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3,013,048 ISOCYANATO SUBSTITUTED ARYL PHOSPHORUS ESTERS

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14 Claims. (Cl. 260-461)

This invention relates to aromatic isocyanates and more particularly to isocyanato aromatic esters, thioesters and amide derivatives of phosphoric acid and thiophosphoric acids.

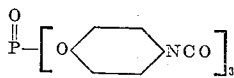
It is an object of this invention to provide isocyanato aromatic phosphoric acid and thiophosphoric acid derivatives. Another object of this invention is to provide isocyanato aromatic phosphoric acid and thiophosphoric acid derivatives which may be used to prepare urethanes having improved flame resistance. Still another object of this invention is to provide a process for the preparation of aryl isocyanato phosphoric acid and thiophosphoric acid derivatives.

These objects and others, which will become obvious from the following disclosure, are accomplished, in accordance with the invention, generally speaking, by providing isocyanato aryl derivatives of phosphoric acids. Thus, this invention contemplates isocyanato aryl phosphorous esters, thioesters and amides having the formula

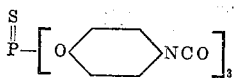


wherein X is oxygen or sulphur, R represents O-aryl, O-aralkyl, O-alkaryl, O-cycloalkaryl, S-aryl, S-aralkyl, S-alkaryl, S-cycloalkaryl, N-(aryl)₂, N(alkyl)(aryl), N(alkyl)₂, N(aralkyl)₂ or N(cycloalkaryl)₂; R' and R'' may be either the same or different and may be R, O-alkyl, O-cycloalkyl, S-alkyl, S-cycloalkyl, N-(alkyl)₂, N-(cycloalkyl)₂; at least one of the aryl radicals contains at least one isocyanato group bonded to a carbon atom of the aromatic ring. The invention therefore contemplates compounds, such as, for example,

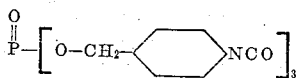
4,4',4''-triisocyanato phenyl phosphate



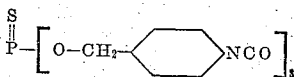
4,4',4''-triisocyanato phenyl thiophosphate



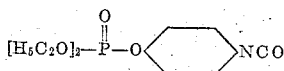
4,4',4''-triisocyanato benzyl phosphate



4,4',4''-triisocyanato benzyl thiophosphate

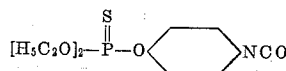


Diethyl-4-isocyanatophenyl phosphoric acid triester

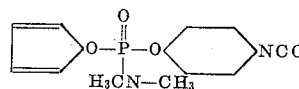


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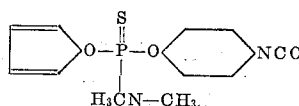
Diethyl-4-isocyanatophenyl thiophosphoric acid triester



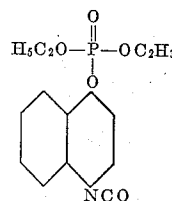
Cyclopentadienyl-4-isocyanatophenyl phosphoric acid triester, dimethyl amide



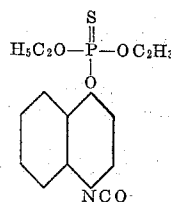
Cyclopentadienyl-4-isocyanatophenyl thiophosphoric acid diester dimethyl amide



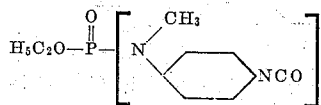
Ethyl, vinyl, 4-isocyanato naphthyl phosphoric acid triester



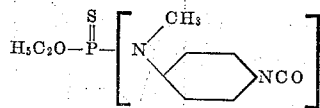
Ethyl, vinyl, 4-isocyanato naphthyl thiophosphoric acid triester



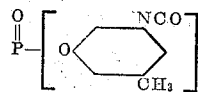
Ethyl phosphoric acid ester-bis (N-methyl-N-4-isocyanatophenyl amide)



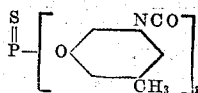
Ethyl thiophosphoric acid ester-bis (N-methyl-N-4-isocyanatophenyl amide)



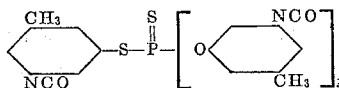
(3-isocyanato-5-methyl phenyl) phosphoric acid triester



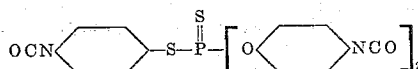
(3-isocyanato-5-methyl phenyl) thiophosphoric acid triester



(3-isocyanato-5-methyl phenyl) dithiophosphoric acid triester.



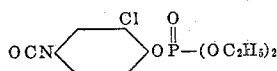
4,4',4''-triisocyanatophenyl dithiophosphate



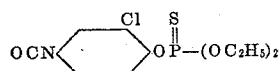
4,4',4''-triisocyanatophenyl tetrathiophosphate



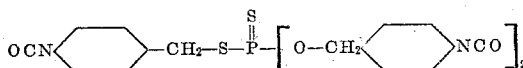
4-isocyanato, 6-chlorophenyl diethyl phosphoric acid triester



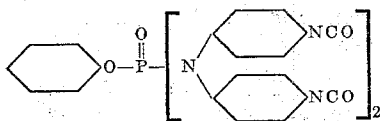
4-isocyanato, 6-chlorophenyl diethyl thiophosphoric acid triester



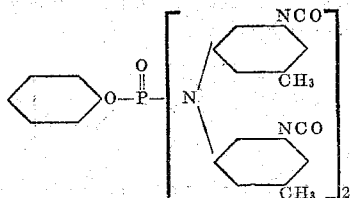
4,4',4''-triisocyanato benzyl dithiophosphate



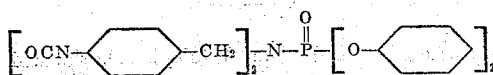
Phenylphosphoric acid ester bis (N,N-4-isocyanato phenyl amide)



Phenyl phosphoric acid ester bis (N,N-3-isocyanato, 5-methyl phenyl amide)

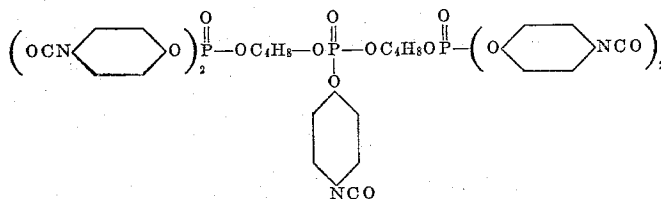
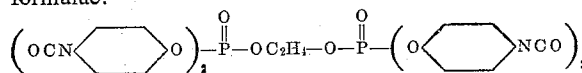


Phenyl phosphoric acid diester, N,N-4-isocyanato benzyl amide



The substituents in the above-mentioned formula may also contain further substituents, such as, for example, halogen, such as chlorine, iodine and bromine; alkoxy, such as, methoxy, ethoxy and propoxy; carboxylic acid

ester, such as, carbomethoxy, carboethoxy and carbobutoxy, and unsaturated hydrocarbon, such as, vinyl, allyl and butenyl, in addition to the isocyanato group which is attached to a carbon atom of an aromatic ring. Further, compounds containing more than one phosphoric acid or thiophosphoric acid nucleus are contemplated by the invention. In such cases R' and R'' may represent radicals of polyhydric alcohols, such as, for example, ethylene glycol, 1,3-propylene glycol, 1,4-butylene glycol and the like, polyvalent amines, such as, for example, N,N-dimethyl ethylene diamine, N,N-diethyl-1,3-propylene diamine, N,N-dimethyl-1,3-phenylene diamine, and the like, linear or branched polyesters, such as, for example, the reaction product of succinic acid with trimethylol propane or ethylene glycol, and the like, polyethers, such as, for example, those obtained from the condensation of alkylene oxides and compounds such as diethylene glycol, polyamides, polyester amides, such as, for example, the reaction product of succinic acid with amino alcohols and more particularly 1-amino, 2-hydroxy ethylene and the like and polythioethers, such as, for example, thioglycols and more particularly thiodiglycol which link two or more phosphoric acid or thiophosphoric acid nuclei through oxygen, sulfur and/or nitrogen atoms. Representative compounds of this type contemplated by the invention are, for example, those having the following formulae:



The new isocyanates are prepared by phosgenating the corresponding amino aryl phosphoric acid derivatives. The amino aryl phosphoric acid derivatives may be prepared by nitration followed by reduction of the corresponding phosphoric acid and thiophosphoric esters, thioesters and amides, such as, for example, triphenyl phosphate, tricresyl phosphate, triphenyl thiophosphate, triphenyl phosphoramidate and the like. Further, the amino derivatives which are phosgenated in accordance with the process of this invention to prepare the new aromatic isocyanates may be prepared by the reaction of phosphoric acid chlorides or substituted phosphoric acid chlorides with nitrophenols and the like, such as, for example, nitro benzyl alcohol, nitro naphthol and nitro methylphenol followed by reduction to the corresponding amines. The following examples illustrate the preparation of representative amino aromatic phosphoric acid and thiophosphoric acid derivatives which may be phosgenated in accordance with the process of the present invention.

Example 1

About 461 g. (1 mol) of p-nitrophenyl-phosphoric acid-triester, prepared by nitration of triphenyl phosphate in nitric acid (density 1.51) at about -5°C . to about 0°C . are dissolved in about 3000 cc. of methanol and introduced into a 7-liter stirrer-type autoclave after adding about 25 g. of fresh Raney nickel. The reduction is completed after about 2-3 hours at a temperature of about 50°C . and a hydrogen pressure between about 20 and about 40 atm.

In working up the product, the reaction mixture is filtered while heating, from the hydrogenation catalyst and the filtrate is cooled with ice. About 105 g. of the p-aminophenyl-phosphoric acid-triester are crystallized out in the form of small needles. After filtering with suction, the remainder of the amino-compound is ob-

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tained by precipitation with water, whereby about another 210 g. crystallize out, so that the total yield is about 315 g. (85% of the theoretical). In this way the substance is obtained in an analytically pure form having sharp melting point. It can be recrystallized from alcohol and is completely soluble in 10% hydrochloric acid and has a melting point of 155° C.

Analysis.—Calculated: C, 58.3%; H, 4.86%; N, 11.31%; P, 8.36%. Found: C, 58.13%; H, 5.0%; N, 11.40%; P, 8.5%.

Example 2

About 195 g. of p-nitrophenyl-thiophosphoric acid-triester, prepared from nitrophenol sodium plus PSCl_3 in xylene (M.P. 181° C.–183° C.) are dissolved in 1.2 liters of methanol and, after adding about 30 g. of Raney nickel, are hydrogenated at a temperature of about 50°–75° C. and at a hydrogen pressure of about 20–40 atm. The absorption of hydrogen is complete after two hours. After filtering, the main quantity of the p-aminophenyl-thiophosphoric acid-triester crystallizes out from the methanol, and the remainder can be obtained by precipitation with water. Yield: 152 g. (97.5% of the theoretical), M.P. 156° C.

Analysis.—Calculated for $\text{C}_{18}\text{H}_{18}\text{O}_3\text{N}_3\text{PS}$: C=56.0%, H=4.6%, N=10.8%, S=8.2%, P=8.0%. Found: C=55.6%, H=4.9%, N=10.8%, S=8.2%, P=8.2%.

Example 3

About 95 g. of diethyl-p-nitrophenyl-thiophosphoric acid-triester, dissolved in about 300 cc. of methanol, are hydrogenated in the presence of about 25 g. of Raney nickel at between about 50° and about 60° C. and under a hydrogen pressure of about 20–40 atm. The hydrogen absorption is complete after three hours. Thereafter the solid material is filtered off from the catalyst and the methanol solution is concentrated. The residue is a reddish-yellow oil which is completely soluble in 10% hydrochloric acid. Yield: 86 g.

Analysis.—Calculated: N=5.7%, S=13.0%, P=12.0%. Found: N=5.56%, S=12.0%, P=12.6%.

Analysis of the phenyl urea (M.P. 108° C.): Calculated — N=7.7%, S=8.8%, P=8.5%. Found—N=7.8%, S=8.3%, P=8.5%.

Example 4

About 302 g. of p-nitrophenyl-phosphoric acid-diester dimethylamide (prepared from N-dimethylamino-phosphoric acid dichloride and nitrophenol sodium, M.P. 148° C.) are hydrogenated in about 1.2 liters of methanol at about 60° C.–75° C. after the addition of about 30 g. of Raney nickel. The hydrogenation is complete after three hours; the solid material is filtered off from the catalyst and the filtrate is concentrated. A light yellow oil which crystallizes on stirring with methylene chloride is left. Yield: 258 g., M.P. 101° C.–103° C. (with decomposition).

Analysis.—Calculated: C=54.6%, H=5.8%, N=13.7%, P=10.1%. Found: C=54.6%, H=5.8%, N=14.2%, P=10.1%.

Example 5

About 268 g. of p-nitrophenyl-phosphoric acid-diester methyl phenylamide (prepared according to Example 4) are hydrogenated and worked up as in Example 4. Yield: 220 g., M.P. 110° C.–111° C.

Analysis.—Calculated: C=61.9%, H=5.4%, N=11.4%, P=8.4%. Found: C=61.9%, H=5.7%, N=11.7%, P=8.5%.

The amino compounds used as starting materials in the process of this invention are more particularly disclosed in copending application S.N. 790,034.

According to the process of the invention, amino aryl phosphoric acid derivatives or amino aryl thiophosphoric acid derivatives are converted to the corresponding isocyanates by phosgenation. Any suitable phosgenation

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method may be used, such as, for example, the cold phase-hot phase phosgenation or even according to the hydrochloride process, the corresponding amine hydrochloride being phosgenated. A suitable phosgenation process is disclosed in U.S. Patent 2,680,127. The process can be carried out either continuously or intermittently. Advantageously, one employs an inert solvent, such as, toluene, benzene, xylene, trichloro ethylene, chlorobenzene, o-dichloro benzene.

The temperature for the phosgenation reaction is not critical. However, it is preferable not to choose too high a temperature for the phosgenation. For this reason, the cold phase-hot phase phosgenation is preferred to the hydrochloride process. In the cold phase-hot phase phosgenation, the mixture of carbamic acid chloride and amine hydrochloride occurs in such a fine suspension that the hot phase phosgenation is completed in a short time. Temperatures between about 80° C. and about 120° C. are preferred in the final phase of the phosgenation, although higher and lower temperatures may be used, if desired.

Recrystallization or distillation of the isocyanates prepared according to the process of this invention is not necessary in most cases, since the products are obtained in a relatively pure form. However, any carbamic acid chloride which may still be present should be destroyed. The excess phosgene may be adequately removed by heating the reaction mixture for a short time at reduced pressure below the boiling point or by blowing an inert gas through the reaction mixture at an elevated temperature.

It was not to be expected that the phosgenation of the amino aryl phosphoric acid ester derivatives and the like would proceed without cleavage of the ester, thioester or amide bonds. However, the process of the invention proceeds in a surprisingly simple and convenient manner. The isocyanato aryl phosphoric acid derivatives are obtained in unexpectedly high yields usually exceeding 80% of the theoretical. The formation of acid chlorides which would be expected from the reaction of phosgene does not take place. Further, the acid chlorides do not appear as secondary products even in small quantities.

In order to better describe and further classify the invention, the following are specific embodiments.

Example 6

About 1.5 liters of substantially anhydrous chlorobenzene are placed in a three-liter flask, cooled to about –10° C. and thereafter about 800 g. of phosgene are introduced and condensed. At the same temperature about 371 g. of finely powdered 4,4',4''-triamino-triphenyl phosphate are added in portions. The mixture is stirred for about four hours in the cold and then left overnight at room temperature. Thereafter, a powerful stream of phosgene is introduced at a temperature of between about 90° C. and about 110° C. until a homogeneous solution is present. The chlorobenzene solution is then blown out with nitrogen and the chlorobenzene distilled off in vacuo. The residue is thereafter treated for approximately another hour at about 160° C. under high vacuum in order to destroy remaining traces of carbamic acid chloride.

The yellow oil which remains is 4,4',4''-triisocyanatophenyl phosphate. It crystallizes after a few days as an analytically-pure white waxy mass. Yield: 380 g. (85% of the theoretical).

Analysis.—Calculated: C, 56.1%; H, 2.68%; N, 9.36%; P, 6.91%; NCO, 28.1%. Found: C, 55.74%; H, 2.60%; N, 9.70%; P, 6.95%; NCO, 28.3%.

Example 7

About 354 g. of p-aminophenyl-thiophosphoric acid-triester are slowly introduced at a temperature of between about minus 5° C. and about 0° C. into a solution of about 600 g. of phosgene in about 2.5 liters of

chlorobenzene and the mixture is left standing overnight in the cold. The temperature is thereafter raised with further introduction of phosgene. After about 6 hours, at a phosgenation temperature of about 100° C. to about 110° C. everything dissolves except for a slight slimy residue, which is filtered off following the addition of substantially anhydrous active carbon. A light-yellow melt, 4,4',4''-triisocyanato phenyl thiophosphate, is left, which soon solidifies into crystalline form. Yield 380 g. (82% of the theoretical), M.P. 84° C.-86° C.

Analysis.—Calculated: C=54.1%, H=2.6%, N=9.05%, P=6.7%, S=6.9%. Found: C=53.9%, H=2.8%, N=9.1%, P=6.9%, S=7.3%.

Example 8

About 700 g. of phosgene are liquified in about 1.5 liters of chlorobenzene at about -10° C. Thereafter, a solution of about 475 g. of diethyl mono-p-amino-phenyl-thiophosphoric acid-triester, dissolved in about 1 liter of chlorobenzene, is added dropwise so that the temperature does not rise higher than about 0° C. After standing in the cold overnight, more phosgene is introduced at about 100° C. to about 110° C. A light clear solution has formed after about 4 hours. This is worked up as in Example 2. About 472 g. of the slightly brownish oily isocyanate are obtained as residue. B.P.: 147° C.-149° C. (with slight decomposition).

Analysis.—Calculated: N=5.2%, P=11.4%, S=11.8%. Found: N=5.3%, P=11.0%, S=11.0%.

Example 9

About 220 g. of (p-aminophenyl)-phosphoric-di-ester-mono-methyl phenylamide are introduced at about 0° C. to a solution of about 500 g. of phosgene in about 2 liters of chlorobenzene. After standing in the cold overnight, the reaction mixture has solidified to a pasty mass which becomes liquid again at about 80° C. More phosgene is introduced for about 4 hours at about 100° to about 110° C. The isocyanate remaining, after distilling off the chlorobenzene, is a light brownish non-crystallizing oil. Yield: 220 g.

Analysis.—Calculated: C=59.8%, H=3.8%, N=10.2%, P=7.5%. Found: C=59.9%, H=3.8%, N=10.0%, P=7.4%.

Although only some of the aforementioned isocyanato aryl phosphoric acid and thiophosphoric acid derivatives were prepared in the foregoing examples, it is to be understood that any of the class of phosphoric acid derivatives more fully disclosed above can be prepared in a similar manner. Further, any of the corresponding amino compounds, more fully disclosed above can be phosgenated in accordance with the process disclosed by the examples to produce the corresponding isocyanato aryl phosphoric acid derivatives.

It is obvious that the process of the invention may be used to produce monoisocyanates, diisocyanates, triisocyanates or higher polyisocyanates. The monoisocyanates and polyisocyanates obtainable by the process of the present invention are useful as starting materials for the manufacture of polyurethane plastics. They may be polymerized by the well-known isocyanate polyaddition process to prepare cellular polyurethanes or homogeneous polyurethanes having improved flame resistance. Coatings produced from the isocyanates of the present invention may be used to replace oil base paint for coating metals or other substrates.

Although the invention has been described in considerable detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for this purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as is set forth in the claims.

What is claimed is:

1. Isocyanato phosphorous compounds having the formula



wherein X is selected from the group consisting of oxygen and sulfur, R is selected from the group consisting of O-aryl, O-aralkyl, O-alkaryl, O-cycloalkaryl, S-aryl, S-aralkyl, S-alkaryl, S-cycloalkaryl, N-(aryl)₂, N-(alkyl)(aryl), N-(alkaryl)₂, N(aralkyl)₂, and N(cycloalkaryl)₂; R' and R'' are selected from the group consisting of R, O-alkyl, O-cycloalkyl, S-alkyl, S-cycloalkyl, N-(alkyl)₂, and N-(cycloalkyl)₂; at least one of the aryl radicals having at least one isocyanato group bonded to a carbon atom of the aromatic ring.

2. 4,4',4''-triisocyanato phenyl phosphate.

3. 4,4',4''-triisocyanato phenyl thiophosphate.

4. Diethyl mono-p-isocyanato phenyl thiophosphoric acid triester.

5. (p-Isocyanato phenyl)-phosphoric-di-ester-mono-methyl phenyl amide.

6. A process for the preparation of isocyanato phosphorous compounds having the formula



wherein X is selected from the group consisting of oxygen and sulfur, R is selected from the group consisting of O-aryl, O-aralkyl, O-alkaryl, O-cycloalkaryl, S-aryl, S-aralkyl, S-alkaryl, S-cycloalkaryl, N-(aryl)₂, N-(alkyl)(aryl), N-(alkaryl)₂, N(aralkyl)₂, and N(cycloalkaryl)₂; R' and R'' are selected from the group consisting of R, O-alkyl, O-cycloalkyl, S-alkyl, S-cycloalkyl, N-(alkyl)₂, and N-(cycloalkyl)₂; at least one of the aryl radicals having an —NCO group bonded to a carbon atom of the aromatic ring, which comprises reacting the corresponding amino aryl phosphate with phosgene.

7. Isocyanato phosphorous compounds having the formula



wherein X is selected from the group consisting of oxygen and sulfur, R is O-aryl and R' and R'' are selected from the group consisting of R, O-alkyl, O-cycloalkyl, S-alkyl, S-cycloalkyl, N-(alkyl)₂, and N-(cycloalkyl)₂; at least one of the aryl radicals having at least one isocyanato group bonded to a carbon atom of the aromatic ring.

8. Isocyanato phosphorous compounds having the formula



wherein X is selected from the group consisting of oxygen and sulfur and R is O-aryl, at least one of the aryl radicals having at least one isocyanato group bonded to a carbon atom of the aromatic ring.

9. Isocyanato phosphorous compounds having the formula



wherein X is selected from the group consisting of oxygen and sulfur, R and R' are O-aryl and R'' is N-(alkyl)-(aryl), at least one of the aryl radicals having at least one isocyanato group bonded to a carbon atom of the aromatic ring.

10. Isocyanato phosphorous compounds having the formula



wherein X is selected from the group consisting of oxygen and sulfur, R is O-aryl and R' and R'' are O-alkyl, said aryl radical having at least one isocyanato group bonded to a carbon atom of the aromatic ring.

11. A process for the preparation of triisocyanato phen-

yl phosphate which comprises reacting a triamino phenyl phosphate with phosgene.

12. A process for the preparation of triisocyanato phenyl thiophosphate which comprises reacting a triamino phenyl thiophosphate with phosgene.

13. Triisocyanato phenyl phosphates.

14. Triisocyanato phenyl thiophosphate.

References Cited in the file of this patent

UNITED STATES PATENTS

2,691,567 Kvalnes et al. ----- Oct. 12, 1954