prevent condensation of excess water and remove the hydrogen chloride formed in the hydrolysis the reaction is run at 150⁰ to 200⁰ C. If the flow of reactants is not strictly regulated, the heat of reaction can cause the temperature to rise above 200⁰ C. Above about 180⁰ C, phoshpine, which is both toxic and pyrophoric, may be formed. In addition, unreacted phosphorus trichloride can be carried out with the off gas reducing the yield of phosphorous acid and contaminating the hydrogen chloride by-product.

Grosse, U.S. Patent 4,834,960, employed steam to finely divide a mixture of phosphorus trichloride and water, but temperatures of 150⁰ to 200⁰ C were required. Lowe, U.S. Patent 5,085,846, prepared phosphorous acid by reacting phosphorus trichloride and water in a continuously recycling loop apparatus. The preferred recycle ratio was 40-150:1, so that equipment to extensively recycle the reaction mixture is required. The phosphorous acid formed typically contained 10-30% water. Consequently, a need exists for a process to produce anhydrous phosphorous acid that does not require temperatures of 150⁰ to 200⁰ C and costly equipment.
The preparation of N-acylaminomethylphosphonic acids from carboxylic acid amides, a suitable formaldehyde source, phosphorous acid, and a carboxylic acid anhydride, as described in U.S. Patent 5,233,080 requires a mixture comprising anhydrous phosphorous acid and a carboxylic acid. Direct production of this mixture from phosphorus trichloride and carboxylic acid would simplify the production of N-acylaminomethylphosphonic acids. Consequently, a need also exists for a process for the direct production of a mixture comprising anhydrous phosphorous acid and a carboxylic acid.

**SUMMARY OF THE INVENTION**

In view of the above needs, the present invention in one of its embodiments is viewed as an improved method of directly producing a mixture of anhydrous phosphorous acid and a carboxylic acid at relatively low temperatures and cost. Thus the present invention provides a method for preparing mixtures of phosphorus compounds comprising the steps of:

(a) reacting phosphorus trichloride with an excess of liquid carboxylic acid, wherein the carboxylic acid is characterized as having a boiling point below 150°C, to form a mixture comprising phosphorous acid, an acyl chloride of the carboxylic acid, hydrogen chloride, the anhydride of said carboxylic acid, and mixed anhydrides of the carboxylic acid and phosphorous acid; and

(b) removing the acyl chloride and hydrogen chloride from the mixture produced in step (a) to form a product stream comprising; phosphorous acid, the anhydride of said carboxylic acid, and mixed anhydrides of the carboxylic acid and phosphorous acid.

In one preferred embodiment, the carboxylic acid is acetic acid. In a further embodiment, a stoichiometric quantity of water is added to the product formed in step (b) to convert the mixed phosphorous acid/carboxylic anhydrides and carboxylic anhydride to an anhydrous mixture of phosphorous acid and carboxylic acid. In a still further embodiment the carboxylic acid is removed to produce anhydrous phosphorous acid. In an additional further embodiment the product formed in step (b) is reacted with acetamide, paraformaldehyde, and acid anhydride to form N-acetylamaminomethylphosphonic acid and the N-acetylaminnomethylphosphonic acid is then hydrolyzed to aminomethylphosphonic acid.
DESCRIPTION OF THE PREFERRED EMBODIMENTS

The reaction, (1), of phosphorus trichloride, PCl₃, with carboxylic acids, RCOOH, is a well known technique for small scale preparation of acyl chlorides (see for example: Organic Syntheses, Coll. Vol., 2, A. H. Blatt, Ed., Wiley, New York, 1943, pp 150-158).

3 RCOOH + PCl₃ ----> 3 RCOCl + H₃PO₃  \hspace{1cm} (1)

As commonly practiced, an excess of phosphorus trichloride is employed in order to obtain the maximum yield of the desired acyl chloride, RCOCl. In such cases, phosphorus trichloride will not be completely converted to phosphorous acid, H₃PO₃. In contrast and according to the instant invention, the use of an excess of carboxylic acid will produce essentially complete conversion to phosphorous acid. This complete conversion to phosphorous acid requires at least three moles, preferably three to ten moles, of carboxylic acid per mole of phosphorus trichloride. Addition of five to eight moles of carboxylic acid per mole of phosphorus trichloride is more preferred.

Liquid carboxylic acids with a boiling point below 150°C are preferred. If the carboxylic acid has a boiling point below 150°C, its acyl halide will have a boiling point below 120°C. Thus, it can be readily separated from the reaction mixture by techniques, such as distillation or scrubbing, that rely on differences in volatility. Preferred carboxylic acids are acetic acid (bp 118°C) and propionic acid (bp 141.1°C). Acetic acid is most preferred because of its ready availability, low cost, and high volatility.

To insure adequate mixing and completeness of reaction in minimum time, the reaction is preferably carried out in the condensed phase in the absence of a solvent by mixing phosphorus trichloride (mp -93.6°C; bp 76.1°C) with the liquid carboxylic acid. Although the reaction may be carried out at any temperature between the freezing point of the reaction mixture and the boiling point of the reactants, temperatures in the range of 0°C to 60°C are preferred.

A competing reaction is reaction, (2), of the acyl chloride with excess carboxylic acid to form the corresponding acid anhydride, RC(O)OC(O)R, and hydrogen chloride.

RCOCl + RCOOH ----> RC(O)OC(O)R + HCl  \hspace{1cm} (2)
The acid anhydride is less volatile than the corresponding acyl halide and carboxylic acid and hence more difficult to separate from the relatively non-volatile phosphorus compounds. In addition, the acid anhydride can react with phosphorous acid to make mixed anhydrides of phosphorous acid and carboxylic acid.

Phosphorous acid is readily regenerated from the anhydrides by addition of water, but this reaction is strongly exothermic and, therefore, inconvenient from a processing standpoint. Consequently, in the production of anhydrous phosphorous acid, carboxylic anhydride formation and subsequent mixed anhydride formation, should be minimized by proper control of the reaction conditions.

If the reaction is carried out below about 60° C, carboxylic anhydride formation is minimized. Reaction temperatures in the range of 20° to 40° C, are more preferred, both for convenience and to minimize side reactions. In this temperature range, reaction is essentially complete in 10 to 30 minutes. Since this reaction is not strongly exothermic, little if any cooling is required.

When reaction is complete, the phosphorus compounds (H₃PO₃, phosphorous acid/carboxylic acid mixed anhydrides) are separated from the chlorine compounds (acyl chloride, HCl). While conventional distillation techniques can be used, distillation may expose the mixed products to elevated temperatures for extended periods of time. Consequently, considerable conversion of the acyl chloride to the corresponding acid anhydride, with the adverse consequence noted above, may occur. Further, long exposure of the reaction mixture to elevated temperatures can produce irreversible conversion of mixed phosphorous acid/carboxylic acid anhydride to diphosphonic acid.

A scrubbing process, in which the reaction mixture is passed downward through a column heated to a temperature above the boiling point of the acyl halide and then to an unheated receiver, is preferred. The efficiency of separation is improved if a gaseous stream is passed through the column counter-current to the liquid flow. While any gas that does not react with the reaction mixture may be used for scrubbing, practical gases are those that are non-toxic, non-flammable, non-explosive, inexpensive, and that do not contain impurities that would contaminate the product stream. Nitrogen is preferred. When a gaseous stream is used for scrubbing, the column is operated above the boiling point of the acyl chloride and below the boiling point of the carboxylic acid.

An alternate technique is to operate the column above the boiling point of the carboxylic acid so that vapors of the carboxylic acid pass upward as the liquid phase passes downward through the column. In this fashion, carboxylic acid vapor
functions as would extrinsic gas, provided that a sufficient excess of carboxylic acid was employed in the original reaction.

Alternatively, additional carboxylic acid vapor can be introduced at the bottom of the scrubbing column. In this case the column is operated either at or above the boiling point of the carboxylic acid. Reduced pressure may be employed to lower the boiling point of the carboxylic acid and thereby produce an upward flow of vapor at a lower temperature.

The product stream, that is, the material entering the receiver, contains carboxylic acid, carboxylic acid anhydride, phosphorous acid, and phosphorous acid/carboxylic acid mixed anhydrides in proportions determined by the manner in which the reaction was carried out and in which the column was operated. As will be apparent to one skilled in the art, the proportion of introduced carboxylic acid vapor passing overhead with the acyl halide relative to that condensing into the downward flowing product stream will be determined by the column temperature, the relative proportions of liquid phase to introduced gas or vapor, and the efficiency of heat transfer inside the column.

In instances in which the phosphorous acid can be used in some subsequent operation as a solution in the carboxylic acid, it is convenient to operate the column in such fashion that the product stream collected at the bottom of the column continues 2 to 6 parts by weight of carboxylic acid for each part by weight of phosphorous acid so that the phosphorous acid (mp about 73° C) does not precipitate in the receiver. When phosphorous acid free of carboxylic acid is desired, the amount of carboxylic acid in the product stream can be reduced by: increasing the column temperature, decreasing the column pressure, increasing the heat transfer capability of the column by increasing its internal surface area, and/or by other methods well known to those skilled in the art.

As will be apparent to one skilled in the art, the amount of acyl halide remaining in the liquid phase is a function of the residence time in the column and the temperature of the column. Trace amounts of chlorine compounds such as acyl chloride and hydrogen chloride may also be present. In general, the latter are undesirable so the column will be operated so as to minimize these impurities. It is an advantage of this process that these impurities can be limited to a concentration of less than 1,000 parts per million (ppm) in the product stream.

For some applications, such as the preparation of N-acylaminomethylphosphonic acids from carboxylic acid amides, a suitable formaldehyde source, phosphorous acid, and a carboxylic acid anhydride (as described more fully in U.S. Patent 5,233,080 herein incorporated by reference for such purpose), the product
stream produced from the process of the instant invention can be used in place of pure phosphorous acid. The amount of carboxylic acid and of carboxylic acid anhydride required by this process is reduced by the amount of these components in the product stream. The amount of acid anhydride required is further reduced by the amount of mixed anhydride in the product stream.

Although the present invention is not intended to be limited to any specific mechanism or theory, it is believed that the mixed phosphorous/carboxylic anhydride is an intermediate in the formation of N-acylaminomethylphosphonic acid. Since the mixed anhydride is present in the product stream, the exotherm encountered in making N-acylaminomethylphosphonic acid is correspondingly reduced, leading to a safer and simpler process.

When the product stream is used in the preparation of an N-acylaminomethylphosphonic acid, a product stream comprising acetic acid, phosphorous acid, acetic anhydride, and mixed acetic acid/phosphorous acid anhydrides, prepared form the reaction of phosphorus trichloride with anhydrous acetic acid is preferred. Paraformaldehyde is the preferred formaldehyde source. Acetamide is the preferred amide. An organic co-solvent, preferably a nitrile, such as acetonitrile or propionitrile, or an ether, such as tetrahydrofuran or dioxane, may also be added. Acetonitrile is the preferred co-solvent. The presence of chlorine containing compounds such as hydrogen chloride and acetyl chloride should be avoided since they can produce carcinogenic bis-(chloromethyl)ether.

N-Acylaminomethylphosphonic acids can be hydrolyzed to aminomethylphosphonic acid under conditions that are well known to those skilled in the art. For example, hydrolysis may be carried out in less than four hours in refluxing 3 to 10% aqueous hydrochloric acid. Aminomethylphosphonic acid is an intermediate in the synthesis of glyphosate.

If an anhydrous mixture of phosphorous acid and carboxylic acid is desired, an amount of water just sufficient to react with the carboxylic acid anhydride and the phosphorous acid/carboxylic acid mixed anhydride may be added to the product stream to hydrolyze these components to phosphorous acid and carboxylic acid. The precise amount of water to be added can be readily determined by proton nuclear magnetic resonance spectroscopic analysis (\(^1\)HNMR) of the product stream. Carboxylic acid anhydride content can be measured by the resonance attributable to protons adjacent to carbonyl at \(\delta\) 2.1-2.5, and the various phosphorus species by resonances in the region around \(\delta\) 5.2 and \(\delta\) 8.7. Other methods of analysis will be apparent to one skilled in the art.
If solvent-free, anhydrous phosphorous acid is desired, the carboxylic acid can be readily removed by conventional separation techniques, such as fractional distillation, especially vacuum distillation, of the carboxylic acid or scrubbing with an inert gas. To minimize phospine formation, these processes should be carried out below 180° C.

Industrial Applicability:
The product stream containing phosphorous acid/carboxylic acid mixed anhydrides may be reacted with paraformaldehyde and acetamide to produce N-acetylaminomethylphosphonic acid, \( \text{CH}_3\text{C(ON)}\text{HCH}_2\text{P(O)(OH)}_2 \); an intermediate for the synthesis of pesticides and corrosion inhibitors. For example, N-acetylaminomethylphosphonic acid can be converted to N-(phosphonomethyl)-glycine, commonly known as glyphosate, a broad-spectrum, post-emergence herbicide. Phosphorous acid is used in the synthesis of various trivalent phosphorus compounds that are used as corrosion inhibitors and metal chelators.

The following examples are presented to more fully demonstrate and further illustrate various individual aspects of the present invention. As such the examples are felt to be non-limiting and are meant to illustrate the invention but are not meant to be unduly limiting in any way. In performing the examples the following general procedures were employed.

General Procedures:
Stripping: The column used in these examples was a five-plate glass Oldershaw column that was jacketed so that temperature could be controlled by circulation of heated oil around the column. Above the column was a condenser and stream splitter so that a desired fraction of the vapor stream could be condensed and removed through a take-off valve and the remainder returned to the Oldershaw column as liquid. The condenser was operated at -10° C to -15° C so that acetyl chloride (bp 52° C) was efficiently condensed while the bulk of the hydrogen chloride vapor passed beyond the condenser into a cryogenic trap or caustic scrubber. An unheated receiver was placed below the column to collect the product stream.

The reaction mixture was introduced at a controlled rate either between the column and condenser or at any desired plate on the column. Carboxylic acid vapor could likewise be introduced at any of these locations. About 90% of the vapors leaving the column were condensed and removed while 10% was returned to the top of the column as condensed liquid.
Provision was made for operation at reduced pressure and for introducing nitrogen gas into the receiver if desired. Unless otherwise noted, all reactions were conducted at atmospheric pressure without nitrogen introduction.

Analysis: The reaction mixture was followed by proton nuclear magnetic resonance. Phosphorous acid has a sharp singlet peak at about δ 8.7 (P-H). Broad multiplets from the phosphorous acid/carboxylic acid mixed anhydrides, which also contain the P-H bond, are also present in this region. Water was added gradually until the broad multiplets from the anhydrides disappeared and the sharp peak grew to a maximum. Since excess water appears as a separate absorption peak in the δ 4-5 region, monitoring this region will confirm that stoichiometry has been reached and the mixture is anhydrous.

Chlorine content was determined by analysis of the hydrolyzed product using an ion-selective electrode.

Example 1

This example illustrates the use of nitrogen gas to remove acetyl chloride and hydrogen chloride from the reaction mixture.

A mixture of 41.7 g (0.695 mole) of acetic acid and 16.8 g (0.122 mole) of phosphorus trichloride was stirred at 20-23° C for 0.5 hr. A stream of nitrogen was established flowing upward through the five-plate glass Oldershaw column at a rate of 27 cm³/min. The column jacket was heated at 120° C. The reaction mixture was fed into the top of the column at a rate of 8.4 g/min. The product collected at the bottom of the column contained phosphorous acid, acetic acid, acetic anhydride, and mixed phosphorus-acetic anhydrides in such amounts that addition of stoichiometric water to hydrolyze the anhydrides would produce an anhydrous solution containing 30% phosphorous acid in acetic acid (84% yield based on phosphorus trichloride). Chlorine content: 1190 ppm.

Example 2

This example illustrates the use of acetic acid vapor to remove acetyl chloride and hydrogen chloride from the reaction mixture.

A mixture of 41.5 g acetic acid (0.692 mole) and 16.5 g (0.120 mole) phosphorus trichloride was stirred at 23-24° C for 0.5 hr. The jacket of the Oldershaw column was heated to 150° C and acetic acid vapor introduced onto the middle plate at a rate of 3.9 g/min. The reaction mixture was introduced at the top of the column at a rate of 5.8 g/min. The product stream collected at the bottom of the column contained acetic acid, acetic anhydride, phosphorous acid and
phosphorous acid/acetic acid mixed anhydrides in such amounts that addition of
stoichiometric water to react with the anhydrides would produce an anhydrous
solution containing 21% by weight phosphorous acid in acetic acid solvent
representing a yield of 93%. Chlorine content: 940 ppm.

Example 3

This example illustrates the use of reduced pressure to separate the
reaction mixture.

A mixture of 83.4 g (1.39 mole) acetic acid and 32.7 g (0.238 mole)
phosphorus trichloride was stirred at 23° C for 1 hr. The jacket surrounding the
Oldershaw column was thermostated at 80° C and the pressure in the column
reduced to 130 mm. The reaction mixture was then introduced at the top of the
column using the differential pressure to cause the liquid to flow through a narrow
orifice into the column at a rate of 4.1 g/min. After addition of the reaction mixture
was complete, 90 mL of acetic acid was added to flush out the lines. The product
stream collected at the bottom of the column contained acetic acid, phosphorous
acid, acetic anhydride and mixed phosphorus/acetic anhydrides in such amounts that
addition of stoichiometric water to react with the anhydrides would produce an
anhydrous solution containing 24% phosphorous acid in acetic acid solvent
representing a yield of 92%.

Example 4

This example illustrates the direct use of the phosphorous acid/mixed
anhydride product stream for further synthesis.

Following the procedure of Example 3, a product stream containing 56.4
mmoles phosphorous acid, 77.0 mmoles phosphorous acid/acetic acid mixed
anhydrides, 37 mmoles acetic anhydride, and 548 mmoles of acetic acid was
prepared.

A mixture of acetonitrile (80 mL), acetic acid (25 mL), 95%
paraformaldehyde (6.64 g, 210 mmole), and acetamide (12.4 g, 210 mmole) was
heated to 85° C for 25 min and then cooled to 20° C. The above product stream was
added while keeping the temperature at 20° C. Then acetic anhydride (44.1g) was
added while still keeping the temperature at 20° C. The mixture was heated to 95° C
for two hours. Proton nuclear magnetic resonance spectroscopy showed that
N-acetylaminomethyl phosphonic acid was produced (124 mmole, 62% based on
formaldehyde and acetamide added). N-acetylaminomethyl phosphonic can be
isolated by removing the solvent and other reactants by vacuum distillation, typically at about 100 mm Hg.

Alternatively, the N-acetylaminomethylphosphonic can be hydrolyzed to aminomethylphosphonic acid. The reaction mixture is concentrated by vacuum distillation, typically at about 100 mm Hg. Hydrolysis is carried out by heating the concentrated reaction mixture at reflux with 5% aqueous sulfuric acid or 5% aqueous hydrochloric acid for about three hours. The progress of the reaction can be followed by proton nuclear magnetic resonance.

Having thus described and exemplified the invention with a certain degree of particularity, it should be appreciated that the following claims are not to be so limited but are to be afforded a scope commensurate with the wording of each element of the claim and equivalents thereof.
I Claim:

1. A process for preparing a mixture of phosphorus compounds comprising the steps of:
   (a) reacting phosphorus trichloride with an excess of liquid carboxylic acid, wherein said carboxylic acid is characterized as having a boiling point below 150°F, to form a mixture comprising; phosphorous acid, an acyl chloride of said carboxylic acid, hydrogen chloride, an anhydride of said carboxylic acid, and mixed anhydrides of said carboxylic acid and phosphorous acid; and
   (b) removing said acyl chloride and hydrogen chloride from said mixture produced in step (a) to form a product stream comprising; phosphorous acid, said carboxylic acid, said anhydride of said carboxylic acid, and mixed anhydrides of said carboxylic acid and phosphorous acid.

2. The process of Claim 1 wherein step (a) is carried out below 60°F.

3. The process of Claim 1 wherein said carboxylic acid is selected form the group consisting of acetic acid and propionic acid.

4. The process of Claim 1 wherein said acyl chloride and hydrogen chloride are removed from said reaction mixture by scrubbing either with a gas that does not react with said reaction mixture or with vapors of said carboxylic acid.

5. The process of Claim 4 wherein said gas is nitrogen.

6. The process of Claim 1 further comprising the step of adding a stoichiometric quantity of water to the product stream formed in step (b) to hydrolyze the anhydrides and form an anhydrous mixture of phosphorous acid and said carboxylic acid.
7. The process of Claim 6 further comprising the step of removing said carboxylic acid from said anhydrous mixture to form anhydrous phosphorous acid.

8. The process of Claim 7 wherein said acyl chloride and hydrogen chloride are removed from said reaction mixture by scrubbing either with a gas that does not react with said reaction mixture or with vapors of said carboxylic acid.

9. The process of Claim 8 wherein said carboxylic acid is acetic acid.

10. The process of Claim 1 further comprising the step of reacting the product stream formed in step (b) with an amide and a formaldehyde source to form an N-acylaminomethylphosphonic acid.

11. The process of Claim 10 wherein step (a) is carried out below 60°C and wherein said acyl chloride and hydrogen chloride are removed from said reaction mixture by scrubbing with a gas that either does not react with said reaction mixture or with vapors of said carboxylic acid.

12. The process of Claim 10 further comprising the step of hydrolyzing said N-acylaminomethylphosphonic acid to form aminomethylphosphonic acid.

13. The process of Claim 10 wherein said carboxylic acid is acetic acid, said formaldehyde source is paraformaldehyde, and said amide is acetamide; wherein step (a) is carried out below 60°C, and wherein said acyl chloride and hydrogen chloride are removed from said reaction mixture by scrubbing with a gas that either does not react with said reaction mixture or with vapors of said carboxylic acid.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

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According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

- Minimum documentation searched (classification system followed by classification symbols)
  - IPC 6 C07F C01B

- Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

- Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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- Further documents are listed in the continuation of box C.

- Patent family members are listed in annex.

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
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Fax (+31-70) 340-3016

Authorized officer

Beslier, L

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