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CHEMISTRY

No. 61

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USSR AND EASTERN EUROPE SCIENTIFIC ABSTRACTS

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USSR UDC 661.183.122

STUDY OF ADSORPTION OF TRACE ADMIXTURES OF VARIOUS SUBSTANCES ON CARBON FIBERS BY GAS ADSORPTION CHROMATOGRAPHY

Minsk IZVESTIYA AKADEMII NAUK BSSR SERIYA KHIMICHESKIKH NAUK in Russian No 2, 1978 pp 56-60 manuscript received 16 Dec 76

YEFIMOVA, T. A., MEYERSON, L. A., ASTAKHOV, V. A. and YERMOLENKO, I. N., Belorussian Technological Institute imeni S. M. Kirov

[Abstract] The study employed a microporous carbon fiber synthesized in the Laboratory of Inorganic and Adsorption-Active Fibers and Films of the Institute of General and Inorganic Chemistry, Academy of Sciences BeloSSR. Tests were made of adsorption of CO, CO_2, NH_3, CH_4, H_2O, acetone, methylethylketone, methyl-, ethyl-, propyl- and isopropyl alcohols, using the LKhM-8MD-1 chromatograph; helium was the gas-carrier. Adsorption isotherms were calculated in the range 100-170°C and at pressures to 10 mm Hg; at this pressure heats of adsorption were assayed from the slope of the isosteres. Adsorption of the substances on the carbon fibers had a nonspecific character. When the chromatographic peaks were symmetrical, heats of adsorption of these substances were determined based on logarithmic dependence of retention volumes on reciprocal of temperature. The relation found between heat, entropy of adsorption and capacity for electron polarization can facilitate prediction of thermodynamic parameters of adsorption. Figures 3; references 5, Russian.

USSR UDC 621.039.325:543.544.6

SORPTION OF URANIUM (VI) WITH AMINOPHOSPHATE AMPHOLYTES FROM SULFURIC ACID SOLUTIONS

Leningrad RADIOKHIMIYA in Russian Vol 20, No 2, 1978 pp 181-188 manuscript received 22 Jul 76

DREYPA, YE. F., PAKHOLKOV, V. S., BALAKIN, V. M., and TESLER, A. G.

[Abstract] Experimental results have been reported of the sorption of uranium (VI), iron (III) and aluminum from sulfuric acid solution using aminophosphate ampholytes. These agents showed characteristic complexing properties, specific towards heavy metals, based on their chelating ability. Aminophosphate ampholytes were obtained by phosphorylating anion exchange resins based on polyethylenepolyamine (AV-16G, AN-31, AN-2F) and anionites of the polymerization type with an acrylate matrix (AN-80-7p, AN-85-7p, AN-86-7p and AN-87-7p) using phosphorous acid in sulfuric acid medium

according to the Kabachnik-Fields reaction. The sorption was made from 0.02 N H_2SO_4 solution of UO_2SO_4, $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$ at different pH values. Distribution coefficients for the ampholytes are higher than for the respective anionites. Sorption of uranium from the polyethylenepolyamine base, using the ampholytes, is not affected by pH or the concentration of H_2SO_4. From the practical side, iron, aluminum and heavy metals are cosorbed with uranium. Isolation of uranium from these admixtures must be made in the desorption phase using a variety of electrolytes. All the ampholytes used are easily obtainable. Figures 4; references 13: 12 Russian, 1 Western.

USSR UDC 541.182.021

DEFORMATION OF DROPS OF LIQUID IN A GAS STREAM

Moscow TEORETICHESKIYE OSNOVY KHIMICHESKOY TEKHNOLOGII in Russian No 2, Mar/Apr 78 pp 297-299 manuscript received 28 Apr 75

KOVALENKO, V. S., Dnepropetrovsk Institute of Chemical Technology imeni F. E. Dzerzhinskiy

[Abstract] The deformation of drops under subcritical conditions such that irreversible deformation and breakup did not occur, was studied by comparing the aerodynamic forces and forces of surface tension. It was assumed that deformation occurs only under the influence of aerodynamic forces; that there is no internal circulation in the drop; that the deformed drop takes on the shape of a compressed ellipsoid, the axis of rotation of which is perpendicular to the direction of the gas stream; that the volume of the drop and the density of the liquid do not change; and that the distribution of pressures on the surface of the drop corresponds to the distribution as a gas stream flows around a sphere. Computer calculations were performed to estimate the influence of individual parameters on the deformation of drops in the transient and self-similar flow modes. Deformation was found to depend greatly on the size and relative speed of movement of the drops through the gas. Deformation also increases with increasing gas density and decreasing surface tension. Figures 3; references 14: 12 Russian, 2 Western.

USSR UDC 541.182.2/.3.001

CALCULATION OF THE FORMATION OF AN AEROSOL

Moscow KOLLOIDNYY ZHURNAL in Russian No 1, Jan/Feb 78 pp 71-75 manuscript received 5 Oct 76

SAMAKHAN, I. I. and SELYAKOV, V. I., Yaroslavl Affiliate of National Scientific Research Institute of Technical Carbon; Moscow Institute of Engineering Physics

[Abstract] In spite of the rather large number of works dedicated to the problem, all known mathematical models of coagulation of aerosols during condensation of vapors or chemical conversions in gas media fail to satisfy the demands of practice as to speed and accuracy of calculations. This work suggests a more general mathematical description of the formation of an aerosol in the case when the mean mass of particles with concentration n_i of class i exceeds the mass of the first particle m_1 by approximately

α^i times, where $\alpha>1$. A system of differential equations is suggested for description of the kinetics of rapid coagulation of particles. Some models previously known are generated by the equations presented as particular cases. The formation of an aerosol of carbon black during thermal decomposition of carbon is used as an example. In the example, numerical integration of the equations demonstrates that the distribution density of the dimensions of particles for comparatively large values of i depends on the selection of the system of equations. This variation is observed only for large values of i, i.e., for comparatively large particles. Figure 1; references 10: 6 Russian, 4 Western.

USSR UDC 541.135.5:546.161

DETERMINATION OF FLUORIDES IN AQUEOUS-ORGANIC SOLUTIONS USING A FLUORIDE-SELECTIVE ELECTRODE

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 33 No 3, Mar 78 pp 506-509 manuscript received 18 Oct 76

GAVA, S. A., POLUEKTOV, N. S. and KOROLEVA, G. N., Physical Chemical Institute, Academy of Sciences UkrSSR, Odessa

[Abstract] This is a study of the influence of various, water-miscible organic solvents on the potential of a fluoride-selective electrode, designed to inquire into possible use of the electrode for direct potentiometric assay of fluoride ions. The fluoride selective electrode, described elsewhere (1976), was based on a monocrystal of LaF_3 with added EuF_2. Analytically pure or chemically pure organic solvents were methanol, ethanol, propanol, acetone and dioxane. Calibrated curves were prepared from 10^{-2}-10^{-5} M standard solutions of NaF which contained 10,30,60 and 90 vol% of an organic solvent. The graduated function of the electrode agrees satisfactorily with the Nernst function in the range 10^{-2} to 10^{-5} M of fluoride ions; values of the angular coefficient are 58 mV for aqueous solutions of NaF and vary from 55 to 62 mV in mixtures of the organic solvents with water. Presence of the organic solvents lowers the values of the Nernst function proportional to the content of these solvents. Direct potentiometric titration of fluoride is possible with only slight error. The fluoride ions do not react with the solvents. Selectivity of the fluoride electrode with respect to chloride, bromide or iodide ions in the presence of the solvents was confirmed. References 4: 3 Russian, 1 Western.

USSR UDC 543.062.543.064

ANALYTICAL PROBLEMS IN CONTROL OF CONTAMINATION OF THE ENVIRONMENT

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 33, No 1, Jan 78 pp 160-170 manuscript received 8 Dec 76

ROVINSKIY, F. YA. and GASILINA, N. K., Institute of Applied Geophysics of the Main Administration of the Hydrometeorological Service, Moscow

[Abstract] The Main Administration of the Hydrometeorological Service is attached to the Council of Ministers USSR. It has organized a state service for monitoring and control of contamination of the environment. This article is a review of problems involved in the work of the service.

The service consists of separate networks for control of air contamination; control of contamination of land water; for control of sea water; for control of soil contamination; and for background survey (biospheric reserves, regional and base stations). The concept of maximum permissible concentrations is the guide. Air control work is undertaken in at least 350 cities. Land water control utilizes 4000 observation sites and over 1200 water source points. Sea water control is performed at various maritime stations and includes inland and shore waters. Potential contaminants of the various environmental objects are listed. Specific methods for assay of contaminants are reviewed. References 97: 25 Russian, 72 Western.

USSR UDC 543.25:543.8

GAS CHROMATOGRAPHIC ASSAY OF TOTAL ORGANIC CARBON IN PURIFIED SEWAGE WATER

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 33, No 1, Jan 78
pp 146-153 manuscript received 15 Apr 76

KHRISTIANOVA, L. A., SERYAKOVA, I. V. and STEN'KO, V. A., Scientific-Research Institute of Communal Water Supply and Purification of Water, Moscow

[Abstract] The Soviet literature has contained many reports on assay of carbon in natural waters but no data on carbon determination in sewage water. A procedure is described for determination of total organic carbon in purified sewage waters which is more direct than biochemical oxygen demand assay, and shorter than the "dry" combustion technique. A standard sample of water (diluted to 10.0 mg/ℓ carbon) is prepared with various C sources, e.g., amino acid, detergent, humic acid. The sample is oxidized by the "wet" procedure with potassium persulfate to carbon dioxide. The CO_2 from the bubble flask reactor is absorbed on Soviet-manufactured polysorb equivalent to porapak Q. CO_2 and O_2 are assayed by gas chromatography. Nitrogen is employed as the gas carrier. Standard curves are prepared, based on combustion of potassium biphthalate and potassium oxalate. Water samples tested were purified biologically at the Tushino Station, Moscow. Sample volumes are 0.3-0.5 ml; the assay required 30 min and can measure 5 mg/ℓ carbon. Figures 5; references 26: 10 Russian, 16 Western.

USSR UDC 543.253:543.8

DIFFERENTIAL OSCILLOGRAPHIC DETERMINATION OF METAPHOS AND HEXACHLOROCYCLOHEXANE IN WATER

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 33, No 1, Jan 78
pp 137-140 manuscript received 24 May 76

SOBINA, N. A., KHEYFETS, L. YA. and ROMANOV, N. A., All-Union Scientific-Research Institute of Water Protection, Kharkov

[Abstract] The sensitivity of polarographic methods at very low concentrations of tested agents has limited use of those methods for assay of chemical contaminants in natural waters. A differential oscillo-polarographic device is described, based on the polarograph PO-5122, to measure low levels of chemical poisons in natural waters. Design of the device is illustrated. The assay procedure is said to be less complex and sufficiently sensitive. Test substances used were the familiar agriculturally-applied metaphos (o,o-dimeltryl-U-(4-nitrophenyl)-thiophosphate and HCCH, at levels of 10^{-8} to 10^{-9} M in river water. Metaphos can be assayed at dilutions of 4.2×10^{-9} M and HCCH at dilutions of 3.4×10^{-8}. The procedure does not require preconcentration. Figures 3; references 6, Russian.

USSR UDC 543.544:543.8

A SIMPLIFIED METHOD FOR THE DETERMINATION OF METHYLMERCURY IN BIOLOGICAL MATERIALS BY GAS CHROMATOGRAPHY

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 33, No 4, Apr 78
pp 812-815 manuscript received 1 Dec 76

GVARDZHANCHICH, I., KOSTA, L. and ZELENKO, V., Ljubljana University
Yugoslavia

[Abstract] In comparison to other metals, mercury is highly volatile and therefore it penetrates rather uniformly into the environment. A method has been developed for the determination of methylmercury in tissue and blood specimens, based on evaporation of methylmercury cyanide formed in the reaction of methylmercury with HCN. The latter is generated "in situ" by reacting $K_4[Fe(CN)_6]$ with sulfuric acid. The methylmercury cyanide is trapped on filter paper impregnated with cysteine, extracted and gas chromatographed. The principle advantage of this method is the ability of using this method in serial determinations, avoiding the troublesome formation of emulsions, typical of all other available methods. Figure 1; references 6: all Western.

USSR UDC 541.122.3:66.062.6:668.531:543.544:628.3

GAS CHROMATOGRAPHIC DETERMINATION OF COMPLEX ESTERS AND TERPENE HYDROCARBONS IN INDUSTRIAL EFFLUENTS AND IN NATURAL WATER RESERVOIRS BY MEANS OF THE HEAD SPACE ANALYSIS

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 33, No 4, Apr 78 pp 794-797 manuscript recieved 18 Feb 77

KOSYUKOVA, L. V. and BELYAYEVA, YU. L., Central Scientific Research and Design Institute of the Forrest Chemical Industry, Gor'ki

[Abstract] In an attempt to increase the analytical sensitivity for ethyl acetate, butyl acetate and terpene alkaloids in industrial effluents, the gas chromatographic analysis of the head space was carried out. The analytical samples were kept at 80-90°C; at these temperatures the equilibrium vapor-liquid is achieved in 10-15 min. Another increase in the sensitivity could be achieved by salting-out process. The sensitivity of this method is 0.005 mg/l and the relative standard deviation ranges from 0.3 to 0.1, with the concentration of the sample varying from 0.01 to 1.0 mg/l. Figures 4; references 5: 4 Russian, 1 Western.

USSR UDC 613.36:663.81]-074:[546.811+546.815

A METHOD FOR DETERMINATION OF MICROQUANTITIES OF HEAVY METALS IN FRUIT JUICES

Moscow GIGIYENA I SANITARIYA in Russian No 3, Mar 78 p 90 manuscript received 4 Dec 77

YES'KINA, O. U., GOZHAYA, L. D. and MANOVA, T. G., Moscow Medical Stomatological Institute

[Abstract] A chemical-spectral method has been developed for the determination of microquantities of heavy metals in fruit juices. The specimen is evaporated, combusted and the residual ash is analyzed on a spectrograph ISP-30. Using a microphotometer MF-4, the intensities are determined at 2833.1 Å for lead, 3247.5 Å for copper and 3262.3 Å for tin. The sensitivity of this method is 10^{-6}%. One Russian reference.

USSR UDC 614.31:637.1:546.815.06

COLORIMETRIC METHOD FOR THE DETERMINATION OF LEAD IN DAIRY PRODUCTS

Moscow GIGIYENA I SANITARIYA in Russian No 3, Mar 78 pp 88-89 manuscript received 14 Dec 77

DAVYDOVA, I. R. and STEPANOVA, N. S., All Union Scientific Research Institute of Dairy Industry, Moscow

[Abstract] A colorimetric method has been developed for detection of lead in various dairy products (milk, yoghurt, condensed and dry milk, etc.) based on coprecipitation of lead sulfate with strontium sulfate, followed by dissolving this precipitate in a solution of sodium hexametaphosphate, development of a color solution and colorimetric determination of the concentration. Comparison of optical densities with calibrated titration curve gave quantitative results. One Western reference.

USSR UDC 615.285.7.017

QUANTITATIVE APPROACH TO THE INVESTIGATION OF THE COMPLEX ACTION OF CHLOROPHOS

Moscow GIGIYENA I SANITARIYA in Russian No 3, Mar 78 pp 83-86 manuscript received 5 Sep 77

SPYNU, YE. I., BOLOTNYY, A. V. and SOVA, R. YE., All-Union Scientific Research Institute of Hygiene and Toxicology of Pesticides, Polymers and Plastics, Kiev

[Abstract] Determination of the complex and combined action of chemicals on the human organism is one of the most difficult tasks in toxicology. Part of the problem is that one deals not with isolated effects but with an interacting, multicomponent system requiring a quantitative analytical approach. Nine groups of animals were used to study the effect of chlorophos, using individual entry routes (by inhalation and by gavage) and combined challenge at three dose levels. The activity of cholinesterase as determined by the Hestrin method was used as the end point indicator of the effect. Analysis of data indicated a 34% effect due to the inhalation route, 39% from the gavage challenge and 19% due to combined action, totalling 92% of the overall effect observed. These experiments can be plotted in an orthogonal matrix in which each factor is varied at three levels. Using a regression analysis, a formula has been developed for the degree of cholinesterase depression in percentages.

On the basis of the orthogonal planning of the experiments, it is possible to describe the effect of pesticide, depending on the route of entry, as well as the effect of complex action, depending on the concentration of the agent. References 5: 4 Russian, 1 Western.

USSR UDC 613.155.3-074

CHROMATOGRAPHIC DETERMINATION OF ORGANIC IMPURITIES IN THE AIR OF RESIDENTIAL AREAS

Moscow GIGIYENA I SANITARIYA in Russian No 1, Jan 78 pp 51-53 manuscript received 28 Mar 77

BULYCHEV, V. P., ZHAROV, V. V., and FINOGENOV, A. M.

[Abstract] Impurities were concentrated by cryogenic treatment (liquid nitrogen) with subsequent chromatographic determination. The impurities were concentrated in a U-shaped trap of stainless steel filled with glass beads 0.5-0.8 mm in diameter. Analysis was performed on a Hewlett-Packard chromatograph model 5754 with an ionization-flame detector. The sensitivity of the method was determined using n-decane. The sensitivity was at least 10^{-5} mg/liter. References 2: Russian.

USSR UDC 614.7:615.277.4:547.231]-074

METHODS OF ANALYSIS OF N-NITROSAMINES IN OBJECTS IN THE ENVIRONMENT

Moscow GIGIYENA I SANITARIYA in Russian No 1, Jan 78 pp 63-68 manuscript received 28 Feb 77

KOSTYUKOVSKIY, YA. L. and MELAMED, D. B., Institute of Nutrition, Academy of Medical Sciences, USSR, Moscow

[Abstract] The methods suggested for separation, purification, and determination of N-nitrosamines were analyzed and critically evaluated, primary attention being given to volatile compounds with water vapor. The compounds were isolated using a combination of distillation with water vapor and extraction by organic solvents. Another group of methods was based on treatment of a specimen with organic solvents. The extracts produced were purified or directly concentrated by successive

washing with dilute of acids and bases. Under optimal conditions, 70-90% of the nitrosamines can be separated from a specimen. TLC and high resolution mass spectrometry are suggested as more effective methods of isolation and analysis of nitrosamines. Chromatography and mass spectrometry allow determination of nitrosamines even in the form of derivatives, which is particularly effective in the analysis of highly polluted objects and nitrosamines of low volatility. Basically new methods using laser radiation, chemiluminescence and raman spectroscopy are also being developed. References 37: 12 Russian, 25 Western.

USSR UDC 613.633+614.715]-073.65

THE USE OF THERMOGRAVIMETRY TO STUDY DUST

Moscow GIGIYENA I SANITARIYA in Russian No 1, Jan 78 pp 68-69 manuscript received 20 May 76

VATSLAV MASHEK, Scientific Research Institute imeni K. Gottvald, CSSR

[Abstract] Dust samples were taken by long-term aspiration through silver membrane filters 1.5 m above ground level. Eighty mg of the material was taken to establish the thermogravimetric (TG) characteristics. This method clearly shows the change in mass of a specimen of dust with rising temperature. Differential thermal analysis (DTA) shows changes in exothermal or endothermal effects, or both, caused by changed in heat content. Dust samples were taken in the streets of an industrial city, in coal mines, at coke plants, in tar battery production shops, at sintering plants and near blast furnaces. The specimens were studied by TG and DTA between 25 and 1000 C at a temperature rate of change of 5°C per minute in a stream of argon at 30 liters/hr. Results of the studies are not given, but it is stated that the use of TG provides additional data on the composition of the dust. A gas chromatograph can identify substances which are liberated as the dust specimens are gradually heated.

USSR

UDC 613.632.4.07

A METHOD OF DETERMINING THE DANGER CLASS OF THE SUM OF VAPORS AND AEROSOLS OF INDUSTRIAL FLUIDS IN THE AIR OF THE WORKING ZONE

Moscow GIGIYENA I SANITARIYA in Russian No 1, Jan 78 pp 71-73 manuscript received 5 Mar 77

KURLYANDSKIY, B. A. and ZAV'YALOV, N. V., Moscow State Sanitary-Epidemiological Station

[Abstract] A formula is presented for the quantitative evaluation of the degree of danger for the sum of vapors and aerosols of toxic industrial fluids. The formula considers the primary hygienic indicators of toxicity (LC_{50}, LD_{50}, C_{cum}, b.p.). Based on this formula, a classification is suggested for the relative toxicities of industrial materials which form aerosols and vapors. The characteristics of a number of industrial materials are presented in a table. In contrast to existing methods of establishment of the danger class, the method suggested allows calculation of the danger class not only for substances for which the MPC has been experimentally determined, but also for all other substances, significantly increasing the reliability of the results of toxic-hygienic consultations. Tables 2; references 5: Russian.

USSR

UDC 614.72-074:546.285-31.06

DETERMINATION OF SILICON DIOXIDE IN THE AIR USING NUCLEAR REACTIONS

Moscow GIGIYENA I SANITARIYA in Russian No 3, Mar 78 pp 73-75 manuscript received 10 Aug 77

KAMIL'DZHANOV, A. KH., MUMINOV, V. A., UBAYDULLAYEV, R. U. and KHAYDAROV, R. A., Institute of Nuclear Physics, Academy of Sciences UzbekSSR, Tashkent; Uzbek Scientific Research Institute of Sanitation, Hygiene and Professional Diseases, Tashkent

[Abstract] The method is based on irradiating air samples containing silicon with a collimated beam of charged deuterium particles of a given energy state, accelerated in a cyclotron, followed by the determination of induced γ-activity. The method is specific, sensitive down to 0.081 μg. In the concentration range of 10^{-3} to 10^{-4} mg the experimental error is less than 15%. References 4: all Russian.

USSR UDC 542.97

PROTEIN-PROTEIN ASSOCIATION IN VARIOUS FORMS OF ENZYME IMMOBILIZATION AND OPTIMUM ACTIVITY OF THE BIOCATALYSTS

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian No 5, 1978 pp 1089-1103

POLTORAK, O. M., CHUKHRAY, YE. S., and PRYAKHIN, A. N., Moscow State University imeni M. V. Lomonosov

[Abstract] Immobilized enzymes have been demonstrated to possess kinetic properties which differ markedly from those of the homologous enzymes in solution, largely due to the fact that the concentration of immobilized enzymes, on or in the carrier, is markedly increased (ca. 10^5-10^6 fold for adsorbed enzymes, and ca. 10^2-10^4 fold for enzymes that are microencapsulated, covalently bound to a carrier, trapped within fibrous structures, etc.). This condition favors not only processes which under normal conditions lead to the formation of quaternary enzymes structures with free energies of formation on the order of 6-10 kcal/mole, but also nonspecific interactions with free energies of 3-5 kcal/mole. The latter type of interactions serve to modify enzyme activities and require novel analyses of such enzyme kinetics in order to optimize immobilized enzyme systems. Based on available experimental data mathematical treatment of such systems is described, with concrete examples provided for hexokinase, glucose-6-phosphate dehydrogenase, alkaline phosphatase, etc. Figures 9; references 22: 2 Western, 20 Russian.

USSR UDC 66.067.38.063.94:668.391

CONCENTRATION OF A PROTEIN EXTRACT BY THE MEMBRANE METHOD

Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 2, 1978 pp 84-86 manuscript received 22 Jun 77

RIZAYEV, N. U., MIRZAAKHMEDOV, M. B., TURAKHODZHAYEV, M. T. and SHAKIROV, T. T., Scientific Research Institute of the Chemistry and Technology of Cotton Cellulose

[Abstract] Extraction of protein from vegetable oil plants is termed an extremely important procedure for acquisition of food protein; the Institute of Chemistry of Plant Substances, AS UkrSSR is cited as the developer of a protein extraction process from oil seed cakes. A method to simplify the stage of concentration of the protein and increase its yield is described in this report. This process employs an ultrafiltration membrane. A laboratory-size ultrafiltration apparatus is depicted;

pressure is produced in the system by a feed-control device ND-63/100 which forces the liquid into the ultrafiltration chamber. The membranes tested include an acetate-cellulose (reverse osmosis) membrane; an acetate-cellulose (ultrafiltration) membrane had the best characteristics for the process. The raw material used was cotton plants. A high degree of separation (100%) of protein is claimed. Figures 1; references 2: 1 Russian, 1 Western.

USSR

UDC 547.92.464

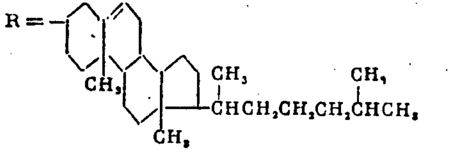
LIQUID CRYSTAL SUBSTANCES. CHOLESTEROL ESTERS OF PERFLUOROALKANE CARBOXYLIC ACIDS

Leningrad ZHURNAL ORGANICHESKOY KHIMII in Russian Vol 14, No 3, Mar 78 pp 544-546 manuscript received 1 Feb 77

MURZA, M. M., BIL'DINOV, K. N. and SHCHERBAKOV, M. S., Bashkir State University imeni 40th Anniversary of October

[Abstract] The importance of cholesterol-containing liquid crystals in instrumentation and in bodily metabolism, and the need for such crystals which will have relatively long effective life are cited. This article reports synthesis of title cholesterol esters, with the general structure:

$CF_3(CF_2)_nCOOR$ ($n = 1 - 6$), $ROOC(CF_2)_mCOOR$ ($m = 2 - 5$).



The structures of the cholesterol-perfluorocarboxylic acid esters have been confirmed by IR spectroscopy; all of the synthesized esters have a IR spectrum band at 1760-1780 cm^{-1} characteristic of valence oscillations of C = 0 of a complex ester, and two bands of average intensity between 1300 and 1050 cm^{-1} corresponding to valence oscillation of C-0-C groups. The esters possess liquid crystal properties. Physical and chemical properties of the esters are tabulated. Synthesis procedures are detailed. References 4: 2 Russian, 2 Western.

USSR UDC 577.150.3

CHANGE IN THE ACTIVITY OF THE SOLUBLE AND BOUND ACID PHOSPHATASE IN AQUEOUS ETHANOLIC SOLUTIONS

Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA in Russian Vol 19, No 1, Jan/Feb 78 pp 20-23 manuscript received 8 Jul 76

GEORGIYEV, G. S., CHUKHRAY, YE. S., ZUBOV, V. P. and POLTORAK, O. M.,
Chair of Physical Chemistry

[Abstract] Activity of the free and bound acid phosphatase was studied in aqueous ethanol solution. The enzyme was adsorbed on the surface of pure silica gel and on silica gel impregnated with a copolymer of maleic anhydride and vinyl palmitic ester. The pH of the solution was maintained at 5.0. There was a distinct difference in the behavior of the soluble and bound enzyme. With increasing concentration of alcohol, the activity of the soluble enzyme remained practically unchanged. The activity of bound acid phosphatase peaked out around 10% EtOH concentration, then dropped to about the starting level. The method used for binding the enzyme to the carrier and its surface differences, if any, did not have any effect on the activity of the enzyme. Figure 1; references 25: 4 Russian, 21 Western.

USSR

UDC 541.136

THE RELATIONSHIP BETWEEN ELECTROCHEMICAL AND CAPILLARY CHARACTERISTICS OF ELECTROCHEMICAL CELLS WITH A CAPILLARY MEMBRANE. GENERAL STATEMENTS

Moscow ELEKTROKHIMIYA in Russian Vol 14 No 4, Apr 78 pp 546-554 manuscript received 14 Oct 76

VOL'FKOVICH, YU. M., Institute of Electrochemistry, Academy of Sciences, USSR, Moscow

[Abstract] The purpose of this investigation is to develop a method of calculation of the variation of voltage on the terminals of an electrochemical group, the primary matrix element of an electrochemical cell with an electrolyte-containing capillary membrane, with constant current density as a function of the electrolyte content. The work also analyzes the influence of the structure of elements included in the electrochemical group on this function. Functional equations are derived relating the electrochemical characteristics with the curve of distribution of pores by radius. The cells discussed include various kinds of batteries, electrolyzers and fuel cells, oxygen and hydrogen concentrators and a number of other electrochemical devices. A method is presented for graphic determination of the variation in cell voltage with electrolyte content. Specific relationships between electrochemical and capillary characteristics of matrix elements of various types will be presented in later reports. Table 1; figures 3; references 14: 12 Russian, 2 Western.

USSR

UDC 541.138.3:546

IONIZATION OF OXYGEN ON POROUS NICKEL ELECTRODES IN A HALF CELL AND A HYDROGEN-OXYGEN FUEL CELL IN KOH MELTS

Moscow ELEKTROKHIMIYA in Russian Vol 14, No 4, Apr 78 pp 501-55 manuscript received 1 Sep 76

BELOKOPYTOV, V. P., OGRYZ'KO-ZHUKOVSKAYA, S. G., and FEDOTOV, N. A., Scientific-Research Institute of Physics and Chemistry imeni L. Ya. Karpov, Moscow

[Abstract] A study is made of the process of ionization of oxygen on porous nickel electrodes with an ordered structure in KOH melts with various oxygen-electrolyte pressure drops and temperatures in a half cell and a hydrogen-oxygen cell modeling a fuel cell. The functional layers of the electrodes were made of smooth and porous nickel foil cut into strips 2 mm wide and 0.5 mm thick (smooth) and 0.1 mm thick (porous).

The smooth nickel strips were corrugated then folded together with the porous nickel strips. Polarization curves were measured potentiostatically. A large number of electrodes were tested in both cells. It was found that studies on partially immersed electrodes, yield information required to create porous electrodes of regular structure with predetermined electrochemical and structural characteristics. In order to improve the characteristics of a moderate-temperature fuel cell using fused potassium alkali as the electrolyte, it is very important to remove water from the anode very actively, for example by circulation of hydrogen on its gas side. Table 1; figures 6; references 7: 4 Russian, 3 Western.

USSR UDC 621.3.035.222;546.57

POWER SOURCES WITH SILVER ELECTRODE

Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian No 10, 1977 pp 2266-2270
manuscript received 20 Oct 76

ANDREYEVA, G. P., VOROB'YEVA, G. B., LEGKIY, I. N. and NIKOL'SKIY, V. A.,
All-Union Scientific Research Battery Institute

[Abstract] Inorganic separators in power sources with silver electrodes, made electrophoretically, react much less with the electrode filling paste --a strong oxidizer--than do organic separators. Data showed that almost 50 percent of electrode energy capacity is lost in storage from the reaction of oxides of silver with hydrated cellulose and its degradation products. The shelf life of batteries fitted with inorganic separators, measured to the loss of half the initial energy capacity, was increased--compared with batteries that had hydrated cellulose film-coated separators, as follows: by 2.1 times for calcium hydroxide and calcium sulfate separator; by 1.8 times for a zirconium oxide separator; and by 1.5 times for a magnesium oxide separator. A thicker inorganic separator extends battery shelf life, but optimal separator thickness for the longest shelf life is attained when the charge voltage drop is not more than 50 mV. Silver electrodes coated with these separators were tested in silver-cadmium batteries. The shelf life of this battery type can be raised to 3 years from the present shelf life of 1 year. Zirconium oxide showed optimal properties as an electrode separator. References 13: 8 Russian, 5 Western.

USSR UDC 547.832

INTERACTION OF THE DERIVATIVES OF ETHYL ETHER OF QUININE ACID WITH PHENYL LITHIUM

Riga KHIMIYA GETEROTSIKLICHESKIKH SOYEDINENIY in Russian No 3, 1978 pp 368-373 manuscript received 8 Jan 77, revised version 9 Aug 77

MASTAFANOVA, L. I., LINBERG, L. F., FILIPENKO, T. YA., YAKHONTOV, L. N., All-Union Scientific Research Chemicopharmaceutical Institute imeni S. Ordzhonikidze, Moscow

[Abstract] The structures of the compounds obtained on interaction of phenyl lithium with ethyl ether of quininic acid and its 1-methyl-2-oxo-derivative and also ethyl ether of 1-methyl-1,2,3,4-tetrahydroquininic acid were established by infrared, paramagnetic resonance and mass spectroscopy. Independently of the solvent (benzene-ether, ether-tetrahydrofurane) and the duration of the process (5 to 17 hours) the same complex mixture of materials is obtained. Efforts were made to separate the products, and the success of this operation was determined by the method of gas liquid chromatography. References 9: 4 Russian, 5 Western.

USSR UDC 547.759.07:543.422.25

STUDIES IN THE FIELD OF 1-AZABICYCLES. VII. SYNTHESIS OF 5-(γ-OXYPROPYL)-1,2-DIHYDROPYRRHOLYSINES AND THE PROPERTIES OF THEIR INTRAMOLECULAR π-HYDROGEN BONDS

Riga KHIMIYA GETEROTSIKLICHESKIKH SOYEDINENIY in Russian No 3, 1978 pp 359-363 manuscript received 26 Jan 77

SKVORTSOV, I. M., ASTAKHOVA, L. N., KUZ'MIN, S. N., YEVTUSHENKO, I. YA., Saratov State University imeni N. G. Chernyshevskiy, Saratov

[Abstract] The reduction of 5-[2-(methoxycarbonyl) ethyl]-1,2-dihydropyrrholysines by lithium alumohydride with 70 to 90 percent yields, 5-(γ-oxypropyl)-1,2-dihydropyrrholysines are obtained which have intramolecular π-hydrogen bonds in dilute solutions. The parameters of the π-hydrogen bonds in the infrared spectra and their enthalpies indicate that among the compounds with aliphatic hydroxyl group and the system of π-electrons, 5-(γ-oxypropyl)-1,2-dihydropyrrholysines have some of the strongest intramolecular π-hydrogen bonds. The physical characteristics and the temperature dependence of the optical density and integral band intensities are tabulated for this compound. References 12: 9 Russian, 3 Western.

USSR UDC 547.75.821.07

DERIVATIVES OF AZAINDOLS. LIII. NEW MEANS OF SYNTHESIZING 6-CHLORO-5-AZAINDOLINE

Riga KHIMIYA GETEROTSIKLICHESKIKH SOYEDINENIY in Russian No 3, 1978 pp 355-358 manuscript received 24 Feb 77

AZIMOV, V. A., GRANIK, V. G., GLUSHKOV, R. G., YAKHONTOV, L. N., All-Union Scientific Research Chemicopharmaceutical Institute imeni S. Ordzhonikidze, Moscow

[Abstract] The synthesis of 2-(cyanocarbamoylmethylene) pyrrholidine (II), 1-dimethylaminomethylene-7-oxo-8-cyano-1,2,3,7-tetrahydro-6-azaindolysine (IV), 2-(cyanocarbethoxymethylene) pyrrholidine (V), 1-ethyl-2-(cyanocarbethoxymethylene) pyrrholidine (VI), 2-(cyanocarbacetylhydrazidomethylene) pyrroholidine (VII) and 1-benzyl-2-(cyanocarbamoylmethylene) pyrrholidine (XI) is described. Condensation of (II) obtained by the interaction of O-methylbutyrolactime (III) with cyanecetamide with diethylacetal dimethylformamide (I) was investigated as a means of synthesizing derivatives of 5-azaindoline not substituted with respected to the pyrrholine nitrogen atom analogously to how the interaction of I with 1-methyl-2-(cyanocarbamoylmethylene) pyrrholidine takes place with respect to the amide group NH_2 with the formation of the corresponding acylformamidine which is easily cyclized into 1-methyl-6-oxi-7-cyano-5-azaindoline. The reaction did not take place as expected and it was finally determined that from III through 1-benzylpyrrholidone-2-, XI and the product of its condensation with I it is possible to synthesize 1-benzyl-6-oxy-7-cyano-5-azaindoline which is converted through 6-oxy-5-azaindoline to 6-chloro-5-azaindoline.

USSR UDC 547.724.1.07

REACTIONS OF AROMATIC AND HETEROAROMATIC COMPOUNDS BEARING ELECTRON ACCEPTOR SUBSTITUTIONS. XII. NEW SYNTHESIS (5-BENZYL-3-FURYL) CARBINOL

Riga KHIMIYA GETEROTSIKLICHESKIKH SOYEDINENIY in Russian No 3, 1978 pp 306-310 manuscript received 26 Jan 77

BELEN'KIY, L. I., GROMOVA, G. P., GOL'DFARB, YA. L., Institute of Organic Chemistry imeni N. D. Zelinskiy USSR Academy of Sciences, Moscow

[Abstract] Simple methods were found for the synthesis of (5-benzyl-3-furyl) carbinol (I) from available furane compounds. The procedures

used to synthesize methyl ester of 4,5-dibromo-2-furanecarboxylic acid (X), the methyl ester of 4-bromo-2-furanecarboxylic acid (XI), 4-bromo-2-furanecarboxylic acid (V), 4-bromo-2-benzoylfurance (VI), 4-bromo-2-benzylfurance (III), 5-benzyl-3-furanaldehyde (VII), (5-benzyl-3-furyl) carbinol (I) and the reduction of 2-benzoylfurane (II) are described. In the five-stage synthesis beginning with 4-bromo-2-furanecarboxylic acid the total carbinol yield was 24 percent. A 77 percent yield of 4-bromo-2-benzoylfurane was obtained by acylation of benzene by the acid chloride, the reduction of which by $AlCl_3$ + $LiAlH_4$ leads to a 75 percent yield of 4-bromo-2-benzylfurane. The 4-bromo-2-benzylfurane is treated with butyl lithium and dimethyl formamide to give 5-benzyl-3-furanaldehyde which is converted quantitatively by $LiAlH_4$ to carbinol. References 18: 4 Russian, 14 Western.

USSR UDC 547.241.233

STUDY OF THE REACTIONS OF AMIDES ON TRIVALENT PHOSPHORUS WITH CARBONYL COMPOUNDS. REPORT 3: REACTION OF 2-ANILIDO-4-METHYL-1,3,2-DIOXAPHOSPHORINANE WITH BENZALDEHYDE

Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 2, 1978 pp 52-54 manuscript received 4 Mar 77

YUSUPOV, M. M., PROSMUSKHINA, L. V. and ROZHKOVA, N. K., Order of Labor's Red Banner Institute of Chemistry of Plant Substances, Academy of Sciences Uzbek SSR

[Abstract] Trivalent phosphorus anilides form corresponding alpha-anilinoalkylphosphates (I) with carbonyl compounds. When 2-anilido-4-5-benzo-1,3,2-dioxaphospholane reacts with aldehydes and ketones, the formation of I is accompanied by simultaneous splitting of the ring by moisture in the air (Yusupov, 1976). This suggested trial of the title reaction in this report. A solution of 2 g. of the anilide and 1 g. benzaldehyde in 6 ml of absolute benzene was heated in a stream of nitrogen for 1.5 hrs. The reaction mixture was precipitated twice from benzene with hexane. The product is a viscous oil which crystallizes on standing. The alcohol-recrystallized product melts at 177-179°. The cyclic structure is retained; inseparable cis and trans isomers are formed. References 7: 6 Russian, 1 Western.

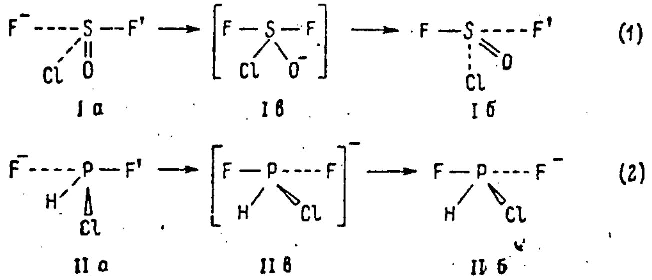
USSR UDC 539.194+547.021

REACTION PATHS OF NUCLEOPHILIC SUBSTITUTION AT THE ATOMS OF SULFUR AND PHOSPHORUS IN SULFINYLIC AND PHOSPHINYLIC GROUPS

Leningrad ZHURNAL ORGANICHESKOY KHIMII in Russian Vol 14, No 3, Mar 78 pp 449-455 manuscript received 17 Feb 77

MINYAYEV, R. M., MINKIN, V. I. and KLETSKIY, M. YE., Scientific-Research Institute of Physical and Organic Chemistry of the Rostov-on-Don State University

[Abstract] The CNDO/2 method (see "Approximate MO Theory," Pople and Beveridge. McGraw-Hill, N. Y., 1970) was the basis of analysis of paths of reaction of nucleophilic substitution at a sulfinylic atom of sulfur and a phosphinylic atom of phosphorus. Models for study of the mechanism of title substitution at the tricoordinated S and P atoms were molecules I and II; the attacking nucleophil was a fluoride ion.



This selection was made due to the common character of the spacial configurations of the starting molecules, the hypervalent intermediate structure and the possibility for stereochemical study of non-equivalent paths of reactions in the approach of the nucleophil to the center under attack. Calculations are displayed as sections of the surfaces of potential energy and in spherical coordinates R, theta and phi (in spheres showing orientation of the molecules SOFCl and PFHCl and the attacking fluoride ion). Three possible reaction paths are calculated corresponding to the movement of the fluoride ion with respect to the three different depressions of the surfaces of potential energy; the paths correspond to strong axial attack on a group. The path of minimal energy of reaction is an axial approach from the side opposite the most electronegative group of the substrate. General principles are discussed. References 15: 5 Russian, 10 Western.

USSR UDC 547.315.2+547.571

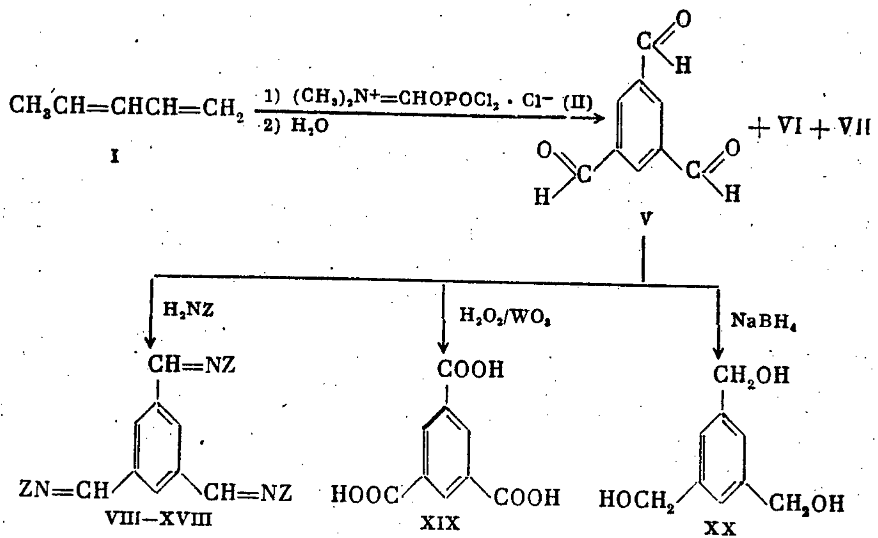
REACTION OF PIPERILENE WITH PHOSPHORUS CHLORIDE-DIMETHYLFORMAMIDE COMPLEXES

Leningrad ZHURNAL ORGANICHESKOY KHIMII in Russian Vol 14, No 3, Mar 78 pp 593-597 manuscript received 14 Feb 77

LONSHCHAKOVA, T. I., BUZYKIN, B. I., LIAKUMOVICH, A. G. and TSIVUNIN, V. S., Kazan Chemical Engineering Institute imeni S. M. Kirov; Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, Academy of Sciences USSR

[Abstract] The reaction of piperilene (I) with the complex of dimethylformamide (DMFA)-phosphorous oxychloride (II) and the complexes DMFA-PCL_3 (III) and DMFA-PCl_5 (IV) has proven to be rather intricate. An unanticipated product was 1,3,5-triformylbenzene (V), in 20-30% yield. The reaction of I and II also yields two other, oligomeric, products (VI)

and (VII) whose structure is still under investigation. The structure of V was confirmed by IR, UV and PMR spectroscopy, synthesis of its anile (VIII), alkylimines (IX-XI), oxime (XII), and hydrazones (XIII-XVIII) by oxidation, with perhydrol in the presence of WO_3, to 1,3,5-benzenetricarboxylic acid (XIX), and reduction, with $NaBH_4$, to 1, 3,5-tris(hydroxymethyl) benzene (XX). Reactions are as follows:



$Z = Ph$ (VIII), Et (IX), Pr (X), t-Bu (XI), OH (XII), NHPh (XIII), $NHC_6H_3(NO_2)_2$ (XIV), $NHCONH_2$ (XV), $NHCSNH_2$ (XVI), NHCOPh (XVII), NHCOPy-3 (XVIII).

Mechanisms of synthesis are discussed. Procedures used are outlined. In other studies, isoprene has been reacted with II-IV, and the products are under examination. References 7: 2 Russian, 5 Western.

USSR UDC 547.298.4

REACTION OF ALKYLHYDRAZINES WITH THE N,N-DIMETHYLAMIDE-PHOSPHORUS OXYCHLORIDE REAGENT

Leningrad ZHURNAL ORGANICHESKOY KHIMII in Russian Vol 14, No 3, Mar 78 pp 622-628 manuscript received 31 Mar 77

SERGUTINA, V. P., ZELENIN, K. N. and KHRUSTALEV, V. A., Military Medical Academy imeni S. M. Kirov

[Abstract] The fact that acylhydrazones are found in nature and are industrially useful prompted efforts to synthesize acylamidrazones. This has been difficult due to the cyclization of the latter--which contain

free N^3H_2 groups--into triazoles, which suggested synthesis of 1,1,3,3-tetra-substituted acylamidrazones. Two such compounds are known to be produced by the reaction of phenyl and benzyl hydrazine with dimethylformamide in the presence of phosphorus oxychloride. The latter reaction has been tested by the authors with a series of alkylhydrazines. The products are 1-acyl-1-alkyl-3,3-dimethylamidrazones; in some cases 1,4-dialkyl-1,4-dihydro-1,2,4,5-tetrazines are formed, as well as acylation products via a mezocarbon atom. The analogs of 1-acryl-1-alkyl-3,3-dimethylamidrazones $(CH_3)_2$ NCR = NNR^1COR^2 are tabulated: in the eight compounds listed, in order R = H, R^1 = methyl, R^2 = H; and, respectively, H, ethyl, H; H, propyl, H; H, isopropyl, H; H, tertiary butyl, H; H, phenyl, H; methyl, propyl, methyl; and, H, propyl, methyl. Structures were established by elementary analysis and IR, UV, PMR, and mass spectroscopy. Experimental procedures are given in detail. References 8: 3 Russian, 5 Western.

USSR UDC 547.26'118

MONOMERIC AND DIMERIC IMIDOPHOSPHATES, DERIVATIVES OF ETHYLENE GLYCOL

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 pp 732-739 manuscript received 2 Aug 76

GULYAROV, V. A., TIKHONINA, N. A., ANDRIYANOV, V. G., STRUCHKOV, YU. T. and KABACHNIK, M. I., Institute of Heteroorganic Compounds, Academy of Sciences USSR

[Abstract] Substituted 2-imine-1,3,2-dioxaphosphalanes $\overline{OCH_2CH_2OP}$ (=NX)Y were synthesized. X and Y are, respectively: $PO(OET)_2$ and NMe_2; $PO(OE_t)_2$ and NEt_2; $PO(OEt)_2$ and OEt; C_6H_5CO and OEt; Ph and NMe_2; Ph and NEt_2; Ph and NBu_2. The products are monomeric when $Y=NR_2$, and dimeric--i.e., they form substituted diazadiphosphetidines--when Y=OR, OPh, SR and F. Figures 1; references 24: 14 Russian, 10 Western.

USSR UDC 547.26'118

REACTIONS OF ISOCYANATES OF DIALKYLPHOSPHOROUS ACIDS WITH ESTERS OF CHLOROACETYLPHOSPHONIC ACIDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 pp 739-743 manuscript received 21 Jun 76

KUNOVALOVA, I. V., BURNAYEVA, L. A., MIKHAYLOVA, N. V. and PUDOVIK, A. N., Kazan State University imeni V. I. Ul'yanov-Lenin

[Abstract] A study was made of the reaction of dialkylisocyanatophosphites with esters of chlorinesubstituted alpha-ketophosphonic acids. Dimethyl and diethylisocyanatophosphites react with dimethyl and diethyl esters of trichloroacetylphosphonic acids via the Perkov reaction to form mixed 0-alkyl-0-alpha-dialkylphosphono-beta, beta-dichlorovinyl esters of isocyanatophosphoric acid. Acid chlorides of mono-, di- and trichloroacetic acids react with two molecules of diethylisocyanatophosphite to form, as end products, the corresponding mixed esters of isocyanatophosphoric acid and phosphaoksazolidinones. Reaction routes are outlined. References 7: 6 Russian, 1 Western (by B. A. Arbusov, 1970).

USSR UDC 541.138.2:547.241

ANODE OXIDATION OF TRIPHENYLPHOSPHINE IN THE PRESENCE OF HALIDE IONS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 pp 743-745 manuscript received 26 Jul 76

KARGIN, YU. M., NIKITIN, YE. V., ROMANOV, G. V., PARAKIN, O. V., LEVSHINA, T. G. and PUDOVIK, A. N., Kazan State University imeni V. I. Ul'yanov-Lenin; Institute of Organic and Physical Chemistry imeni A. Ye. Arbusov, Kazan Affiliate, Academy of Sciences USSR

[Abstract] Electrochemical oxidation of aromatic phosphines in non-nucleophilic medium and the formation of intermediary cation radicals can be used to accomplish a variety of reactions involving electrochemical nucleophilic substitution (1) and addition (2).

$$Ph_3P - 2e + Nu^- \xrightarrow{-H^+} NuC_6H_4PPh_2 \longrightarrow \text{продукты дальнейшего замещения,} \quad (1)$$

$$Ph_3P - 2e + 2Nu^- \longrightarrow Ph_3PNu_2. \quad (2)$$

The effect of the nature of the nucleophilic agent on the direction of the process has been examined. Electrochemical oxidation of triphenyl phosphine in the presence of halide ions, involves anode addition with the formation of triphenylhalogenphosphorane which is then converted to triphenylphosphinic oxide.

$$Ph_3P \xrightarrow{-2e,\ 2Hlg^-} Ph_3PHlg_2 \xrightarrow{H_2O} Ph_3PO$$

Figures 1; references 4: 2 Russian, 2 Western.

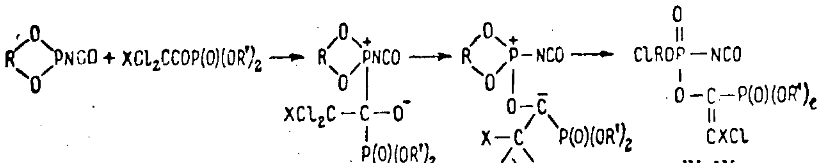
USSR UDC 547.26'118

REACTION OF DIISOCYANATES OF ALKYLPHOSPHOROUS AND OF MONOISOCYANATES OF GLYCOLPHOSPHOROUS ACIDS WITH ESTERS OF CHLOROACETYLPHOSPHONIC ACIDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48 No 4, Apr 78 pp 746-749 manuscript received 22 Sep 76

KONOVALOVA, I. V., BURNAYEVA, L. A., NOVIKOVA, N. K., CHERKINA, M. V., MONAKHOVA, T. G. and PUDOVIK, A. N., Kazan State University imeni V. I. Ul'yanov-Lenin

[Abstract] The reactions of diisocyanates of methyl and ethylphosphorous acids with dimethyl and diethyl esters of trichlorophosphonic acids were studied. These reactions proceed primarily in the direction of a Perkov rearrangement with formation of alpha-dialkylphosphone-beta, beta-dichlorovinyl esters of diisocyanatophosphoric acid. In the reaction of monoisocyanates of ethylene-,1,2-and 1,3-propyleneglycolphosphorous acids with esters of di- and trichloracetylphosphonic acid the reactions also follow the Perkov rearrangement, under controlled conditions. In reactions of cyclic isocyanates with alpha-halogen carboxylic compounds, stabilization of the intermediary bipolar ion occurs with opening of the ring per the Perkov reaction:


IV-IX

$R = CH_2{-}CH_2,\ CH_2{-}CH_2{-}CH_2,\ \underset{CH_3}{CH}{-}CH_2;\ R' = CH_3, C_2H_5.$

References: 4 Russian.

USSR UDC 547.26'118:54.49

SPECTROSCOPIC STUDY OF THE STRUCTURE OF PHENYLSUBSTITUTED TRI- AND TETRA-COORDINATED PHOSPHORUS AND COMPLEXES OF THEM WITH TIN HALIDES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 pp 749-753 manuscript received 15 Nov 76

YARKOVA, E. G., NAZIPOV, SH. M., SOBANOVA, O. B., MURATOVA, A. A. and PUDOVIK, A. N., Kazan State University imeni V. I. Ul'yanov-Lenin

[Abstract] IR spectral data for $(C_6H_5)_nE$ compounds (E=O, S, N, P; n=2,3) help to define their benzene ring orientation. In this work the orientation of the benzene rings (theta angle) was determined for oxides of diphenylmethylphosphine and in their complexes with tin chloride and bromide, SnX_41L_2. The values are tabulated. For $SnX_4 \cdot L_2$ complexes their ionic or cis and trans geometric structure can be decided by comparison with the initial ligands. Figures 2; references 13: 9 Russian, 4 Western.

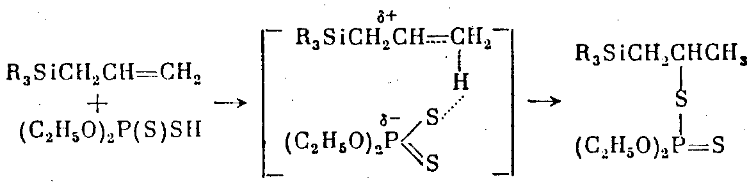
USSR UDC 547.26'118+547.345

KINETICS AND MECHANISM OF REACTION OF ADDITION OF DIETHYLDITHIOPHOSPHORIC ACID TO ALLYLSILANES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 pp 753-757 manuscript received 14 Oct 76

KUTYREV, G. A., NIGAMETZYANOV, R. T., CHERKASOV, P. A. and PUDOVIK, A. N., Kazan State University imeni V. I. Ul'yanov-Lenin

[Abstract] A study was made of the addition of the title acid to various allylsilanes; the order of addition of dithiophosphorus acids to trialkylallylsilane has previously been shown to follow Markovnikov's law. The reactivity of the allylsilanes was found to be increased by the addition of electron-donor substituents at the silicon atom. An electrophilic mechanism of addition of dithioacids to the allylsilanes is preferred. An asynchronic mechanism with fractioned distribution of charges in the transitional state is suggested:



Figures 3; references 16: 11 Russian, 5 Western.

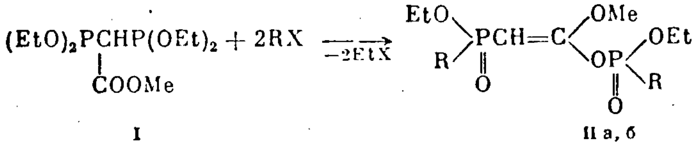
USSR UDC 547.241

REACTION OF TETRAETHYLCARBOMETHOXYMETHYLENE-1,1-DIPHOSPHONITE WITH ALKYL HALIDES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78
pp 757-764 manuscript received 23 Aug 76

NOVIKOVA, Z. S., SKOROBOGATOVA, S. YA. and LUTSENKO, I. F., Moscow State University imeni M. V. Lomonosov

[Abstract] Carbalkoxymethylenephosphonites with the general structure $[(RO)_2P]_2CHCOOR$ have been shown by the authors to react in the Arbusov rearrangement, with alkyl halides:



$RX = ClCH_2OCH_3$ (a), CH_3I (б).

Cleavage of the phosphorus--carbon bond in an intermediate stage of the reaction may be assumed to take place in one of three schemes:

Схема 1

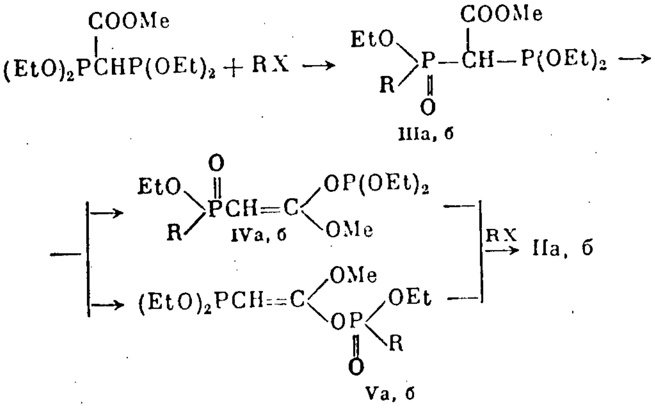


Схема 2

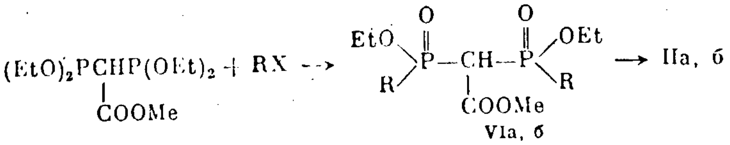
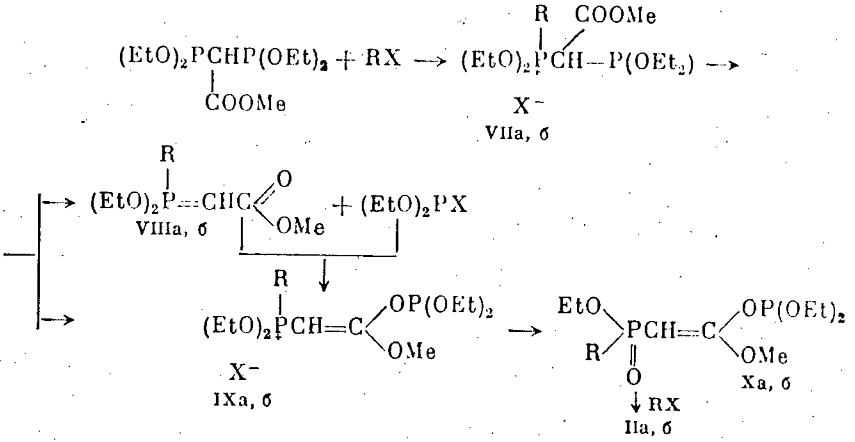


Схема 3



The present article describes the Arbusov reaction of the title compound with alkyl halides wherein a O-substituted compound of phosphorylated alkylacetate is formed. The phosphorus-carbon bonds in the diphosphorus (III,V) substituted acetates in reactions with various nucleophilic reagents were found to be highly labile and led to cleavage of the group with a tri-coordinated atom of phosphorus. References 7: 5 Russian, 2 Western.

USSR UDC 547.26'118

DIALKOXYPHOSPHINES. V. ADDITION OF DIALKOXYPHOSPHINES TO SCHIFF BASES AND DIAZO COMPOUNDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 pp 765-767 manuscript received 19 Nov 76

LUTSENKO, I. F., PROSKUNINA, M. V. and KARLSTEDT, N. B., Moscow State University

[Abstract] The addition of the title compounds to compounds with short N-C and N-N bonds was studied, e.g., addition of the compounds to Schiff bases benzalaniline and benzylidenebutylamine in the absence of acid-base catalysts. The reaction is exothermic and requires 20-30 hours. In the addition of dibutyoxyphosphine to diphenyldiazomethane the reaction proceeds at room temperature. Hence the addition occurs under mild conditions. PMR data and elementary analysis of the products are presented. References 5: 3 Russian, 2 Western (one of these is by the title authors).

USSR UDC 547.241

PREPARATION AND PROPERTIES OF PHOSPHORUS-CONTAINING OXIMES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 pp 767-774 manuscript received 29 Oct 76

BORISOVA, YE. YE., VAFINA, N. M., ZABLIKOVA, T. A., IL'YASOV, A. V., TRUTNEVA, YE. P. and SHERMERGORN, I. M., Kazan Veterinary Institute imeni N. E. Bauman

[Abstract] Earlier work is cited to indicate that the title oximes can be prepared when nitroolefins react with esters of trivalent phosphorus acids. A series of compounds so prepared is tabulated. When trimethylphosphite reacts with omega-nitrostyrene or p-fluoro-omega-nitrostyrene in alcohol or ether, dimethyl esters of alpha-styrolphosphonous acid and alpha-(p-fluorophenyl) vinylphosphonous acid are prepared--in addition to the phosphorus-containing oximes. Various syntheses are cited for preparation of analogously-reacting substituted omega-nitrostyrenes with phosphites in alcohols. Figures 3; references 9: 6 Russian, 3 Western.

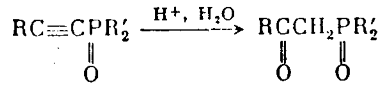
USSR UDC 547.341:541.454+541.67

PROTONIZATION OF BETA-CARBONYLIC PHOSPHORYLIC COMPOUNDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 pp 774-777 manuscript received 10 Nov 76

SKVOTSOV, N. K. and IONIN, B. I., Leningrad Engineering Institute imeni Lensovet

[Abstract] Products of the following hydration reaction have been studied.



$$\underset{\text{Ia—IIIa}}{RC{\equiv}C\underset{\underset{O}{\|}}{P}R'_2} \xrightarrow{H^+,\ H_2O} \underset{\text{I—III}}{R\underset{\underset{O}{\|}}{C}CH_2\underset{\underset{O}{\|}}{P}R'_2}$$

Ia—IIIa I—III

$R = Ph$ (I), Me (II), NEt_2 (III); $R' = Et$ (I), OMe (II), OEt (III).

Analysis of the changes in chemical shifts of the protons of the different groups and changes in the chemical shifts of phosphorus with increase in degree of protonization of these compounds (I, II and III) are used to define the direction of linkage of the proton and to estimate basicity of the compounds. Parameters of protonization are tabulated for I to III.

Protonization occurs at the oxygen of the phosphorylic group in I and II, and at the oxygen of the carbonylic group in III. References 13: 7 Russian, 6 Western.

USSR UDC 547.463.1+546.185

TRIBROMOPHOSPHAZODICYANOETHYLENES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 pp 778-780 manuscript received 23 Nov 76

KUKHAR', V. P. and PAVLENKO, N. G., Institute of Organic Chemistry, Academy of Sciences UkrSSR

[Abstract] A convenient synthesis of the tribromo title derivatives, as opposed to less difficult trichloro derivatives, has been sought. Reactions studied include treatment of sodium and silver tricyanomethane, and, 1-amino-1-bromo-2,2-dicyanoethylene with phosphorus pentabromide to form 1-tribromophosphazo-1-bromo-2,2-dicyanoethylene; chlorine and brominetricyanomethane react with phosphorus tribromide to yield the corresponding tribromophosphazoethylenes; the tribromophos phazo-1-bromo-2,2-dicyanoethylene, similar to the trichlorophosphazo analogs, reacts readily with water, alcohols and amides. The bromine atoms at the phosphorus atom are less mobile than chloride. References 8: 5 Russian, 3 Western.

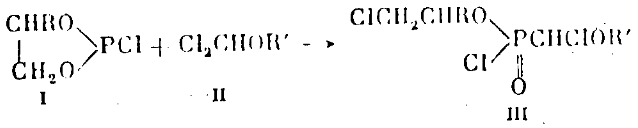
USSR UDC 547.241

REACTION OF ALKYLENEGLYCOLCHLOROPHOSPHITES WITH DICHLOROMETHYLALKYL ETHERS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 pp 780-783 manuscript received 22 Jan 77

KRUTSKIY, L. N., KRUTSKAYA, L. V., GORYACHEVA, O. L., ZYKOVA, T. V. and TSIVUNIN, V. S., Kuzbas Polytechnical Institute

[Abstract] Ethylene- and 1,2-propyleneglycolchlorophosphites were reacted with dichloromethylpropyl and -butyl ethers, in continuation of a series of analogous reactions under study by Krutskiy. The reaction occurs by heating equimolar amounts of I and II at 110-120°C for 15-18 hours to yield beta-chloroalkyl ether acid chlorides of alkoxychloromethylphosphonic acids:



Products were separated by vacuum distillation and structures established by IR spectra (in a UR-20) and PMR (in a MNR-5535 spectrometer). Figures 1; references 3: Russian.

USSR UDC 546.185

CONVENIENT SYNTHESIS AND STRUCTURE OF DIALKYL ESTERS OF ARENESULFONYLAMIDOPHOSPHORIC ACIDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 pp 783-787 manuscript received 17 Jan 77

KOZLOV, E. S., KOLESNIK, N. P. and SHOKOL, V. A., Institute of Organic Chemistry, Academy of Sciences UkrSSR

[Abstract] The title compounds, $ArSO_2NHP(O)(Oalk)_2$ were reported by Shevchenko (1974) to be good extraction reagents for many metals and hence useful in industry and in synthetic work. Their preparation was expensive and difficult. Continued efforts at synthesis has led to a simplified approach to their preparation by reaction of dialkylphosphates and a mixture of arenesulfamide and powdered KOH or NaOH in CCl_4. The esters were shown by IR spectroscopy to possess a predominantly amide structure. Figures 2; references 8: 7 Russian, 1 Western.

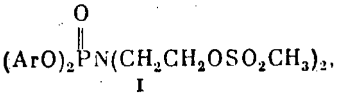
USSR UDC 547.26'118.07

UV SPECTRA OF PHOSPHORYLATED ESTERS OF METHANESULFONIC ACID AND p-TOLUENESULFONEHYDRAZIDES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 pp 788-790 manuscript received 27 Jun 77

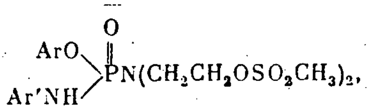
TITARENKO, I. P. and PROTSENKO, L. D., Kiev Scientific Research Institute of Pharmacology and Toxicology, Ministry of Health UkrSSR

[Abstract] This is a report on UV spectra of three types of compounds.



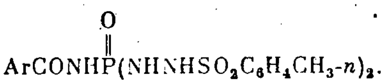
$(ArO)_2\overset{\overset{O}{\|}}{P}N(CH_2CH_2OSO_2CH_3)_2,$

I



$\begin{matrix}ArO\\ Ar'NH\end{matrix}\!\!>\!\overset{\overset{O}{\|}}{P}N(CH_2CH_2OSO_2CH_3)_2,$

II



$ArCONH\overset{\overset{O}{\|}}{P}(NHNHSO_2C_6H_4CH_3\text{-}n)_2.$

III

The spectra were taken in methanol, using the CF-4 spectrophotometer--Tikarenko.

UV absorption cuves of (1) diaryl esters of N,N-bis(2-methanesulfonyloxyethyl) amidophosphoric acid, (2) aryl esters of N-arylamido-N^1,N^1-bis(2-methanesulfonyloxyethyl) aminophosphoric acids and (3) bis-p-toluenesulfonehydrazides, are depicted; the substituents attached to the phosphorus atom define the shape of the curves. Figures 3; references 8: Russian.

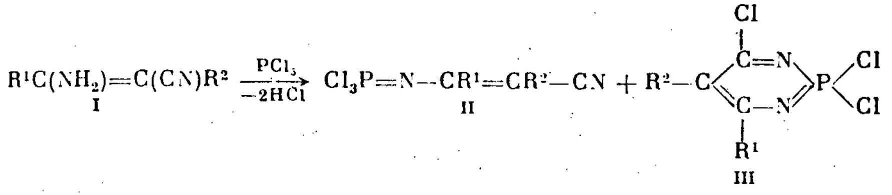
USSR UDC 547.879+547.241

REACTION OF PHENYLTETRACHLOROPHOSPHORANE WITH CYANAMINOALKENES

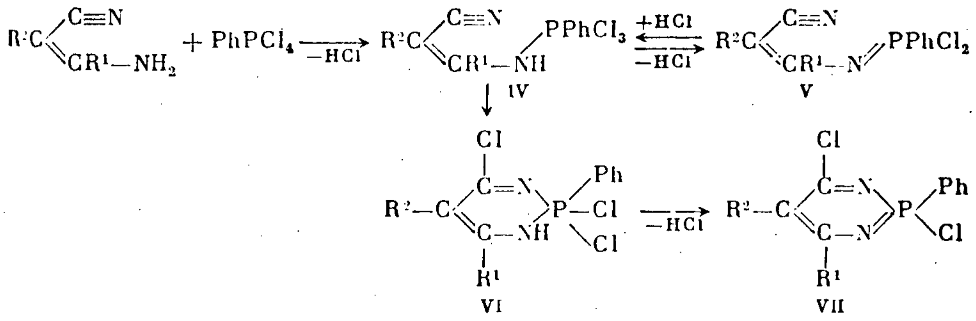
Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 pp 799-803 manuscript received 12 Jul 76

KORNUTA, P. P. and KUZ'MENKO, L. S., Institute of Organic Chemistry, Academy of Sciences UkrSSR

[Abstract] This is a continuation of earlier work which established that PCl_5 reacts with monocyanoaminoalkenes (Ia) to form a mixture of trichlorophosphazo compounds (II) and diazaphosphorines (III); PCl_5 with dicyanoaminoalkenes (Ib) yields only III:



Reactions of Ia or Ib with phenyltetrachlorophosphorane are reported here:



The products formed are 2,4-dichloro-2-phenyl-1,3,2-diazaphosphorines. The chlorine atoms of the latter readily exchange with nucleophilic reagents. References: 5 Russian.

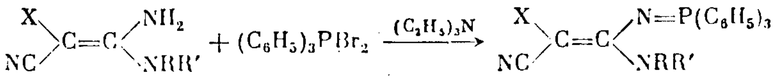
USSR UDC 577.415.1+546.185

SUBSTITUTED TRIPHENYLPHOSPHAZOETHYLENES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 pp 803-805 manuscript received 24 Feb 77

BODNARCHUK, N. D. and YATSISHIN, A. A.

[Abstract] Phosphorus pentachloride readily reacted with 2,2-dicarbalkoxy-N-alkylketenaminals to yield hydrogen chloride, ethyl chloride and a tarry reaction mixture. However, individual products of phosphorylation could not be separated. Triphenyldibromophosphorane reacted with keteneaminals in the presence of triethylamine to yield triphenylphosphazoethylenes (IIa-g)



Ia–г IIa–г

а, $X = COOC_2H_5$, $R = R' = H$;
б, $X = COOC_2H_5$, $R = H$, $R' = C_4H_9$;
в, $X = COOC_2H_5$, $R = R' = CH_3$;
г, $X = CN$, $R = R' = CH_3$.

Keteneaminals, with various substituents in the beta-position, which contain one or two primary aminogroups, enter into this reaction; only one molecule of triphenyldibromophosphorane participates. Structures of IIa-g are indicated by the preparation procedure, elementary analysis and IR spectra. When triphenylphosphazoethylanes are subjected to the action of Cl_2, the latter attaches at the ethylene bond which splits with formation of triphenylphosphazodimethylaminodichloromethane. References: 4 Russian.

USSR UDC 547.26.119

REACTION OF TRIALKYLARSENATES WITH ARSENIC TRIHALOGENIDES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 pp 805-808 manuscript received 23 May 77

GAMAYUROVA, V. S., ALADZHIYEV, M. M. and CHERNOKALSKIY, B. D., Kazan Chemical Engineering Institute imeni S. M. Kirov

[Abstract] The following course is suggested for the reaction of trialkylarsenates and arsenic trifluoride:

$$(RO)_3AsO + AsF_3 \longrightarrow «FAsO(OR)_2» + F_2AsOR$$

When trialkylarsenates were reacted with electrophilic reagents, e.g., arsenic-trichloride or tribromide, at a 1:1 ratio the corresponding halogenalkyls were formed. The latter were immediately blown off to prevent their reaction with the trialkylarsenate. Dihalogen derivatives of alkylarsenious acids were produced which were identified by element analysis and comparison of properties with those of compounds in the literature. When tributylarsenate was reacted with arsenic tribromide, bromide derivatives of dibutylarsenious acid were analogously prepared. Crystalline products were also obtained in this reaction, with the elementary composition $RAsO_3$. Molecular weights indicated they were predominantly dimers, dialkylmetaarsenates, previously not described in the literature. The reactions are discussed and synthesis procedures given. References 14: 5 Russian, 9 Western.

USSR UDC 547.242

SYNTHESIS AND EXCHANGE OF THE ANION OF METHYLDI (alpha-NAPHTHYL)ALKYLARSONIUM IODIDES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 pp 809-811 manuscript received 17 Jan 77

GIGAURI, R. D., INDZHIYA, M. A., CHERNOKAL'SKIY, B. D. and CHACHAVA, G. N.

[Abstract] Trialkylarsines are known to be more active than the corresponding aromatic analogs in the reaction of tertiary arsines with electrophilic agents, viz., halogen alkyls and alkylenes, halogen-substituted alcohols, ester, etc., with formation of arsonium salts. This prompted study of alkylation of di(alpha-naphthyl)alkylarsines (I) and examination of the products. (I) does not react with alkyl chlorides or bromides but will react with methyl iodide, in anhydrous benzene, at room temperature to yield the title compounds. Alkyl components (methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl and isopentyl), yields, and physical and chemical properties are tabulated. The procedure of exchange of anions of the arsonium salts will yield the corresponding perchlorates: when the methyldi (alpha-naphthyl) alkylarsonium iodides are reacted with aqueous solutions of magnesium perchlorate, good yields of the corresponding arsonium perchlorates are obtained. Physical and chemical properties of the latter are also listed. References 9: 6 Russian, 3 Western.

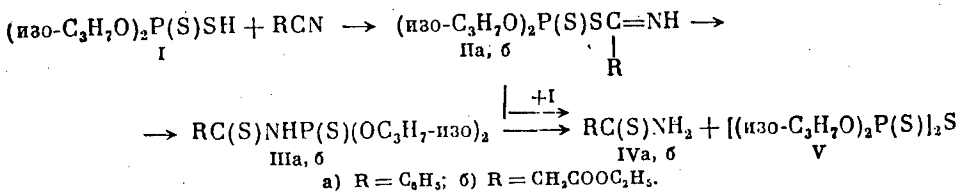
USSR UDC 547.26'118

REACTION OF PHOSPHORUS DITHIOACIDS WITH NITRILES OF CARBOXYLIC ACIDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 p 926 manuscript received 13 Apr 77

PUDOVIK, A. N., CHERKASOV, R. A., ZIMIN, M. G. and ZABIROV, N. G., Kazan State University imeni V. I. Ul'yanov-Lenin

[Abstract] It had been shown by Pudovik (1973) that diisopropyldithiophosphoric acid (I) reacts with benzonitrile to form, among other products, O,O-diisopropyl-S-benzimidoyldithiophosphate (IIa). It has subsequently been found that (IIa) rearranges to N-(O,O-diisopropylthiophosphonyl) thiobenzamide (IIIa). Equimolar quantities of (I) and benzonitrile yield several other products: thiobenzamide (IVa), tetraisopropyltrithiopyrophosphate (V).



$$\underset{\text{I}}{(\text{изо-}C_3H_7O)_2P(S)SH} + RCN \longrightarrow \underset{\text{IIа, б}}{(\text{изо-}C_3H_7O)_2P(S)S\underset{\substack{|\\ R}}{C}{=}NH} \longrightarrow$$

$$\longrightarrow \underset{\text{IIIа, б}}{RC(S)NHP(S)(OC_3H_7\text{-изо})_2} \xrightarrow{+I} \underset{\text{IVа, б}}{RC(S)NH_2} + \underset{\text{V}}{[(\text{изо-}C_3H_7O)_2P(S)]_2S}$$

а) $R = C_6H_5$; б) $R = CH_2COOC_2H_5$.

References 4: 2 Russian, 2 Western.

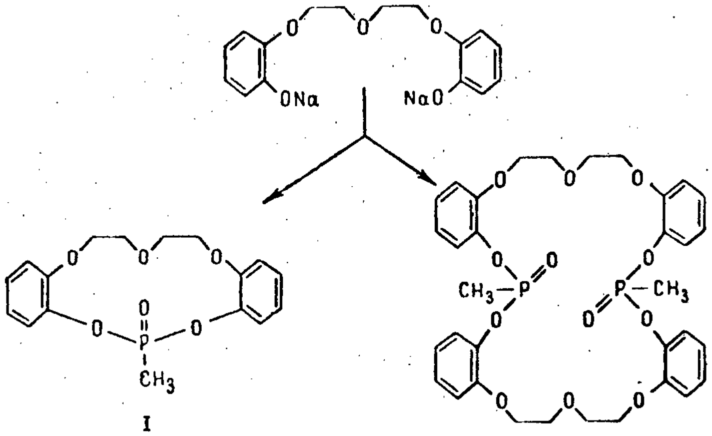
USSR UDC 547.26'18

A NEW PHOSPHORUS-CONTAINING MACROCYCLIC (CORONA)

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 p 927 manuscript received 10 May 77

KUDRYA, T. N., SHTEPANEK, A. S. and KIRSANOV, A. V., Institute of Organic Chemistry, Academy of Sciences UkrSSR

[Abstract] The disodium salt of 2,2-(oxydiethylenedioxy)diphenol reacts with the acid dichloride of methylphosphonic acid to yield a mixture from which two crystalline compounds have been isolated. Details of reaction are given:



I

II

Compound I had been earlier isolated and described. The yield (11%), and element analysis for compound II are given. It melts at 216-218°C. Reference: 1 Russian.

USSR UDC 66.094.17:546.98:547.241

AMIDOPHOSPHONITE COMPLEXES OF Cd^{2+}

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 p 928 manuscript received 18 Apr 77

D'YAKONOV, A. N. and ZAVLIN, P. M., Leningrad Institute of Cine-Engineers

[Abstract] Complex compounds $(Cd(C_6H_11P(NHC_4Ha)_2)_4)$ $(NO_3)_2$ were prepared by reaction of $Cd(NO_3)_2$ and cyclohexylphosphonic acid amides. IR and NMR spectroscopy revealed that the unshared pain of nitrogen electrons participate in the formation of the coordination bond. This is expressed with displacement of valency oscillations of the NH group of the complexes as compared with the initial ligands in the IR spectra, and is confirmed by absence of marked displacement of the chemical shift of P31 in the compared compounds. Procedures for synthesis are outlined; element analysis, IR spectroscopy (UR-20 instrument) and NMR spectroscopy (at 11 MHz) confirmed structure.

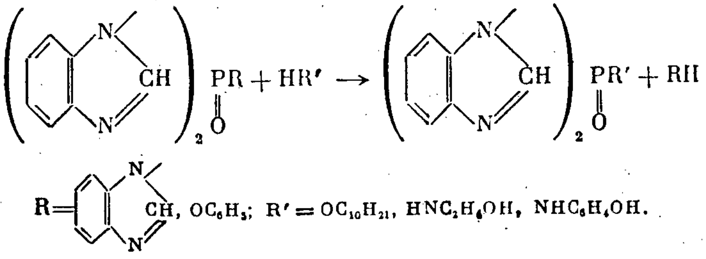
USSR UDC 547.26'118

REACTION OF PHOSPHORYLATED BENZIMIDAZOLES WITH NUCLEOPHILIC REAGENTS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 pp 928-929 manuscript received 28 Apr 77

MATEVOSYAN, G. L., MATYUSHICHEVA, R. M. and ZAVLIN, P. M., Leningrad Institute of Cine-Engineers; Leningrad Agricultural Institute

[Abstract] Phosphorylated benzimidazole derivatives warrant interest because of their potential in plant growth regulation. In this contribution to their study, tri(1-benzimidazolido) phosphate (I) and di(1-benzimidazolido) phenylphosphate (II) were treated with alcohols, amines, aminoalcohols and aminophenols. (I) phosphorylates aniline and ethanolamine but practically does not react with alcohols. When (II) reacts with aniline, the benzimidazol group is substituted. Reaction of (II) with alcohols proceeds as follows:



Reaction quantities in reactions of (I) and (II) are given. structures of products are confirmed by chemical analysis, IR and UV spectra and thin layer chromatography.

USSR UDC 541.183.02

EFFECT OF NUMBER OF PHOSPHOROXIDE MONOLAYERS ON THE CATALYTIC ACTIVITY OF VANADIUM-PHOSPHORUS-CONTAINING SILICA GELS PREPARED BY MOLECULAR SUPERPOSITION

Leningrad ZHURNAL OGSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 p 941 manuscript received 4 Nov 77

POSTNOVA, A. M. and KOL'TSOV, S. I., Leningrad Engineering Institute imeni Lensovet

[Abstract] The catalytic properties of vanadium-phosphorus-containing silica gels suffer from ill-defined surface positioning of the active components. The method of molecular superposition has made it possible to optimally position a system of oxide monolayers, in a definite sequence and with defined composition and structure, and subsequently, to regulate the activity of the catalyst. The use of phosphoroxide monlayers under a monolayer of vanadium increased catalytic activity almost threefold. Optimal composition of the $P_2O_5 . V_2O_5$ components can be achieved by the molecular superposition procedure for synthesis of the catalyst. References 5: 4 Russian, 1 Western.

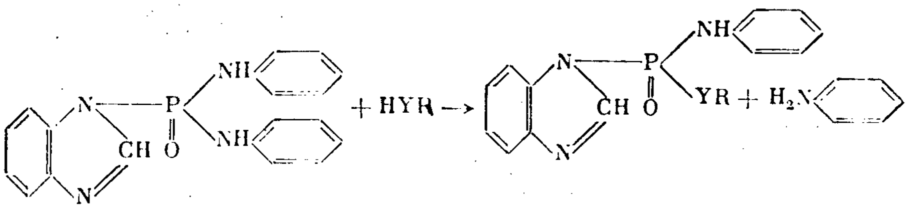
USSR UDC 547.26.11

REACTION OF DIANILIDE(1-BENZIMIDAZOLIDO)PHOSPHATE WITH NUCLEOPHILIC REAGENTS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 pp 941-942 manuscript received 18 Jul 77

MATEVOSYAN, G. L., MATYUSHICHEVA, R. M. and ZAVLIN, P. M., Leningrad Agricultural Institue; Leningrad Institute of Cine-Engineers

[Abstract] This work continues the search for physiologically-active benzimidazole derivatives with the capacity for plant growth regulation. Reactions of the title compound with alcohols, phenols, amines, amino-alcohols and aminophenols proceeds as shown.



YR = $C_{10}H_{21}O$, C_6H_5O, *n*-ClC_6H_4NH, HOC_2H_4NH, *n*-HOC_6H_4NH.

Reaction conditions and quantities used are presented in detail. IR--UR-20 apparatus--, UF--SF-16 apparatus--, and thin layer chromatography--Silufol-254--data confirmed composition, structure and individuality of the products.

USSR UDC 547.241

REACTION OF TETRAKIS (TRIFLUOROMETHYL)CYCLOTETRAPHOSPHINE WITH FLUOROIODOALKANES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 pp 942-943 manuscript received 4 Nov 77

LAVENT'YEV, A. N., MASLENNIKOV, I. G. and SOCHILIN, YE. G., Leningrad Engineering Institute imeni Lensovet

[Abstract] Curves of the title reaction of $(CF_3P)_4$ with fluoroiodoalkanes correspond to a first order reaction. A study was made of partial order of reaction based on one of the components; the relation of rate of

consumption of the cyclotetraphosphine at the initial moment in time on the magnitude of its initial concentration--which was varied within the limits of 0.07 to 0.29 mol/1--was calculated. The order, based on the cyclotetraphosphine, appeared to be 1. The reaction apparently proceeds with intermediate formation of a molecular complex whose breakdown determines the rate of the entire process. References: 2 Russian.

USSR UDC 547.495.1

ACID CHLORIDES OF 0-ALKYL-N-ALKYL-N-(ALKOXYCARBONYL)-AMIDOPHOSPHORIC ACID

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 p 943 manucript received 11 Jul 77

GAMALEYA, V. F. and SHOKOL, V. A., Institute of Organic Chemistry, Academy of Sciences UkrSSR

[Abstract] Shokol refers to an earlier (1966) synthesis of dialkyl esters of N-alkyl-N-(alkoxycarbonyl)-amidophosphoric acid by reaction of trialkylphosphites with esters of N-chloro-N-alkylcarbamic acid. Further, dialkylchlorophosphites--which are less nucleophilic than the trialkylphosphites--also reacted readily with the N-chloro acid; the reaction proceeds more slowly, to produce the title compounds. IR and NMR spectra confirmed the chemical structures of the products which are colorless liquids soluble in most inert organic solvents. References: 1 Russian.

USSR UDC 542.91:547.1'128'118

THE INTERACTION OF TRIS(TRIMETHYLSILYL)PHOSPHATE WITH SALTS OF INORGANIC AND ORGANIC ACIDS

Moscow IZVESTIYA AKADEMII NAUK SSSR--SERIYA KHIMICHESKAYA in Russian No 1, Jan 78 pp 219-220 manuscript received 25 May 77

VORONKOV, M. G., ROMAN, V. K. and SENATORSKAN, V. N., Irkut Institute of Organic Chemistry, Siberian Department, Academy of Sciences USSR

[Abstract] In contrast to bis(trimethylsilyl)sulfate, tris(trimethylsilyl)phosphate is not cleaved by alkali metal chlorides, bromides or iodides and does not react with Na_2SiF_6 or NH_4BF_4. NaF cleaves it to form trimethylsilyl

fluoride, while nitrates and acetates or alkali metals give the corresponding trimethylsilyl derivatives. The nitrate derivative is unstable and decomposes to yield hexamethyldisilane. No reaction was seen with salts or permanganic, prussic, thiocyanic, carbonic, sulfurous or hydrosulfuric acids. References 7: 6 Russian, 1 Western.

USSR UDC 541.6:543.422.4:547.;'118

THE VIBRATIONAL SPECTRA AND STRUCTURE OF ACYLPHOSPHINES

Moscow IZVESTIYA AKADEMII NAUK SSSR--SERIYA KHIMICHESKAYA in Russian No 1, Jan 78 pp 97-103 manuscript received 4 Oct 76

RAZUMOVA, YE. R., EL'NATANOV, YU. I., SHIKHALIYEV, SH. M. and KOSTYANOVSKIY, R. G., Institute of Chemical Physics, Academy of Sciences USSR, Moscow

[Abstract] In order to determine whether an amide linkage, demonstrated during the flat inversion transition, exists in the pyrimidal acylphosphine, the vibrational spectra of $MeCOPMe_2$, $MeCOP(iC_3H_7)_2$, $MeCOP(tC_4H_9)_2$ and $Me_3CCOP(tC_4H_9)2$ were studied and analyzed. Infrared and Ramen laser spectra were used for assigning bands and the number of polarized and depolarized lines for each part of the $CC(O)PC_2$ skeleton. The presence of depolarized and polarized lines in the P-C band of the Ramen spectra of all compounds studied demonstrated that these compounds have a plane of symmetry through the CC(O)P atoms which corresponds to the absence of an amide linkage. Assignments were confirmed by calculation of normal vibrational frequencies based on electrographic data. Figures 1; tables 4; references 15: 7 Russian, 8 Western.

USSR UDC 541.49:546.765:547.52/59:546.183

ARENEPHOSPHITE- AND ARENEPHOSPHINITECHROMDICARBONYL COMPLEXES WITH MEDIUM SIZE CHELATE RINGS

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 239, No 6, 21 Apr 78 pp 1363-1366 manuscript received 18 Jan 78

NESMEYANOV, A. N., KRIVYKH, V. V. and RYBINSKAYA, M. I., Institute of Heteroorganic Compounds, Academy of Sciences USSR

[Abstract] Arene $Cr(CO)_2PR_3$ complex chelates are most stable when the ring has five or six members, but the seven membered ring chelate is

more stable than the corresponding areneolefinchromdicarbonyl chelate. Eight and nine membered rings were synthesized from arylalcohol chromtricarbonyl complexes treated with diphenylchlorphosphite or diphenylchlorphosphine in the presence of triethylamine in ether. Chelate rings were formed after irradiation. Yields were equivalent to those for five to seven membered rings. The ease of formation of these chelates is due to the stability of the Cr-P bond with low transannular interaction. Two ortho methyl groups on the arene lead to a very low yield for the eight membered chelate caused by steric effects. Structural confirmations were done by elemental analysis, IR, PMR and mass spectrometry. Tables 2; references 9: 2 Russian, 9 Western.

USSR

THE SPECIFIC INTERACTION OF 0,0-DIALKYL-S-LUPINANETHIOPHOSPHATES, 0,0-DIALKYL-S-EPILUPINANETHIOPHOSPHATES AND THEIR IODOMETHYLATES WITH CHOLINESTERASE

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 239, No 6, 21 Apr 78
pp 1346-1349 manuscript received 8 Dec 77

ABDUVAKHABOV, A. A., DALIMOV, D. N., ASLANOV, KH. A., SADYKOV, A. S., ROZENGART, V. I., MIKHAYLOV, S. S. and GODOVIKOV, N. N., Institute of Heteroorganic Compounds, Academy of Sciences USSR, Moscow, Department of Bioorganic Chemistry, Academy of Sciences Uzbek SSR, Tashkent

[Abstract] A series of 0,0-dialkyl-S-lupinanethiophosphates and 0,0-dialkyl-S-epilupinanethiophosphates were synthesized from potassium 0,0-dialkylthiophosphate and bromlupinane or bromepilupinane. Methyl iodide was then used to produce the iodomethylates. The anticholinesterase activity of these compounds was studied with human erythrocyte acetylcholinesterase (AChE) and horse serum butylcholinesterase (BuChE) by evaluating the bimolecular rate constants. It was found that the constant increased with increasing length and branching of the alkoxy radical and was higher for the iodomethylates than for the uncharged analogues. This positive charge may orient the inhibitor at the anionic site of the enzyme or have an inductive effect on the thioester group facilitating phosphorylation. Increasing activity with chain length is also due to orientation. The reactivity with butylcholinesterase was more strongly dependent on chain length than with AChE and less dependent on the presence of charge. Isoamyl derivatives were the most inhibitory. Compounds with a lupinane fragment were more selective towards BuChE due to their axial substituent at the C-7 of the transquinolizide system, while epilupinine derivatives with an equitorial substituent were more specific towards AChE. The data indicate that these phosphorganic compounds are strong AChE and BuChE inhibitors. Figures 1; tables 2; references 12: 9 Russian, 3 Western.

USSR UDC 546.18

REACTION OF PHOSPHORUS PENTACHLORIDE WITH IMIDOYLAMIDINES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78
pp 1181-1182 manuscript received 8 Jun 77

KORNUTA, P. P. and KOLOTILO, N. V., Institute of Organic Chemistry,
Academy of Sciences Ukrainian SSR

[Abstract] Imidoylamidines reacted with equimolar quantities of phosphorus pentachloride yielded a series of triazaphosphorenes. The following R-1,3,5-triaza-2-phosphorenes were obtained: R= 2,2-dichloro-4,6-bis-(trichloromethyl)-, m.p. 76-79°C (b.p. 105-108°C/0.05 mm), R= 2,2-dichloro-4,6-bis(trifluoromethyl)-, m.p. 89-92°C; R= 2,2-dichloro-4-trifluoromethyl-6-trichloromethyl-, m.p. 40-43°C (b.p. 47-49°C/0.05 mm) and R= 2,2-dichlor-4-phenyl-6-trichloromethyl-m.p. 112-114°C. References 2: 1 Russian, 1 Western.

USSR UDC 547.26'118

SYNTHESIS OF ALKYL ESTERS OF BIS(HYDROXYMETHYL)PHOSPHINIC ACID

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78
pp 1182-1183 manuscript received 13 Jun 77

ROMANENKO, V. D., KORNUTA, P. P. and MARKOVSKIY, L. N., Institute of
Organic Chemistry, Academy of Sciences Ukrainian SSR

[Abstract] Esterification of bis(hydroxymethyl)phosphinic acid with orthoformate esters in presence of dimethylformamide at 90-120°C gave alkyl esters of bis(hydroxymethyl)phosphinic acid. To isolate this product, it had to be first converted to a distillable trimethylsilyloxymethyl derivative and regenerated by treatment with methanol. The following esters have been obtained: methyl: n_D^{20} 1.4808, d_4^{20} 1.3635, ethyl: n_D^{20} 1.4765, d_4^{20} 1.2895, propyl n_D^{20} 1.4715, d_4^{20} 1.2251 and butyl n_D^{20} 1.4680, d_4^{20} 1.1750. One Western reference.

USSR UDC 542.91:547.1'116

A NOVEL C-P HETEROCYCLE - 5,11-DIHYDRO-6,11-DIOXO-11-PHENYLDIBENZ-[b,e]AZA-5,11-PHOSPHEPINE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 p 1187
manuscript received 22 Jun 77

PETROV, K. A., CHAUZOV, V. A., LEBEDEVA, N. YU. and KOSTROVA, S. M.

[Abstract] Heating 5,10-dihydro-5-phenyldibenz[b,e]phosphoren-10-one-5-oxide with hydroxylamine hydrochloride in pyridine converts it to an oxime, m.p. 261°C, which under the action of polyphophoric acid rearranges to 5,11-dihydro-6,11-dioxo-11-phenyldibenz[b,e]aza-5,11-phosphepine (I), m.p. 324°C - a novel C-P heterocyclic compound. Treatment of I with sodium hydride in dimethylformamide followed by alkylation with CH_3I gave N-methyl-5,11-dihydro-6,11-dioxo-11-phenyldibenz[b,e] aza-5,11-phosphepine, m. p. 230-233°C. One Russian reference.

USSR UDC 547.241

BIPHILICITY OF DIALKYLIODOPHOSPHINES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 p 1188
manuscript received 30 Jun 77

KABACHNIK, M. M., PRISHCHENKO, A. A., NOVIKOVA, Z. S. and LUTSENKO, I. F., Moscow State University imeni M. V. Lomonosov

[Abstract] It has been shown that dialkyliodophosphines react with electrophilic as well as with nucleophilic reagents much more readily than tricoordinated phosphorus acid chlorides. For example, dialkyliodophosphine reacted with methyl iodide to yield trialkyliodophosphorane. On the other hand, dialkyliodophosphines also react via the Arbuzov reaction with tricoordinated phosphorus acid esters to yield unsymmetrical diphosphine monoxides. References 4: 3 Russian, 1 Western.

USSR

UDC 547.241

CHLOROMETHYLATION OF DIALKYLARYLPHOSPHINES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 p 1180 manuscript received 30 May 77

KORMACHEV, V. V., MITRASOV, YU. N. and KUKHTIN, V. A., Chuvash State University imeni I. N. Ul'yanov

[Abstract] Hydrogen chloride was bubbled into a mixture of diethyl-4-methoxyphenylphosphine oxide, formaldehyde and hydrochloric acid at 70°C for 3.5 hrs. Neutralization and extraction of the reaction mixture produced diethyl-3-chloromethyl-4-methoxyphenylphosphine oxide m.p. 98°C (b.p. 181-182°C/0.5 mm). The dipropyl homologue, under similar conditions, yielded the chloromethylated derivative melting at 42-44°C (b.p. 176-178° C/0.2 mm). Under these conditions no reaction took place with the oxides of diethylphenyl-, diethyl-p-tolyl-, dimethyl-p-cumenyl-, or dimethyl-2,4-xylylphosphines. Three Russian references.

USSR

UDC 546.185

REACTION OF DIALKYLCYANAMIDES WITH PHOSPHORUS TRICHLORIDE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 p 1179 manuscript received 30 May 77

SHEVCHENKO, V. I., PISANENKO, N. P. and KOSINSKAYA, I. M., Institute of Organic Chemistry, Academy of Sciences Ukrainian

[Abstract] Phosphorus trichloride reacts exothermally with dialkylcyanamides to yield N,N-dialkyl-N'-dichlorophosphoriminocarbamic acid chlorides. These acid chlorides can be converted to N,N-dialkyl-N'-tetrachlorophosphoriminocarbamic acid chlorides using Cl_2 of PCl_5. With a 2:1 ratio of PCl_5 they yield hexachlorophosphorates, and when oxidized with NO_2, they produce N,N-dialkyl-N'-dichlorophosphonyliminocarbamic acids. Two Russian references.

USSR UDC 546.92-386.535.843

REACTION OF POTASSIUM TETRATHIOCYANATOPLATINUM WITH TRIALKYLPHOSPHITES IN BENZENE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 p 1178 manuscript received 26 May 77

TROITSKAYA, A. D., SENTEMOV, V. V., SADAKOVA, G. P. and ALPAROVA, M. V., Izhevsk Agricultural Institute

[Abstract] The reaction of $K_2[Pt(SCN)_4]$ (I) with trialkyphosphites (TAP) in benzene was studied by IR spectroscopy. When a ten-fold excess of triethyl or tripropyl phosphite (TEP or TPP respectively) was used, the initial product was $[Pt(TAP)_2(NCS)_2]$ which after about 24 hrs converted to $[Pt(TAP)(NCS)_2]_2$ (II) (TAP= TEP or TPP). With a 20-30 fold excess of TEP, the product was $[Pt(TEP)_4](NCS)_2$. With 10, 20 or 30 fold excess of triisopropylphosphite only the II type complex was formed. One Russian reference.

USSR UDC 547.257.2

REINECKE COMPLEXES WITH AMINES CONTAINING A FERROCENE FRAGMENT

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 pp 1177-1178 manuscript received 24 May 77

GAPONIK, P. N., LESNIKOVICH, A. I. and ORLIK, YU. G., Byelorussian State University imeni V. I. Lenin

[Abstract] Ferrocene amines were reacted with Reinecke salts in alcohol to yield three products, depending on the ratio of the reagents used: ferrocenylmethyldimethylammonium[tetrathiocyanato-N-diaminochromate(III)], (1,1'-diethylferrocenylmethyl)-dimethylammonium-[tetrathiocyanato-N-diaminochromate (III)] or (1,1'-diethylferrocenomethyl)dimethylammonium-[tetrathiocyanato-N(1,1'diethylferrocenylmethyl) dimethylamineaminochromate-(III)]. The first two compounds are solid crystalline materials with decomposition points of 120 and 150°C respectively; the third compound is tarry. References 5: 1 Polish, 4 Western.

USSR UDC 546.183 + 547.297

DIALKYLPHOSPHITE ADDITION PRODUCTS WITH ORGANIC ACIDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78
pp 1176-1177 manuscript received 24 May 77

KIM, T. V., IVANOVA, ZH. M. and GOLOLOBOV, YU. G., Institute of Organic Chemistry, Academy of Sciences Ukrainian SSR

[Abstract] Diethylphosphite and other acid phosphites form addition products with strong organic acids $(C_2H_5O)2PHO\cdot RCOOH$. Identical products are also obtained in the reaction of triethylphosphite with carboxylic acids. Even when a large excess of triethylphosphite is used, only half of the organic acid is used up to dealkylate the phosphite: the other half binds to the acid phosphite which is formed in the above process to again give the addition product. One Russian reference.

USSR UDC 547.242

SYNTHESIS OF ARSENIC CONTAINING ION EXCHANGE RESINS BASED ON STYRENE-DIVINYLBENZENE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78
pp 1088-1092 manuscript received 18 Mar 77

LASKORIN, B. N., CHERNOKAL'SKIY, B. D., MIFTAKHOVA, R. G., STUPIN, N. P., RYABOVA, YE. K., MUGINOVA, S. M. and GARIYEVA, F. R.

[Abstract] Arsenic containing ion exchange resins were obtained by reacting R_2AsLi (I) with a styrene-divinylbenzene copolymer. These resins could be then oxidized to yield materials containing arsine oxide groups (II) or they could be reacted with methyl iodide in sealed ampules at room temperature to yield resins with quaternary arsonium base (III). Dimethylsulfate did not alkylate the resin. The structure of porous copolymers depended on the pore forming agent. When chloro and bromoarsines were compared as arsenating agents, the bromo homologue was much more effective. By means of potentiometric titration the basicity of these resins was determined; the following was the order of increasing strength: $\underline{I} < \underline{II} < \underline{III}$. Figure 1; references 20: 8 Russian, 1 Czech, 11 Western.

USSR UDC 541.127:547.242

NUCLEOPHILIC CENTER IN S_N2 REACTIONS OF THE ESTERS OF TRIVALENT ARSENIC ACID

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 pp 1083-1088 manuscript received 9 Mar 77

VALIULLINA, V. A. and CHERNOKAL'SKIY, B. D., Kazan' Chemical-Technological Institute imeni S. M. Kirov

[Abstract] Esters of the trivalent arsenic acid have two nucleophilic reaction centers: the oxygen and the arsenic atoms, both with unshared electron pairs. This leads to two possible reactions in the first stage of a nucleophilic attack on the saturated carbon atom of an alkyl halide, yielding an oxonium or an alkoxyarsonium derivative. To answer this question, the kinetics of this reaction was studied. The results have shown that the first stage of the reaction of dialkyl-, alkylphenylarsinic acid as well as alkylarsonic acid esters is the formation of alkoxyarsonium salts. In the process, rate constants and activation parameters of the ethyl iodide reaction with some of trivalent arsenic esters have been determined. Figures 3; references 23: 19 Russian, 4 Western.

USSR UDC 547.242

OXIDATION OF ALKYLDI(o-TOLYL)ARSINES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 pp 1080-1082 manuscript received 17 Jan 77

GIGAURI, R. D., CHERNOKAL'SKIY, B. D., INDZHIYA, M. A., GODERDZISHVILI, L. I. and GVILAVA, E. YE., Tbilisi State University, Kazan' Chemical-Technological Institute imeni S. M. Kirov

[Abstract] Butyldi(o-tolyl)arsine was oxidized with $KMnO_4$ at room temperature to yield 5-butyl-2,7-dioxo-3,8-dibenz-1,6-dioxa-5-arsaspiro[4,4]nona-3,8-diene. This must have occurred via an intramolecular dehydration of the intermediate product--the oxide of butyldi-(o-carboxyphenyl)arsine. Figure 1; references 11: 6 Russian, 5 Western.

USSR UDC 547.1'118

REACTION OF PHOSPHORUS CONTAINING POLYSULFIDES WITH DERIVATIVES OF TRIVALENT PHOSPHORUS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 pp 1078-1080 manuscript received 28 Mar 77

TOLMACHEVA, N. A., KHASKIN, B. A. and MEL'NIKOV, N. N.

[Abstract] The reaction of phosphorus containing polysulfides with trivalent phosphorus compounds occurs in two stages: when tri- and tetrasulfides are reacted with equimolar quantities of di- and trialkyl phosphites, one sulfur atom is split off the sulfides, yielding di- and trisulfides. When excess of di- and trialkylphosphites is used, the trisulfide formed reacts further to produce thiopyrophosphates and esters of thio- and dithiophosphoric acid. References 8: 4 Russian, 1 Polish, 3 Western.

USSR UDC 542.91 + 547.1'118

MECHANISM OF THE SELENO-SELENOL ISOMERIZATION OF β, γ-UNSATURATED ESTERS OF THE PHOSPHORUS-SELENIUM ACIDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 pp 1073-1078 manuscript received 19 Mar uu

NURETDINOV, I. A., BUINA, N. A. and BAYANDINA, YU. V., Institute of the Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan' Branch of the Academy of Sciences USSR

[Abstract] There are basically two possible mechanisms for the seleno-selenol isomerization of β, γ-unsaturated phosphorus-seleno acids: via a 6 membered cyclic transfer of the electrons (analogously to the isomerization of β, γ-unsaturated esters of thiophosphoric acid) and via an alkylation of the unsaturated phosphorus acid (this route being also possible through an intramolecular path). To study this, a series of crotyl and γ-chlorocrotyl esters of phosphorus-selenoacids has been synthesized. The experiments have shown that the rearrangement occurs via inter- or intramolecular alkylation. The substituents on the double bond show a lesser effect on the isomerization than the substituents on the phosphorus atom. Figure 1, references 7: 5 Russian, 2 Western.

USSR UDC 547.1'118

ELECTRONIC EFFECTS OF THE SUBSTITUENTS IN PHOSPHORUS SELENOACID CHLORIDES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 pp 1071-1073 manuscript received 9 Mary 77

NURETDINOV, I. A., LOGINOVA, E. I. and BAYANDINA, YE. V., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan' Branch of the Academy of Sciences USSR, Physical-Technical Institute, Kazan' Branch of the Academy of Sciences

[Abstract] The effect of the substituents at the phosphorus atom on the P(Se) bond in selenoorganophosphoric compounds was studied using NMR^{31}P and IR spectroscopic methods. The spin-spin interaction constant J(PSe) was found to be related to the number of chlorine atoms in the molecule. It appeared that the effect of the substituents at the phosphorus atom was additive. For chlorine, the group contribution to the value of spin-spin nuclear interaction ^{31}P and ^{77}Se in a selenoorganophosphoryl group was found to be 350 Hz. Analyzing a series of selenophosphonic acids and acid chlorides, it has been established that substituents at the phosphorus atom have an inductive effect on the interaction of nuclei ^{31}P and ^{77}Se in the selenophosphoryl group and on the distribution of electronic density of the chlorine atom in the P-Cl group. References 10: 7 Russian, 1 Polish, 3 Western.

USSR UDC 543.422:547.1'118

IR SPECTROSCOPIC STUDY OF THE COMPLEXES OF PHOSPHORYL COMPOUNDS WITH PHENOL

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 pp 1053-1057 manuscript received 23 Nov 76

RAYEVSKIY, O. A., GILYAZOV, M. M. and LEVIN, YA. A., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan' Branch of the Academy of Sciences USSR

[Abstract] The shift in the IR valence vibration frequency ν(OH) is commonly used in analyzing intramolecular interactions in organophosphoric compounds. The data available, however, are far from being abundant and uniform. In this study the relationship of $\Delta\nu$(OH) to the structure of a large number of phosphoryl compounds has been established, the data being obtained under standardized conditions. About 250 compounds were investigated: dialkyl(aryl)phosphites, monoalkyl(aryl)-phosphonites,

dialkyl(aryl)- and trialkyl(aryl)phosphine oxides, acid halides, esters and amides of phosphonic, phosphinic and phosphoric acids, etc. The dependence of ν(OH) on the concentration was investigated using trimethylphosphate and phenol as model compounds. It has been established that, in order to obtain $\Delta\nu$(OH) values independent of concentration, one had to work with phenol solutions which did not lead to selfassociation; the phosphoryl compound should be of low concentration, so as not to affect the dielectric permeability of the solution. The $-\Delta H$ values of the phosphoryl compounds with substituents capable of only inductive effects correlated closely with the Taft constants σ^*. The enthalpy of the complex formation of phenol with phosphoryl compounds correlated with Kabachnik's constant σ^{Φ}. Figures 2; references 18: 11 Russian, 7 Western.

USSR UDC 547.241 + 541.69

SYNTHESIS AND THE REPELLENT PROPERTIES OF THE ORGANOPHOSPHORIC DERIVATIVES OF HEXAMETHYLENIMINE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 pp 1058-1061 manuscript received 16 Nov 76

GRECHKIN, N. P., GUBANOVA, G. S. and KASHAFUTDINOV, G. A., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan' Branch of the Academy of Sciences USSR

[Abstract] A series of hexamethylenamides was obtained by the reaction of phosphorus acid chlorides with hexamethylenimine (I). Trialkylphosphites reacted with chloroacetic acid hexamethylenamide to yield hexamethylenamides of the dialkylphosphonoacetic acid. Hexamethyleniminoethanol was obtained by the reaction of I with ethylene oxide. All of the products were tested for their repellent activity. Hexamethyleneamidophosphates showed considerable repellent activity, which was lowered by introduction of increased number of I rings. The persistence of the repellent activity increased with increased length of the alkoxy radicals. The repellent activity was closely related to the evaporation rate of the test compound. References 5: all Russian.

USSR UDC 547.557 + 547.466.22 + 546.183 + 541.127

N-MONOALKYLSUBSTITUTED X-AMINOCARBOXYLIC ACID ESTERS. COMMUNICATION 2. IMINE FORMATION OF N-PHOSPHORYLATED DERIVATIVES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 pp 1061-1065 manuscript received 19 Nov 76

NESTEROVA, L. I., KASUKHIN, L. F., PONOMARCHUK, M. P. and GOLOLOBOV, YU. G., Institute of Organic Chemistry, Academy of Sciences Ukrainian SSR

[Abstract] Searching for new effective fungicides, N-phosphorylated aminoacetates were synthesized. A mixture of ethanol and triethylamine added to a solution of $Cl_2PN(isoPro)CH_2COOEt$ in anhydrous ether yielded 0,0-diethyl-N-isopropyl-N-ethoxycarbonylmethylamidophosphite (I); when 4 equivalents of Et_2NH were used instead of ethanol, the product was N,N-tetraethyl-N-isopropyl-N'-ethoxycarbonylmethyltriamidophosphite (II). Addition of PhN_3 to I in benzene produced 0,0-diethyl-(N-isopropyl-N-ethoxycarbonylmethyl)amido-N'-phenylimidophosphate, and PhN_3 added to II yielded (N,N-tetraethyl-N'-isopropyl-N'-ethoxycarbonylmethyl)triamido-N"-phenylimidophosphate. No biological data are reported. The inductive and resonance components of the electron accepting ability σ^{Φ} of isopropyl-(ethoxycarbonylmethyl)amino group were determined by the kinetic method. The values agree with their transmolecular interactions with the phosphorus atom. References 13: 10 Russian, 3 Western.

USSR UDC 547.557 + 546.185 + 541.127

IMINATION OF N-(0,0-DIETHYLPHOSPHORYL)-N-METHYLAMIDOPHOSPHITES USING PHENYLAZIDE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 pp 1065-1071 manuscript received 19 Feb 77

KLEPA, T. I., KASUKHIN, L. F., PONOMARCHUK, M. P. and GOLOLOBOV, YU. G., Institute of Organic Chemistry, Academy of Sciences Ukrainian SSR

[Abstract] 0,0-Diethyl-N-methylamidophosphate was reacted with diethylchlorophosphite in presence of triethylamine to yield 0,0-diethyl-N-methyl-N-(0',0'-diethylphosphoryl)amidophosphite, which upon addition of phenylazide gave 0,0-diethyl-[N-methyl-N-(0'0'-diethylphosphoryl)]-amido-N'-phenylimidophosphate. Essentially in the same manner the following two compounds were obtained: 0-ethyl-[N,N,N'-trimethyl-N'-(0,0'-diethylphosphoryl)]diamido-N"-phenylimidophosphate and N,N,N',N',N"-pentamethyl-N"-(0,0-diethylphosphoryl)triamido-N"'-phenylimidophosphate.

The inductive and resonance components of the electron accepting ability σ^{Φ} were determined for the substituent $(EtO)_2P(O)NMe$ using the kinetic method. The values obtained support the possibility of intramolecular coordination of the phosphoryl oxygen atom with the neighboring phosphorus atom. References 15: 12 Russian, 3 Western.

USSR UDC 547.26'118

REACTION OF DIALKYLPHOSPHOROUS ACID ISOCYANATES WITH TRIMETHYLPYRUVIC ACID NITRILE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78
pp 1013-1020 manuscript received 25 Feb 77

KONOVALOVA, I. V., GAREYEV, R. D., BURNAYEVA, L. A., FASKHUTDINOVA, T. A. and PUDOVIK, A. N., Kazan' State University imeni V. I. Ul'yanov-Lenin

[Abstract] The reaction of monoisocyanate of the dimethylphosphorous acid with the nitrile of trimethylpyruvic acid was studied in detail. On the basis of the IR, NMR ^{31}P spectroscopical data and thermographic analysis, the following compounds were identified as the reaction products: 2-alkoxy-2-oxo-3-alkyl-5-cyano-5-tert-butyl-2-phosphaoxazolidine-4-ones, 4-alkyl-3-alkoxy-2-cyano-2-tert-butyl-3-oxophosphazolidin-5-ones and 3,5-dialkoxy-2-cyano-2-tert-butyl-3-oxophosphaoxaz-4-oles as mixtures of configurational isomers. When the nitrile of trimethylpyruvic acid was reacted with diethyl-, dipropyl-, diisopropyl- and dibutylisocyanatophosphites, the reaction was much slower, requiring several hours of heating to 90°C, the isolation of final products being complicated by tarring. According to the NMR ^{31}P, IR and PMR data, the reaction occurred by an analogous scheme, except that the ratio of the final products was different. References 5: 4 Russian, 1 Western.

USSR UDC 547.241. + 547.571

α-AMINOBENZOYLPHOSPHINES. SYNTHESIS AND SOME OF THEIR PROPERTIES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78
pp 1008-1013 manuscript received 25 May 77

PUDOVIK, A. N., ROMANOV, G. V. and POZHIDAYEV, V. M., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan' Branch of the Academy of Sciences USSR

[Abstract] α-Aminobenzoylphosphines (I) were obtained by the reaction of diphenyl- and tert-butylphenylphosphines with benzylidenemethylamine, aniline, p-toluidine, p-anisidine and p-bromoaniline homologues. Heating I with equimolar quantity of sulfur or selenium yields respective sulfides and selenides of tertiary phosphines. Heating a mixture of α-N-p-tolylaminobenzyl-tert-butylphenylphosphine with methyl iodide to 80-90°C yields dimethyl-tert-butylphenylphosphonium iodide; at room temperature no reaction is observed. Analogous behavior occurs in case of α-N-phenylaminobenzyldiphenylphosphine. Thermograms of individual I show an endoeffect of melting and an exoeffect corresponding to the formation of nitrogen free product, to which the structure of 1,2-bis(diphenylphosphino)-1,2-diphenylethylene was assigned. References 12: 5 Russian, 7 Western.

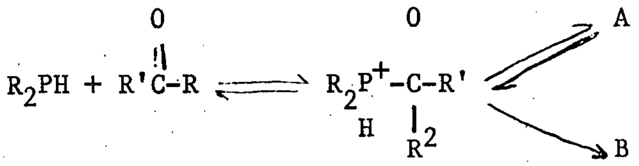
USSR UDC 541.438.1

α-HYDROXYALKYLPHOSPHINES, THEIR FORMATION AND THERMAL TRANSFORMATIONS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 pp 1001-1008 manuscript received 9 Dec 76

PUDOVIK, A. N., KONOVALOVA, I. V., ROMANOV, G. V., POZHIDAYEV, V. M., ANOSHINA, N. P. and LAPIN, A. A.

[Abstract] Thermal behavior of α-hydroxyalkylphosphines in presence of catalysts has been investigated. Specifically, the study included reactions of diphenylphosphine with the esters of pyruvic, benzoylformic, aceto- and benzoylphosphonic acids, with diacetyl, acetaldehyde, as well as with the nitriles of benzoylformic, pyruvic and trimethylpyruvic acids. The products of these reactions are α-hydroxyphosphines which on heating convert to tertiary phosphine oxides. Analysis of the results led to the postulation of the following mechanism:



$$R_2PH + R'\overset{O}{\overset{\|}{C}}-R \rightleftharpoons \underset{H}{R_2P^+}-\overset{O}{\underset{R^2}{C}}-R' \begin{matrix} \nearrow A \\ \searrow B \end{matrix}$$

which then convert to a stable α-hydroxyalkylphosphine (A) or tertiary phosphine oxide (B). Figures 2; references 19: 13 Russian, 6 Western.

USSR UDC 542.952.1:547.1'118

REACTIONS OF TRIVALENT PHOSPHORUS ACID AMIDES WITH β-PROPIOLACTONES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 pp 997-1001 manuscript received 3 Jan 77

BATYYEVA, E. S., AL'FONSOV, V. A. and PUDOVIK, A. N., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan' Branch of the Academy of Sciences USSR

[Abstract] A detailed study of the reactions of amidophosphites with β-propiolactone was carried out. Hexamethyltriamidophosphite (I) reacted with lactone yields tetramethyldiamidophosphite and acrylic acid dimethylamide with heat evolution. This occurs via an isomerization of β-propiolactone to acrylic acid followed by its reaction with amidophosphite. Analogously, I reacted with acrylic acid to yield the same final products. When 0,0-diethyl-N-diethylamidophosphite was reacted with β-propiolactone, formation of 0,0-diethyl-0-acroylphosphite was registered on the NMR ^{31}P spectrum. In general, the reactions of P^{III} acid amides with acrylic acid are complex. At the first stage of reversible protonation of the amidophosphite nitrogen atom takes place forming an anhydride and an amine. The dealkylation and carboamidation products obtained result from side reactions. Formation of analogous products in the reaction of P^{III} acid amides with β-propiolactone occurs via the isomerization of β-propiolactone to acrylic acid. References 11: 8 Russian, 3 Western.

USSR UDC 547.558.1

SYNTHESIS AND SOME REACTIONS OF DIETHOXY- AND DIPHENOXYPHOSPHINE SUBSTITUTED PHOSPHORANE-PHOSPHONIUM SALTS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 pp 991-997 manuscript received 14 Jan 77

MASTRYUKOVA, T. A., LEONT'YEVA, I. V., ALADZHEVA, I. M., SVOREN', V. A., PETROVSKIY, P. V., LUTSENKO, A. I. and KABACHNIK, M. I., Institute of Metal Organic Compounds, Academy of Sciences USSR

[Abstract] Experimental results have been reported of the synthesis and reactivity of phosphorane-phosphonium salts containing ethoxy and phenoxy groups at the trivalent phosphorus atom. These compounds have been obtained by reacting hexaphenylcarbodiphosphorane with diethyl- and diphenylchlorophosphite. The nucleophilicity of trivalent phosphorus atom in this salt is lower: the reaction with methyl iodide occurs at the trivalent phosphorus atom, but it is a slow reaction. Sulfur adds to this salt also via the trivalent phosphorus. Protonation at low temperatures occurs at the phosphorus atom; with increasing temperature, the C-protonated form is obtained. However, it is unstable and breaks down to phosphorane-phosphonium salt and chlorophosphine, leading to an irreversible shift of the equilibrium. Figure 1; references 9: 2 Russian, 1 Polish, 6 Western.

USSR UDC 547.76'118

REACTION OF 2-CHLORO-1,2-OXA-4-PHOSPHOLENES WITH ORTHOCARBONYL COMPOUNDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 pp 984-990 manuscript received 27 Dec 76

ARBUZOV, B. A., VIZEL', A. O., SHCHUKINA, L. I. and ZYABLIKOVA, T. A., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan' Branch of the Academy of Sciences USSR

[Abstract] Even though the reactions of trivalent phosphorus acid halides with orthocarbonyl compounds were known for over a century, their mechanism was not studied in detail. This report concerns the reaction of triethylorthoformate with 2-chloro-3,3,5-trimethyl-1,2-oxa-4-phospholene, - a trivalent phosphorus acid halide containing a five membered heterocycle with one oxygen atom in the ring. Equimolar quantities of the reagents were mixed and heated with and without an inert solvent. The reaction

is complex, occuring in stages: at room temperature actually no reaction takes place; with heating 2-ethoxy-1,2-oxa-4-phospholenes are formed first, which then convert to 2-oxo-2-alkoxymethyl derivatives by the Arbuzov reaction. The reaction is slowed down when two methyl groups occupy the third carbon atom of the phospholane ring. At elevated temperatures the oxaphospholene ring is cleaved, accompanied by numerous side reactions. References 12: 4 Russian, 8 Western.

USSR UDC 547.241

PHOSPHORUS CONTAINING SULFOXONIUM YLIDES. COMMUNICATION 2. PROPERTIES OF YLIDES STABILIZED WITH PENTACOVALENT PHOSPHORUS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 pp 978-984 manuscript received 22 Dec 76

LYSENKO, V. P., BOLDESKUL, I. YE., LOKTIONOVA, R. A. and GOLOLOBOV, YU. G., Institute of Organic Chemistry, Academy of Sciences Ukrainian SSR

[Abstract] A series of stable C-acylated ylides was synthesized by reacting phosphonylsulfonium ylides (I) with equimolar quantities of phenylisocyanate. In these compounds the anion charge on the ylide carbon atom is stabilized by phosphorus and carbonyl containing groupings. The C-acylated ylides can also be obtained by the reaction of sulfoxonium methylide with acetic anhydride. With acids I forms phosphorus containing sulfoxonium salts, and with aldehydes - respective B -hydroxy C-acylated ylides. Diethylphosphonylsulfoxoniummethylide reacted easily with azides and diazomalonate to yield the phosphazo- and phosphazine compounds containing sulfoxonium methylide group. Based on the pK_a values, the following is the order of decreasing delocalization ability of tetracoordinated phosphorus towards the anion charge of the phosphorylated sulfoxonium ylides.

$\geqq P\text{-}N\text{-}Tos > \geqq P{=}NN{=}C(CO_2C_2H_5)_2 > \geqq P{=}O > \geqq P{=}N\text{-}C_6H_5$.

References 11: 6 Russian, 5 Western.

USSR UDC 547.26'118

REACTIONS OF PHOSPHORUS DITHIOACIDS WITH BENZANILINE AND BENZALMETHYLAMINE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 pp 1020-1025 manuscript received 27 Jan 77

ZIMIN, M. G., ZABIROV, N. G., CHERKASOV, R. A. and PUDOVIK, A. N., Kazan' State University imeni V. I. Ul'yanov-Lenin

[Abstract] The reaction of benzalaniline and benzalmethylamine with dimethyl-, diethyl-, dipropyl-, and diisopropyldithiophosphoric acid as well as with diphenyldithiophosphinic acid and the thermal stability of the products formed have been reported. On the basis of the IR, NMR ^{31}P and PMR spectral data, the initial products are the dithiophosphate salts of benzalaniline or benzalmethylamine, which eventually convert to 0,0-dialkyl esters of S-[N-phenyl(methyl)benzylamino]-dithiophosphoric acids. A number of thermal decomposition reactions for these compounds has been reported, in most cases the major product being 0,0-dialkyl esters of S-alkyldithiophosphoric acid. References 12: 4 Russian, 8 Western.

USSR UDC 547.26'118

INCOMPLETE HYDROLYSIS OF ALKYL-, CYCLOALKYL- AND ARYLDICHLOROPHOSPHINES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 pp 1048-1053 manuscript received 6 Apr 77

ANDREYEV, N. A., GRISHINA, O. N. and SMIRNOV, V. N., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan' Branch of the Academy of Sciences USSR

[Abstract] Incomplete hydrolysis of methyl-, cyclohexyl- and phenyldichlorophosphines was studied by means of ^{31}P NMR spectroscopy. The hydrolysis of methyl dichlorophosphine occurs in stages, first leading to the formation of methylphosphonous acid chloride; then, with increasing temperature, the methylphosphonous acid anhydride is obtained. This product also proved to be unstable, disproportionating to $(CH^3P)_n$ and $(CH_3PO)_n$. An analogous situation was observed with cyclohexyl and phenyldichlorophosphines. These findings indicate that changes of the viscosity, solubility and the ability to phosphorylate, occurring in phosphonous acid anhydrides on storage, are due to disproportionation and not to polymerization, as claimed by some. Figure 1, references 17: 10 Russian, 7 Western.

USSR UDC 547.241.547.34

REACTION OF CARBON TETRACHLORIDE WITH PHENYL ESTERS OF SOME PHOSPHINIC ACIDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 pp 1046-1048 manuscript received 14 Feb 77

KHARRASOVA, F. M., YEFIMOVA, V. D. and SALAKHUTDINOV, R. A., Kazan' Chemical-Technological Institute imeni S. M. Kirov

[Abstract] Experimental results have been reported on the reaction of CCl_4 with phenyl esters of diethyl-, phenylethyl-, p-tolylethyl-, p-bromophenylethyl-, p-chlorophenylethyl- and bis-p-bromophenylphosphinous acids. The immediate reaction product was a tarry substance which could not be distilled. However, when the reaction was run in presence of benzaldehyde, the products were: phenyl ester of the phosphinic acid, benzal chloride and β, β-dichlorostyrene. References 9: 8 Russian, 1 Western.

USSR UDC 547.26'11

REACTIONS OF PHOSPHORUS DITHIOACIDS WITH THE NITRILES OF BENZOYLFORMIC AND PYRUVIC ACID

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 pp 1025-1031 manuscript received 24 Feb 77

CHERKASOV, R. A., KUTYREV, G. A., KARELOV, A. A., YARKOVA, E. G. and PUDOVIK, A. N., Kazan' State University imeni V. I. Ul'yanov-Lenin, Kazan' Institute of Organic and Physical Chemistry, Academy of Sciences USSR imeni A. Ye. Arbuzov

[Abstract] The reaction of 0,0-dimethyl- and 0,0-diisopropyldithiophosphoric acids with the nitriles of benzoylformic and pyruvic acids was studied. Combining equimolar quantities of diisopropyldithiophosphoric acid with benzoylcyanide at room temperature leads to the formation of 5-(0,0-diisopropyldithiophosphoryl)-2-benzoyl-4H-6-phenyl-1,3,4-oxadiazine (I) and bis(diisopropylthiophosphoryl)disulfide (II). Evidently the first step in this reaction is the addition of the dithioacid to the C≡N group of the ketonitrile; the ketoimidoyl obtained reacts further to yield the above end products I and II. Reaction of dimethyldithiophosphoric acid (III) with the nitrile of benzoylformic acid is so rapid that without a solvent, extensive tar formation takes

place; the yield of the disulfide is only about 20%. When III was reacted with the pyruvic acid nitrile, the reaction also occurred along addition to the nitrile group, but then dealkylation of the dithiophosphate moiety took place. References 22: 9 Russian, 1 Polish, 12 Western.

USSR UDC 547.341

REACTIVITY AND STRUCTURAL CHARACTERISTICS OF THE PHOSPHORYLATED CARBONYL COMPOUNDS. COMMUNICATION 15. INVESTIGATION OF THE REACTION OF PHOSPHORYLATED ALDEHYDES WITH β-DICARBONYL COMPOUNDS AND CYANOACETIC ESTER

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78
pp 1032-1036 manuscript received 20 Dec 76

SOKOLOV, M. P., LIORBER, B. G., RAZUMOV, A. I., MOSKVA, V. V., BULATOVA, Z. YA. and ZYKOVA, T. V., Kazan' Chemical-Technological Institute imeni S. M. Kirov

[Abstract] Continuing their studies of the reactivity of phosphorylated carbonyl compounds, a series of unsaturated phosphorylated β-dicarbonyl and cyanocarbonyl derivatives were obtained by reacting phosphorylated aldehydes with acetylacetone, dimedone, and acetoacetic as well as cyanoacetic esters (in the presence of catalytic amounts of pyridine). The products exist in keto-enol equilibrium mixtures, this aspect being discussed in another paper. The reaction mechanism depends on the structural characteristics of the aldehydes as well as on the acidity of the reagents with an active methylene group. References 7: 5 Russian, 2 Western.

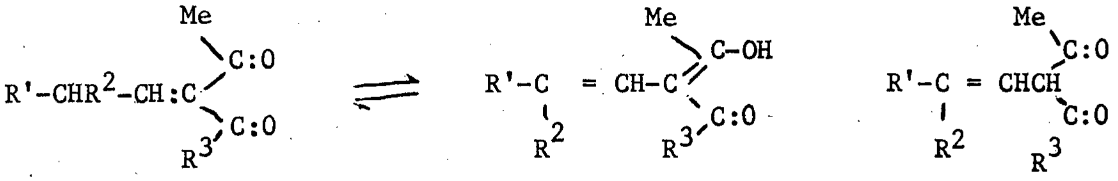
USSR UDC 547.241

REACTIVITY AND STRUCTURE OF PHOSPHORYLATED CARBONYL COMPOUNDS. COMMUNICATION 16. INVESTIGATION OF THE TAUTOMERISM OF PHOSPHORYLATED β-DICARBONYL COMPOUNDS, DERIVATIVES OF ACETOACETIC ESTER AND ACETYL ACETONE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78
pp 1036-1041 manuscript received 20 Dec 76

SOKOLOV, M. P., LIORBER, B. G., RAZUMOV, A. I., MOSKVA, V. V., BULATOVA, Z. YA., ZYKOVA, T. V. and SALAKHUTDINOV, R. A., Kazan' Chemical-Technological Institute imeni S. M. Kirov

[Abstract] Phosphorylated β-dicarbonyl compounds, derivatives of acetoacetic ester and acetyl acetone, exist in tautomeric equilibrium:



Using NMR$^{1}_{H}$, ^{31}P and IR spectroscopic methods, it has been shown that they exist in keto-enol equilibrium, the relative proportions of these forms depending on the nature of β-dicarbonyl compound, on the substituents at the phosphorus atom, basicity of the P:O group, etc. The enol form of the phosphorylated derivatives of acetoacetic ester has been found to be stabilized principally by the intermolecular bonds, while the enol form of acetyl acetone - by intramolecular H-bonds. Figure 1; references 6: 3 Russian, 3 Western.

USSR UDC 547.241'547.341

REACTION OF PHOSPHONOUS ACID ESTERS WITH CARBON TETRACHLORIDE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 5, May 78 pp 1041-1046 manuscript received 4 Dec 76

KHARRASOVA, F. M., YEFIMOVA, V. D., YEREMINA. M. M. and SALAKHUTDINOV, R. A., Kazan' Chemical-Technological Institute imeni S. M. Kirov

[Abstract] Differential-thermal analysis was used to determine the temperature at which phenyl esters of alkyl and arylphosphonous acids showed a tendency towards reacting with CCl_4. In contrast to alkyl halides, this reaction is quite complicated, occurring at temperatures above 160°C. Triphenylphosphite did not react with CCl_4 even at 350°C. Using NMR ^{31}P spectroscopy, it was shown that the reaction product of diphenyl ester of butylphosphonous acid with CCl_4 contained as many as 6 different compounds. Other reaction products were so tarry that no NMR spectrum could be obtained. When the reaction was carried out in the presence of benzaldehyde, the products were phosphonic esters, benzal chloride and dichlorostyrene. References 22: 15 Russian, 7 Western.

USSR UDC 541.127.546.21:538

RATES OF OXYGEN EXCHANGE BETWEEN PHOSPHOMOLYBDOVANADIUM HETEROPOLYANIONS AND WATER BASED ON NMR of ^{17}O

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 240, No 1, May/Jun 78
pp 128-131 manuscript received 30 Dec 77

FEDOTOV, M. A. and MAKSIMOVSKAYA, R. I., Institute of Catalysis, Siberian Department of the Academy of Sciences USSR, Novosibirsk

[Abstract] Phosphomolybdovanadium heteropolyacids (HPA) are used as reversible oxidants in liquid-phase oxidation of olefines (Matveyev, 1977). Understanding of the kinetics of these reactions requires knowledge of the makeup and structure of HPAs and of their anions and their kinetic properties in solution. The present study has used NMR ^{17}O to study the kinetics of isotopic exchange of ^{16}O-^{17}O between atoms of the oxygen of a (phosphorus, molybdenum and vanadium) heteropolyanion and atoms of the oxygen of the molecules of solvent-water. The oxygen atoms, which occupy various positions in the heteroanion, will give NMR lines differing due to chemical shift; rates of exchange of the structurally different atoms of oxygen can be measured, after ^{17}O enrichment in the water solution. Measurements were made of NMR spectra and rates of enrichment, by ^{17}O, of the heteropolyanion makeup of $PMo_{12-n}V_nO_{40}^{(n+3)-}$ (n=0,1,2) and $V_{10}O_{28}^{6-}$ (heteropolyanion-0,-1,-2 and decavanadate, respectively. These measurements yielded rate constants and insight into the composition and structure of the heteropolyanions under conditions similar to those in catalytic processes. The data are expected to contribute to an understanding of the kinetics of the catalysis and of HPA oxidation-reduction reactions. Figures 2; references 12: 7 Russian, 5 Western.

USSR UDC 546.881.5'776'185:538

STUDY OF THE STATE OF PHOSPHOMOLYBDOVANADIUM HETEROPOLYACIDS IN AQUEOUS SOLUTIONS USING THE NMR METHOD

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 240, No 1, May/Jun 78
pp 117-120 manuscript received 30 Dec 77

MAKSIMOVSKAYA, R. I., FEDOTOV, M. A., MASTIKHIN, V. M., KIZNETSOVA, L. I. and MATVEYEV, K. I., Institute of Catalysis, Siberian Department of the Academy of Sciences USSR, Novosibirsk

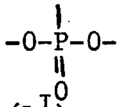
[Abstract] The title compounds with the general formula $H_{3+x}(PMo_{12-x}VxO_{40})$ are presently used as reversible oxidants in catalytic oxidation of olefines in solution. Relation of the oxidation-reduction properties and the structure of heteropolyacids (HPA) requires resolution of the task of identifying them in solutions and this is made difficult because of the similarity in properties and capability of interconversion of the HPAs with different x. The NMR method is applicable here and has been used to examine ^{31}P, ^{51}V and ^{17}O solutions of phosphomolybdovanadium HPA, where x=0,1,2,3 (thus, HPA-1, HPA-2 and HPA-3). The NMR spectra revealed that aqueous solutions of HPA contain a mixture of HPAs of different composition, and that chemical shifts in the lines are a function of the acidity of the solution, varying in character with a different x. Since HPA shows different composition, depending on method of synthesis, preparation of pure HPAs of definite structure requires use of purity control, e.g., by NMR, in addition to chemical analytical control. Spectra of HPA-1, HPA-2, and HPA-3 are shown. Figures 2; references 12: 7 Russian, 5 Western.

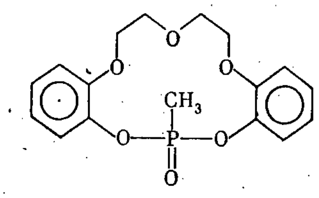
USSR UDC 546.33-386+546.34-386

COMPLEX COMPOUND OF PHOSPHONYL-CONTAINING MACROCYCLIC LIGANDS WITH ALKALI METAL IONS

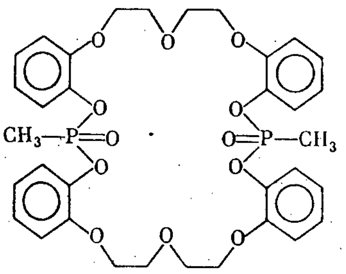
Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 240, No 1, May/Jun 78
pp 100-103 manuscript received 27 Jan 78

YATSIMIRSKIY, K. B., Academician, Academy of Sciences UkrSSR, SINYAVSKAYA, E. I. and KUDRYA, T. N., Institute of Physical Chemistry imeni L. V. Pisarzhevskiy, Academy of Sciences UkrSSR, Kiev

[Abstract] This is a study of complex formation by alkali metal salts with ligands which contain one or two  $-O-\overset{|}{\underset{\overset{\|}{O}}{P}}-O-$ groups, have different sizes of macrorings and are monomeric (L^{I}) or dimeric (L^{II}) forms of macrocyclic polyether:



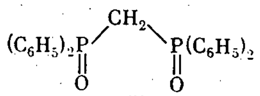
(L^I)



(L^{II})

$(C_6H_5)_3P{=}O$

(L^{III})



$(C_6H_5)_2\underset{\overset{\|}{O}}{P}-CH_2-\underset{\overset{\|}{O}}{P}(C_6H_5)_2$

(L^{IV})

Results are compared with those of complexes formed by alkali metals with non-cyclic ligands which have one or two P=O-groups (L^{III}) and (L^{IV}). The reactions are run in a non-aqueous medium with acetates of a number of alkyl metals and with halides of lithium for which the great effect of complex formation is seen among the alkali halides. The capacity of these ligands to form complexes is measured by comparison of the magnitude of the stability constant of complexes obtained by measurement of the electrical conductivity of solutions. Phosphoryl-containing ligands with different macroring sizes differ in melting point, MW and solubility in organic solvents. Infra-red spectra of phosphoryl-containing macrocyclic ligands L^I and L^{II} are shown in the free state and after complex formation with LiCl and apparently reveal different conformation of ligand molecules and presence of an intra-molecular hydrogen bond. Stability of the complexes in terms of nature of the anion is discussed. The macrocylic ligand L^{II} forms a more stable complex than the non-cyclic chelate-forming compound L^{IV}. Figure 1; references 8: 5 Russian, 3 Western.

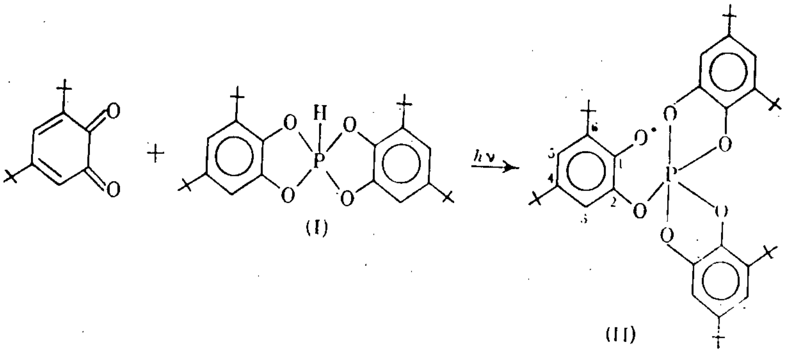
USSR UDC 541.515

FREE RADICALS WITH A SIX-COORDINATED PHOSPHORUS ATOM WITH UNSYMMETRICAL LIGANDS

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 240, No 1, May/Jun 78 pp 92-95 manuscript received 26 Dec 77

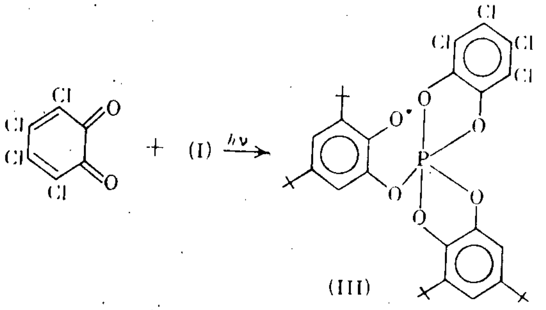
PROKOF'YEV, A. I., KHODAK, A. A., MAL'YSHEVA, N. A., PETROVSKIY, P. V., BUBNOV, N. N., SOLODOVNIKOV, S. P. and KABACHNIK, M. I., Academician, Institute of Heteroorganic Compounds, Academy of Sciences USSR, Moscow

[Abstract] Work by Prokof'yev's group in 1976 showed that 3,6-di-ter-butyl orthoquinone, and orthochloranil, react with bis-3,6-di-ter-butyl-1-2-phenylenedioxyspirophosphorane under UV radiation, to form free radicals with a six-coordinated phosphorus atom. Specific line breadths in the EPR spectra of these radicals indicated intramolecular exchange of the unpaired electron and bond in these radicals--a circulating or wandering, valency. The present article reports a study of the EPR spectra of radicals synthesized analogously when 3,5-di-ter-butyl-orthoquinone, and orthochloranil, react with bis-(3,5-di-ter-butyl-1,2-phenylenedioxy)-spirophosphorane (I). These reactions proceed as follows:

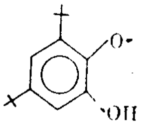


(I)

(II)



(III)



(IV)

где + — трет бутил

The course of these reactions shows the actual preparation of a six-coordinated phosphorus atom and makes it possible to examine the influence of unsymmetrical ligands on the nature of the intramolecular exchange of the free valency and bond. EPR spectra of radicals II and III, recorded for various temperatures (-100 up to -40°C), display a narrowing of line breadth with rise in temperature. The changes, which are reverisble with change in temperature, indicate the presence of inter-ligand exchange of the unpaired electron and bond, where the unpaired electron circulates around the ligands participating in the exchange. In compound IV there is no intramolecular migration of hydrogen atoms. Figures 2; references 4: 3 Russian, 1 Western.

USSR UDC 542.91:547.335.2'161:547.1'118

REACTION OF PERFLUORO-2-AZAPROPENE WITH TRIALKYLPHOSPHITES

Moscow IZVESTIYA AKADEMII NAUK SSSR--SERIYA KHIMICHESKAYA in Russian No 10, 1977 pp 2379-2381 manuscript received 26 Apr 77

GONTAR', A. F., TIL'KUNOVA, N. A., BYKHOVSKAYA, E. G. and KNUNYANTS, I. L., Institute of Organoelemental Compounds, Academy of Sciences USSR

[Abstract] Perfluoro-2-azapropene was found to be more electrophilic than perfluoroisobutylene, the most electrophilic of the nonfunctional fluoroolefins. When perfluoro-2-azapropene was treated with trialkylphosphites, the reaction products were trialcoxyperfluorazapropenylfluorophosphoranes; the latter are stable intermediates of the Arbuzov reaction. Though stable at room temperature, when heated above 120°, trialcoxyperfluorazapropenylfluorophosphoranes decompose to yield alkyl fluoride, dialkylfluorophosphate and trifluoromethylisonitrile. References 9: 6 Russian, 3 Western.

USSR UDC 519.281.2:541.6:547.29.314

BIOLOGICAL ACTIVITY - A FUNCTION OF THE STRUCTURE. COMMUNICATION 2. HANSCH MODEL FOR γ-BUTYROLACTONES

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IMENI D. I. MENDELEYEV in Russian Vol 23, No 2, 1978 pp 225-226 manuscript received 26 Sep 77

[Abstract] β-Substituted γ-butyrolactones exhibit convulsive activity with toxic doses ranging from 3 to 200 mg/kg, depending on the substituent in the β-position. An attempt was made to construct a mathematical model based on the Hansch method for consideration of structure-activity relationship. When linear relationship of the biological activity to the additive constant of hydrophobic property of the substituents was considered, the model was unsatisfactory. However, when secondary order regression was applied, the model showed satisfactory relationship of the hydrophobic factor to biological activity. References 5: all Western.

USSR UDC 616.71-006-073.916:546.18-32(047)

ALKYLENEDIPHOSPHONIC ACIDS AND THEIR DERIVATIVES - OSTEOTROPIC AGENTS

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 12, No 5, May 78 pp 25-32 manuscript received 21 Jun 77

KORSAKOV, M. V. and IVIN, B. A., Scientific Research Institute of Oncology imeni Prof. N. N. Petrov, Leningrad

[Abstract] A review of biological activity of the alkylenediphosphonic acids (APA) has been given, concentrating on geminal diphosphonic acids with a P-C-P bridge. APA's are capable of forming chelating complexes because of their two geminal electron accepting phosphonic groups. The strongest complexes were found to be formed on the basic side of the pH scale. APA's are also isoelectronic analogues of pyrophosphoric acid. Among a number of synthetic approaches, the most universal ones are based on the reaction of phosphorus trihalide with compounds containing electron accepting functional groups. APA's exhibit a wide range of biological activities, depending on their structure. They have been used in treating problems of Ca^{2+} and phosphate metabolism, treatment of osteoporosis and as antimetabolites of pyrophosphates. Technecium diphosphates are currently used as agents of choice in diagnosis of bony metastases of carcinoma of the breast, lung and prostate. However, little is known about their transport mechanism and metabolism in the bones. References 29: 5 Russian, 24 Western.

USSR UDC 615.31:547.751'918].015.11

INVESTIGATION OF THE BIOLOGICAL ACTIVITY OF INDOLE NUCLEOSIDES. STRUCTURE-BIOLOGICAL ACTIVITY RELATIONSHIPS

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 12, No 5, May 78 pp 33-38 manuscript received 29 Dec 77

DOBRYNIN, YA. V., NIKOLAYEVA, T. G., MUKHANOV, V. I., YARTSEVA, I. V., MINIKER, T. D., EKTOVA, L. V., TOLKACHEV, V. N., CHKANIKOV, N. D. and PREOBRAZHENSKAYA, M. N., Scientific Center of Oncology, Academy of Medicinal Sciences USSR Moscow

[Abstract] Four groups of indole glycosides were studied: (I) 1-glycosides of unsubstituted indole with different alkyl components; (II) various glucopyranosylindoles with substituents in position 3; (III) indole arabinosides with substituents in the pyrrole and in benzyl rings; and (IV) arabinopyranosyl-5 and -6-nitroindoles. The following three compounds were synthesized for the first time: 1-α-L-arabinopyranoside-5(6)-amino-, -5(6)-nitro- and -3-bromo-6-nitroindoles. Cytotoxic activity of these agents was investigated on standard monolayer cell cultures of human ovarian carcinoma. In the I group of compounds only indole-1-α-L-arabinoside showed moderate cytotoxic activity. Modification of the pyrrole ring showed no effect on the biological activity, while introduction of substituents into the benzyl ring increased the cytotoxic effect; the strongest effect being noticed in case of indole-1-α-L-arabinopyranosides with a nitro group in the 5 or 6 position. Group IV compounds showed lower cytotoxicity. References 11: 10 Russian, 1 Western.

USSR UDC 615.31:547.784.6

SYNTHESIS OF 2-MERCAPTOIMIDAZOLE DERIVATIVES AND THEIR BIOLOGICAL PROPERTIES

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 12, No 5, May 78 pp 59-62 manuscript received 23 Sep 77

POVSTYANOY, M. V., PRIYMENKO, B. A., and KOCHERGIN, P. M., Kherson Branch of the Odessa Technological Institute, Zaporozhe Medical Institute

[Abstract] A series of 2-mercaptoimidazoles was synthesized. Using the Anschnitz and Schwickerath method, 2-methylmercapto-4,5-diphenyl-imidazole was obtained (I). To get the 2-benzylmercapto-4,5-diphenylimidazole (II) 4,5-diphenylimidazolone-2-thione was reacted with benzyl chloride in presence of alcoholic NaOH at 60-65°C. A 5-6 hr reaction of methyl iodide or alkyl epoxide with I or II in alcoholic NaOH solution yielded a series of 1-methyl(β-hydroxyalkyl)-2-alkylmercapto-4,5-diphenylimidazoles. Addition of hydrogen peroxide to I dissolved in glacial acetic acid yielded 4,5-diphenylimidazolyl-2-methylsulfone. And finally, addition of acetic acid α-bromoketone or its ethyl ester to I or II in sodium ethoxide solution followed by refluxing for 10-15 hrs, yielded N-substituted- and 4,5-diphenylimidazolyl-2-methylsulfones. All synthesized compounds exhibited weak to moderate fungistatic and bacteriostatic activity. Three of them showed moderate hypotensive effect. References 7: 5 Russian, 2 Western.

USSR UDC 615.31:547.914.2

BIOLOGICAL ACTIVITY AND TOXICITY OF MALEOPIMARIC ACID DERIVATIVES

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 12, No 5, May 78 pp 70-72 manuscript received 9 Nov 77

SVIKLE, D. YA., PRIKULE, A. YA., SHUSTER, YA. YA. and VESELOV, D. YA., Institute of the Wood Pulp Chemistry, Academy of Sciences Latvian SSR, Riga, Riga Medical Institute

[Abstract] A series of N-substituted maleopimaric acid (MPA) imides has been synthesized and their antimicrobial and toxic activity was investigated. The experimental results showed that N-substituted imides of MPA possessed selective antimicrobial activity, being well tolerated by laboratory animals. Some agents from this group could be selected on the basis of their ability to suppress bacterial flora during the fermentation process of citric acid. References 17: 4 Russian, 2 Czech and 11 Western.

USSR UDC 615.35.036.8:681.3

STATISTICAL ANALYSIS OF THE DATA BASE OF BIOLOGICALLY ACTIVE COMPOUNDS. COMMUNICATION 2. PROGNOSTICATION OF THE BIOLOGICAL ACTIVITY BY THE METHOD OF SUBSTRUCTURAL ANALYSIS

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 12, No 5, May 78 pp 88-92 manuscript received 7 Dec 77

AVIDON, V. V., AROLOVICH, V. S., KOZLOVA, S. P. and PIRUZYAN, L. A., Scientific Research Institute of the Biological Studies of Chemical Compounds, Moskovskaya Oblast'

[Abstract] In a preceeding paper, the authors discussed basic principles in creating a data bank of medicinally and biologically active agents, containing structural and pharmacological information. Since the data in such a bank would be the product of many investigators, an attempt was made to develop a method for using these data in prognosticating biological activity of new chemical entities. To achieve this goal, it has been proposed to use a variant of the so-called "substructural analysis." In this particular case, the substructures could be equated to the descriptors used in coding the structures. A substructural analysis program has been written for the calculation of information evaluation of a given activity. On the basis of such a program it could be possible to predict what type of activity one would expect from a given structure. The method was tested retrospectively on the available bank of data, by extracting the test compound from the bank prior to developing the normalized indexes. It has been claimed that on this basis one could narrow down the number of tests for a group of active agents. References 8: 5 Russian, 3 Western.

USSR UDC 582.232.11

INTERRELATION BETWEEN THE STRUCTURE OF TRANSITION METAL CHELATE COMPOUNDS AND THEIR TOXICITY FOR CHLORELLA

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 240, No 1, May/Jun 78 pp 96-99 manuscript received 2 Jan 78

RUKHADZE, YE. G. and BARASHKOV, G. K., Moscow State University imeni M. V. Lomonosov

[Abstract] Chelates of copper, cobalt, zinc, cadmium, lead and chromium have been examined to identify toxicity of typical chelates for Chlorella

pyrenoidosa Strain 82 in the log phase of growth, and to shed light on the relation of structure to physiological activity. Toxicity was measured on the basis of effect on cell growth in 4 days (Barashkov method, 1977). Toxicity was expressed in terms of C_{cr} (the critical concentration of the investigated compound, which is equal to the concentration in mg/l that decreases--by 5% as compared to the control--the rate of division of cells in a trial suspension); toxicity was also expressed as T_c "toxic-units" (for copper sulfate the "toxic unit" is one). In addition to the simple ionic bond compound [e.g. $Cu(NO_3)_2$ pr $CuCl_2$], Cu-ligand types tested included a) complex compounds, dichloride-bis-alpha-picolinate of copper, b) monochelates, c) bis-chelates and d) molecular complexes with transitional charge. Data tabulated include C_{cr} and T_c as a function of Cu-ligand covalency, toxicity and structure of metallocyclic N-alkyl-(aralkyl)-salicylalamines of copper, toxicity of bi-nuclear chelate compounds of copper and C_{cr} and T_c as a function of the constant of stability of copper chelate compounds and electron-donor and electron-acceptor substituents in the ligands. Some comparisons of the order of toxicity of the metals tested were made. References 14: 7 Russian, 7 Western.

USSR UDC 614.777+612.6]:547.263

THE MPC OF ISOPROPYL ALCOHOL FOR BODIES OF WATER CONSIDERING THE EFFECT ON THE GONADS AND PROGENY

Moscow GIGIYENA I SANITARIYA in Russian No 1, Jan 78 pp 8-11 manuscript received 15 Feb 77

ANTONOVA, V. I. and SALMINA, Z. A., Institute of Biophysics, Ministry of Public Health, USSR, Moscow

[Abstract] A study was made of the influence of isopropyl alcohol on the function of the gonads, the reproductive function of animals and the development of their progeny, as well as the embryotoxic effect of the alcohol. The alcohol was administered in the experiments before pregnancy, during pregnancy and during both times. The reproduction function of the animals was studied during the sixth month of chronic exposure by comparison of experimental females with experimental males, experimental females with control males, control females with experimental males and control females with control males. Doses used were 1008 and 252 mg/kg for 20 and 45 days, 1800 mg/kg for 3 months, and in the chronic experiment 18, 1.8, 0.18 and 0.018 mg/kg. It was concluded that the existing maximum permissible concentration (MPC) of isopropyl alcohol for bodies of water does not disrupt the reproductive function of the animals and is safe for the progeny. The threshold concentration on the basis of taste was found to be ineffective. Tables 3; references 6: 5 Russian, 1 Western.

USSR UDC 678.4:547.391:615.9

EVALUATION OF THE TOXICITY OF ACRYLIC ACID NITRILE

Moscow KAUCHUK I REZINA in Russian No 3, 1978 pp 29-31 manuscript received 2 Jun 77

STASENKOVA, K. P., BONDAREV, G. I. and MURAV'YEVA, S. I., Nutrition Institute, Academy of Medicinal Sciences USSR; Institute of Industrial Hygiene and Professional Diseases, Academy of Medicinal Sciences USSR

[Abstract] Experimental results have been reported on the investigation of chronic and acute toxicity of acrylic acid nitrile. The experiments were carried out on rats and guinea pigs. The agent was administered parenterally, by gavage, by inhalation and topically. The results obtained showed that acrylonitrile is a highly toxic, dangerous compound. Clinically, the symptoms of acute poisoning were the same regardless of the route of administration: in 3-5 min the animals exhibited irregular breathing, after 20 min convulsions occurred, and in about 1-4 hrs after the exposure - death. The lowest single dose causing toxic manifestations was 7.5 mg/kg. In the subacute experiments with inhalation, the agent showed cumulative properties, so that a dose of 20 ± 5 mg/m^3 already was responsible for toxic symptoms. References 10: 6 Russian, 2 Polish, 1 Czech, 1 Western.

USSR UDC 613.32:[615.285.7+661.185

STABILITY OF SOME PESTICIDES IN WATER

Moscow GIGYENA I SANITARIYA in Russian No 4, 1978 pp 104-105 manuscript received 14 Jun 77

AKIMOV, A. M. and BABICH, A. I., Volga Scientific-Research Institute of Hydrotechnology and Melioration, Engels, Saratovskaya Oblast'

[Abstract] Water stability of the most widely used pesticides: hexachlorocyclohexane, chlorophos, metaphos and 2,4-D was studied under conditions of their concurrent presence in test samples. Also, the effect of sulfanol NP-1 detergent on these pesticides was investigated. The experiments were carried out in aquariums containing dechlorinated tap water only and in aquariums modelling natural water reservoirs (containing tap water, lake sand and algae). The most stable pesticide was hexachloran which was found in water throughout the entire experiment (360 days). Less stable were 2,4-D, chlorophos and metaphos in that order. A large portion of the chemicals decomposed early in the experiment, their rate of breakdown during the first days increased with increasing concentration in water. At the same time the quantity of material retained in water increased with increasing concentration. In water reservoir models the chemicals were less persistent than in pure water, but with introduction of sulfanol NP-1 their persistence increased in all cases. No references.

USSR UDC 614.7:615.285.7]-07

THE LEVELS OF PESTICIDES USED IN A GIVEN AREA AS AN INDICATOR OF PESTICIDE CONTAMINATION

Moscow GIGIYENA I SANITARIYA in Russian No 4, 1978 pp 95-97 manuscript received 11 Jul 77

YAKUBOV, A. YA., Tadzhik Scientific-Research Institute of Epidemiology and Hygiene, Dushanbe

[Abstract] Based on the analysis of the volume of pesticides used in 34 regions of Tadzhik Republic, five zones of pesticide contamination have been identified, corresponding to the quantities of these chemicals applied per hectare. In the first zone (4.4 kg/ha) the following fungicides were used: sulfur and copper preparations, phosphamide and hexachlorocyclohexane. Recent years showed a marked drop in the use of chemicals. In the second zone (8.9 kg of chemicals per hectare)

the agents used include fungicides, inorganic preparations and chloroorganic pesticides. The third zone utilized primarily inorganic agents, defoliants and chloroorganic as well as organophosphoric pesticides. Most of these compounds were non-persistent; 22.7 kg were applied per hectare. The fourth zone (28.8 kg/ha) employed fungicides, defoliants and insecticides; the assortment in the fifth zone was similar to that in the third zone, the total volume applied was in excess of 35 kg per hectare. The residual quantities of these chemical agents in air, water and soil were found to be related to the total quantity used per year. Therefore it has been proposed that the reverse should also be true and from the levels used, charts could be prepared reflecting environmental contamination. References 8: all Russian.

USSR UDC 614.839.532:[632.95 + 668.8]

SUPPRESSING OF DUST EXPLOSIONS IN SEALED CONTAINERS

Moscow KHIMICHESKAYA PROMYSHLENNOST' in Russian No 2, 1978 pp 105-107

VODYANIK, V. I. and KOZHUSHKOV, N. P.

[Abstract] Currently used systems for suppressing explosions, both of domestic and foreign origin, were reviewed. A novel model for suppressing explosions, developed at the All-Union institute of Safety Technology for the Chemical Industry and some experimental results obtained with it are described. It consisted of a 10 m^3 cylinder, an atomizer, an explosion sensor, a hydro-bomb, an irrigator, a pyrotechnic charge, a pressure sensor and an oscillograph. It was shown that water is the best agent for fire extinguishing during quenching of dust explosions. Figures 4; references 6: 6 Russian, 2 Western.

USSR UDC 621.869.88:661.41-911.4

ACCIDENT PREVENTION MEASURES FOR CHLORINE CONTAINERS

Moscow KHIMICHESKAYA PROMYSHLENNOST' in Russian No 3, 1978 pp 202-205

TIMOFEYEV, A. F., KIRYUKIN, G. V., LAZINTSEV, D. N., MIKHEL', M. L., FROLOV, N. S. and KHAIN, P. G.

[Abstract] A technical description of chlorine containers is presented. In spite of the precautionary measures, a number of explosive accidents have occurred. Among several possible causes, the following have been cited: faulty construction leading to mechanical cracks, impurities in the liquid chlorine or in the inert gas maintained over the surface of the liquid, overfilling of the containers, formation of hydrogen, and hydrocarbon impurities from compressor lubricants, etc. The pressure inside such containers is related to the level of filling and to storage temperature. To prevent accidents, strict adherence to regulatory measures must be observed. Figures 4; references 6: 5 Russian, 1 Western.

USSR UDC 547.241+547.435+547.571+597.299.66

SEARCH FOR NEW POTENTIAL PESTICIDES OF PREPARATIONS TO COMBAT COTTON DISEASES

Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 2, 1978 pp 70-79
manuscript received 8 Feb 77

MAKSUDOV, N. KH., MAKHAMATKHANOV, M. M., ARIPOV, A. and SEYTKASYMOV, ZH., Tashkent Order of Labor's Red Banner Institute of Irrigation Engineers and Mechanization of Agriculture

[Abstract] Organophosphorus compounds, derivatives of aminoalcohols and dithiocarbaminoacid, have already been synthesized by the authors and tested for pesticide activity. In the present work, a new series of pesticides, growth regulators and defoliants have been synthesized, including derivatives of chloromethylphosphonic acid, chloroethylphosphonic acid, dithiophosphonic acids with amines, aminoalcohols and dithiocarbalinic acid. The large number of compounds produced are tabulated, indicating specific substituents, physical and chemical properties, formulas and IR spectra. All products were tested for growth regulation, defoliant and fungicidal properties. Some compounds exhibit high biological activity. References 25: 7 Russian, 18 Western.

USSR UDC 661.632.951

NEW DIRECTIONS IN SYNTHESIS AND UTILIZATION OF PYRETHROIDES

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IMENI D. I. MENDELEYEV in Russian Vol 23, No 2, 1978 pp 170-178

PROMONENKOV, V. K. and KOROTKOVA, O. A., All-Union Scientific-Research Institute of Chemical Plant Protective Agents

[Abstract] The search for non-toxic insecticides continues. One of the more promising groups consists of the analogues of natural pyrethrins - the so called pyrethroides. They are safe agents because they break down rapidly in the warm blooded organisms and are excreted just as rapidly. However, their synthesis is complex and therefore they are expensive. This review covers recent work in the synthetic approaches to the intermediate compounds necessary for the production of pyrethroides: chrysanthemum monocarboxylic acid (CMA) and its analogues. The ability to produce a number of such agents led to a discovery of many CMA analogues which surpassed the parent compound by their toxic and paralytic activity, while retaining low toxicity towards warm blooded organisms. References 85: 3 Russian, 82 Western.

USSR UDC 632.936

POSSIBILITIES OF PRACTICAL APPLICATION OF FEROMONES

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IMENI D. I. MENDELEYEV in Russian Vol 23, No 2, 1978 pp 179-188

KONDRAT'YEV, YU. A., LEBEDEVA, K. V. and PYATNOVA, YU. B., All-Union Scientific-Research Institute of Chemical Plant Protective Agents

[Abstract] A new methodology has been developed for the protection of enviroment and plants from various pests: control of living organisms by chemical substances. Many natural agents of chemical communication may be used to interact with living organisms and plants. Among such agents feromones play an important role. By means of such agents it is possible to control behavior of various pests, decrease their numbers and maintain the population on a safe level. This is done by luring these pests into traps, by desorienting them and by interrupting their mating. The new analytical techniques were very helpful in isolating and identifying feromones of some 42 types of insects. These agents are completely safe, since they were being excreted into the environment ever since the first insects inhabited this planet. References 184: 7 Russian, 177 Western.

USSR UDC 632.95.54.66

BASIC TENDENCIES MANIFESTED IN THE SEARCH FOR NEW PESTICIDES

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IMENI D. I. MENDELEYEV in Russian Vol 23, No 2, 1978 pp 136-142

MEL'NIKOV, N. N., All-Union Scientific-Research Institute of Chemical Plant Protective Agents

[Abstract] A review of the state of art has been given for pesticides, herbicides, insecto-acaricides and fungicides. Data have been tabulated reflecting annual expenditures for various agents, assortments of toxic agents and patents covering a variety of chemicals. In spite of this tremendous shopping list, developmental studies continue in this area, concentrating on lower toxicity, absence of teratogenic and carcinogenic effects, minimal effects on human beings chronically exposed to these agents and absence of toxic metabolites. A stress is made on higher activity coupled with specificity, on economical advantages, storage and transportation stability, non-corrosiveness and availability of inexpensive starting material. The most intensive studies are in the area of

organophosphoric compounds. Some of the more interesting novel developments are in the area of hormones and pheromones, rapidly decomposing heterocyclic compounds and in agents related to ureas and thioureas. References 61: 22 Russian, 39 Western.

USSR UDC 632.954

NOVEL SYNTHETIC PLANT GROWTH REGULATORS AND HERBICIDES

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IMENI D. I. MENDELEYEV in Russian Vol 23, No 2, 1978 pp 149-159

BASKAKOV, YU. A., All-Union Scientific-Research Institute of Chemical Plant Protective Agents

[Abstract] A review of primarily western literature covering the period from 1970 to 1977. The study is devoted to novel synthetic plant growth regulators and herbicides. The following topics have been discussed: simple and complex phenolic ethers; carboxylic acids and their simple derivatives; haloacetanilides; heterocyclic carboxylic acids and their derivatives; dinitroanilines and dinitrophenylhydrazines; onium compounds; alkyl esters of acylcarbonic acids; urea derivatives; nitrogen heterocyclic compounds; oxygen containing heterocycles, and metal organic compounds. The fact that many of these agents have rather simple structures led the author to conclude that a rescreening of the early pesticide candidates should be carried out testing for growth inhibiting properties. The development of herbicides reached the saturation point, so that the future trend will be in the direction of growth regulators and systemic fungicides. References 52: 3 Russian, 49 Western.

USSR UDC 547.953+547.455

A NOVEL APPROACH TO THE SYNTHESIS OF GLYCOPHOSPHOLIPIDS

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IMENI D. I. MENDELEYEV in Russian Vol 23, No 2, 1978 pp 220-221 manuscript received 28 Jun 77

NIFANT'YEV, E. YE., PREDVODITELEV, D. A. and SHIN, V. A., Moscow State Pedagogical Institute imeni V. I. Lenin

[Abstract] The synthesis of a novel glycerophospholipid (1,2-distearoyl-rac-glycero-3)-(D-galacto-6-)-phosphate has been described.

Hexaethyltriamidophosphorous acid was used as the starting phosphorylating substance; its three amido groups being sequentially substituted by benzyl alcohol, a sugar and by 1,2-distearoylglycerine, the unsymmetric phosphite obtained was then oxidized to a phosphate, and upon removal of the protective groups, 1,2-distearoylglycerine was obtained. All reactions took place under mild conditions with high yields at the crucial points. References 2: both Western.

USSR UDC 519.281.2:541.6:547.87

BIOLOGICAL ACTIVITY - A FUNCTION OF THE STRUCTURE. COMMUNICATION I. FREE-WILSON MODEL FOR BICYCLIC ORTHOESTERS

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IMENI D. I. MENDELEYEV in Russian Vol 23, No 2, 1978 pp 224-225 manuscript received 26 Sep 77

YEZHOV, V. V., DAN'SHIN, B. I., POTASHNIKOV, P. F. and SOKOL'SKIY, G. A.

[Abstract] The Free-Wilson mathematical model was used in an attempt to correlate the biological activity with the 1- and 4-substituents of 1R-4R'-2,6,7-trioxabicyclo[2.2.2]octanes. On the basis of this analysis, biological activity of any homologous bicyclic ester could be predicted. According to this model, the strongest activity should have been exhibited by 1-butyl-4-isopropyl-2,6,7-trioxabicyclo[2.2.2]octane, and the weakest by 1-ethyl-4-methyl substituted homologue. Analysis of the data showed however that there is no linear correlation between the 1,4-substituents and the biological activity. Accordingly, another model, such as perhaps the Hansch model, should be tried. References 3: all Western.

USSR UDC 541.67.32

REACTION OF LANTHANIDE SHIFTING REAGENTS WITH ORGANOPHOSPHORIC COMPOUNDS

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IMENI D. I. MENDELEYEV in Russian Vol 23, No 2, 1978 pp 234-235 manuscript received 18 Jul 77

GALAKHOV, I. V., VERENIKIN, O. V. and KNUNYANTS, I. L

[Abstract] PMR spectra were obtained for a series of methylphosphonic esters in presence of tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium. Upon addition of lanthanide shifting reagents,

these compounds with a chiral phosphorus atom exhibited anisochronic effect of the diastereotopic Me-groups connected with the prochiral center, appearing on the spectrum in form of two doublets. Cooling the samples to -90°C does not lead to the appearance of nonequivalence of diastereotopic nuclei; heating these compounds to 100°C does not remove the anisochronic effect, showing that the restricted internal rotation does not apply in such cases. References 3: all Western.

USSR UDC 632.934

PROMISING SYSTEMIC FUNGICIDES AND MERCURY-FREE SEED TREATING AGENTS

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IMENI D. I. MENDELEYEV in Russian Vol 23, No 2, 1978 pp 202-208

ADREYEVA, YE. I., All-Union Scientific-Research Institute of Chemical Plant Protective Agents

[Abstract] A review of a series of systemic fungicides has been reported, covering the following agents: benamyl, topsin, vitawax, piperazine derivatives, pyrimidine analogues, esters of thiocarboxylic acids, as well as derivatives of 1,2,4-triazole, tetrazole, hydantoin, thiourea, etc. New systemic fungicides and contact agents with novel mechanism of action will reduce or even eliminate adaptability of the microorganisms to these agents. Systemic fungicides show higher prophylactic activity than the contact chemicals. Because of rapid penetration into the plan, they are not affected by weather conditions and do not require uniform coverage of the entire surface being treated. To avoid the problem of adaptability, more research should be carried out on new systemic fungicides with different reaction mechanisms. References 75: 28 Russian, 47 Western.

USSR UDC 632.95.577.4

PESTICIDES AND THE PROTECTION OF ENVIRONMENT

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IMENI D. I. MENDELEYEV in Russian Vol 23, No 2, 1978 pp 208-214

MEL'NIKOV, N. N.

[Abstract] For many centuries industrial and agricultural developments were taking place at the expense of the contamination of human environment.

Only recently interest was aroused concerning this problem, especially the problem of environment contamination with chloroorganic pesticides. The author noted certain interesting facts: with increased use of the pesticides, their content in human diet and in human milk diminished considerably during the past decade. While DDT does accumulate in sheep's fat, methoxychlor does not. In spite of increased use of pesticides in the USA, there is a tendency to lower cancer incidence there. The contamination of environment with pesticides was discussed with considerably emotions in the past. Actually, when applied improperly, high toxic levels of these agents did accumulate in the surrounding atmosphere. Nevertheless, even then pesticides constitute only a fraction of the total contamination, when other sources are considered. With proper selection of chemicals and adherence to sound application methods, the accumulation of pesticides in the environment could be totally avoided. To support this, statistics have been cited showing increased numbers among wild animals in Germany, Czechoslovakia and other countries as compared to the late thirties levels. References 176: 24 Russian, 152 Western.

USSR UDC 632.95.025

SOME DIRECTIONS FOR A RATIONAL SYNTHESIS OF NOVEL ORGANOPHOSPHORIC INSECTO-ACARICIDES

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IMENI D. I. MENDELEYEV in Russian Vol 23, No 2, 1978 pp 160-169

MASTRYUKOVA, T. A. and KABACHNIK, M. I., Institute of Metal Organic Compounds

[Abstract] The empirical search for new agents which predominated in the past has to yield to some rational approaches, because it became continuously less cost-effective. There are other approaches possible, based on detailed studies of comparative physiology and biochemistry of various organisms, based on the mechanism of action, different metabolic pathways and on mathematical models. Two of the most crucial factors that must be considered in designing new agents are the specificity of action and safety to human operators. One way of achieving lower toxic effects is based on synthesis of agents which break down to subcomponents which already exist in nature. Increase in the selectivity should be based on individual approaches to specific pests, based on the following reactions: phosphatase hydrolysis, carboxyesterase hydrolysis, carboxyamidase hydrolysis, or oxidative activating modification of the already known effective insector-acaricides. Even though the science is not ready yet to design structures with specific activities, certain narrowing of possibilities is within reach. This review covers primarily

organophosphoric agents, because the authors believe that they are the most promising ones. References 49: 25 Russian, 24 Western.

USSR

UDC 632.934 + 614

CURRENT GOALS OF THE MEDICAL INVESTIGATION OF PESTICIDES AIMED AT THE SAFETY OF THEIR APPLICATION

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IMENI D. I. MENDELEYEV in Russian Vol 23, No 2, 1978 pp 123-129

MEDVED', L. I., KAGAN, YU. S., SPYNU, YE. I. and BURYY, V. S., All-Union Scientific-Research Institute of the Hygiene and Toxicology of Pesticides, Polymers and Plastics

[Abstract] The coordinate hygienic and toxicological studies of pesticides, Public Health Ministry chartered in 1954 a Committee for the Study and Regulation of the Use of Poisonous Chemicals. Then in 1964, the All-Union Scientific-Research Institute of the Hygiene and Toxicology of Pesticides, Polymers, and Plastics was organized in Kiev. The staff of this Institute drafted a set of proposals which then was officially promulgated by the Public Health Ministry in form of "Methodological Guidelines" for Hygienic Evaluations of New Pesticides. These guidelines provide precautionary measures for the investigations of all possible pathogenic properties of pesticides: toxic, cumulative, embryotoxic, gonadotoxic, mutagenic, blastomogenic and ellergenic. This paper reviews the requirements placed on modern pesticides and their toxicological and hygienic evaluation. Following aspects are being covered: physical and chemical properties; toxicity towards human and animal species; danger of acute poisoning; chronic toxicity; remote effects of pesticides and hygienic aspects of pesticide application. In spite of definite progress in the area of lowering the incidence of acute poisoning, the long term safety still needs to be studied. References 23: all Russian.

USSR UDC 632.937

SUCCESSFUL DEVELOPMENT OF AN INTEGRATED METHOD FOR PLANT PROTECTION

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IMENI D. I. MENDELEYEV in Russian Vol 23, No 2, 1978 pp 130-135

FADEYEV, YU. N. and NOVOZHILOV, K. V., All-Union Academy of Agricultural Sciences imeni V. I. Lenin

[Abstract] Introduction of pesticides provided an easy method of controlling undesirable agents in agriculture. However, it soon led to new problems connected with the toxicity of these chemicals. Currently the most effective method of controlling weeds and pests is based on the so called integrated systems of plant protection, which aim at long term protection of the surroundings by controlling weeds at a safe level. Integrated systems of plant protection utilize special agrotechnical methods of prophylaxis and suppression of the development of individual weeds and pests; cultivation of resistant varieties; preservation and activation of natural entomophages and other organisms regulating the growth of phytopathogens and weeds, and detailed analysis of agrobiocenosis prior to selection of biological or chemical agents. A number of examples has been reviewed for optimal application of various chemicals. All of these examples point out that integrated control measures should be based on a detailed knowledge of the biology and ecology of a particular culture being treated, knowledge of the surrounding fauna and specific field conditions. It should not be rigid, but dynamic, adjusting to the specific problems and our enlarging knowledge. References 25: 23 Russian, 2 Western.

USSR UDC 632.95.025.8

RESISTANCE OF ARTHROPODA AND METHODS FOR OVERCOMING THIS PROBLEM

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVY IMENI D. I. MENDELEYEV in Russian Vol 23, No 2, 1978 pp 196-201

ROSLANTSEVA, S. A., All-Union Scientific-Research Institute of Chemical Plant Protective Agents

[Abstract] The number of arthropoda strains resistant to insectoacaricides is growing continuously. This started with the chloroorganic insecticides and soon expanded to the organophosphoric agents when they replaced the ineffective organohalides. Cases of such resistance

development have been cited for a number of geographical areas, for different chemicals, and a variety of biological species. The ability to develop resistance to toxic chemicals appears to be a general biological effect observed also in other biological forms: weeds and microorganisms. The best way to avoid development of the resistance is to alternate the toxic agents used to control the pests. The chemicals have to be carefully selected, taking into consideration the cross-resistance, mechanism of action and genetic characteristics of the species population. References 151: 61 Russian, 3 Czech, 1 Polish, 86 Western.

USSR UDC 632.934 + 632.7

PESTICIDES USED TO CONTROL ARTHROPODA - CARRIERS OF HUMAN DISEASE

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IMENI D. I.
MENDELEYEV, in Russian Vol 23, No 2, 1978 pp 189-195

DERBENEVA-UKHOVA, V. P. and USPENSKIY, I. V., Institute of Medical
Parasitology and Tropical Medicine imeni Ye. I. Martsinovskiy

[Abstract] The past decade witnessed a radical change in the attempts to control arthropoda. The goal of current control measures is not total eradication of a given species over certain area, but reduction of the population to safe levels. Hence the attack centers on diminishing the reproductive potential of such pests. Such an approach necessitates a detailed study of pesticides and a search for novel agents - the so-called pestistatics. A series of pesticides has been discussed: DDT, metoxychlor, hexachlorocyclohexane, dichlorophos, and other organophosphoric agents. Among the pesticides, the authors reviewed growth regulators and agents controlling physiological development (derivatives of juvenile hormone), chemical sterilants and sex attractants. References 136: 44 Russian, 92 Western.

USSR UDC 547.996:632.936.2

A NEW SYNTHESIS OF DISPALURE -- A GYPSY MOTH (PORTHETRIA DISPAR) SEXUAL ATTRACTANT

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 239, No 6, 21 Apr 78 pp 1377-1380 manuscript received 12 Dec 77

TOLSTIKOV, G. A., ODINOKOV, V. N., GALEYEVA, R. I., BAKEYEVA, R. S. and RAFIKOV, S. R., Institute of Chemistry, Bashkirskiy Branch, Academy of Sciences USSR, Ufa

[Abstract] A simple new synthesis for disparlure, Z-7,8-epoxy-2-methylactadecane, with no steps requiring stereochemical control, has been developed. Z,Z-1,5-cyclooctadiene is subjected to selective ozonolysis with the aid of $NaBH_4$ to produce the diol, which is brominated with PBr_3, reacted with heptyl- and then isobutylmagnesium bromide and the epoxide formed by reaction with monoperphthalic acid. A yield of 25% was obtained. Structures were confirmed by IR, mass spectrometry and PMR. The preparation obtained demonstrated attractant activity for male gypsy moths in field trials identical to that of a known sample of disparlure. Extraction and alumina column chromatography were used for product purification and GC on 15% Apiezon L for analysis. References 14: 7 Russian, 7 Western.

USSR UDC 678.686-404.9.004

NEW COLD-CURING EPOXY ADHESIVES AND THEIR USE IN THE ECONOMY

Moscow PLASTICHESKIYE MASSY in Russian No 4, 1978 pp 52-53

KRUGLOV, B. I., BABICH, T. S., KULIK, T. A., and SIMONOV, V. A.

[Abstract] Types UP-5-177 and UP-5-177-1 epoxy adhesives can cure in water or on moist surfaces. These adhesives consist of modified epoxy resins plus a special curing agent, UP-5-159, which is insoluble in water and compatible with epoxy resins. These adhesives have good adhesion strength following curing in air or in water. They are already in use for the repair of parts of ships and other metal products which will be exposed to water. A series of similar adhesives has been developed, and their characteristics are presented. Curing time varies with the type of curing agent used. Service life is over 5 years with a constant static load of up to 262 kgf/cm^2.

USSR UDC 678.686.004

NEW EPOXY MATERIALS

Moscow PLASTICHESKIYE MASSY in Russian No 4, 1978 pp 51-52

KRUGLOV, B. I., SOLONITSYNA, V. A., KOSMYNIN, V. V., VEYKSHA, S. S., and SHOSTIK, G. S.

[Abstract] The use of epoxy compounds is expanding. Compounds such as types UP-592-10, UP-592-10/1 and UP-5-105-1A are used for insulation of pipes, finishing of cracks, sealing of instruments, and production of anticorrosion coatings. The physical, mechanical and electrical properties of cured epoxy compounds are presented. The use of compounds type UP-503A and UP-503B can increase the reliability and durability of electronic and electrical equipment operating at high temperatures. These single-component, fast-curing epoxy compounds are produced by combining ED-20 and ED-16 resin with a latent curing agent. They have low viscosity at their usage temperatures of 80-100 C, but cure rapidly at 180-200 C (2-3 hours).

USSR UDC 678.743.22.004.14(045)

METALLOPLAST -- A NEW STRUCTURAL MATERIAL

Moscow PLASTICHESKIYE MASSY in Russian No 4, 1978 pp 50-51

OVCHINNIKOV, YU. V., STESIKOV, V. P., CHERKASHIN, YE. N., CHANTSEVA, A. S., PARFENOVA, T. N., SHUMNAYA, V. A., BAKANOV, S. I., KOKHNO, YU. A., GELLER, YE. M., ZASLAVSKAYA, O. B., SHTEKHNO, O. N., MOVSHCHOVICH, V. S., and SULIZ, V. G.

[Abstract] The most progressive method of corrosion protection is application of protective polymer coatings to metals. The combination of a metal with a polymer coating actually produces a new material -- a metalloplast -- with the high strength and rigidity of the metal and the corrosion-resistant and decorative properties of the polymer. The areas of application of various metalloplasts are determined primarily by the properties of the polymer films. At present, PVC films have been developed for general purpose metalloplasts. These films are nontoxic, chemically stable and have high strength. Metalloplast can be used to replace stainless steel in the manufacture of ventillation system ducts for galvanic chemical production shops. The basic physical and chemical characteristics of the films (0.2-0.3 mm thick) are presented. Higher-strength films have been developed for use in the machine-building industry.

USSR UDC 536.7:546.791.4'131

ENTHALPY OF THE FORMATION OF URANIUM TETRACHLORIDE

Leningrad RADIOKHIMIYA in Russian Vol 20, No 2, 1978 pp 211-213
manuscript received 2 Nov 76

SUGLOBOVA, I. G. and CHIRKST, D. E.

[Abstract] Uranium tetrachloride can be obtained in highly purified state and therefore is used widely as a standard. In the past the enthalpy of its formation has been determined independently by four investigators to be 251.2 ± 0.3 kcal/mole. Recently a quite different value was reported, throwing some doubt on the earlier measurements; the new value was 243.6 ± 0.6 kcal/mole. This paper reports yet another determination, to clarify the matter. The enthalpy of the formation of uranium tetrachloride was determined by measuring the heats of solution of 0.005 M Na_2SiF_6 and $1.5 \cdot 10^{-6}$ M H_2PtCl_6 in 4 M HCl, saturated with argon. Precautions were taken to avoid oxidation with air oxygen. On the basis of the experimental data the enthalpy of the formation of uranium tetrachloride was established to be 251.4 ± 1.0 kcal/mole. References 10: 2 Russian, 8 Western.

USSR UDC 542.61:546.791

EXTEACTION OF SULPHITE COMPLEXES OF URANIUM (VI)

Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 23, No 1, Jan 78
pp 126-129, manuscript received 15 Sep 76

SHEVCHUK, I. A., PALIY, A. I. and BUTYUGIN, A. V., Donetsk State University

[Abstract] A study was made of the extraction of sulphite complexes of uranium (VI). Sulphite-acid complexes of uranium at pH 3-6 are more completely extracted than sulphate complexes. Methods of equilibrium shift and analysis of the organic phase are used to establish the composition of the extracting associate. The log of the extraction constant is 3.09 ± 0.09. Uranium is extracted from sulphite solutions by chloroform solutions of secondary amines with a long alkyl chain. Figures 4; table 1; references: 3 Russian.

USSR UDC 628.16.081.9

WATER DEMINERALIZATION BASED ON THE USE OF COUNTERCURRENT ION EXCHANGE COLUMNS WITH HIGH SPECIFIC EFFICIENCY

Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 51, No 1, Jan 78
pp 96-100 manuscript received 2 Feb 77

MEDVEDEV, G. A., GORSHKOV, V. I., MURAV'YEV, D. N., FERAPONTOV, N. B., and KASPAROVA, O. O., Moscow State University imeni M. V. Lomonosov

[Abstract] The conventional method for water demineralization employs stationary ion exchange resin columns. In this study countercurrent upward movement of the solution was employed, coupled with periodic lowering of the ion exchange resin column and removal of the spent layer. The upward movement of the solution kept the column pressed against the filter on top of the column; stopping the solution flow lowered the resin column for the removal of spent material. The system has been described in detail. The countercurrent columns showed definite advantages over the stationary ones: continuous flow, simple control and automation, smaller operational area and less resin used per operation. In general, the countercurrent process is also economically more advantageous. Figures 2; references 4: 3 Russian, 1 Western.

USSR UDC 663.631:621.57

CRYSTALLIZATION METHODS OF DESALINIZATION OF SEA AND BRINE WATERS AND PURIFICATION OF WASTE WATER

Kiev VISNYK AKADEMIYI NAUK UKRAYINS'KOYI RSR in Ukrainian No 2, 1978
pp 41-54

ALEKSEYEV, V. P. and SMIRNOV, L. F.

[Abstract] The problem with desalinization is mainly one of economics. In the USSR, the cost per cubic meter of ordinary tap water is from 3 to 8 kopecks. In contrast, the cost per cubic meter of desalinized water in operational or planned distilling units is 45 to 76 kopecks. Of the many methods which are suitable for industrial use (distillation, electrodialysis, reverse osmosis and crystallization), the least economical method is crystallization. Electrodialysis and reverse osmosis are primarily suitable for desalinizing slightly saline water (about 0.5%). Methods of distillation (evaporation, adiabatic boiling, steam compression distillation, freezing) are the most highly developed. The crystallization process follows this pattern: 1. crystals of ice or hydrates are formed; 2.

crystals are separated and washed from solution; 3. crystals are melted. Soviet distillation apparatus is compared with units produced by such US manufacturers as Struthers, Blau-Knox, IDE, AVCO, Syracuse University, Koppers, etc. References 22: 9 Russian, 13 Western.

USSR UDC 613.32:547.412.721.4

HYGIENIC STANDARDIZATION OF TETRACHLOROPROPENE IN WATER RESERVOIRS

Moscow GIGIYENA I SANITARIYA in Russian No 4, 1978 pp 15-18 manuscript received 30 Jun 77

FEDYANINA, V. N., PAVLENKO, M. N., KURYSHEVA, N. G., EZROKH, T. I., and RAMUL', N. YU., Novosibirsk Scientific-Research Institute of Sanitation

[Abstract] Tetrachloropropene (TCP), a widely used chemical in polymer synthesis, affects the taste of water in higher concentrations. Its odor can be detected at 0.17 mg/l. TCP is a moderately toxic agent; its LD_{50} for rats is 1070 mg/kg and for mice 800 mg/kg. Clinically, the central nervous system is affected by TCP and dystrophic changes are observed in the liver. The cumulative effect of TCP was moderate; changes were observed in the activity of alanine aminotransferase and oxidase. In acute experiments doses of 1/2 LD_{50} exhibited strong inhibitory activity towards all endoplasmatic reticulum enzymes. On the basis of the experimental data obtained, the maximum permissible dose of TCP was established at 0.2 mg/l. References 3: all Russian.

USSR UDC 613.32:[628.162.96:546.621

HYGIENIC JUSTIFICATION FOR THE MAXIMUM PERMISSIBLE RESIDUAL QUANTITY OF A NEW REAGENT IN DRINKING WATER - ALUMINUM CHLOROXIDE

Moscow GIGIYENA I SANITARIYA in Russian No 4, 1978 pp 12-15 manuscript received 22 Apr 77

KOROLEV, A. A. and KRASOVSKIY, G. N., I Moscow Medical Institute imeni I. M. Sechenov

[Abstract] Aluminum chloroxide (ACO) is a new reagent for treating drinking water; this study aimed at the determination of maximum

permissible dose for ACO. The LD_{50} of ACO was 5200 mg/kg for mice, 4320 mg/kg for rats and 5430 mg/kg for guinea pigs. It did not exhibit cumulative activity. In chronic experiments doses of 1 mg/kg showed no effect on test animals. When 10 mg/kg dose was used, changes were observed in the activity of alkaline phosphatase and transaminase. Some gonadotoxic activity was manifested and the condition-reflex activity was affected. Overall, a 1.5 mg/l dose has been recommended as the maximum permissible level. References 5: all Russian.

USSR UDC 614.777:351.777.613.12:547.233

HYGIENIC STANDARDIZATION OF CHLOROCHOLINE CHLORIDE IN WATER RESERVOIRS

Moscow GIGIYENA I SANITARIYA in Russian No 4, 1978 pp 8-12 manuscript received 31 Oct 77

VASILENKO, V. YE., I Moscow Medical Institute imeni I. M. Sechenov

[Abstract] Chlorocholine chloride (CCC) is a plant growth regulator promoting grain growth under poor weather conditions. It is a microcrystalline, hydroscopic material soluble in water and quite stable in aqueous medium. Its odor can be detected in 4 mg/l concentrations, its taste - at 5 mg/l. CCC slows down biochemical processes of oxygen consumption and depress saprophytic microflora. The LD_{50} of CCC ranges from 410-47- mg/kg for rats, mice and guinea pigs. It has a cumulative action although no deaths were observed among the experimental animals. On the basis of sanitation-toxicological experiments, the maximum permissible level of CCC in water has been set at 0.2 mg/l. Figure 1; references 13: 12 Russian, 1 Western.

USSR UDC 621.359.7:541.183.7:546.212

ELECTROSORPTIVE AND FILTRATION METHODS OF WATER DESALINATION

Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian No 10, 1977 pp 2211-2216 manuscript received 4 May 76

KROKHV. V. V.

[Abstract] Three methods of water desalination in conventional installations are described: electrosorptive, mixed ion-exchange/electrosorptive and filtration. The plastic column in the electrosorptive method passes

purified solution successively through two upper chambers filled with activated charcoal electrically charged from the outside. Column dimensions are: diameter 12.8 cm; height 50 cm; chamber height 16 cm. The electrode spacing is 11 cm. Multiple repetition of the electrosorption-desorption-scrubbing cycle desalinates the solution to a high degree. A modification of this method is the plastic four-section electrosorptive column: multilayer capron netting sections the column into four parts. Electrosorption occurs in one section, while desorption of ions with recharging of the electrosorbent takes place in the next section. The four-section interior, turning at 500-600 rpm, feeds relatively desorbed water through valves at the bottom. Other modifications are presented. The electrosorbent is activated charcoal plus deferruginated coarse-grained KSK silica gel. Efficiency ratings for the methods are given: from 1.7 g/(hr•kg of sorbent) to 0.14 g/(hr•kg), calculated for the removal of tetraethylammonium chloride. References 5: Russian.

USSR UDC [66.061.8:532.712](047)

OSMOTIC EXTRACTION OF A SOLVENT - A NOVEL METHOD FOR WATER DESALINATION AND FOR CONCENTRATION OF SOLUTIONS

Moscow KHIMICHESKAYA PROMYSHLENNOST' in Russian No 3, 1978 pp 188-191

KUL'SKIY, L. A., KNYAS'KOVA, T. V. and ZARITSKIY, YE. G.

[Abstract] The authors reviewed a number of western literature references on water desalination methods, mostly of U.S. origin. Evidently none were covered in the Soviet literature as yet. Principal schematics for the osmotic solvent extraction process have been analyzed, pointing out suitable extracting solutions and methods for the removal of the solvent. The osmotic method is based on the passage of a solvent through a semipermeable membrane into the extracting solution with a higher osmotic pressure, followed by separation of the solvent and of the extracting solution. The method is potentially applicable in many situations, from water desalination to regeneration of expensive reagents. Figures 3; references 18: all Western.

USSR UDC 532.71:66.066.6

THE ADDITIVE PROPERTY OF PERMEABILITY OF GAS-SEPARATION MEMBRANES

Moscow TEORETICHESKIYE OSNOVY KHIMICHESKOY TEKHNOLOGII in Russian No 2, Mar/Apr 78 pp 285-286 manuscript received 1 Jun 76

VOLGIN, V. D., POLYAKOV, S. V. and SHADRIN, L. G., Moscow Institute of Chemical Machine Building

[Abstract] It is often assumed that the permeability of membranes with respect to gas mixtures can be calculated by addition of the permeabilities for the individual components. However, this has not yet been proven. A study was made of the separating effect of polyvinyltrimethylsilane membranes for mixtures of nitrogen, carbon dioxide and helium with oxygen. Two-layer membranes were used with a pressure difference of 700 mmHg, created by a vacuum pump. It was found that the permeability of polymer membranes does not follow equations derived from the assumption of simple diffusion. Tables 2; references 4: 2 Russian, 2 Western.

USSR UDC 541.182.65:66.076.3:11:539.141

STUDY OF PROCESSES OF SEEPAGE OF COLLOIDAL AND BIOLOGICAL SUSPENSIONS THROUGH NUCLEAR FILTERS

Moscow KOLLOIDNYY ZHURNAL in Russian No 1, Jan/Feb 78 pp 59-62 manuscript received 14 Oct 76

MCHEDLISHVILI, B. V., BRESLER, S. YE., KOLIKOV, V. M., MOLODKIN, V. M., FLEROV, G. N., BARASHENKOV, V. S., TRET'YAKOVA, S. P., SHCHEGOLEV, V. A., KOZLOVA, T. I., AKSENOVA, T. A., and KOROLEV, M. B., Polytechnical Institute imeni Kalinin, Leningrad, Joint Institute for Nuclear Research, Dubna, and Institute of Poliomyelitis and Viral Encephalitis, Academy of Medical Sciences, USSR, Moscow

[Abstract] Results are presented of a study of the structure and filtration properties of nuclear filters, their permeability and selectivity. Methods of their sterilization and regeneration are also analyzed. Filters made of lavsan film 10-12 μm in thickness were studied. The film was bombarded with xenon or argon ions accelerated in the U-300 cyclotron of the Nuclear Reactions Laboratory at JINR. The pore diameter varied between 0.05 and 3.1 μm. Analysis of the curves of distribution of pore sizes indicates the possibility of organizing a highly effective process of separation and concentration of colloidal solutions if the variation in pore size can be kept between 1 and 5%. Experiments involved filtration of solutions of latexes and viruses confirm this possibility. Tables 2; figures 4; references 4: 3 Russian, 1 Western.

USSR

CENTENNIAL ANNIVERSARY OF THE BIRTH OF PROFESSOR I. P. LOSEV

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IMENI D. I. MENDELEYEV in Russian Vol 23, No 2, 1978 p 215

PRESIDIUM OF THE ALL-UNION CHEMICAL ASSOCIATION IMENI D. I. MENDELEYEV

[Abstract] Professor I. P. Losev, one of the most distinguished scientists in the area of the chemistry of high molecular compounds, was born on 16 January 1878. He worked at the Moscow Chemical-Technological Institute imeni D. I. Mendeleyev from 1923 to his death. From 1932, I. P. Losev chaired the department of the Technology of Organic and Metal Organic High Molecular Weight Compounds. He was the first in the USSR to initiate studies on the synthesis of polyurethanes, polycarbonates and on ion exchange resins. In his work, he was able to combine research studies with industrial developments in the field of plastics. He was active in the revolutionary movement from 1906 on. He received a number of the USSR medals for his scientific contributions. His name will always be remembered warmly.

USSR

IN HONOR OF THE 80TH ANNIVERSARY OF THE BIRTH OF BORIS ARISTARKHOVICH DOGADKIN, 20 MARCH 1898-13 OCTOBER 1977

Moscow KOLLOIDNYY ZHURNAL in Russian No 1, Jan/Feb 78 pp 184-187

THE EDITORS OF THE KOLLOIDNYY ZHURNAL, The Department of Polymer Chemistry and Physics of the Moscow Institute of Precision Chemical Technology imeni M. V. Lomonosov

[Abstract] B. A. Dogadkin was well-known both in the Soviet Union and abroad. He was the author of textbooks on the chemistry and physics of rubber and elastomers, and a scientific researcher for 50 years. Dogadkin was the initiator of Soviet studies on emulsion polymerization and the inventor of an industrial method of the production of synthetic latex. His work covered practically the entire area of the chemistry and technology of elastomers, from the synthesis of rubber to the development of the physical and chemical principles of processes of treatment of elastomers and the study of their structure and properties. In recent years, Dogadkin suggested that vulcanization be considered a multistage, microheterogeneous colloid chemical process. He also studied the mechanism of structuring of rubber under the influence of alkylphenol

derivatives and polyhalides. His work represents a fundamental contribution to the theory and practice of vulcanization. A cycle of work performed by Dogadkin and others led to the discovery of the now widely known regularities of the fatigue endurance of rubber. He was one of the first researchers to use methods of manufacture of products directly from latexes. The name of Professor Dogadkin is connected with an entire era in the development of science and the industry of processing of polymers.

USSR

TO THE MEMORY OF STEPAN NIKOLAYEVICH DANILOV

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 48, No 4, Apr 78 pp 947-949

ANIKEYEVA, A. N., PLISKO, YE. A., LAZAREV, S. YA. and ALIYEVA, G. S.

[Abstract] Death came on 4 February 1978 to 90-year-old Prof., Dr. Chem. Sci., S. N. Danilov, chief editor of this journal, 1914 graduate of St. Peterburg's University and recipient of RSFSR, TatarASSR and USSR honors. He taught at Leningrad and, during WWII, in Kazan. He was an organic chemist who made major contributions in the field of cellulose and high molecular weight compounds. His editorial association with this journal lasted from 1946 to the end of his life. He was mentor for more than 100 candidate and doctorate dissertations; over 1000 specialists owe him a debt of gratitude for his teaching and inspiration. Over 40 of his publications deal with the history of the nation's chemical effort.

USSR UDC 547.7

SIXTH INTERNATIONAL CONGRESS ON THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

Riga KHIMIYA GETEROTSIKLICHESKIKH SOYEDINENIY in Russian No 3, 1978
pp 419-421

YAKHONTOV, L. N.

[Abstract] Brief abstracts are presented of some of the reports given at the Sixth International Congress on the Chemistry of Heterocyclic Compounds held 9-13 June 1977 in Teheran at the College of Pharmacy of Teheran University. The reports include a talk by G. Rapoport on the possibility of stereospecific synthesis based on optically active amino acids, a report by J. Kutni on synthetic studies in the series of alkaloids exhibiting effectiveness in the clinical treatment of malignant neoplasms, a report by G. Shantavi on new synthetic studies in the series of benz(a) and indolo [2,3-a] quinolysidines connected, in particular, with a new approach to the complete synthesis of reserpin, a report by R. Schmidt on carbane ion heterocyclic systems discussing the 8 π-electron heterocycles forming certain anions, the report by M. Protiva on studies aimed at finding new psychotropic compounds in the series of dibenzo [b, f] thiepines and their analogs, L. Townsend on the relation of the structure and biological activity in the series of aza, desaza and aza-desazaguanines and hypoxanthins and also their β-D-ribofuranosides, the report by K. Potts on the development of the chemistry of heterocycles containing nitrogen and phosphorus as heteroatoms, the report by I. Lalezari on the synthesis of polyazasteroids, selenoazasteroids, and so on, the report by P. Kazulokos on obtaining thiazolo and thiadiazolosteroids, the report by R. Moffet on finding psychotropic compounds in the series of benzdiazepines, M. Zhinich on finding new psychotropic compounds in the benzdiazepine series, a report by Kochetkov on the fluorescent tagging of nucleotides based on the reaction of aminopurines and aminopyrimidines with chloracetaldehyde and related compounds. The seventh international congress on the chemistry of heterocyclic compounds is planned for 1979 in Florida.

YUGOSLAVIA UDC 615.9:547+577.1

THE CHEMISTRY AND BIOLOGY OF AMANITE TOXINS

Zagreb KEMIJA U INDUSTRIJI in Serbo-Croatian No 12, 1977 pp 673-679
manuscript received 14 Feb 77

WIELAND, THEODORE, The Max Planck Institute for Medical Research, Heidelberg

[Abstract] The poisonous amatoxins and phallotoxins in fungi Amanita phalloides and other fungi in the Amanita genus are discussed. On the molecular level, amatoxins are a group of bicyclic octopeptides causing progressive liver and kidney damage in mice, then death in a hepatitic coma, total degeneration of the liver parenchyma and necrosis of tubules. The chemistry and correlation between the structure and toxicity of amatoxins are discussed, with the indication that a sulphur-bearing bridge is a key to the toxicity and that a lateral chain in the molecular structure causes the toxicity. Methods for inhibiting toxicity are discussed. Phallotoxins are heptapeptides that cause rapid death in mice when applied intraperitoneally, are shown to be secondary to the effects of the fungus since they do not absorb well in the gastroduodenal tract. Aspects of the toxicology and chemistry of phallotoxins are discussed. With chemical alterations toxicity was eliminated. Both toxins form a firm bond with certain albumins, but a covalent bond does not develop. Figures 7; references 24: all Western.

HUNGARY UDC 622.276.654(439):66.023

REACTOR TYPES USED FOR THE DEVELOPMENT OF OIL RECOVERY BY IN SITU COMBUSTION

Budapest MAGYAR KEMIKUSOK LAPJA in Hungarian Vol 33, No 2-3, 1978 pp 138-147

KASSAY, Arpad, Industrial Research Laboratory for Petroleum and Natural Gas Mining (OGIL), Budapest

[Abstract] Studies carried out at the OGIL aimed at characterization of the in situ combustion method are described. Chemical reactors are suitable for these studies. However, the process can only be approximated since it takes place in a porous medium, heat transfer occurs both by conduction and convection, a large combustion front moves in three immiscible media (oil, water and gas), and since there is both evaporation and condensation of oil and water. Preliminary studies indicate that combustion-tube reactors are the most suitable reactor types for the study. Various types of such reactors were developed by the OGIL for the NIM [Ministry of Heavy Industry] since 1969. The design criteria and the methods of study are described. The two approved reactors are adiabatic and heat-loss types. The tests described dealt with the liquid-state oxidation of hydrocarbons at temperatures of up to 260°C. The article also described briefly the reactor instrumentation (for the measurement and recording of the temperature, pressure, through-put velocity of the gases, and the specific gravity of the oil produced). Commercial instruments were used throughout. Figures 6; tables 3; references 35: 2 Hungarian, 5 Russian, 28 Western.

CSO: 1841

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