

Anhydrides of Phosphono Isobutyric Acid .

colorless liquids which can be distilled under reduced pressure. They hydrolyze comparatively readily with water. The thermal stability increases with an increasing number of methyl groups in the ester group. During the preparation of the trimethyl ester of the phosphono isobutyric acid with PCl_5 at 70°C it was found that to the acid chloride another substance is formed which has a melting point of $161 - 162^\circ\text{C}$. It is formed from the initial ester by intramolecular cyclization to form a cyclic anhydride because of an intramolecular reaction of the phosphono isobutyric acid. The acid chloride of the diethyl ester of the phosphono isobutyric acid also decomposes on continuing heating up to $150 - 170^\circ\text{C}$ and ethyl chloride and an intramolecular anhydride of the P-ethyl ester of the phosphono isobutyric acid are formed. The inner anhydrides of 1-phosphono isobutyric acid readily hydrolyze with water and yield two-basic acids the titration of which consumes exactly 2 equivalents of alkali. The P-methyl-phosphono isobutyric acid methyl-ester was separated in the form of a silver salt. On alkylation of this salt with methyl iodide the authors obtained trimethyl esters of the phosphono isobutyric acid.

SUBMITTED:
Card 2/2

SV 79-29-5-19 '75

5(3)

AUTHORS:

Petrov, K. A., Nepmysheva, A. A.

TITLE:

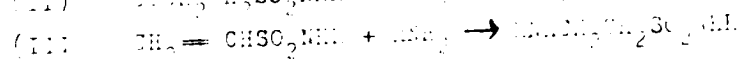
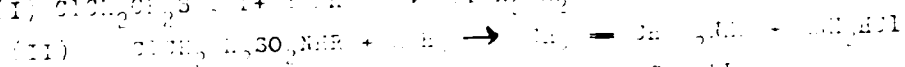
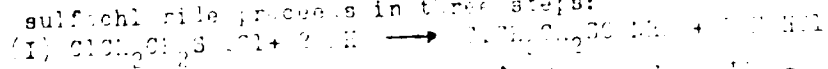
Reaction of Aliphatic Amines With β -Chloro-Ethane-Sulfochloride
(Reaktsiya alifaticheskikh aminov s β -khloretansul'fokhloridom)

PERIODICAL:

Zhurnal obshchey khimii, 1951, Vol 29, Nr 5,
pp 1494 - 1496 (USSR)

ABSTRACT:

In the present paper the conditions were investigated under which by the action of dimethyl- and diethyl amine upon β -chloro-ethane-sulfochloride vinyl-sulfodialkyl-amides and dialkyl-amino-ethane-sulfodialkyl-amides are formed. The yields are about 5%. The reaction was carried out in ether or chloroform at different temperatures (from -10 up to +60°C) and at a molar ratio of sulfochloride: amine = 1:3. In all cases identical products were obtained. Probably the reaction of amines with β -chloro-ethane-sulfochloride proceeds in three steps:



Card 1,2

Reaction of Aliphatic Amines With 3-Chloro-ethane-
Sulfochloride

S. V. T. - 1958 - 28

From data published and the results obtained in this work it may be concluded that the reactions (I) and (II) proceed at a high rate. The reaction rate of (III) depends on the nature of the amine. Dialkyl-amine-ethane-sulfochloride can be obtained by the addition of dialkyl amines to vinyl-ethane-sulfochloride at room temperature. There are references, I believe, in the Soviet literature.

SUBMITTED: March 25, 1958

Card 2, 2

Combination of Dialkyl Phosphorous Acids with
Alkyl Isothiocyanates

317, 318, 319, 320, 321, 322

phosphono-thioformic acid can only be distilled after washing the reaction mass with water. The reaction of the phosphites with isothiocyanates was carried out with methyl and allyl-isothiocyanates. In the latter case the addition took place both at the C=C and at the N=C bond. In the first case the esters of the γ -isothiocyanate propyl phosphinic acid must be formed, in the second the esters of the allyl-amido-phosphono-thioformic acid (Scheme 2). The latter esters are determined by hydrolysis of the reaction products with hydrochloric acid, in which connection phosphoric acid is obtained, as was expected, which was separated in the form of the trianiline salt. The alkyl-amido-phosphono-thioformates are viscous, yellow liquids with a strong unpleasant odor, which are easily soluble in organic solvents. When heated with hydrochloric acid (1:1) they are hydrolyzed to give ortho-phosphoric acid. The constants of the compounds synthesized are given in the table. There are 6 table and 6 references, 5 of which are Soviet

Card 2/3

5 (3)

AUTHORS:

Petrov K. A. Meymysheva, A. A.

SIV/79-23 6 11 72

TITLE:

Mixed Anhydrides of Carboxylic Acids and of the Acid Esters of Phosphoric- and Methyl Phosphinic Acid (Smeshannyye anhidridy karbonovykh kislot i kislykh efirov fosfornoj i metilfosfinovoy kislot) A New Method for the Production of Pyro-Phosphates (Novyy metod polucheniya pirofosfatov)

PERIODICAL:

Zhurnal obshchey khimii 1958 Vol 29 Nr 6 pp 1822 - 1826 (USSR)

ABSTRACT:

Among the organic derivatives of the anhydrides of the phosphoric acids there is a great number of physiologically active compounds in the field of biochemistry and agriculture. At present in addition to the well investigated pyro-phosphates and thiopyro phosphates only the mixed anhydrides of the carboxylic acids of the phosphites the anhydrides of the carboxylic acids and of the thionephosphates (i.e. the dialkyl-acyl-phosphites and dialkyl-acyl-thione phosphates) are known (Refs 1-4). In the present paper the authors describe the synthesis of the dialkyl-acyl-phosphates hitherto unknown and their properties. These compounds were obtained by reaction of the silver salts of the carboxylic acids with the acid chlorides of the

Card 1/3

Mixed Anhydrides of Carboxylic Acids and of the Acid
Esters of Phosphoric and Methyl Phosphinic Acid. A
New Method for the production of pyro-phosphates

phosphates or alkyl phosphates with an inert solvent at 40°. The end product was a practically pure acyl phosphate which was confirmed by the analysis (quantitative yields of phosphorus and acetyl group). The dialkyl-acyl phosphates are thermolabile compounds. In the vacuum distillation they decompose according to scheme 1. This behavior of the acyl phosphates was used by the authors in the synthesis of various pyro-phosphates which can be obtained in one single run without separation of the acyl phosphates. The reaction of the acid chlorides of the phosphate esters with silver acetate took place by heating in benzene. After separation of the precipitate and after distillation of the solvent the rest was fractionated; thus the acetic anhydride and the pyro-phosphates were separated. The yields in pyro-phosphates were 40-95%. The tetraethyl pyro-phosphate was obtained in good yield according to scheme 2 by reaction of silver or lead carbonate with diethyl-chloro-phosphate. The attempt to use instead of these salts sodium

Card 2/3

Mixed Anhydrides of Carboxylic Acids and of the Acid Esters of Phosphoric- and Methyl Phosphinic Acid. A New Method for the Production of Pyro-Phosphates SOV/79-24-6-11/72

potassium salts was a failure. The formation of the pyro-phosphates on the thermal decomposition of the acyl phosphates is only possible if the latter do not contain any alkyl amide groups. The alkyl-amido-acyl-phosphates decompose according to scheme 4. The constants of the compounds synthesized are given in the tables. There are 2 tables and 6 references, 4 of which are Soviet.

SUBMITTED: August 9 1958

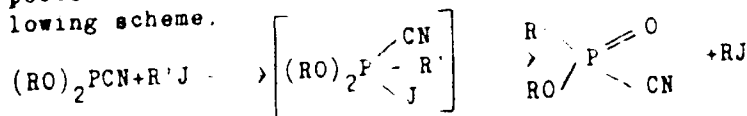
Card 3/3

AUTHORS: Petrov, K. A., Gatsenko L. G., SCV/79-29-6-12/72
 Neymysheva A. A.

TITLE: Esters of the Alkyl-cyano phosphinic Acids (Efiry alkiltsian-
 fosfinovykh kislot)

PERIODICAL: Zhurnal obshchey khimii : 1959 Vol 29. Nr 6. pp 827 - 831
 (USSR)

ABSTRACT: In addition to the authors' papers (Ref 1) the influence exer-
 cised by the alkyl halides upon the dialkyl-cyano-phosphites
 was investigated in this paper. The authors assumed that this
 reaction takes place according to the rearrangement of Arbuzov,
 and esters of the alkyl cyano-phosphinic acids were to be ex-
 pected which was confirmed experimentally according to the fol-
 lowing scheme.



N.-propyl-methyl-cyano-phosphinate was thus formed under pres-
 sure at 160° within 8-10 hours from di-n.-propyl-cyano-phosphite
 with the 3-4 fold quantity of methyl iodide, the structure of

Card 1/2

Esters of the Alkyl-cyano-phosphinic Acids

SOV/79-23-6-12/72

which was confirmed by the analysis (80% yield). Chlorine, when reacting with it in the presence of an equimolar quantity of PCl_3 , yields methyl-phosphinic acid-dichloride the constants of which are in agreement with the data published (Ref 2) (Scheme 2). The synthesis suggested of the alkyl-cyano-phosphinates is of general character. These esters are colorless liquids, soluble in organic solvents and hydrolyze readily with water and alkali lyes. The dialkyl-cyano-phosphites used as initial products were obtained by substitution of the CN-group for the chlorine in the dialkyl-chloro-phosphites by means of silver cyanide in ether on heating. Alkyl-cyano-phosphites are liquids of unpleasant phosphine odor, soluble in organic solvents which form solid complex salts with cuprous chloride. There are 3 references, 1 of which is Soviet.

SUBMITTED: March 20, 1958

Card 2/2

5(3)

AUTHORS:

Petrov, K. A., Neymysheva, A. A.

SOV, 7, 1977, 1167-1177

TITLE:

Carbylaminochlorides (Carbilyaminochlorides). I. Aliphatic
Carbylaminochlorides (I. Alifatskiye karbilyaminochlorides)

PERIODICAL:

Zhurnal obshchey khimii, 1977, Vol. 50, No. 7, pp. 1167-1177 (USSR)

ABSTRACT:

According to references 1, 2, 3, only β -chloroethylamine and methyl carbylaminochloride are known compounds. Little investigated aliphatic carbylaminochlorides, which, however, are little investigated. In the present paper the hitherto unknown methyl carbylaminochloride and the intermediate product obtained by an improved method in the synthesis of methyl carbylaminochloride as well as some properties of aliphatic carbylaminochlorides are described. Methyl carbylaminochloride was obtained by the chlorination of methyl isothiocyanate in ether at C^0 . The authors used a characteristic property, i.e. to free iodine from sodium iodide and potassium iodide, (1 mol : 1 mol), for a quantitative determination of methyl-, ethyl-, and β -chloroethyl carbylaminochloride. This process is shown below.

Aromatic carbylaminochlorides in this case are not described.

Card 1/2

Carbylaminohalides. I. Aliphatic Carbylaminochlorides 3077 - 1-7-19 83

in contrast to aliphatic carbylaminochlorides. In this respect trichloro methyl carbylaminochloride occupies an intermediate position between aliphatic and aromatic compounds. In contrast to aromatic carbylaminochlorides, methyl- and trichloro methyl carbylaminochloride do not react with H_2S ; with CuS and copper sulphides in solutions they react only at higher temperatures (above 100°). In the action of uridine on trichloro methyl carbylaminochloride always a complete substitution of chlorine atoms takes place. From the reaction products probably the guanidine derivatives (I) and (II) with equal empirical formulas were obtained, however, they were not further investigated. The syntheses of trichloro methyl mercaptan described in publications (refs 1, 4) are very complicated and produce low yields. By modifying Milton's synthesis (ref 4) it was possible to increase considerably the yield, i.e. by reducing the amount and concentration of nitric acid as well as by longer heating of the reaction mass (see experimental part). There are 6 references.

SUBMITTED: March 20, 1983

Card 2/2

5(3)

AUTHORS:

Petrov, K. A., Noymsheva, A. A.

3077-1-7-1959

TITLE:

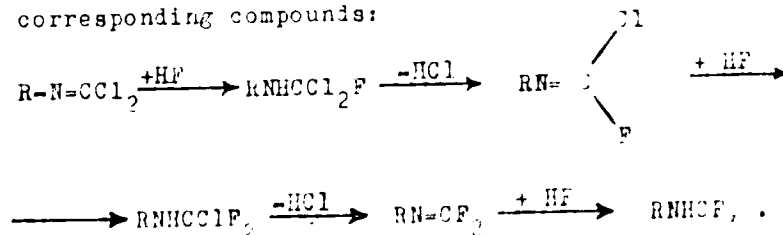
Carbylaminohalides (Karbilaminohalogenidy). II. Synthesis of Secondary Amines With a Trifluoromethyl Group (II. Sintez vtorichnykh aminov s triflormetil'noy gruppy)

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol. 32, No. 7, pp. 3077-3081 (USSR)

ABSTRACT:

This synthesis was carried out by the authors by reaction of hydrogen fluoride with carbylaminochlorides. Secondary amines with a trifluoro methyl group on the nitrogen are formed as a consequence of the subsequent affiliations of HF to carbylaminohalides and the separation of hydrogen chloride from the corresponding compounds:



Card 1/3

Carbylaminochlorides. II. Synthesis of Secondary Amines
With a Trifluoromethyl Group

SOV, 74-10-7-16/81

Carbylaminochlorides react vigorously with HF at low temperatures in this connection, according to the reaction conditions, secondary amines or polymers of carbylamino fluorides are formed. The reaction of hydrogen fluorides with phenyl, p-tolyl-, β -chloroethyl-, and trichloromethyl carbylaminochloride led to the following compounds: phenyl trifluoromethylamine (68,5 %), p-tolyltrifluoromethylamine (70 %), hexafluorodimethylamine (85 %), and acid fluoride of β -chloroethylcarbamio acid. In the reaction of aniline with phenyl trifluoromethylamine only one fluorine atom is replaced by the aniline residue, and only by the action of water diphenyl urea is formed (Scheme 2). The ease with which hexafluorodimethylamine is formed in the reaction of HF with trichloromethylcarbylaminochloride is explained by scheme 3. In the energetic reaction of β -chloroethyl carbylaminochloride with HF at low temperature, without solvent and with an excess of HF, diffusibly separable polymers of β -chloroethyl carbylaminochloride are formed. In the action of aniline on acid fluoride of β -chloroethyl carbylaminochloride β -chloroethyl urea is formed. The hydrolysis of

Card 2/3

Carbylaminoalides. II. Synthesis of Secondary Amines With a Trifluoromethyl Group

hexafluoroisopropylamine is illustrated by example 4.
There are 5 references, none of which is Soviet.

SUBMITTED: March 25, 1959

Card 3/3

Sov. Chem. Rev. 1967, 36, 1

AUTHORS: Petrov, K. A., Noykovaeva, A. A.

TITLE: Caroylamino-fluorides III. A New Method of Synthesis of Caroylamino-fluorides

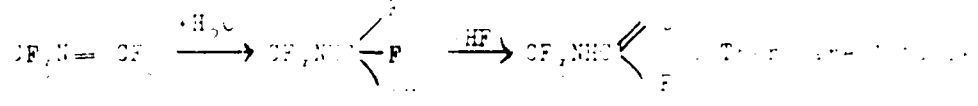
PERIODICAL: Journal. Sov. Chem. Rev., 1967, Vol. 36, No. 1, pp. 1-10. See also p. 10.

ABSTRACT: The synthesis of caroylamino-fluorides was reviewed. Caroylamino-fluorides (1-2) and others are of limited value since they are hydrolyzed to caroylamino-fluorides, and can only be applied to the synthesis of caroylamino-fluorides which contain a non-fluorinated radical which is directly bonded to the nitrogen. The caroylamino-fluorides already known are listed in the table. In the present paper, a new method of synthesizing the caroylamino-fluorides is described which is based on the elimination of hydrogen fluoride from secondary amines containing a trifluoromethyl group. Such amines can be synthesized. Ref. 1 by reaction of the caroylamino-chlorides with a trialkylamine. Benzyl-trifluoromethylamine and hexafluoro-isopropylamine were dehydrofluorinated. On heating the former with potassium fluoride up to 140-150° without a solvent for 4-5 hours, the pure caroylamino-fluoride is formed. It boils at 49°/1 mm Hg, and is rather well preserved in a closed container, even without a stabilizer.

Card 1 of 2

Carbonylamine Halides III. A New Method of Synthesizing $CF_3N=CF_2$ and $CF_3N=CF$ Carbonylamine Halides

... on heating with quinoline, no hydrogen fluoride is
... By passing the hexafluoro-diamidylamine vapor
... through a column filled with granulated K_2CO_3 and
... water at 10-15°C, trifluoro-methyl-carbonylamine
... obtained (the yield is similar to a product of known
... (Kochi et al. 1971). Attempts to obtain carbonylamine
... substitution of the fluorine in carbonylamine
... by other different halogens, were carried out
... trifluoro-methyl-carbonylamine with water and
... vigorously with ammonia, sulphides with water
... NH_4^+ . The carbonylamine halides were purified



... and ...

Submitted: ...

... 3

5(3)

SOV 79-73-9-46/78

AUTHORS:

Petrov, K. A., Nemyshneva, A. A.

TITLE:

Synthesis of the Derivatives of Phosphor Sulfonic Acid

PERIODICAL:

Zhurnal Obshchey Khimii, 1969, Vol. 39, No. 3, pp. 506-507
(USSR)

ABSTRACT:

Apart from a patent describing the synthesis of vinyl phosphonosulfonates by reacting dialkyl phosphites with sulfones (Ref. 1), the phosphor sulfonic acids are only little investigated. In the present paper the synthesis of similar compounds is made by the addition of dialkyl phosphites to the derivatives of vinyl sulfonic acid. Esters, dialkylamides and the fluorides of vinyl sulfonic acid were used for the reaction with phosphites; however, in all cases derivatives of ethylene phosphonosulfonic acid resulted. The dialkyl phosphites and the dialkyl amides of vinyl sulfonic acid in the presence of sodium alcoholate in heating to 110° within 6 hours, and esters of dialkylamides of ethylene phosphonosulfonic acid are formed in yields of 60-70%. Unlike dialkylamides the fluorides of vinyl sulfonic acid with the dialkyl phosphites in the absence of sodium alcoholates. In this connection the introduction of fluorine considerably intensified the activity of

Card 1/3

SCV, 79-13-2-10-16

Synthesis of the Derivatives of Phosphorothioic Acid

the double bond. The reaction takes place at 110°C and is described by the scheme $(RC)_2PCH_2CH_2CHCO_2F \rightarrow RC_2PCH_2CH_2CHSO_2F$. In the

action of 11-(n-undecylthio)disulphide on sodium diethyl phosphate, methyl-S-butyl disulphide (Scheme 1) resulted instead of the expected compound. Di-(n-undecyl)propyl disulphide reacts with triethyl phosphite under the formation of triethyl thiophosphate. The same result is obtained with S-acid fluorides of the elements of the 16th and 17th groups of the periodic table. The reaction of KF with chloro-substituted compounds especially with such having a mobile chlorine atom a substitution of the chlorine atom by fluorine takes place at the beginning of the hydrochloric acid and the following fluoride is formed:

$$CH_2ClCH_2R + KF \rightarrow CH_2FCH_2R + KCl$$

Hydrogen fluoride is separated by KF and these compounds with a double bond are formed:

$$CH_2FCH_2R + KF \rightarrow CH_2=CHR + KF.HF$$

Thus in this case a derivative fluorination is observed. The following fluorination is also

Card 2/3

SOV, 20-22-2-16/76

Synthesis of the Derivatives of P... A...

Submitted to ...

SUBMITTED: July 11, 1976

Part 3,3

SC7 79-11-17 79

3(3)

AUTHORS:

Petrov, K. A., Neymyadova, A. A.

TITLE:

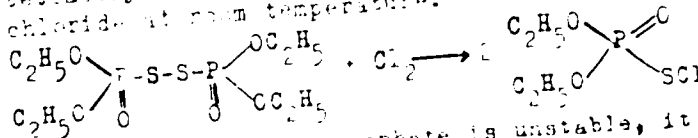
S- Chlorodiethyl Thiophosphate

PERIODICAL:

Zhurnal Obshchei Khimii, 1959, Vol 29, Nr 2, pp 1010-1011 (USSR)

ABSTRACT:

The present paper deals with the synthesis of S-chlorodiethyl thiophosphate and its properties. It is made by reacting tetraethyl bisulfite (Ref 1) with chlorine or ethylchloride at room temperature.



S-chlorodiethyl thiophosphate is unstable, it loses its chlorine rather rapidly and passes into an undistillable liquid. It shows strong similarity with sulphene chlorides with respect to its chemical properties and its reactivity. Thus it separates iodine from acidified potassium iodide solutions and passes into disulphide (Scheme 2). It adds to styrene and cyclohexene and reacts with diazomethane under the formation of

Card 1/3

SOV, 79-29-9-47 76

S-Chlorodiethyl Thiophosphate

O,O-diethyl-S-2-chloroethyl phosphite and similar compounds. Like the sulphene chlorides (Ref 3), it reacts with dialkyl phosphites. The reaction with diethyl phosphite yields tetraethyl thiopyrophosphate (S. 194-3). The assumed structure of tetraethyl thiopyrophosphate agrees with the data of the preceding paper, where it was shown that sulphene chlorides which have the same functional S-Cl-group as S-2-chloroethyl thiophosphate react with acid and neutral phosphites under the formation of thioesters of phosphoric acid and thiopyrophosphates (Ref 3). Opinions diverge concerning the structure of thiopyrophosphate. This structure, thiopyrophosphate which is obtained by the reaction with H₂S with diethyl thiopyrophosphate and pyrophosphate is described in the literature (Ref 4). It is described the same structure if it forms the salt of sulfur diethyl tetraethyl phosphite (Ref 5). According to G. S. Sviridov it has the structure (Ref 6). S. 194-3, A. Ya. and B. A. Aronov assume also that tetraethyl thiopyrophosphate is obtained by different methods and is the same substance because of the different method of production it shows the same constant. There are 9 references, 4 of which are Soviet.

Car 7/3

PETROV, K. A.

43

PHASE I BOOK EXPLOITATION

SOV.6034

Konferentsiya po khimii i primeneniyu fosfororganicheskikh soyedineniy. 2d.
Kazan', 1959

Khimiya i primeneniye fosfororganicheskikh soyedineniy. trudy (Chemistry
and Use of Organophosphorus Compounds. Conference Transactions) Moscow.
Izd-vo AN SSSR, 1962. 630 p. Errata slip inserted. 2800 copies printed.

Sponsoring Agency Akademiya nauk SSSR. Kazanskiy filial.

Resp. Ed. A. Ye. Arbuzov, Academician, Ed. of Publishing House: L. S.
Povarov. Tech. Ed.: S. G. Tikhomirova.

PURPOSE: This collection of conference transactions is intended for chemists,
process engineers, physiologists, pharmacists, physicians, veterinarians,
and agricultural scientists.

COVERAGE: The transactions include the full texts of most of the scientific
papers presented at the Second Conference on the Chemistry and Use of

Card 1/14

Chemistry and the Use of Organophosphorus (Cont.)

SOV. 6034

Organophosphorus Compounds held at Kazan' from 2 Nov through 1 Dec 1959. The material is divided into three sections: Chemistry, containing 67 articles, Physiological Activity of Organophosphorus Compounds, containing 26 articles, and Plant Protection, containing 12 articles. The reports reflect the strong interest of Soviet scientists in the chemistry and application of organophosphorus compounds. References accompany individual reports. Short summaries of some of the listed reports have been made and are given below.

TABLE OF CONTENTS (Abridged)

Introduction (Academician A. Ye. Arbuzov)

3

TRANSACTIONS OF THE CHEMISTRY SECTION

Gefter, Ye. L. [NII plastmass (Scientific Research Institute of Plastics, Moscow)]. Some Prospects for the Industrial Use of Organophosphorus Compounds

46

Card 2/4

Organic and the Use of Organic Compounds (Cont.)

SO 604

substituted phosphoric and phosphonic acids, as well as phosphonates containing catalysts, have been synthesized and studied.

Pol'skii, K. A., V. A. Parshina, and G. I. Dan'ko. Phosphorus-Containing Polyester and Polyamide Resins.

200

Bis-(p-*tert*-butylphenoxy)phosphonic acid, diesters, and salts thereof, as amides and chlorides, have been obtained and for the first time described in the scientific literature. Organic phosphorus polyesters and polyamides based on them were given. Diethylolglycol hexamethylene diamine and bis-(p-*tert*-butylphenoxy)phosphonic acid and a number of forming fibers were also obtained and described.

Pol'skii, K. A., E. Ye. Nefant'eva, and I. I. Sopykova. Application of Anionic Rearrangement to the Synthesis of Polyphosphonates.

202

Phosphorus-containing vinyl phosphonates have been subjected to anionic rearrangement to give polyphosphonates with a regular structure. The phosphonates polymerize under the action of methyl lithium

CI 1174

53830
53630

3,190,000
B020, B000

AUTHORS Petrov, K. A., Nifant'ev, E. Ye.

TITLE Phosphorus-containing Polymers. I. Synthesis and Polymerization of Ethylene Alkyl phosphates.

PERIODICAL. Vysokomolekulyarnyye soedineniya, 1960, Vol. 2, No. 4, pp 417-420

TEXT. Neutral phosphates are well-known compounds used in industry and agriculture. But so far no phosphates had been synthesized which contain in the molecule a five-membered cyclic ester grouping, nor high molecular phosphates that had not been condensed via the vinyl ester groups. In the present paper, a simple process is suggested for the preparation of ethylene alkyl phosphates and their polymerization. These were synthesized by oxidation of ethylene alkyl phosphites with nitrogen dioxide. The cyclic phosphates synthesized were used by the authors to obtain polymers containing phosphorus. They also found that cyclic phosphates (contrary to phosphonates) form higher-molecular compounds.

Card 1/2

Synthesis and polymerization of ethylene
alkyl phosphates

37,140,80
BOSTON

polymerization under the same conditions with a degree of polymerization
of 10-14. The resultant polymers maintained the same molecular weight
and the same properties as found in experiments without or with
catalysts sodium. High-molecular phosphates are neutral and have a
polyester structure. The high-molecular phosphates described in this
paper may be used as plasticizers. The experimental part describes the
preparation of ethylene hexyl phosphite, ethylene phenyl phosphite, and
ethylene alkyl phosphates (Table 1), the conditions of polymerization,
ethylene alkyl phosphates and the properties of the polymers (Table
2) as well as the reaction of polyethylene propyl phosphate with phosphorus
pentoxide. It is shown that ethylene alkyl phosphates polymerize
without standing or heating. It was also found that the yield of
ethylene alkyl phosphates obtained by the above described process is
90-95%, and that on polymerization the latter form an ester
molecular weight of 2,000-3,000 by cleavage of the phosphate group.
There are 2 tables and 3 references (Soviet, U.S.S.R., and British).

SUBMITTIF Docid: 11

TIMOSHEV, V.G.; PETROV, K.A.; RODIONOV, A.V.; BALANDINA, V.V.; VOLKOVA, A.A.;
YEL'KINA, A.V.; MAGHIBEDA, Z.I.

Extraction capacity of neutral, oxygen-containing organic substances.
Radiokhimiia 2 no.4:419-425 '60. (MIRA 13:9)
(Extraction (Chemistry))

82817

2109
2209

15 8114

AUTHORS: Petrus, K. A. Nifant'eva, E. A.

TITLE: Phosphorus Polymers. II. Use of Phosphinic Chlorides for Synthesizing Polyphosphinites

PERIODICAL: Vysokomolekulyarnaya Khimiya, 1964, 7, No. 1, pp. 66-78

TEXT: The authors used the Arsenow reaction for synthesizing phosphinic esters. Polymerization occurs on heating 1 mole of phosphinites with 0.001 - 0.1 mole of methyl iodide in a sealed tube. Polyphosphinites are formed with a molecular weight of 1000. hitherto unknown cyclic phosphinites were obtained by reacting phosphinites with 1,4-dioxane in the presence of tertiary amines. 1,3-butylene phosphinite and phenylphosphinite are formed in the reaction with CH_2I_2 as a rearranged alkylation reaction with

Card 1/2

43817

Phosphorous Polymers. II. Use of the
Artuzov Rearrangement for Synthesizing
Polyphosphonates

S. I. ZIL'BERMAN
V. A. POKHODIN

$$R \begin{array}{c} \diagup \\ \text{C} \\ \diagdown \\ \text{CH}_2 \end{array} \text{P}=\text{O} \left[\text{-(CH}_2\text{)}_n \text{-P} \begin{array}{c} \diagup \\ \text{O} \\ \diagdown \\ \text{R} \end{array} \text{O} \right]_m \text{-CH}_2 \text{R}$$

The structure of the central member could be proved by cleaving the methyl phosphonate phosphinite polymer by means of sodium hydroxide solution. The methyl-phenylpropylphosphinite was obtained. The results of polymerization of phosphite esters with the use of methyl iodide are given in a table. There are references to Soviet and US.

K

SUBMITTED: January 1967

Card 2/3

PETROY, K.A.; SHEVCHENKO, V.B.; TIMOSHEV, V.G.; MAKLYATEV, F.A.; FOKIN,
A.V.; RODIONOV, A.V.; BALANDINA, V.V.; YEL'KINA, A.V.; MAGNIBEDA,
Z.I.; VOLKOVA, A.A.

Alkyl phosphonates, diphosphonates, and phosphine oxides as
extracting agents. Zhur.neorg.khim. 5 no.2:498-502
F '60. (MIRA 13:6)

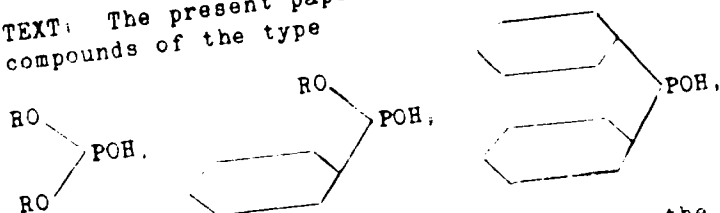
(Phosphonic acid) (Phosphine oxide)
(Extraction(Chemistry))

SHEVCHENKO, V.B.; SHMIDT, V.S.; MENAROKOMOV, E.A.; PETROV, K.A.

Extraction of nitric acid with tri-n-octylamine. Zhur. neorg.
khim. 5 no.8:1852-1856 Ag '60. (MIRA 13:9)
(Nitric acid) (Octylamine)

S/079/60/030/04/40/060
B001/B016

AUTHORS: Petrov K A, Urbanskaya, O S
 TITLE: Amidation Reaction of Some Compounds of Trivalent Phosphorus
 PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 4, pp 1255-1258
 TEXT: The present paper deals with the reaction of chloramine with compounds of the type



which led to a new method of synthesizing the amides of phosphoric and phosphinic acid. The direct amidation of compounds of trivalent phosphorus could be useful for the synthesis of compounds with the phosphamide group. This group, like the sulfamide group, may impart

Card 1/3

1979.

S, 079, 60, 030, 04, 07, 000
BCC, BO, 1

53832

AUTHORS: Petrov, K. A., Parshina, V. A.

TITLE: Phosphatic Polyester- and Polyamide Resins

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 4, pp. 1341-1344

TEXT: It was the aim of the investigation under review to carry out the synthesis of organophosphorus condensation polymers of the type of polyester and polyamides. Ethylene glycol, diethylene glycol, hexamethylene diamine and the ester of the dibasic acid bis-(p-carbomethoxy phenyl)-methyl phosphin-oxide were used for the condensation. Polymers (I), (II), (III) are described. The characteristic feature of these polymers is the circumstance that there are atoms of pentavalent phosphorus in their chain, which are linked by phosphocarbon compounds. Thus, polymers (I) and (III) differ from "Terylene" and "Nylon" by the fact that the radicals of bis-(p-carboxyphenyl)-methyl phosphin-oxide replace the radical of terephthalic acid in the chain of the former and the radical of adipic acid in the chain of the other. With respect to heating and reacting with various reagents containing organophos-

S/079/60/030/05/42/074
B005/B016

5.3630

AUTHORS:

Petrov, K. A., Maklyayev, F. L., Bliznyuk, N. K.

TITLE:

Diphosponates. I. Esters of Methylene Diphosphonic Acid

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, No. 5, pp. 1602-1608

TEXT: The authors of the present paper investigated the alkylation of sodium dialkyl phosphites with chloro-methyl-phosphinic esters (Michaelis-Becker Reaction). It was possible to clarify the side reactions which accompany this reaction. In some cases, the yield of alkylation products (tetraalkyl methylene diphosponates) could be raised. When treating sodium diethyl phosphite with the diethyl ester of chloro-methyl-phosphinic acid, a considerable quantity of a solid substance which is not distillable, and substances with a lower boiling point than that of the diphosponate result in addition to the corresponding diphosponate. The authors indicated that the solid product is a mixture of the sodium salts of the esters of methylene diphosphonic acid, ethyl phosphinic acid, and chloro-methyl-phosphinic acid. The low-boiling liquid by-product mainly consists of the diethyl esters of ethyl- and chloro-methyl phosphinic

Card 1/3

Diphosphonates I Esters of Methylene
Diphosphonic Acid

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acid. The formation of these by-products is due to the alkylation of the sodium dialkyl phosphites by the resultant esters of the alkyl-phosphinic acids (Ref 5) In a schematical survey, the equations for the formation of all possible products of reaction of sodium diethyl phosphite with the diethyl ester of chloro-methyl-phosphinic acid are summarized. This reaction was accomplished under considerably varied conditions. The separation of the reaction products encountered with great difficulties. The procedure of separation is described in detail. The yield in diethyl phosphonate was 30-50% depending on the reaction conditions, calculated for the initial sodium diethyl phosphite. The structure of the by-products is given. In some cases, the alkylation of sodium dialkyl phosphite by the product of the principal reaction, which represents a disturbing side-reaction, may be checked to a large extent by choosing suitable conditions; a complete elimination of this side reaction is hardly possible. The chloro-methyl-phosphinic esters which were used as initial products for the synthesis of methylene diphosphonates were obtained by esterification of the corresponding diacid chlorides with alcohols. By some modifications of the reaction conditions of a method described in publications (Ref 7), the yield of the esterification could be increased to 90-95%. Table 1

Card 2/3

Diphosphonates I Esters of Methylene
Diphosphonic Acid

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B005/B016

presents 5 esters of chloro-methyl-phosphinic acid which have not yet been described. Boiling point, refractive index, density and molecular refraction are given for each ester. In an experimental part, all reactions performed are described in detail. In Table 2 yields and P- and Cl-contents are given for 4 esters from Table 1. A Ye Arбузов is mentioned in the present paper. There are 2 tables and 7 references, 3 of which are Soviet.

SUBMITTED: May 26, 1959

Card 3/3

S/079/60/030/05/43/C74
BC05/BC16

5363:

AUTHORS: Petrov, K. A., Maklyayev, P. L., Bliznyuk, N. K.

TITLE: Diphosphonates II Synthesis of Esters of Ethylene- and Methyl Ethylene Diphosphonic Acid

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, No 5, pp 1608-1614

TEXT: The authors of the present paper showed that the synthesis of esters of ethylene diphosphonic acid may be performed by means of the ~~Michaelis-Becker~~ reaction. All difficulties connected with the use of this reaction could be overcome by determining the optimum temperature range and the optimum order in mixing the reagents. On reaction of sodium dialkyl phosphites with 1,2-dihalogen alkanes, olefins only result at too high temperatures whereas at low temperatures mainly the corresponding diphosphonates are formed. The order observed when combining the reagents exerts considerable influence upon the direction of the reaction of sodium diethyl phosphite with 1,2-dichloro ethane. The best yield of the corresponding diphosphonate (57.5%) is obtained by adding slowly the benzenic solution of sodium diethyl phosphite to dichloro ethane heated to 50-55°.

Card 1/3

Diphosphonates. II Synthesis of Esters of Ethylene and Methyl Ethylene Diphosphonic Acid S/079/60/030/05/43/074
B005/B016

The chloro-ethyl phosphinic esters do not result in these reactions as the mobility of the halogen in these esters is higher than in the 1,2-dihalogen alkane. In the reaction of sodium diethyl phosphite with dichloro ethane, the diethyl ester of ethyl phosphinic acid and a mixture of salts of ethylene diphosphonic esters and ethyl phosphinic esters are obtained as by-products. The formation of these by-products is due to alkylation of sodium diethyl phosphite by the tetraethyl ester of ethylene diphosphonic acid which results as principal product of the reaction, or by the diethyl ester of ethyl phosphonic acid. The corresponding reaction schemes as well as the structural proof of these side-products are given. By the afore-mentioned alkylation of sodium dialkyl phosphites with dichloro ethane, also the tetraisopropyl ester of ethylene diphosphonic acid was synthesized which has not yet been described in publications. By the reaction of sodium dialkyl phosphites with allyl phosphonates in the presence of sodium alcoholates, esters of methyl ethylene diphosphonic acid were produced. The rate of this reaction does not so much depend on temperature but rather on the quantity of the alcoholate acting as a catalyst. Finally, esters of allyl phosphinic acid were formed by treating sodium dialkyl phosphites with allyl bromide. This reaction has

Card 2/3

Diphosphonates. II. Synthesis of Esters of
Ethylene- and Methyl Ethylene Diphosphonic Acid

S/079/60/030/05/43/074
B005/B016

been investigated previously (Ref 8) By modification of some reaction conditions, the yield of this synthesis could be increased from 57 to 72.5% In an experimental part, all syntheses performed are described in detail. In the present paper, M. I. Kabachnik (Ref 7) is mentioned. There are 9 references, 7 of which are Soviet

SUBMITTED May 26, 1959

Card 3/3

S 3630

S/079/60/030/06/05/009
B002/B016

AUTHORS: Petrov, K. A., Maklyayev, F. L., Bliznyuk, N. K.

TITLE: Diphosphonates. 3. Synthesis of O- and S-Bisphosphonates

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 6, pp. 1960-1964

TEXT: In the present paper the synthesis of compounds of the type $[(RO)_2P(O)(CH_2)_n]_2O$ and $[(RO)_2P(O)(CH_2)_n]_2S$ is described. So far, there are but little data available on it, since its complete performance has met with difficulties. It is generally based on an alkylation of diethyl sodium phosphite by means of dichloro and dibromo-dimethyl ethers. The resultant precipitate is difficultly separated from the solution, but a distillation without preceding separation involves further interaction of the NaCl or NaBr salts formed in the reaction with the diphosphonate, in which connection the disodium salts of the ethers result. The formation of these sodium salts is confirmed by the alkylation reaction (Refs. 1,2,5) of sodium dialkyl phosphites by means of esters of alkyl phosphinic and diphosphinic acids, which was already known to the

Card 1/3

Diphosphonates. 3. Synthesis of O- and
S-Bisphosphonates

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B002/B016

authors. The synthesis of the O- and S-diphosphonates is now studied on the reaction of sodium dialkyl phosphites with dichloro-dimethyl- and α, β' -dichloro-diethyl ethers, further with dichloro-dimethyl- and α, β' -dichloro-diethyl sulfides. In all cases the esters of the di-phosphonic acid were obtained. The afore-mentioned difficulties when separating the reaction product were eliminated by adding so much water, that the resultant salt is dissolved. The purely organic layer was washed out with alkali and water. To prevent decomposition after the distillation, the latter must be performed on a small quantity of anhydrous Na_2CO_3 .

K_2CO_3 . The resultant O- and S-bisphosphonates represent high-boiling, thermostable, viscous liquids which are not or only sparingly soluble in water, but well soluble in organic solvents. The properties of the compounds synthesized are presented in the table. The following compounds were obtained: Bis(diisopropyl phosphono)dimethyl ether, yield 70%; bis(dibutyl-phosphono) dimethyl ether, 69.3%; bis(diisopropyl-phosphono) diethyl ether, 37.8%. By slowly adding Chlorex during the latter reaction, the yield could be increased up to 57.2%. Bis(dibutyl phosphono)

Card 2/3

Diphosphonates. 3. Synthesis of O- and
S-Bisphosphonates

S/079/60/030/06, 05. 009
B002/B016

diethyl ether, 46.8%, and the corresponding sulfides with the yields:
bis(diethyl-phosphono)dimethyl sulfide 57%, bis(dibutyl-phosphono)dimethyl
sulfide 50.8%, the tetraethyl ester of diphosphono-dimethyl sulfide 71%.
bis(diisopropyl-phosphono)diethyl sulfide 39.5%, and bis(dibutyl-
phosphono)diethyl sulfide 35.2%. There are 1 table and 6 references:
5 Soviet and 1 American.

SUBMITTED: May 26, 1959

Card 3/3

S/000/00/000/000/000/XX
B000/B000

AUTHORS Petrov K. A. Bliznyak N. K. and Lysenko T. N.

TITLE Reaction of Sodium Dialkyl phosphites¹ and Sodium Monoalkyl phosphates with Alkyl Magnesium Halides

PERIODICAL Zhurnal khimicheskoy fiziki 1960 Vol. 30 No. 6
pp. 1964-1968

TEXT. Dialkyl phosphinic acids of the type RR'P(O)CH₃ have scarcely been investigated, since their synthesis is rather difficult. Of the various known methods for their synthesis, the authors selected the one by G. M. Kosolapoff (Ref. 1) which involves the reaction of Grignard reagents with dialkyl phosphites and subsequent oxidation of the resulting dialkyl phosphinoylides (Refs. 2, 3). When studying the reaction, the authors had to employ a large excess of the above reagent, and found that dialkyl phosphites split up the alkyl magnesium halide into the corresponding hydrocarbon according to Scheme 1:
$$(RO)_2P(O)CH_3 + 3R'MgX \rightarrow R_3C-P(O)MgX + R'H + 2ROMgX$$
 Thus, the authors

Card 1/1

Reaction of Sodium Dialkyl phosphites and Sodium Monoalkyl phosphonates With Alkyl Magnesium Halides S/O79/60/030/066/025/033/XX
BOO7/BO55

obtained 60% butane in the reaction of diethyl phosphite with butyl magnesium bromide according to Kislapff. To avoid this inexpedient waste of organomagnesium compound the author used the sodium salts of dialkyl phosphites instead of the free acids since the former do not split up the organomagnesium compound and dialkyl phosphinic acids are formed. Alkyl magnesium halides with sodium dialkyl phosphites form salts of dialkyl phosphinic acids according to Scheme 2:

$$(RO)_2P(OR')Na + 2R''MgX \longrightarrow R''_2P(OR')Na + 2ROMgX$$
 As was expected according to

the reaction by Michaelis Becker treatment of the reaction product obtained from sodium diethyl phosphite and hexyl magnesium bromide with methyl iodide gave a precipitate of methyl dihexyl phosphin oxide. Alkylation of the mixed magnesium salt obviously occurs as a side reaction: $ROMgX + CH_3I \longrightarrow ROCH_3 + MgXI$. The reaction of dialkyl phosphites and their salts with Grignard reagents is a convenient method of synthesizing dialkyl phosphinic acids but gives only acids with two equal alkyl groups. With a view to obtaining a generally applicable

Card 2/4

Reaction of Sodium Dialkyl phosphites and
Sodium Monoalkyl phosphonates With Alkyl
Magnesium Halides

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B001/B055

method for the synthesis of these acids, the authors studied the reac-
tion of the etherates of alkyl phosphinic acids (Ref. 5 Scheme 6) with
alkyl magnesium bromides which is however very difficult and gives
low yields (Ref 4) There are 1 table and 6 references. 2 Soviet and
4 US

SUBMITTED. June 15 1959

Card 3/3

DATE: AT 1 11 1951

SECRET

MEMORANDUM FOR THE DIRECTOR
SUBJECT: [Illegible]

[Illegible typed text follows]

CH [Illegible] N [Illegible] [Illegible]

[Illegible handwritten notes and signatures]

Styrene Amide Phosphate

1950
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If no alcoholate is used as a catalyst, the yield is small. A small yield of N, N', N'', N'''-tetraethylphosphoric acid was obtained by reacting the acid tetraethylphosphoric acid with ethyl alcohol. This reaction should be carried out in a dry benzene solution. The product is a colorless oil. The fractional crystallization of the tetraethylphosphoric acid from benzene. The results of this work are reported in Soviet Journal of US, and Japanese.

SUBMITTED August 1950

Card 1/1

03-10-1960
21 1960

ANTHORS: Petrov, K. A., Bliznyuk, N. K., Korotkova, V. I.
TITLE: Reaction of the Acid Chlorides of Phosphoric Acid and Alkyl Phosphinic Acids With Alkyl Magnesium Bromides
PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 32, No. 1, pp. 2995-2999

TEXT: Proceeding from the papers of Refs. 1-6 that deal with the smooth formation of the trialkyl phosphine oxides from phosphorus oxychloride and organo-magnesium compounds (Scheme 1), the authors tried to increase the yields of dialkyl phosphinic acids. They showed that the reaction of the acid chlorides of the pentavalent phosphoric acids with alkyl magnesium bromides does not come to an end, and found the reasons why. Also in the case of lower boiling of the acid chloride with excess organo-magnesium compound a certain amount of dialkyl phosphinic acid forms besides phosphine oxide. The yield of the mentioned acid increases considerably if alkyl magnesium halides of isostructure are used. Thus, according to Ref. 1 the reaction of phosphorus oxychloride with n-butyl

Card 1/3

Reaction of the Acid Chlorides of Phosphoric
Acid and Alkyl Phosphinic Acids With Alkyl
Magnesium Bromides

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R001, R064

magnesium bromide gives rise to 50-60% tri-n-butyl phosphine oxide and 15-25% di-n-butyl phosphinic acid. Under the same conditions, except for the use of isobutyl magnesium bromide, the oxide yield is reduced to 25-30%, and that of the acid increased to 30.5%. Apparently, the authors of Ref. 1 regarded the mixture of trialkyl phosphine oxide and dialkyl phosphinic acid as pure oxide. The formation of considerable amounts of dialkyl phosphinic acids besides the oxides in the Grignard reaction may be explained by the fact that the intermediate products (the dialkyl phosphonates) react with magnesium halides and pass over into the complexes $R_2P(O)Cl \cdot MgXCl$ that are insoluble in ether and which in turn react difficultly under heterogeneous conditions with the alkyl magnesium halides. This circumstance permits stopping most of the reaction during the intermediate stage and thus to obtain the dialkyl phosphinic acids and their derivatives. On treating phosphorus oxychloride or the acid dichloride of methyl phosphinic acid with alkyl magnesium bromides, in the molar ratio 1 : 2 and 1 : 1, with subsequent hydrolysis, dialkyl phosphinic acids were obtained in approximately the same yields as in the blocking

Card 2/3

Reaction of the Acid Chlorides of Phosphoric Acid and Alkyl Phosphinic Acids With Alkyl Magnesium Bromides

SECRET
R001 B 64

of the chlorine atom with pyridine (Ref. 6) (Scheme 3). On treating the above complex with alcohol in the presence of triethylamine the ester of dialkyl phosphinic acid is obtained in good yields (Scheme 3). The reaction of alkyl dichloro phosphates and acid chloride esters of methyl phosphinic acid with Grignard reagents gave rise to esters of dialkyl phosphinic acids (Table) (Scheme 4). There are 1 table and 7 references. 1 Soviet, 5 US, and 1 German.

SUBMITTED: August 17, 1959

Card 3/3

15 5540 2109.2209, 1526

3107940 013 004 018 11
B-11 B-11

AUTHORS: Petrov, K. A., Parshina, V. A., Daruze, G. A.
TITLE: Phosphorus-containing Polyesters and Polyamide Resins
PERIODICAL: Zhurnal obshchey khimii, 1968, Vol. 4, No. 1,
pp. 3000-3004

TEXT: As was already previously shown by the authors, the polyamide- and polyester resins synthesized from diamines or glycols and phosphine oxides (containing two carboxyl groups), are capable of developing fibers (Ref. 1). The present investigation deals with the synthesis of the hitherto unknown organo-phosphorus polymers that differ essentially from the polymers obtained from phosphine oxides. The initial substances of condensation were ethylene glycol, diethylene glycol, hexamethylene diamine and bis (p - carboxyphenyl) phosphinic acid or its methyl ester. Three polymers (I), (II), (III) are described. It is characteristic of these polymers that their chain contains the radicals of bis(p-carboxyphenyl) phosphinic acid with the unesterified phosphorus group in the case of the polymers (I) and (II), and in the case of the polymer (III) in the form of an ammonium salt. Thus, the first two polymers are weak acids, and the

Card 1/2

Phosphorus-containing Polyesters and Polyamide Resins

0 079 60 040 000 000 010
R001/R004

latter is an ammonium salt. The authors assume that fiber formation can be attained in this case not only by pressing the melt through the spinneret, but also from the alkaline solution, with subsequent acid treatment. These polyesters and polyamides are obviously cationites, of the phosphate resin type, that are capable of ion exchange. The utilization of these resins for precipitation and separation of the rare elements is possible. The most important initial products for synthesizing the organo-phosphorus polyesters and polyamides containing bis-(p-carboxyphenyl) phosphinic acid, was obtained by oxidizing the di-p-tolyl phosphinic acid and identified as some hitherto unknown derivatives (salts, esters, acid chlorides). The polyesters of bis-(p-carboxyphenyl) phosphinic acid were obtained by longer heating of the bis-(p-carboxyphenyl) phosphinic acid with ethylene glycol or diethylene glycol in the presence of zinc borate and pentaerythrite. The polyester resins are separated from the acidified alkaline solutions in the form of amorphous powders. There are 7 references: 1 Soviet, 2 US, 1 British, and 1 German.

SUBMITTED: August 18, 1954

Card 2/2

87534
S 107/10 100 100 100
300 100 100

53630

AUTHORS: Petrov, K. A., Maklyayev, P. L., Nymysheva, A. A., and Bliznyuk, N. K.

TITLE: Synthesis of N-Chloro Phosphamides

PERIODICAL: Zhurnal Obshchey Khimii, 1964, Vol. 36, No. 10, pp. 4060 - 4064

TEXT: The authors synthesized various N-chloro phosphamides and developed a general method. The initial phosphamides were obtained by reacting the amine with the corresponding acid chlorides in ether or chloroform (Refs 2-4). Table 1 lists the constants of the obtained known initial phosphamides. The substitution of chlorine for the hydrogen atoms in the alkyl amide group of phosphamide took place under the action of an excessive alkaline solution of sodium hypochlorite upon the chloroform solution of the respective phosphamide. The N-chloro amides were obtained by chlorination of phosphamide with phosphorus pentachloride in the presence of sodium acetate or zinc oxide in carbon tetrachloride. The N-chloro phosphamides are obtained by extracting the reaction mass

Card 1/3

Synthesis of N-Chloro Phosphamides

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with chloroform or CCl_4 by shaking the extraction flask and the subsequent removal of the solvent at room temperature in vacuum (with the aid of a rotary distillation). The diphenyl acid phosphate which is insoluble in water and CCl_4 , was chlorinated with aqueous chlorine in a mixture of CCl_4 and water (1 : 2) in the presence of an excess of sodium acetate. All N-chloro phosphamides have a strong odor, yellowish liquids, soluble in organic solvents (some of them in water). Under the action of a sulfur form solution of N-chloro phosphamide upon a potassium iodide solution in acetic acid medium, iodine is quantitatively separated, which is titrated with hyposulfite; thus, it is possible to determine active chlorine. N-chloro phosphamides (derivatives of methyl phosphonate) proved to be the least stable. They decompose already after 10 days, the content of active chlorine being reduced by 10%. N-chloro dimethyl and diphenyl phosphate in which the chlorine content is 1.2% and 1.7% respectively, proved to be the most stable. The content of active chlorine in N-dichloro dimethyl dimethyl phosphonate was reduced by 1/3 after 30 days. The constants of the N-chloro phosphamides are given in Table V. I. Vinyukin (1956). V. M. Golovinskiy, 1957. Zhurnal A. I. N. 1957, 10, 10.

Card 2/1

Synthesis of N-Chlorosuccinimide

67834
S 24,760 210 101 101
8001 B064

took part in the experiments. There are 2 tables and 4 references.
1 Soviet, 1 US, 1 British, and 1 German.

SUBMITTED: February 18, 1964

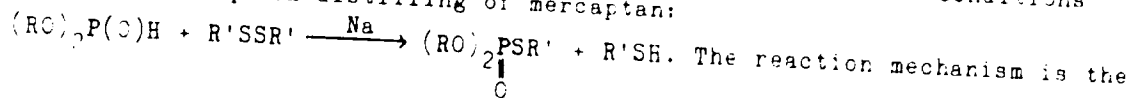
Card 3/3

S/079/61/011/01/01/01-
B001/B066

AUTHORS: Petrov, K. A., Bliznyuk, N. K., and Mansurov, I. Yu.
 TITLE: Reactions of Acid Phosphites, Thiophosphites, Phosphonites, and Dialkylphosphine Oxides With Disulfides
 PERIODICAL: Zhurnal obshchey khimii, 1961, Vol. 31, No. 1, pp. 176 - 179

TEXT: Following their study in Ref. 1 on the reaction of sodium dialkylphosphites with disulfides the authors found that disulfides react with acid phosphites, thiophosphites, phosphonites, and dialkylphosphine oxides in the presence of catalytic quantities of metallic sodium (in some cases even without it) giving the corresponding thiol derivatives. The corresponding thiophosphate can be obtained nearly quantitatively by allowing an equimolecular mixture of acid phosphite and dialkyl disulfide to react with a small quantity of Na (0.1 - 0.3 mole%) under conditions that permit a quick distilling of mercaptan:

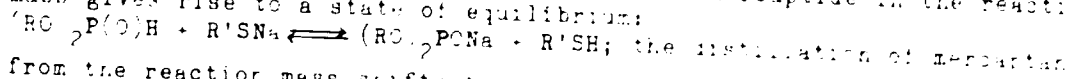
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Card 1/1

Reactions of Acid Phosphites, Thiophosphites, S/079/01/011/00000000
 Phosphonites, and Dialkylphosphine Oxides With B 01/B066
 Disulfides

following: when the above mixture is treated with catalytic Na, dialkylphosphite forms a salt which reacts with the disulfide according to the above equation; the presence of phosphite and mercaptide in the reaction mass gives rise to a state of equilibrium:



the distribution of mercaptan from the reaction mass shifts the equilibrium to the right. The reaction proceeds more smoothly, if the resultant mercaptan has a low boiling point, and is rendered difficult if the boiling points are close to each other. Dialkyl thiophosphites readily react with disulfides even with small sodium admixtures, and give dithiophosphates. Monoalkylphosphonites (which are less acid) also react smoothly with disulfides to form thiophosphonates. Dialkylphosphine oxides which have no acid properties but are suitable reducing agents, give thiophosphonates in fair yield without Na: $\text{R}_2\text{P}(\text{O})\text{H} + \text{R}'\text{SSR}' \longrightarrow \text{R}_2\text{PSR}' + \text{R}'\text{SH}$. The reactions of disulfides with

acid phosphites and phosphonites are determined by the acidic and reducing properties of the latter. There are suitable and references:

Card 2/2

Reactions of Acid Phosphites, Triphosphites, S₂O₃²⁻,
Phosphonites, and Dialkylarsine Oxides With B₂S₃, B₂O₃,
Disulfides

* Soviet, * US, and * Polish.

SUBMITTED: February 1, 1966

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Card 2/2

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S/079/61/031/001/001/001
B001/B066

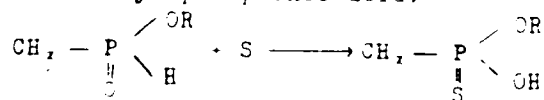
53630

AUTHORS: Petrov, K. A., Bliznyuk, N. K., Studnev, Yu. N., and Kolomiyets, A. F.

TITLE: Monoalkoxy-methyl Thiophosphonates and Monoalkoxy-methyl Phosphonites

PERIODICAL: Zhurnal obshchey khimii, 1961, Vol. 31, No. 1, pp. 179 - 184

TEXT: In order to simplify the synthesis of the above compounds described in Refs. 1 - 4, the authors studied the addition reaction of sulfur to the monoesters of methyl phosphinic acid:



X

The rate of this reaction depends, above all, on the nature of the solvent to be applied. This reaction, for instance, proceeds rapidly and smoothly in dioxane, but does not take place at all in ether. Like dialkyl phosphites (Ref. 6), also alkyl phosphonites add sulfur in ethereal solution.

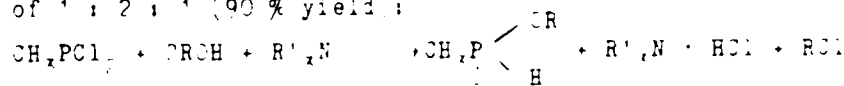
Card 1/3

88489

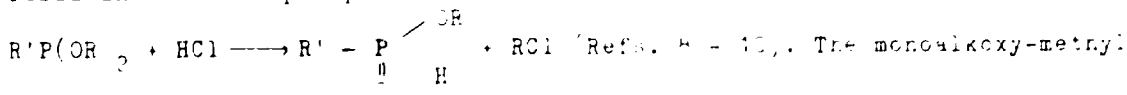
S/279/61/011/001/012/005
B001/B006

Monoalkoxy-methyl Thiophosphonates and
Monoalkoxy-methyl Phosphonites

only in the presence of bases (triethylamine). The reaction rate of sulfur, which is higher with monoalkyl phosphonites than with dialkyl phosphonates, corresponds to the change of the electron density on the phosphorus atom. The structures of the resultant monoalkyl thiophosphonic acids were confirmed by their conversion to salts and esters. The novel monoesters of methyl phosphinic acid were obtained by reaction of methyl-dichlorophosphine with alcohols in the presence of tertiary amines in a molar ratio of 1 : 2 : 1 (90 % yield):



Not only the tertiary amine serves as a HCl acceptor, but also the resultant neutral phosphonite (Refs. 8 - 10), according to the reaction



phosphonites well soluble in organic solvents are stable compounds which do not change for years in pure condition. The yields of monoalkyl phosphonites

Card 2/1

Monoalkoxy-methyl Triphosphonates and
Monoalkoxy-methyl Phosphonites

88483

S/079/61/031/001/017/005
B001/B066

phonites were between 75 and 90 %. There are 1 table and 16 references:
2 Soviet, 6 US, and 1 Polish.

SUBMITTED: February 1, 1966

X

Card 3/3

89515

53630

S/079/61/031/002/008/019
B118/B208

AUTHORS: Petrov, K. A., Neymysheva, A. A., Ponenko, M. G.,
Chernushevich, L. M., and Kuntsevich, A. D.

TITLE: Reaction of N-chloroimides of carboxylic acids with trialkyl-,
halogen-, and cyano phosphites

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 2, 1961, 516-522

TEXT: The authors studied the reaction of N-chloroimides of esters of acetic
and carboxylic acids with trialkyl-, halogen-, and cyano phosphites. Con-
trary to the vigorously reacting sulfene chlorides, chloramines, and alkyl
hypo-chlorites, the reaction of N-chloroethyl acetamide with triethyl
phosphite proceeds smoothly and with little heat evolution. Separation of
ethyl chloride occurs only on prolonged heating at 60-70°C. This reaction
probably takes place in two stages: ✓

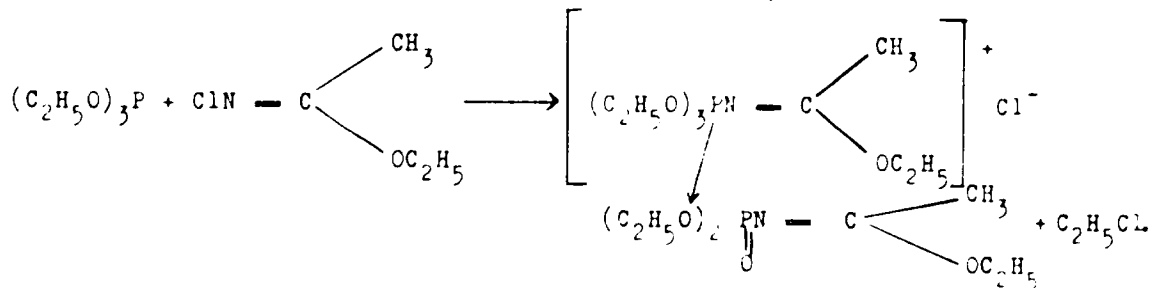
Card 1/4

89515

S/079/61/C31/OC2/OC8/C19

B118/B208

Reaction of N-chloroimides ...



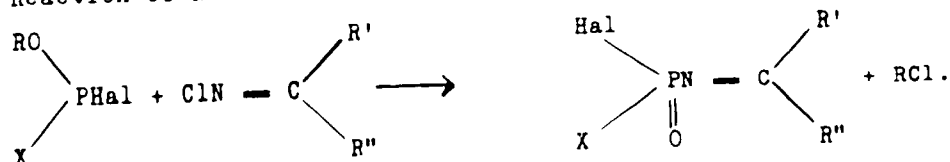
The free phosphonium compound was not obtained. Chloroimides of carboxylic acid esters react more vigorously with phosphites; main products are the esters of dialkoxy-methylenamide of phosphoric acid. The chloroamides react with dialkyl chloro and dialkyl fluoro phosphites, alkyl dichloro and alkyl difluoro phosphites in a similar manner, giving the corresponding halogen amidophosphates in yields of between 27.5 and 70.5%.

Card 2/4

89515

S/079/61/031/002/CC8/C19
B118/B208

Reaction of N-chloroimides ...



Dialkyl fluoro phosphites give with chloroimides rather stable phosphonium compounds. Prolonged heating of the phosphonium compounds reduces the yield of fluoro phosphates; the reaction mixture was, therefore, distilled in vacuum after heating for 1-2 hr at 40-50°C. The fluoro amidophosphates are thermostable and are slowly hydrolyzed with water. When treating difluoro amidophosphates with aqueous alkali lyes at low temperatures, only one fluorine atom is hydrolyzed. On the action of a calculated quantity of sodium alcoholate in the solvent, only one fluorine atom is substituted by the alkoxy radical. Chloro amidophosphates are not thermostable, contrary to fluoro amidophosphates, distill only in high vacuum, and are easily hydrolyzable even at room temperature. When treating chloro amidophosphates with potassium cyanate in water at 5°C, the cyano group is substituted for chlorine, in addition to hydrolysis; in this way, the ethyl ester of

Card 3/4

89515

S/079/61/031/002/008/019
B118/B208

X

Reaction of N-chloroimides ...

diethoxy-methylenamide of cyano phosphoric acid results in a 20% yield. By reacting chloroimides with cyano phosphites, cyano amidophosphates are obtained according to Arbuzov's rearrangement (Ref. 2) in yields between 30 and 50%. Dialkoxy-methylenamides of dicyano phosphoric acid are unstable and decompose with separation of gaseous products. There are 1 table and 4 references: 2 Soviet-bloc.

SUBMITTED: February 15, 1960

Card 4/4

PETROV, K.A.; BLIZNYUK, N.K.; SAVOSTENOK, V.A.

Reactions of sulfenamides with compounds of trivalent phosphorus.

Dokl. Akad. Nauk SSSR 244:1361-1366, 1979.

(Sulfenamides)

(Phosphorus organic compounds)

PETROV, K.A.; NEYMYSHEV, A.A.; DOTSEV, G.V.; VARICH, A.G.

Reactions of sulfenyl chlorides and N-chloramines with phosphorus
trichloride, dichlorophosphines, and red phosphorus. Zhur. ob.
khim. 31 no.4:1366-1371 Ap '61. (MIRA 14:4)
(Chloramine) (Sulfenyl chloride)
(Phosphorus organic compounds)

PETROV, K.A.; NIFANT'YEV, E.Ye.; NIKITINA, R.F.

Synthesis of diaryl phosphates and aryl phosphonates, and some
of their properties. Zhur.ob.khim. 31 no.5:1705-1709 My '61.
(MIRA 14:5)

(Phosphoric acid) (Phosponic acid)

PETROV, K.A.; NIFANT'YEV, E.Ye.; LYSENKO, T.N.

New synthesis of dialkyl phosphates. *Zhur.ob.khim.* 31 no.5:1709-
1711 My '61. (MIRA 14:5,

(Phosphoric acid)

PETROV, K.A.; NIFANT'YEV, E.Ye.; GOL'TSOVA, R.G.

Interesterification of methyl phosphonites. *Zhur.ob.khim.*
31 no.7:2367-2370 JI '61. (MIRA 14:7)
(Phosphonic acid) (Esterification)

PETROV, K.A.; NIFANT'YEV, E.Ye.; GOL'TSOVA, R.G.

Interesterification of monoethyl methylphosphinite with glycols.
Zhur.ob.khim. 31 no.7:2370-2373 J1 '61. (MIRA 14:7)
(Phosphinic acid) (Esterification) (Glycols)

PETROV, K.A.; NIFANT'YEV, E.Ye.; LYSENKO, T.N.; YEVLAKOV, V.P.

Synthesis of esters of phosphorous and phosphinic acids by
alcoholysis of their amides. Zhur.ob.khim. 31 no.7:2377-2380
Jl '61. (MIRA 14:7)
(Phosphorous acid) (Phosphinous acid)

25370

S/079/61/031/008/008/009
D215/D304

53630

AUTHORS: Petrov, K.A. and Parshina, V.A.

TITLE: Reactions of Phosphines I, Reactions primary aliphatic phosphines with aldehydes and ketones

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 8, 1961, 2729-2731

TEXT: In this experimental work the authors studied the reaction of propylphosphine with formaldehyde, acetaldehyde, benzaldehyde, and acetophenone; they proved that primary phosphines easily react with different aldehydes and ketones. With formaldehyde the reaction proceeds according to the scheme.

$C_3H_7PH_2 + 3CH_2O + HCl \rightarrow C_3H_7P(CH_2OH)_3Cl$ With other carbonylic compounds the reaction sometimes stops on the first or second alkylation stage, it depends on the reagents as well as the solvent used; e.g. propyl phosphine with benzaldehyde in aqueous alcohol solution with HCl forms propyltri-(phenylmethylol) phosphonium chloride, but in absolute ether

Card 1/2

25371

S/079/61/031/008/009.009
D215/D304

5636

AUTHORS: Petrov, K.A., Nifant'ev E.Ye., Gol'tsova, R.G.
and Gubin, G.V.

TITLE Investigating the chemical properties of acid bis-
esters of ethylene glycol and methylphosphine acid

PERIODICAL: Zhurnal obshchey khimii, v. 31 no. 8, 1961, 2732-2735

TEXT: In previous publications, the authors have shown that acid bis-
methylphosphonites could be prepared by esterification of the mono-
ethylester of methylphosphinic acid with glycols. In the present in-
vestigations they studied some reactions of the simplest of these com-
pounds, obtained by esterification with ethylene glycol. The follow-
ing reactions were studied. 1) Oxidation of bismethylphosphinite
[Abstractor's note. Called subsequently "the starting product"] with
nitrogen oxides to the corresponding ester of bismethylphosphoric acid,
according to scheme (NI). The obtained product is highly hygroscopic
and reacts as a dibasic acid. 2) The reaction of the starting product

Card 1/2

Investigating the chemical...

25211
S/079/61/031/008/009/009
D215/D304

with sulfur; they did not succeed with the product itself, only with its sodium salt which was obtained from the product and sodium methoxide in dry methyl alcohol and could be isolated. (N2). 3) The reaction with dibutyldisulfide and methylthiocyanate (N3). 4) chlorination of the starting product which was successful with chlorine, but not with SO_2Cl_2 ; only a monochloride was obtained with chlorine which was oxidized to a corresponding phosphonic acid (N4). 5) Aminomethylation with tetraethyldiaminomethylene; with equimolar amounts of reagents they obtained monomethyl diethylamino phosphonate (N5). In the last two reactions the two phosphonic groups showed a different reactivity, only one of them taking part in the reaction. There are 5 references: 3 Soviet-bloc and 2 non-Soviet-bloc. The references to the English-language publications read as follows: L.W. Daasen, J. Am. Chem. Soc. 80, 5301, 1958. E.K. Fields, J. Am. Chem. Soc. 74, 1528, 1952.

SUBMITTED: July 27, 1960

Card 2/2

S/079/61/031/009/001/012
D15/D306

AUTHORS: Petrov, K.A., Nifant'yev, E.Ye., and Khorkhoyanu, L.V.

TITLE: Peresterification of esters of dialkyl-phosphinous acids with glycerine derivatives

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 9, 1961, 2889 - 2894

TEXT: In the present work the authors studied peresterification of dialkyl- and diarylphosphinous acids with glycerine derivatives containing one free hydroxyl group for use in insect repellent compounds. The reaction of 1,2-diphenylideneglycerine with 1,2-isopropylideneglycerine was studied. The compounds were found to react readily with simpler esters, methylethyl-, dipropyl- and diphenylphosphinous acid. Glycerine derivatives with free secondary hydroxyls such as 1,3-benzylideneglycerine reacted less readily, but still gave good yields of the corresponding phosphinites. The phosphinites of the glycerine series provide novel compounds which

Card 1/6

Peresterification of esters ...

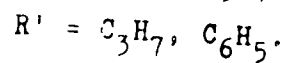
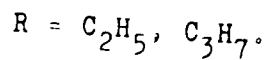
S/079/61/031/009/001/012
D215/D306

are either liquids or crystalline solids having unpleasant odours. They oxidize easily in air but remain stable in an inert gas atmosphere; their chemical properties are similar to those of simpler dialkyl- and diarylphosphinous acids and in oxidizing medium and in the presence of sulphur convert to the corresponding phosphonates and thiophosphonates. The synthesized phosphinites react according to Arbuzov's reaction forming phosphine oxides and corresponding halogen derivatives. The peresterification and alkylation of phosphinites may be used in preparing some halogen derivatives from polyatomic alcohols if the former are difficult to produce. In the present work the authors also investigated this reaction in order to produce more complex halogen derivatives of the polyatomic alcohols. The propyl dipropylphosphinite and ethyl diphenylphosphinite necessary for this reaction were prepared by reacting Menshutkin acid chlorides with organomagnesium compounds at -70°C



Card 2/6

Peresterification of esters ...

S/079/61/031/009/001/012
D215/D306

(1)

The first of the esters obtained has been unknown so far, and the second used to be prepared by more complex methods. The peresterification reaction was conducted by heating equimolecular quantities of the phosphinite and the glycerine derivative in a dry nitrogen stream with a small piece of sodium, distilling the required quantity of alcohol and finally vacuum distilling the residue. Time, temperature, yields and constants of the compounds obtained are given in tabulated form. In further experiments the propyl ester of dipropylphosphinous acid was oxidized with nitrogen oxides at $-10^{\circ}C$ until a permanent green coloration was obtained. Vacuum distillation of the solution yielded the propyl ester of dipropylphosphinic acid with high purity; b.pt. $103-104^{\circ}C/1$ mm Hg, $n_D^{20} - 1.4418$, $d_4^{20} - 0.9543$, and having an empirical formula

Card 3/6

Peresterification of esters ...

S/379/61/031/009/001-011
D215/D306

$C_9H_{21}O_2P$. The ester is colorless, odorless, insoluble in water, and soluble in ether, benzene, carbon tetrachloride and petroleum ether. Similarly oxidations of 1,2-isopropylidene glycerine ester and the 1,3-benzylideneglycerine ester of dipropylphosphinous acid were carried out to yield respectively esters of dipropylphosphinic acid, $C_{12}H_{25}O_4P$, b.pt. 143-144°/0.2 mm,

n_D^{20} - 1.4530, d_4^{20} - 1.0376 and $C_{16}H_{21}O_4P$ b.pt. 117-118°/10⁻⁴ mm

n_D^{20} - 1.5190. Both esters are insoluble in water and petroleum ether and soluble in alcohol, acetone, benzene, chloroform and carbon tetrachloride. Addition of sulphur to both propyl- and 1,2-isopropylideneglycerine esters of dipropylphosphinous acid was conducted by heating the esters with thoroughly dry sulphur at 140-142°C (exothermic reaction). The corresponding sulphur derivatives have b.pts. 81-82°C/0.5 mm and 141-140°C/1 mm respectively, unpleasant odors, and are both insoluble in water and soluble in

Card 4/6

Peresterification of esters ...

S/079/61/031/009/001/012
D215/D306

common organic solvents. Propyl-, 1,2-isopropylidenglycerine- and the 1,3-benzylidenglycerine esters of dipropylphosphinous acid undergo the Arbuzov rearrangement with methyl iodide to yield respectively dipropylmethylphosphine oxide, b.pt. 91-93°C/1 mm, m.pt. 39-39.5°C, the above oxide and 2,2-dimethyl-4-iodomethyldioxolene-1,3 b.pt. 81-83°C/9 mm n_D^{20} - 1.5038, and the oxide as before and 2-phenyl-5-iodo-dioxan b.pt. 117-120°C/9 mm, n_D^{20} - 1.4983. The preparation of propyl ester of dipropylphosphinous acid and the ethyl ester of diphenylphosphinous acid was carried out by reacting the corresponding alkyl (propyl or ethyl) dichlorophosphite, pyridine, alcohol and propyl- or phenylmagnesium bromide respectively in ether at -65°C. Distillation of the reaction mixture yields in the first case the propyl ester of dipropylphosphinous acid b.pt. 70-71°C/7 mm, n_C^{20} - 1.4430, d_4^{20} - 0.8475 MR_{found} 54.64, MR_{calculated} 54.94, which is a mobile liquid with unpleasant smell which igni-

Card 5/6

Peresterification of esters .

S/079/61/031/009 10.10.10
D215/D306

tes in air and which is insoluble in water but soluble in common organic solvents; in the second case the ethyl ester of diphenylphosphinous acid b.p. 127-128°C/1 mm, n_D^{20} = 1.5910. There are table and 8 references: 4 Soviet-bloc and 4 non-Soviet-bloc. The references to the English-language publications read as follows: U.S. Patent 2,588,407; E. Baer, H.L. Fischer, J. Am. Chem. Soc. 70, 609, 1948; C.N. Smith, D. Burnett, J. Econ. Entomol. 42, 434, 1949; T.H. Bevan, T. Malkin, D.B. Smith, J. Chem. Soc. 1955, 1383.

SUBMITTED: September 5, 1960

Card 6/6

27506

S/079/61/031/009/007/112
D215/D306

54300 2209 2409

AUTHORS: Petrov, K.A., Smirnov, V.V., and Yemel'yanov, V.I.

TITLE: Alkylation and arylation of white phosphorus

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 9, 1961,
3027 - 3030

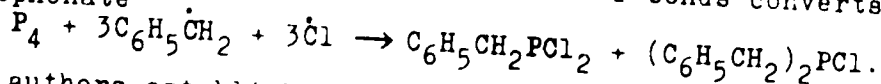
TEXT: The authors for the first time carried out direct alkylation and arylation of white phosphorus without catalysts or activating additives. Heating benzyl chloride with white phosphorus at 300°C for 4 hrs. gave benzyldichlorophosphine. It may be assumed that alkylation and arylation reaction proceed according to a free radical mechanism as in both alkyl and aryl halides. C - Halogen bond may undergo homolytic splitting. The free radicals formed attack the white phosphorus molecule, whose structure is a tetrahedron with P atoms at each apex; this decomposes into two P₂ molecules only at 800°C. In the initial stages of alkylation and arylation the splitting of P - P bond occurs under the action of free radi-
Card 1/4

Alkylation and arylation of ...

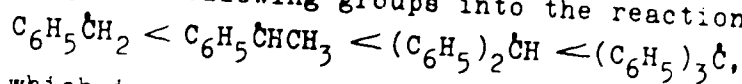
27506

S/079/61/031/009/007/012
D215/D306

als to form a tetraphosphorus - alkyl - or aryl halide which on renewed attack causing breaking of P - P bonds converts to a halo-phosphonate



The authors established a relation between the stability of the free radical and the minimum temperature, at which the reaction occurs by introducing the following groups into the reaction



the stability of which increases from left to right. The temperature of the reaction decreases on passing from haloderivatives forming less stable radicals, to haloderivatives giving more stable radicals; for benzyl chloride the temperature is 300°C, for 1-chlorophenylethane 270°C, for diphenyl-chloromethane 250°C, and for triphenylchloromethane 225°C. Aralkylation of white phosphorus with benzyl chloride was conducted in a sealed tube heated at 300°C for 4 hrs. Distillation yielded three fractions, the second

Card 2/4

27506

S/079/61/031/009/007/012

D215/D306

Alkylation and arylation of ...

being identified as benzyl dichlorophosphine. This was dissolved in CCl_4 and nitrogen oxides passed through the solution to give benzylphosphinic acid dichloride, b.pt. $130^\circ\text{C}/2$ mm. Hydrolysis of the latter by refluxing with water yielded white crystalline benzylphosphinic acid, m.pt. $166-166.5^\circ\text{C}$. The third fraction, b.pt. $234-236^\circ\text{C}/12$ mm was identified as dibenzylchlorophosphine. The distillation residue after boiling with alkaline H_2O_2 , neutralization and acidification gave dibenzylphosphinic acid. Arylation of white phosphorus with bromobenzene using a similar method gave phenyldibromophosphine, diphenylbromophosphine and triphenylphosphineoxide. Arylation with m-bromotoluene gave m - tolyldibromophosphine b.pt. $110-111^\circ\text{C}/2$ mm and di-m-toluylbromophosphine, b.pt. $141-142^\circ\text{C}/2$ mm. Alkylation with n-octyl bromide produced n-octyldibromophosphine b.pt. $72^\circ\text{C}/22$ mm and di-n-octylbromosphosphine b.pt. $140^\circ\text{C}/11$ mm. There are 10 non-Soviet-bloc references. The references to the English language publications read as follows: O. Masson, J.B. Kirkland, J. Chem. Soc., 55, 118, 1870; F.W. Bennet, H.J. Emeleus, R

Card 3/4

Alkylation and arylation of ...

27506

S/079/61/031/003/007/012
D215/D306

N. Haszeldine, J. Chem. Soc., 1565, 1953; British Patent 707961,
1954; Ch.a., 48, 10642, 1954.

SUBMITTED: September 5, 1960

Card 4/4

15 8150

1372, 2209, 2409

27508

S/079/61/031/009/009/17
D215/D306

AUTHORS: Petrov, K.A., Gavrilova, A.I., Shatunov, V.K., and
Korotkova, V.P.

TITLE: Diethyleneimides of β -aminoethylphosphinic and
thiophosphinic acids. II

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 9, 1961,
.3076 - 3081

TEXT: The present work is a continuation of an earlier work, in which the authors showed that diethyleneimido vinylphosphonates and vinylthiophosphonates as well as esters of vinylphosphinic acid form addition compounds with mercaptans and alcohols to form corresponding ethyleneimides of alkylphosphinic and alkylthiophosphinic acids. In continuing the investigations, the authors studied the addition of secondary and primary amines to diethyleneimides of vinylphosphinic and vinylthiophosphinic acids. The amines used were diethylamine, ethyleneimine, piperidine, morpholine, dibenzy-
Card 1/3

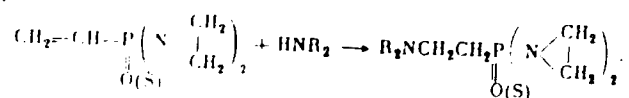
Diethyleneimides of ...

27508

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D215/D306

amine and allylamine; they were found to add to imides of vinylphosphinic and vinylthiophosphinic acids to form imides of β -aminoethylphosphonates and thiophosphonates, according to the following reaction:



Diethylamine, piperidine and ethyleneimine readily combine at room temperature over a period of 1.5-2 days or at 40-50°C. for 4-5 hrs. Dibenzylamine and allylamine react in the presence of catalytic quantities of sodium alcoholate. In all cases it is advisable to use equimolecular quantities without a solvent. Addition of amines to the imides of the acids is more difficult than in the case of the addition of amines to neutral esters of the acids. The addition products of piperidine, morpholine and diethylamine with the imides of the acids were purified by vacuum distillation (10⁻⁴ mm); the products of the other amines decomposed on distilling. All di-

Card 2/3

27508

S/079/61/031/009/009/012
D215/D306

Diethyleneimides of ...

ethylene-imides of aminophosphonates and aminothiophosphonates were viscous, colorless liquids, soluble in benzene, chloroform, ether and alcohol and are stable at temperatures below 0°C. Prolonged storing at room temperature results in gradual polymerization which is due to the opening of the ethyleneimide rings and results in the production of linear polymers either without a phosphorus residue or with the phosphorus residue binding the main chains of the macromolecule. The compounds which were prepared and their properties are summarized in tabulated form. Preparation of compounds 1-7 and 9 was conducted at room temperature and of compounds 8, 10, and 11 at 80°C in the presence of sodium ethoxide. There are 2 tables and 3 Soviet-bloc references.

SUBMITTED: September 5, 1960

Card 3/3

15 8150

27509

S/079/61/031/009/010/012
D215/D306

AUTHORS: Petrov, K.A., Gavrilova, A.I., Shatunov, V.K., and Korotkova, V.P.

TITLE: Diethyleneimides of alkyl- and alkenylthiophosphinic and phosphinic acids. I

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 9, 1961, 3081 - 3085

TEXT: The authors studied the properties of diethyleneimides of alkyl- and alkenylthiophosphinic and allylphosphinic acids, and investigated the addition of mercaptans and alcohols to diethyleneimides of vinylphosphinic and vinylthiophosphinic acids. Their aim was to prepare imidophosphonates and thiophosphonates containing ether and thioether groups in a radical bonded with phosphorus through carbon. Diethyleneimides of alkyl- and alkenylthiophosphinic and allylphosphinic acids were prepared by reacting the corresponding acid chlorides with ethyleneimine in dry benzene or ether

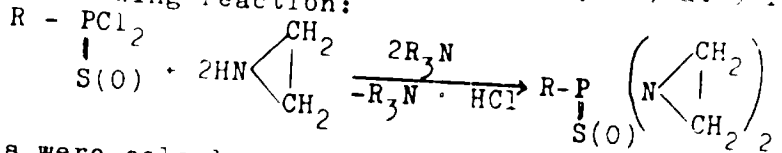
Card 1/3

27509

S/079/61/031/029/017.012
D215/D306

Diethyleneimides of alkyl- ...

in the presence of a tertiary base (HCl acceptor) at 60°C according to the following reaction:



The products were colorless liquids, readily soluble in water and organic solvents; some of them crystallized on prolonged standing. Almost all the compounds distilled in vacuum, the one exception being the diethyleneimide of 8-chloroethylthiophosphinic acid which polymerizes at 100-102°C and 10⁻⁴ mm pressure probably due to HCl splitting off which initiates spontaneous polymerization. The properties and yields of some of the prepared phosphinates and thiophosphinates are given in tabulated form. Diethyleneimides of vinylphosphinic and thiophosphinic acids form addition products with mercaptans and alcohols. With mercaptans the reaction occurs at 60°C and is complete in 14-15 hrs. or less if catalytic quantities of sodium alcoholate is present. Ethylmercaptan adds more

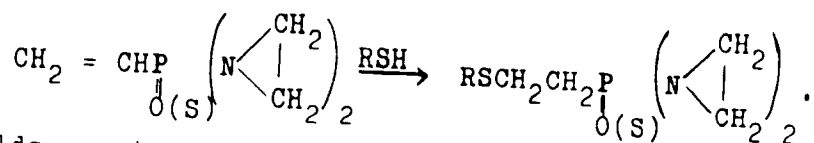
Card 2/3

27509

S/079/61/031/009/010/012
D215/D306

Diethyleneimides of alkyl- ...

easily than butyl mercaptan and in general the reaction proceeds as follows:



The yields are in the region of 50-60 %. Alcohols unlike mercaptans add less readily and it was possible to obtain only small yields of ethyl and butyl alcohol addition products, only after prolonged heating in the presence of alcoholates. Better yields were obtained by reacting alcoholates with diethyleneimides of β -chloroethylphosphinic acid. There are 2 tables and 3 references: 2 Soviet-bloc and 1 non-Soviet-bloc. The reference to the English-language publication reads as follows: U.S. Pat. 2,654,738, 1953; U.S. Pat 2,672,459, 1952.

SUBMITTED: September 5, 1961

Card 3/3

PETROV, K.A.; NIFANT'YEV, E.Ye.; KORENOYANO, L.V.; KRUSKOV, A.I.

Reesterification of esters of dialkyl- and diarylphosphinic acids.
Zh. obshch. khim. 1966, 40(3):379-380, 5 figs. (MIR, 1966,
(Phosphinic acid) (Esterification)

PETROV, K.A.; NIFANT'YEV, E.Ye.; GOL'TSOVA, R.G.

Re-esterification of phosphinothioic and phosphonothioic esters
with alcohols. Zhur.ob.khim. 31 no.10:3174-3177 0 '61.

(MIRA 14:10)

(Phosphonothioic acid) (Phosphinothioic acid) (Alcohols)

FETROV, K.A.; PARSHINA, V.A.; GAYDAMAK, V.A.

Reactions of phosphines. Part 2: Reactions of primary aromatic
phosphines with aldehydes and ketones. Zhur.ob.khim. 31 no.10:
3411-3414 0 '61. (MIRA 14:13)

(Phosphine) (Aldehydes) (Ketones)

PETROV, K.A.; YEVDKOV, V.P.; SERGEYEVA, L.N.; LEDOVSKIKH, V.A.

2, 4, 5-trichlorophenyl esters of methylthiophosphinic and
methylphosphinic acids. Zhur.ob.khim. 31 no.10:3414-3417 0 '61.
(MIRA 14:10)

(Phosphinothioic acid) (Phosphinic acid)

PETROV, K.A.; PARSHINA, V.A.

Reactions of phosphines. Part 3: Reactions of secondary phosphines
with aldehydes and ketones. Zhur.ob.khim. 31 no.10:3417-3420

● '61. (MIRA 14:10)

(Phosphine) (Aldehydes) (Ketones)

PETROV, K.A.; PARSHINA, V.A.

Reactions of phosphines. Part 4: Properties of methylolphosphonium
chlorides and methylolphosphines. Zhur.ob.khim. 31 no.10:3421-
3424 0 '61. (MIRA 14:10)
(Phosphonium compounds) (Phosphine)

PETROV, K.A., ELIZN'UK, N.K., SAVOSTENOK, V.A.

"Reactions of sulfenamides with compounds of trivalent phosphorus."

zhurnal "Rizheniye neorganicheskikh soedinenii" (Journal of Inorganic Chemistry) No. 1, 1964, p. 100. Application of organic phosphorus compounds. A. G. Petrukhin, V. A. Savostenok, N. K. Elizn'uk, K. A. Petrov. Acad. Sci. USSR Div. Chem. USSR, 1964.

Collection of organic phosphorus compounds of the Institute of Chemistry of the USSR Academy of Sciences.