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USSR Report

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ADSORPTION

UDC 541.183

METHANE ADSORPTION ON ZEOLITE NAX AT SUB-CRITICAL AND SUPER-CRITICAL TEMPERATURES

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 5, May 85 (manuscript received 9 Feb 84) pp 974-978

CHKHAIDZE, E. V., FOMKIN, A. A., SERPINSKIY, V. V. and TSITSISHVILI, G. V., Institute of Physical Chemistry, USSR Academy of Sciences, Moscow

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[Abstract] Measurement of CH 4 adsorption on zeolite NaX in a pressure interval from approximately 0.1 Pa up to approximately 20 MPa and a temperature range from 120 K up to 600 K showed that adsorption isosteres are linear in these pressure and temperature intervals. Adsorption isosteres are interrupted at the pressure line of saturated methane vapor and then continue linearly in the super-critical region. The first adsorbed molecules at sufficiently low temperatures are adsorbed on deep potential wells, naturally realizing a Langmuir model of adsorption on the zeolite. Figures 6; references 16: 8 Russian, 8 Western. [299-2971]

ALKALOIDS

UDC 547.94:543.51

MASS SPECTROMETRIC STUDY OF NEW ALKALOIDS OF FAMILY LILIACEAE

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 1, Jan-Feb 85 (manuscript received 19 Dec 83) pp 3-11

TIMBEKOV, E. Kh. and SADYKOV, A. S., Order of Friendship of the Peoples Institute of Textile and Light Industries imeni Yudash Akhunbabayev, Tashkent

[Abstract] A review of research conducted on Colchicum L. and Merendera Ramond of the family Liliaceae and tropolone alkaloids covers basic methods of fragmentation, analytical indicators of the individual structural types and the dissimilarities due to the disposition of functional groups, substituents and degree of unsaturation of the separate rings. Despite the structural differences of these alkaloids, mass spectrometry may be successfully used to determine structural type as well as the individual elements of the structure. Figures 8; references 28: 22 Russian, 1 Czech, 5 Western. [288-12765]

UDC 547.944/945

ALKALOIDS OF HAPLOPHYLLUM PERFORATUM

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 2, Mar-Apr 85 (manuscript received 6 Nov 84) pp 273-274

RAZAKOVA, D. M., BESSONOVA, I. A. and YUNUSOV, S. Yu., Order of Labor Red Banner Institute of Chemistry of Plant Substances, UzSSR Academy of Sciences, Tashkent

[Abstract] Previously, scimmianine, evocsine, perfamine, flindersine, haplamine and lignane eudesmine alkaloids were detected in the above-ground portion of haplophyllum perforatum gathered during the budding stage and at the start of flowering. In the present work, scimmianine, flindersine, haplamine, exocsine and eudesmine were detected in the same portions of the same plant gathered during the end of the flowering stage. References 5: 4 Russian, 1 Western. [289-12765]

UDC 947.944/945

ALKALOIDS OF HYOSCYAMUS PUSILLUS

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 2, Mar-Apr 85 (manuscript received 26 Nov 84) p 274

ARIPOVA, S. F., Order of Labor Red Banner Institute of Plant Substances, UzSSR Academy of Sciences, Tashkent

[Abstract] A study of the alkaloid composition of hyoscyamus pusillus L. Sp. pl. (henbane) showed that this plant contains hyoscine, hyoscinamine and apohyoscine. Although this plant grows widely in Central Asia, this was the first time that the above-ground portion was studied for alkaloid content. Reference 1 (Russian). [289-12765]

ANALYTICAL CHEMISTRY

UDC 665.61.033.55:543.42

DETERMINATION OF VANADIUM AND NICKEL IN GAS OIL FRACTIONS BY ATOMIC ABSORPTION SPECTROSCOPY

Moscow NEFTEKHIMIYA in Russian Vol 25, No 2, Mar-Apr 85 (manuscript received 10 Apr 84) pp 159-162

ZAMILOVA, L. M., BIKTIMIROVA, T. G. and SOKOLOVA, V. I., Bashkir Scientific Research Institute of Oil Refining

[Abstract] Flameless atomic absorption spectroscopy was employed for the determination of vanadium and nickel in gas oil fractions obtained from Astrakhan and Western Siberian crude, shortening the time of analysis 5-to 10-fold. For the selection of optimal analytical conditions, trials were conducted with combustion temperatures of $600-1000^{\circ}$ C, below the atomization temperatures of 2600° C for vanadium and 2400° C for nickel. Systematic errors due to metal admixtures were eliminated by conducting combustion at 1000° C or by the use of a deuterium label. Recovery studies demonstrated that the lower limit of vanadium detection (10 g sample adjusted to 25 ml with xylene) was 5 x 10^{-6} %, and for nickel 2.5 x 10^{-6} %. The standard curves were reproducible, indicating that hydrocarbons and other metals did not significantly affect the results and that any analyzed oil product can serve for the construction of standard curves. Figures 1; references 12: 1 Czech, 7 Russian, 4 Western. [284-12172]

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UDC 546.664

LUMINESCENCE OF DYSPROSIUM IN YTTRIUM ORTHOBORATE

Kiev DOKLADY AKADEMII NAUK UKRAINSKOY SSR: SERIYA B. GEOLOGICHESKIYE, KHIMICHESKIYE I BIOLOGICHESKIYE NAUKI in Russian No 4, Apr 85 (manuscript received 19 Jul 84) pp 50-52

DOTSENKO, V. P., YERMAKOVA, S. V., YEFRYUSHINA, N. P. and ZHIKHAREVA, Ye. A., Physical-Chemical Institute, UkSSR Academy of Sciences, Odessa

[Abstract] Yttrium orthoborates activated by dysprosium- $Y_{1-x}Dy_xB0_3$ -were prepared by sintering their oxides with boric acid, first at 900° C for 2 hours and then at 1200° C for 2-3 hours. Dy concentrations were x = 10^{-5} to 10^{-1} at. fraction. The spectra of luminescence for photoand x-ray excitation were similar, with two groups of lines in the regions 450-490 nm and 560-590 nm, caused by transitions of ${}^{4}F_{9/2}$ to ${}^{6H}_{15/2}$ and ${}^{6H}_{13/2}$ respectively. For Dy³⁺, energy migration accounts for part of the concentration quenching, along with direct donor-acceptor reactions by dipoledipole mechanisms. No shifts or new groupings were noted within the Dy concentration range above. The macroparameter of the quenching (γ) was graphed, allowing calculation of the microparameter, C_{da} = 18 x 10^2 (A6/mks). Figures 4; references 5: 4 Russian, 1 Western. [271-12672]

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BIOCHEMISTRY

UDC 547.964.4

NOVEL STRUCTURAL ANALOG OF HUMAN INSULIN: ASPARTYL-B³⁰-INSULIN

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 4, Apr 85 (manuscript received 12 Jun 84) pp 948-949

SHVACHKIN, Yu. P., NIKITINA, A. M., FUNTOVA, S. M., KRASNOSHCHEKOVA, S. P., FEDOTOV, V. P. and IVANOVA, A. I., Institute of Experimental Endocrinology and Hormone Chemistry, USSR Academy of Medical Sciences, Moscow

[Abstract] A previously-undescribed analog of human insulin--aspartyl- B^{30} insulin--has been synthesized by a combination of enzymatic and chemical techniques. The essential steps consisted of replacement of the threonine moiety at B^{30} by aspartic acid, using trypsin transamidation of porcine insulin, and chemical removal of protective groups. Convulsive trials conducted on mice showed that the analog possessed 100% of the biological activity of an international standard. References 2: 1 Russian, 1 Western. [282-12172]

UDC 547.926+577.17

BIOLOGICAL ACTIVITY OF PHYTOECDISTEROIDS AND THEIR DERIVATIVES IN IN VITRO TESTS ON DROSOPHILA MELANOGASTER CELLS

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 2, Mar-Apr 85 (manuscript received 25 Apr 84) pp 223-226

KRAMEROV, A. A., POLUKAROVA, L. G., MUKHA, D. V., GVOZDEV, V. A., GOROVITS, M. B. and ABUBAKIROV, N. K., Order of Labor Red Banner Institute of Chemistry of Natural Substances, UzSSR Academy of Sciences, Tashkent

[Abstract] A study of the specific biological activity of several natural ecdisteroids and their derivatives obtained from plants growing in Central Asia shows that they only slightly inhibit cell growth and do not initiate metamorphosis in imago discs. Apparently, the specific biological activity of ecdisteroids depends on the availability of hydroxyl groups reacting with the receptors. References 15: 8 Russian, 7 Western. [289-12765]

CATALYSIS

UDC 547.534.2'021/023:542.952:661.862.65:546.161

ISOMERIZATION OF ALKYL AROMATIC HYDROCARBONS ON ALUMINOSILICATE CATALYST MODIFIED WITH NI AND Cu COORDINATION COMPOUNDS

Moscow NEFTEKHIMIYA in Russian Vol 25, No 2, Mar-Apr 85 (manuscript received 28 May 84) pp 163-166

KOZLOV, N. S., OSINOVIK, Ye. S., PRYAKHINA, N. Ya., SEN'KOV, G. M. and GORBATSEVICH, M. F., Institute of Physico-organic Chemistry, Belorussian SSR Academy of Sciences

[Abstract] An assessment was made of the effects of addition of Cu[BF4] or Ni[SiF₆] to aluminosilicate on the isomerization of several alkyl aromatic hydrocarbons (benzene, toluene, ethylbenzene, trimethylbenzyme and o-, p- and m-xylene) at 273°K under atmospheric pressure in hydrogen. Modification of the catalyst was shown to increase its efficiency in isomerization, with 0.5-2.0% Cu[BF4] increasing the target product of p-xylene 5.1-5.7%. In the presence of high concentrations (10%) of Ni[SiF₆] an undesirable increase in toluene prevails as a result of demethylation of xylenes, while with 1% Ni[SiF₆] the p-xylene yield from the alkyl aromatic hydrocarbons increases by 9.1% over unmodified aluminosilicate. The data indicate that the presence of [BF₄]⁻ or [SiF₆]⁻ anions on the surface of the catalyst enhances the efficiency of aluminosilicate in isomerization reactions, with the formation of p-xylene proceeding primarily as isomerization of m-xylene. References 17: 2 Polish, 10 Russian, 5 Western. [284-12172]

UDC 547.31:542.941.7:546.74

ACTIVITY OF NICKEL CATALYSTS IN LIQUID-PHASE HYDROGENATION OF 1-HEXENE

Moscow NEFTEKHIMIYA in Russian Vol 25, No 2, Mar-Apr 85 (manuscript received 4 Jun 84) pp 167-171

KUZNETSOVA, N. N., DOBROSERDOVA, N. B., MALAKHOVA, N. V. and LUNIN, V. V., Moscow State University imeni M. V. Lomonosov

[Abstract] Nickel catalysts prepared by different methods were tested for their efficiency in liquid-phase hydrogenation of 1-hexene, employing previously described techniques [Dobroserdova, NB, et al., Neftekhimiya, 23(2): 172-176, 1983]. Kinetic data obtained with Raney nickel, ZrNi, HfNi and Ni/ZrO₂ showed that the highest specific activity was exhibited by ZrNiH_{2.8}. The hydrogen of the hydride phase was largely uninvolved in olefin hydrogenation at room temperature, with its primary function limited to forming active catalytic surface sites. Analysis of the kinetic data in relation to oxidation-reduction treatment used to form the intermetallic hydrides demonstrated that activity was predicated on hydride component of the catalyst. Loss of activity with time appears to be due to ordering of the surface microstructure and disappearance of defects with the assumption of an equilibrium state. References 12 (Russian). [284-12172]

UDC 547.313:542.941.7:66.094.173

HYDROGENATION OF 1-HEXENE IN BENZENE ON MODIFIED Pt/A1203 CATALYSTS

Moscow NEFTEKHIMIYA in Russian Vol 25, No 2, Mar-Apr 85 (manuscript received 2 Apr 84) pp 172-175

MARYSHEV, V. B., GRISHCHENKO, A. V., ZHARKOV, B. B., POLYAKOV, A. A. and FEDOROV, V. S., All-Union Scientific Research Institute of Petrochemical Processes, Leningrad

[Abstract] Studies were conducted on the regulation of the selectivity of Pt/Al₂O₃ catalysts in the hydrogenation of 1-hexene in benzene by the addition of a second metal (Cd, Cu, Pb, Sn) to create bimetallic catalysts. Analysis of the catalytic efficiencies at 180°C under 1.5 MPa hydrogen with a 1-hexene:benzene:octane ratio of 1:2:2 demonstrated that addition of a second metal depressed the activity of the catalyst in the hydrogenation of 1-hexene. However, selectivity in the hydrogenation of the olefin increased, indicating that hydrogenation of the aromatic hydrocarbon was inhibited to a greater extent. Cadmium was most effective in promoting selective hydrogenation of 1-hexene. In the Pt-Cd system the reaction was first order in 1-hexene and zero order in benzene. The introduction of 0.2 atoms of Cd per one atom of Pt was sufficient to decrease benzene hydrogenation 2-fold.

Analysis of adsorption data showed that increased selectivity of 1-hexene hydrogenation was due to a four-fold decrease in benzene adsorption to the catalytic surface as a result of Cd addition. Figures 2; references 5: 2 Russian, 3 Western. [284-12172]

UDC [547.31+547.52/.59]:66.094.173

HYDROGENATION OF UNSATURATED AND AROMATIC COMPOUNDS ON POLYMERIC CATALYSTS

Moscow NEFTEKHIMIYA in Russian Vol 25, No 2, Mar-Apr 85 (manuscript received 9 Dec 83) pp 176-178

KARAKHANOV, E. A., LOKTEV, A. S., PSHEZHETSKIY, V. S. and DEDOV, A. G., Moscow State University imeni M. V. Lomonosov

[Abstract] Polymeric Rh and Pd catalysts were prepared and tested for efficiency in hydrogenation of 1-hexene, cyclohexene, cyclopentadiene, 1,5cyclooctadiene, benzene, nitrobenzene and aniline at 20-30°C under atmospheric pressure. The polymeric matrix consisted of styrene-maleic acid or maleic acid-methyl methacrylate copolymers, and polyacrylic acid and polyvinylpyrrolidone polymers. Hydrogenation of olefins to the corresponding alkanes proceeded with virtually 100% efficiency in water-alcohol medium. The Rh catalysts were particulary effective in the hydrogenation of cyclic dienes to cycloalkanes, and in the hydrogenation of benzene. Hydrogenation of aniline was insignificant, while the nitro group of nitrobenzene was reduced to an amino group over Rh and Pd catalysts. The key advantage of these catalysts was their solubility in water-alcohol mixtures and ease of isolation by pH adjustment. References 1 (Russian). [284-12172]

UDC 547.217.1:542.941.8:66.095.252.7

MODIFIED Pt/A1203 CATALYST FOR DEHYDROCYCLIZATION OF n-HEPTANE

Moscow NEFTEKHIMIYA in Russian Vol 25, No 2, Mar-Apr 85 (manuscript received 15 Oct 84) pp 179-182

KOMAROV, V. S., PRYAKHINA, N. Ya., STEPANOVA, Ye. A., KOZLOV, N. S. and SEN'KOV, G. M., Institute of General and Inorganic Chemistry and Institute of Physico-organic Chemistry, Belorussian SSR Academy of Sciences

[Abstract] Studies were conducted on the modification of Pt/Al₂O₃ catalysts with TiO₂ in order to obtain efficient dehydrocyclization of n-heptane with catalysts containing less Pt, a metal in short supply. Preparation and testing of catalysts containing 5-15 wt% TiO₂ showed that

catalytic activity was retained and even improved in the face of a reduction in the Pt component from 0.6 to 0.4 wt%, in reactions carried out under 0.6 MPa hydrogen, 530°C, and a $H_2:C_7H_{16}$ ratio of 4:1. Maximum activity was obtained with catalysts containing 10-15 wt% TiO₂, with the effects of TiO₂ ascribed to promoting greater dispersion of Pt particles on the Al_2O_3 carrier. Large-pore samples containing 15 wt% TiO₂ were effective in catalyzing the formation of aromatic hydrocarbons and products of isomerization and dehydrocyclization as a result of limitation of diffusion factors that inhibit these reactions. References 9: 8 Russian, 1 Western. [284-12172]

UDC 547.313:542.941.1

LIQUID-PHASE HYDROGENATION OF OLEFINS ON NICKEL HYDRIDE CATALYSTS

Moscow NEFTEKHIMIYA in Russian Vol 25, No 2, Mar-Apr 85 (manuscript received 15 Dec 83) pp 183-187

YUFFA, A. Ya., LEBEDEVA, N. N. and LISICHKIN, G. V., Tyumen State University; Moscow State University imeni M. V. Lomonosov

[Abstract] Comparative studies were conducted on the efficiency of surface fixed NiCl2-LiAlH4 impregnated and homogenous NiCl2-LiAlH4 catalysts in the hydrogenation of 1-hexene, cyclohexene and cyclopentadiene at 20°C by H2 under atomspheric pressure in organic solvents. Maximal activity was seen with Silochrome C-120-fixed catalyst at a Al:Ni ratio of 1.1:1, for the impregnated catalyst with a ratio of 1.8:1, and with the homogenous catalyst at a ratio of 1:1. Thermodesorption studies indicated that the hydride phase of the fixed catalyst consisted of NiH_{0.8} and that of the impregnated catalysts was at ca. 200:1. Activity of the fixed catalyst was due to surface phenomena on the support, whereas in the impregnated catalyst the nickel hydride leached into the solution and imparted to the latter catalytic activity. Figures 4; references 8: 6 Russian, 2 Western. [284-12172]

UDC 547.216:66.095.252.7:542.976:546.92

EFFECTS OF GERMANIUM AND ZIRCONIUM ON PLATINUM CATALYST IN DEHYDROCYCLIZATION OF n-HEXANE

Moscow NEFTEKHIMIYA in Russian Vol 25, No 2, Mar-Apr 85 (manuscript received 25 May 83) pp 188-191

NADIROV, N. K., VOZDVIZHENSKIY, V. F., KONDRATKOVA, N. I. and FATKULINA, A. A., Institute of Chemistry of Oil and Natural Salts, Kazakh SSR Academy of Sciences

[Abstract] Pt/Al203 catalysts were modified with Ge and Zr and analyzed for their efficiency in catalyzing dehydrocyclization of n-hexane at 520°C under atmospheric pressure. Introduction of Ge or Zr to a Ge:Pt or Zr:Pt ratio of ca. 1-2:1 resulted in a sharp increase in the yield of benzene, accounting for ca. 40-60% of the transformation. However, a marked decrease in dehydrocyclization was noted when the Ge:Pt or Zr:Pt ratio exceeded 2. The increased efficiency of dehydrocyclization under appropriate conditions was attributed to the establishment of a system of zero-charged and oxidized Pt clusters with a small effective positive valence. Figures 1; references 11: 7 Russian, 4 Western. [284-12172]

UDC 541.64:543.544:547.538.241

OLIGOMERIZATION OF PHENYLACETYLENE ON FUSED IRON CATALYST

Moscow NEFTEKHIMIYA in Russian Vol 25, No 2, Mar-Apr 85 (manuscript received 16 Feb 84) pp 199-205

SLIVINSKIY, Ye. V., VOYTSEKHOVSKIY, Yu. P., ZVEZDKINA, L. I., LOKTEV, S. M., FIKHTE, B. B. and SHISHKINA, M. V., Institute of Petrochemical Synthesis imeni A. V. Topchiyev, USSR Academy of Sciences

[Abstract] To assess the various steps involved in the oligomerization of olefins, a relatively inefficient catalyst used in fatty acid synthesis was selected (Fe-SiO₂-V₂O₅-Al₂O₃-K₂O; 95-96.5% Fe, 0.5-1.0% K₂O) to facilitate the isolation and identification of intermediate products. Oligomerization of phenylacetylene on the fused Fe catalyst was conducted at 150°C under 10 MPa nitrogen, with the isolated oligomers identified by mass, PMR, NMR and IR spectroscopies. Tabulation of the spectral data and analysis of corresponding structures led to the conclusion that oligomerization of phenylacetylene. A scheme for the proposed steps is provided. Figures 1; references 19: 5 Russian, 14 Western. [284-12172]

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UDC 547.535:542.952

TRANSFORMATION OF ALKYLBENZENES ON POLYFUNCTIONAL Mo/MORDENITE CATALYST IN HYDROGEN

Moscow NEFTEKHIMIYA in Russian Vol 25, No 2, Mar-Apr 85 (manuscript received 27 Jan 84) pp 211-217

CHIZHOV, V. B. and RABINOVICH, G. L., "Angarsknefteorgsintez" Production Association; All-Union Scientific Research Institute of Petrochemical Processes

[Abstract] Detailed analysis was conducted on the primary transformations of C9 aromatic hydrocarbons on Mo/mordenite catalyst, with the reactions conducted at 420-460°C under a pressure of 4.6 MPa and a short contact time. The primary reactions involved in the transformation of pseudocumene were isomerization and disproportionation, leading to the formation of xylenes, and tetramethylbenzenes. The rate of isomerization in this case was greater than that of disproportionation of methylbenzenes, m-, p- and o-Ethyltoluenes first underwent hydrodealkylation with removal of the ethyl group, with the resultant toluene undergoing transalkylation and isomerization. The primary transformation of cumene involved hydrodealkylation with the formation of benzene and propane. The rate ratios for the removal of the isopropyl, ethyl and methyl groups from cumene, ethyltoluenes and pseudocumene were 19:7:1, corresponding to the stability ranking of the carbonium ions: isopropyl>ethyl>methyl. Figures 1; references 11: 6 Russian, 5 Western. [284-12172]

UDC 547.313:541.128.12

ADDITION OF ACETALDEHYDE TO ETHYLENE ON COMPLEX CATALYSTS

Moscow NEFTEKHIMIYA in Russian Vol 25, No 2, Mar-Apr 85 (manuscript received 9 Apr 84) pp 218-223

GVOZDOVSKIY, G. N., KOSHELEV, Yu. N., TARASOV, B. P., MARAKAYEV, T. A., DEVEKKI, A. V. and MUSHENKO, D. V., All-Union Scientific Research Institute of Petrochemistry, Leningrad

[Abstract] Spectrophotometric studies were conducted on the catalytic complexes formed among cobalt acetate, potassium bromide and N-bromosuccinamide used to catalyze the addition of acetaldehyde to ethylene in acetic acid. Evaluation of the electronic spectra indicated that in the catalytic composition and in the reaction mixture several species of coordinated compounds are formed as a result of binary interactions, and that catalytic efficiency is predicated on such complexes. Kinetic studies demonstrated that, in the reaction, oxygen functions in the initiation of the addition and

accelerates the formation of methyl ethyl ketone at the time or rormation of the radical chain. Studies of monoaddition reactions with ethylene, propylene, butene and hexene leading to the formation of the respective methyl alkyl ketones showed that with an increase in the length of the hydrocarbon radical of the alpha-olefin the effective rate constant diminishes, presumably due to increased shielding of the double bond by the alkyl. Figures 4; references 9: 8 Russian, 1 Western. [284-12172]

UDC 546.217.2:542.924:661.183.6

CRACKING OF ISOOCTANE ON HIGH-SILICA ZEOLITES

Moscow NEFTEKHIMIYA in Russian Vol 25, No 2, Mar-Apr 85 (manuscript received 13 Oct 83) pp 224-227

YUSHCHENKO, V. V., TOPCHIYEVA, K. V. (deceased), MEGED', N. F. and LIMOVA, T. V., Moscow State University imeni M. V. Lomonosov; Grodno State University

[Abstract] A comparative analysis was conducted on the cracking of isooctane on high-silica zeolite (ultrasil [sic]), faujasite or aluminosilicate, at 350-490°C. Evaluation of the product yields and the rates of conversion, demonstrated that on ultrasil the rate constants was several orders of magnitude lower than on calcium-decationated faujasite or amorphous alum inosilicate. This difference in the rate constants was attributed to the inaccessibility of the internal channel surface of ultrasil to isooctane. Consequently, only the upper surfaces of the channels are available for isooctane conversion, while internally located surfaces are involved only in secondary transformations involving relatively unbranched products of primary cracking. This would explain the relatively high energy of activation for the cracking of isooctane on ultrasil of 80 kJ/mole. References 13: 10 Russian, 3 Western. [284-12172]

UDC 665.644:549.67

MOLECULAR SHAPE SELECTIVITY OF ZEOLITES USED IN CRACKING

Moscow NEFTEKHIMIYA in Russian Vol 25, No 2, Mar-Apr 85 (manuscript received 8 Jun 84) pp 228-233

TSYBULEVSKIY, A. M. and DANILUSHKINA, K. P., All-Union Scientific Research and Planning Institute of Gas Processing, Krasnodar

[Abstract] A comparative analysis was conducted on the cracking characteristics of zeolites, aluminosilicate and faujasite in terms of molecular

shape selectivity. Cracking studies were conducted on binary cystems at 500°C involving n-octane and 2,2,4-trimethylpentane (TMP), 2-methylpentane and TMP, and 2,4-dimethylhexane and TMP. Comparison of the rate constants in conjunction with an analysis of diffusion factors and the effects of various carriers (methane, propane) showed that molecular shape selectivity applies not only to the various zeolites (CaA, CaE), but also to the large-pore synthetic faujasites. Product selectivity of low-MW olefins from n-octane cracking on zeolites is determined by intracrystalline diffusion of feedstock molecules and products in the zeolite spaces. Selectivity can be enhanced by dilution of the feedstock with low-MW gases having a small effective diameter, or by induction of a network of secondary pores in the catalyst. Figures 4; references 14: 11 Russian, 3 Western. [284-12172]

UDC 547.592.2:542.973:542.943.4

COUPLING OF LIQUID-PHASE OXIDATION-EPOXIDATION OF CYCLOHEXENE IN CYCLOHEXANOL ON HETEROGENOUS CATALYSTS

Moscow NEFTEKHIMIYA in Russian Vol 25, No 2, Mar-Apr 85 (manuscript received 13 Jun 83) pp 237-243

BERENTSVEYG, V. V., CHAN BIK NGA, CHEMLYEVA, T. A. and BARINOVA, T. V., Moscow State University imeni M. V. Lomonosov

[Abstract] A mathematical analysis was conducted on the coupling of liquid phase oxidation-epoxidation of cyclohexene in the presence of cyclohexanol over the bifunctional catalyst: Cr(III)-iminodiacetate complex on silica and MoO₃ on silica. Studies of reactions at 75°C and in the presence of cyclohexanol approaching 5 mole% revealed that cyclohexenol, cyclohexenone and cyclohexene oxide constituted the primary products. The binary catalytic system evidenced a synergistic effect, which in part was ascribed to generation of additional cyclohexenol in the coupled process. Figures 3; references 8: 5 Russian, 3 Western. [284-12172]

UDC 541.49:547.89

HIGH-MOLECULAR-WEIGHT CATALYSTS IN ORGANIC SYNTHESIS. VIII. POLYMERIC CROWN ETHERS AS CATALYSTS OF O- AND N-ALKYLATION REACTIONS

Riga IZVESTIYA AKADEMII NAUK LATVIYSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 2, Mar-Apr 85 (manuscript received 4 Dec 84) pp 215-220

KLYAVIN'SH, M. K., ROSKA, A. S. and ZITSMANIS, A. Kh., All-Union Scientific Research Institute of Applied Biochemistry of the Scientific Production Association "Biokhimreaktiv."

[Abstract] Polymeric catalysts simplify production processes and are particularly attractive for expensive or difficult to produce compounds. Poly-(dibenzo-18-crown-6) was obtained by dispersion polycondensation with formaldehyde in a variety of different media and subsequent granulation of the resulting gel. The granules effectively catalyzed O-alkylation of phenols and naphthols, particularly in solvents which caused them to swell significantly (200-340%). They were adaptable to three-phase catalysis, leading to alkylation of polycyclic substrates (e. g., with anthrone). Alkylation of alcohols was also successfully carried out with concentrated (50%) alkali solutions using an excess of the alkylating reagent. The granules also catalyzed N-alkylation of heterocyclic amines such as indole and, in three-phase reactions, carbazole and 3-methylpyrazole. Figures 3; references 11 (Russian).

[287-12672]

UDC 541.128.13:542.943.7:541.127:546.11.027:546.733'732-31

FACTORS WHICH DETERMINE ACTIVITY OF CATALYSTS OF VARIOUS CHEMICAL TYPES IN HYDROGEN OXIDATION REACTIONS. PART 1: OXIDATION AND ISOTOPE EXCHANGE OF HYDROGEN OVER COBALT MONOXIDE-OXIDE

Moscow KINETIKA I KATALIZ in Russian Vol 26, No 2, Mar-Apr 85 (manuscript received 13 Oct 83) pp 320-326

DOLGIKH, L. Yu., IL'CHENKO, N. I. and GOLODETS, G. I., Institute of Chemical Physics imeni L. V. Pisarzhevskiy, UkSSR Academy of Sciences, Kiev

[Abstract] The oxidation of hydrogen is a convenient system for studying those group factors which determine the catalytic activity of substances during gas-phase oxidation. A mechanism is proposed for hydrogen oxidation over cobalt monoxide-oxide catalyst that is based on kinetic data of the $2H_2 + O_2 = 2H_2O$ reaction and isotope exchange in $H_2 + D_2 = 2HD$. At low temperatures the reaction consists of alternate reduction-reoxidation of surface hydrogen adsorbed in the molecular form, while at high temperatures and low P_{02}/P_{H_2} values the mechanism includes dissociative chemsorption of

hydrogen. Figures 4; references 13: 11 Russian, 2 Western. [291-12765] UDC 541.128.13:542.943.7:546.11.027:546.92

FACTORS WHICH DETERMINE ACTIVITY OF CATALYSTS OF VARIOUS CHEMICAL TYPES IN HYDROGEN OXIDATION REACTIONS. PART 2: OXIDATION AND ISOTOPE EXCHANGE OF HYDROGEN OVER PLATINUM

Moscow KINETIKA I KATALIZ in Russian Vol 26, No 2, Mar-Apr 85 (manuscript received 23 Nov 83) pp 327-333

GOLODETS, G. I., IL'CHENKO, N. I. and DOLGIKH, L. Yu., Institute of Chemical Physics imeni L. V. Pisarzhevskiy, UkSSR Academy of Sciences, Kiev

[Abstract] A study was made of the kinetics of oxidation of hydrogen and the mixture $H_2 + D_2$ over platinum, and isotope exchange of hydrogen and oxygen under conditions of oxidative catalysis. A mechanism is proposed for hydrogen oxidation which includes dissociative hydrogen chemosorption and reaction of oxygen with adsorbed hydrogen atoms. All of the kinetic data may be quantitatively described if it is assumed that the heat of hydrogen adsorption increases linearly with the degree of surface filling with oxygen. This corresponds to a model of induced surface non-uniformity. A value of 0.56+0.07 was determined for transfer coefficient from experimental data. Figures 4; references 9: 7 Russian, 2 Western. [291-12765]

UDC 541.128.35:546.74:546.11. 27

EFFECT OF CARRIER ON CATALYTIC PROPERTIES OF NICKEL CATALYSTS IN REACTION OF LOW TEMPERATURE ISOTOPE EXCHANGE IN MOLECULAR HYDROGEN

Mosciw KINETIKA I KATALIZ in Russian Vol 26, No 2, Mar-Apr 85 (manuscript received 22 Mar 84) pp 363-367

PEREVEZENTSEVA, N. N. and ZHAVORONKOVA, K. N., Moscow Chemical-Technological Institute imeni D. I. Mendeleyev

[Abstract] A study was made of the relationship between specific catalytic activity ($C_{\rm SP}$) and temperature for nickel catalysts on silica, alumina and kieselguhr carriers, and nickel black in hydrogen-deuterium exchange reactions at 66-273 K. Two distinct types of temperature functions, i.e., with and without a break in the curve were found to exist. Heating in hydrogen at 450 K results in a break in the temperature/ $C_{\rm SP}$ curve for all types of nickel catalysts. This phenomenon is discussed from the standpoint of the participation of various forms of adsorbed hydrogen in the exchange reaction. Figures 3; references 15: 10 Russian, 5 Western. [291-12765]

UDC 541.128.35:542.91:541.451:539.217

SYNTHESIS AND STUDY OF HIGH TEMPERATURE CARRIERS BASED ON MAGNESIUM AND ALUMINUM OXIDES

Moscow KINETIKA I KATALIZ in Russian Vol 26, No 2, Mar-Apr 85 (manuscript received 31 Jan 84) pp 429-435

IVANOVA, A. S., DZIS'KO, V. A., MOROZ, E. M. and URZHUNTSEVA, A. Ya., Institute of Catalysis, Siberian Department, USSR Academy of Sciences, Novosibirsk

[Abstract] A study was made of the effects of the nature and ratio of initial components and calcining temperature on the phase composition and structural-mechanical properties of magnesium and aluminum oxides. In all cases a solid solution having spinel structure with cationic vacancies was formed. The number of these vacancies decreases when re-precipitated aluminum hydroxide + hydrated clay or gamma-alumina are substituted with re-precipitated aluminum hydroxide alone, with increase in MgO content and with increasing calcining temperature. Samples containing hydrated clay had maximum surface area. Total pore size decreases with increasing MgO content and calcining temperature. Figures 2; references 11: 9 Russian, 2 Western. [291-12765]

UDC 541.128.13:547.216:549.67:539.217

EFFECT OF POROUS STRUCTURE OF ZEOLITE-CONTAINING CATALYSTS ON THEIR ACTIVITY AND SELECTIVITY. ZEOLITE-CONTAINING CATALYSTS BASED ON ZEOLITE Y

Moscow KINETIKA I KATALIZ in Russian Vol 26, No 2, Mar-Apr 85 (manuscript received 25 Apr 84) pp 442-445

ROSOLOVSKAYA, Ye. N. and BARSUKOV, O. V., Chemical Faculty, Moscow State University imeni M. V. Lomonosov

[Abstract] Catalytic activities and selectivities were determined for catalysts containing zeolite CaY-78 and amorphous alumina-silicates of various compositions and pore structure in n-hexane conversion reactions at 400°. The difference in activity and selectivity of zeolite in zeolite-containing catalysts in comparison to zeolite with no matrix is apparently due to the blocking of part of the zeolite with the matrix material and the presence of matrix-zeolite cationic transitions. Figures 1; references 7: 6 Russian, 1 Western.

[291-12765]

UDC 66.092:541.128

EFFECTS OF MOLYBDENUM OXIDE ON ACTIVITY OF ZEOLITE CATALYSTS

Baku AZERBAYDZHANSKIY KHIMICHESKIY ZHURNAL in Russian No 1, Jan-Feb 85 pp 17-19

SHARIFOVA, E. B., ZEYNALOVA, F. A., ASKEROVA, A. I. and ZUL'FUGAROV, Z. G., Institute of Inorganic and Physical Chemistry, Azerbaijan SSR Academy of Sciences

[Abstract] Trials were conducted under laboratory conditions of zeolite catalysts enriched with 7, 10, or 15 wt% MoO₃ in the pyrolysis of benzine to low MW olefins at 650°C and volumetric flow rates of 1.3-5 h⁻¹. Increasing the MoO₃ content resulted in a decrease in the gaseous products and coke, but the concentration of low MW olefins in the gas increased. Increasing the MoO₃ content favored an increase in the yield of propylene and the butylenes, and diminished ethylene production. In general, gases accounted for 50.0-88.00 wt% of the product of pyrolysis, with the low MW C₂-C₄ olefins representing 63.6-78.3% of the gaseous products. References 2 (Russian). [303-12172]

UDC 541.127.015

OXIDATION OF BUTYL ALCOHOLS ON OXIDE CATALYST

Baku AZERBAYDZHANSKIY KHIMICHESKIY ZHURNAL in Russian No 1, Jan-Feb 85 pp 20-24

AL'ZIYUD, M. A., ALIYEV, E. A. and ADZHAMOV, K. Yu., Azerbaijan Institute of Oil and Chemistry imeni M. Azizbekov

[Abstract] Studies were conducted on the rates of dehydration and oxidative dehydrogenation of butyl alcohols on Sn-Mo-O catalyst to determine the efficiency of the catalyst for this series of compounds. Reactivity in dehydration was found to follow the following ranking: n-butanol<sec-butanol< iso-butanol<tert-butanol. In terms of oxidative dehydrogenation the ranking followed the following sequence: n-butanol>iso-butanol>sec-butanol>tertbutanol. The two series were interpreted on the basis of the induction effects of alkyl groups, which weaken as the carbon chain is lengthened. Figures 4; references 6 (Russian). [303-12172]

UDC 547.551+547.31

ALKENYLATION OF ANILINE BY ISOPRENE OVER ALUMINOSILICATE-ZEOLITE CATALYST ZEOKAR-2

Baku AZERBAYDZHANSKIY KHIMICHESKIY ZHURNAL in Russian No 1, Jan-Feb 85 pp 25-27

MAGERRAMOV, M. N., LYUTFALIYEV, A. G., KHALILOVA, R. A. and DADASHEVA, I. Sh., Azerbaijan State University imeni S. M. Kirov

[Abstract] Optimal conditions were determined for the alkenylation of aniline by isoprene over aluminosilicate-zeolite catalyst Zeokar-2. Under the selected conditions of 140°C, an aniline: isoprene 4:1 ratio, and 45.5 wt% catalyst, the yield of monopentenylaniline was 64.7%. Product distillation and chromatographic and IR analysis yielded composition data of 58.9% N- and 41.1% C-pentenylanilines. References 5 (Russian). [303-12172]

UDC 66.56.4

CHEMICAL COMPOSITION OF CATALYTIC CRACKING PRODUCTS OF SULFUROUS OIL VACUUM DISTILLATE

Baku AZERBAYDZHANSKIY KHIMICHESKIY ZHURNAL in Russian No 1, Jan-Feb 85 pp 28-31

BASILI, I. K. and SEID-RZAYEVA, E. M., Institute of Petrochemical Processes, Azerbaijan SSR Academy of Sciences imeni Yu. G. Mamedaliyev

[Abstract] A chemical analysis was conducted on products obtained by catalytic cracking over zeolytes of the vacuum distillate of sulfurous crude, covering a temperature range of 460-520°C at a pilot plant. Tabulated data are presented on the chemical composition of the different fractions obtained by cracking. With the use of zeolite-based catalysts, the yield of the gasoline fraction can be improved by 3.1 wt%, with the octane rating ranging from 80.3-81.0. References 3: 2 Russian, 1 Western. [303-12172]

19

UDC 541.128

REACTION OF N₂0 WITH NiCr₂0₄

Baku AZERBAYDZHANSKIY KHIMICHESKIY ZHURNAL in Russian No 1, Jan-Feb 85 pp 32-36

VUD, M. E. and GASAN-ZADE, G. Z., Institute of Oil and Chemistry imeni M. Azizbekov

[Abstract] Since nitrogen oxide decomposes over nickel oxide but not chromium oxide, trials were conducted over a wide temperature range to determine its decomposition on NiCr204. Decomposition of N20 commences at 350°C with a reaction rate of 3.2 x 10^{-14} moles/cm² x sec. The formation of more 0_2 than accounted for by the decomposition indicates that 0_2 is released from the catalyst. At temperatures below 350°C, heterogenous reoxidation of reduced catalyst takes place. Figures 3; references 7: 5 Russian, 2 Western. [303-12172]

UDC 541.128:549.67

STUDY OF CATALYTIC PROPERTIES OF Fe³⁺- AND Cu³⁺-SILICATES WITH ZEOLITE STRUCTURES

MOSCOW IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 5, May 85 (manuscript received 28 Sep 84) pp 978-983

VOSTRIKOVA, L. A., YECHEVSKIY, G. V., NOSYREVA, G. N. and IONE, K. G., Institute of Catalysis, Siberian Department, USSR Academy of Sciences, Novosibirsk

[Abstract] Selectivity of reactions of synthesis of hydrocarbons from methane in the presence of Fe and Cu silicates with a structure of zeolites obtained under hydrothermal conditions as a function of the Fe_2O_3 and CuOlevel in them is described and discussed. Silicates with zeolite type ZSM crystalline structure were obtained by hydrothermal synthesis in the presence of A1(III), Fe(III) and Cu(II) salts. Increase of the Fe(III) level and Cu(II) level in the alumosilicates reduces the selectivity of the latter for aromatic products of methanol conversion. Aromatic hydrocarbon synthesis by the ferrosilicates is not observed. It was assumed that introduction of Fe^{3+} and Cu^{3+} decreases the value of n in the active center of alumosilicate $Si(OA1)_{4-n}$ and this reduces the rate of redistribution of hydrogen in the unsaturated intermediate compounds forming during methanol conversion. Figures 2; references 16: 6 Russian, 10 Western. [1841-2791]

UDC 66.012.46

RAISING COKING RESISTANCE OF NICKEL CATALYSTS FOR HYDROCARBON CONVERSION

Kiev KHIMICHESKAYA TEKHNOLOGIYA in Russian No 3, May-Jun 85 (manuscript received 28 Nov 84) pp 9-12

VESELOV, V. V., DENBNOVETSKAYA, Ye. N. and ZAYCHUK, I. A., Institute of Gas, UkSSR Academy of Sciences, Kiev

[Abstract] The resistance of nickel-on-alumina catalysts to coking has been observed to increase as the ratio of the surface area of the carrier to that of the nickel catalyst increases. This phenomenon is explained on the basis of mathematical equations derived from a model system and experimental data obtained from a catalyst used to treat a 1:4 methane/carbon dioxide mixture. Figures 5; references 2: 1 Russian, 1 Western. [293-12765]

UDC 66.074.3

STUDY OF CRUST TYPE CATALYSTS FOR PURGING OFF-GASES OF OXIDES OF NITROGEN

Kiev KHIMICHESKAYA TEKHNOLOGIYA in Russian No 3, May-Jun 85 (manuscript received 29 Nov 84) pp 13-15

TERESHCHENKO, A. D., SHEVEL', A. A. and VESELOV, V. V., Institute of Gas, UkSSR Academy of Sciences, Kiev

[Abstract] One disadvantage of employing catalyst APK-2 to purge off-gases of oxides of nitrogen in dilute nitric acid production is the high palladium content. In the present work it is shown that this catalyst can be successfully replaced with a so-called "crust" type catalyst, where only the outermost layer of the catalyst particles contain noble metal. Such catalysts require much less palladium with no loss in activity. Figures 4; references 6 (Russian). [293-12765]

UDC 66.092.89

EFFECT OF NATURE OF CARRIER ON COKING RESISTANCE OF NICKEL CATALYSTS FOR NAPHTHA CONVERSION

Kiev KHIMICHESKAYA TEKHNOLOGIYA in Russian No 3, May-Jun 85 (manuscript received 29 Jul 84) pp 15-17

ISMAILOVA, P. L., KHAMZINA, A. Kh. and TALIPOV, G. Sh., All-Union Scientific Research Institute of Chemical Technology; Institute of the Medical Industry, Tashkent

[Abstract] Selection of an effective carrier for coke-resistant naphtha conversion remains a pressing problem. In the present work a study was made of the effects of specific surface of the carrier, structural states of the nickel ion and the nature of the nickel sites formed on the carrier surface on the coking of nickel naphtha conversion catalysts. Catalyst carriers included C-18, $MgAl_2O_4$, gamma- and alpha-alumina, GIAP-8 and K-5A. The results show that the formation of a free NiO phase on the catalyst surface coincides with a marked increase in the coking rate, regardless of the chemical nature of the carrier. Figures 2; references 9: 5 Russian, 4 Western. [293-12765]

UDC 543.8

MECHANISM OF CATALYST REGENERATION IN ULTRASONIC FIELD

Kiev KHIMICHESKAYA TEKHNOLOGIYA in Russian No 3, May-Jun 85 (manuscript received 16 Nov 84) pp 17-19

ROMENSKIY, A. V., POPIK, I. V., LOBOYKO, A. Ya. and ATROSHCHENKO, V. I., Severodonets Production Association "Azot"

[Abstract] A study was made of catalyst poisoning as caused by the blocking of the active surface by solid particles from the reaction mixture, and by filling of the catalyst pores. The mechanism of ultrasonic catalyst regeneration was studied by using a palladium catalyst (APK-2) used to purge off-gases from oxides of nitrogen, and a catalyst (PK-3) used to purge oxygen from nitrogen. The former is poisoned sulfur present in natural gas, and the latter with ferrous oxide. In an ultrasonic field, the particles are broken down by cavitational erosion and acoustic currents. References 6 (Russian). [293-12765]

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CHEMICAL INDUSTRY

PROGRESS IN CHEMICAL INDUSTRY

Kiev POD ZNAMENEM LENINIZMA in Russian No 8, Apr 85 pp 46-48

[Article by V. Kostenko, Chief of the Chemical Industry Department of the Ukrainian SSR State Planning Committee (Gosplan): "The Chemical Industry" under the rubric "26 May - Chemistry Day"]

[Text] In developing productive power and meeting the material demands of society, there has long since been an important role played by chemical methods of production. Even in the last century K. Marx and F. Engels noted that all progress in the area of chemistry "multiplies the number of useful substances and the number of useful applications of known substances..." (K. Marx and F. Engels, "Works", Vol. 23, p 619).

At its present stage, our native chemical industry, due to constant support from the Communist Party and the government, has become a powerful raw materials base for the chemicalization of all branches of the economy.

In the last ten to fifteen years the volume of production of various types of chemical products in the nation has almost doubled. In such areas as the output of ammonia, mineral fertilizer, sulfuric acid, and soda ash, the Soviet Union leads the world. There has been a sharp decline in the difference in production levels between the USSR and the USA.

Simultaneously there have been significant progressive changes in the techniques, technology, and production structure of the branch due to the creation of new manufactures and even sub-branches. This has made possible an improvement in quality factors.

A worthy contribution to solving the tasks of chemicalization of the economy has been made by the workers of the Ukrainian SSR, which has an abundance of chemical raw materials, energy resources, qualified cadres, and many customers for the branch's products. In all there are processed here about 20 percent of the USSR's total output of chemical production, including 50 percent of its sulfur; 40 percent of its white pigments; 23 percent of its soda ash; and more than 23 percent of its everyday chemical products.

The republic's chemical industry is developing within the framework of the unified national complex with consideration of the interests of the entire nation and the needs for complex development of the region's productive forces. The volume of branch production in the UkSSR already exceeds the all-union production level of 1963.

During the 11th Five-Year Plan the collectives of chemical and petrochemical industry enterprises have been completing a widespread construction program. In four years the basic production capacity of the branch has been increased by 25 percent. There have been expenditures on facilities at production projects of more than 2,500,000,000 rubles in capital investments.

In the beginning of March of this year, the CPSU Central Committee congratulated those who took part in the construction when there was completion of the facilities and there was start-up of complexes for producing ammonia and carbamide at Production Associations [PO] "Stirol" in Gorlovka and "Azot" in Dnepropetrovsk, and at the Odessa "Priportovyy" Plant. The chemists finished the latter eight months ahead of schedule and reached planned capacity in the new carbamide complex of 1,000 tons of production per day. The collectives of "Stirol" and "Azot" have assumed an obligation for the month to surpass their output schedule for planned productivity.

In this five-year plan there have been construction start-ups of such production complexes as the carbamide facility at PO "Azot" in Severodonetsk and the caustic soda facility at PO "Khlorvinil" in Kaluga, the capability to produce chemical fibers in Zhitomir and Chernigov, and plastics and synthetic resins in Shostka, Borislav, and at the Cherkassy PO "Azot".

Together with the creation of new capabilities there has been uninterrupted growth in the volume and tempo of work on reconstruction and technical reequipping, witnessed by the growth in capital investments directed toward these ends. While in the 1971 to 1975 period they comprised 15 percent of the volume of all capital investments, from 1976 to 1980 they comprised 17.3 percent, and in the four years of the current five-year plan they are more than 30 percent of all capital outlay.

There has been success in completing reconstruction, for example, at PO "Khimprom" in Sumy, at "Azot" in Severodonetsk, at "Stirol" in Gorlovka, at the Lisichansk Soda Plant, and at artificial fibers enterprises in Cherkassy and Chernigov, at the Belaya Tserkov PO for tires and rubber and asbestos articles, and at Dnepropetrovsk PO "Dneproshina". There have been good results from reconstruction at the PO "Svema" in Shostka, and at enterprises for plastics production in Priluki and Kharkov, and for everyday chemicals in Simferopol and Uzhgorod.

Reconstruction has accounted for almost all of the growth in the volume of production at the named enterprises without increasing the number of workers. This is especially important when labor resources are in short supply.

As reconstruction is one of the factors in accelerating scientific and technical progress in the economy, the chemical industry itself relies heavily on achieving it. Technical reequipment is taking place in such main directions as the changeover to new high-quality raw material sources such as natural gas, native sulfur, hydrocarbon raw materials, and the use of units and technological lines for strengthening unified capacity, and the introduction of low-expenditure technology and complex use of raw materials and collateral products.
Due to this there has been a broadening in assortment, an increase in output, and an improvement in production economy of many basic chemical products, in particular in fertilizer, organic semifinished products and polymer materials.

As was envisaged in the basic directions for development of the economy, the growth of production potential takes place on the basis of use of equipment with increased individual capacity. For example, this year the updated units will account for about 50 percent of several types of plastics and more than 70 percent of the ammonia, sulfuric acid, carbamide; while ten years ago the share of production of these very important types of production at large units was 20 to 25 percent.

The creation of production facilities based on increased individual capacity provides significant growth in the productivity of labor. As a result of the last four years the increase in industrial production at Ministry of Chemical Industry [MinKhimProm] facilities in the UkSSR was accomplished with no increase in work force. Furthermore, highly productive units have allowed us to decrease the specific capital expenditures and costs and to save energy resources.

During this period there have been adapted new types of production, for example, cordage and technical fibers with improved properties for tires and transporter tapes, various types of chemical fibers, textile enhancement substances, varnishes, and dyes. Plastics production has grown by 41 percent. There is constant growth in the assortment of production.

Workers in the branch actively participate in meeting the Food Program. The volume of production of mineral fertilizer in the republic has grown by 28 percent compared to 1980, and there has been particular growth in the production of complex and combined fertilizers, and they have achieved the output of new effective means for crop protection - "polikhom" [unidentified substance] and "polikarbatsin" [apparently polycarbacine. According to the Soviet Chemical Encyclopedic Dictionary, this is a complex compound of Ziram and N,N'-bis-thiocarbamoy] disulfide, and probably used as a fungicide.]

Enterprises of the chemical industry furnish agriculture with materials for improving the soil - "phosphogips" [a phosphated gypsum], and calcium sulfate concentrates. At the Sumy PO "Khimprom" there was start-up of a production facility for feed phosphates, and they are starting to produce pyrosulfite, a protector of feeds.

A great deal of attention is paid to production of consumer goods, plans for which from year to year are exceeded. In 1984 they were produced at a value of 39,700,000 rubles above the plan. At the same time there was perfected the output of new compounds of everyday chemistry with previously established improvements in demanded properties, such as "Lotoa-avtomat AS-83" [presumably a laundry detergent], "Das" low foaming paste [presumably toothpaste] and others.

In all during 1981 to 1984 there was put into production 44 specific goods of everyday chemistry. Among these is a substance for optical surface

"Vanavan", which is produced by the Uzhgorod Everyday Chemical Plant, and which was awarded a gold medal at the 1984 exposition in Bratislava.

[Insert: "Figures and Facts" under the rubric "Into your Notebook"]

- In our nation the chemical industry as an important factor in raising the effectiveness of the entire economy is developing at a very rapid rate.

Thus, while the volume of production of all of the USSR's industries rose 98 percent between 1970 and 1983, the chemical and petrochemical industries grew by 151 percent including fertilizer production for foodstuffs, and by 129 percent respectively. Chemical fibers and thread grew by 181 percent, synthetic resins and plastics by 114 percent, synthetic dyes by 160 percent, and chemical- pharmaceuticals by 229 percent.

- Last year construction was started on facilities for caustic soda, varnish and paints, synthetic dyes, fiberglass production and so on. Specifically, there were brought on-line facilities for producing synthetic ammonia at PO "Azot" in Kemerovo, and for capron synthetic thread at the Barnaul Synthetic Fibers Plant.

These very important types of goods were produced: synthetic resins -- 4,800,000 tons, or 109 percent of 1983 production; mineral fertilizer (converted 100 percent for foodstuffs) 30,800,000 tons; caustic soda 3,000,000 and chemical fibers and thread 1,400,000 tons; chemical means for plant protection (in conventional units) 567,000 tons, or 104 percent of 1983 production for each of these four products; and 63,700,000 automobile tires.

- The chemical and petrochemical industries account for more than 10 percent of basic production resources for the nation's industry. Increasing labor productivity in this branch by only one percent adds 490,000,000 rubles in additional production per year.

There is a great deal of result from sparing use of chemical products. Saving one percent of them on a national scale amounts to hundreds of billions of rubles. For example, saving by the population and secondary reprocessing of one ton of polyethylene yields output of 800 kilograms of product, for which there would otherwise be used about five tons of petroleum. At the enterprises of Glavneftekhimprom [the Chief Directorate for Petrochemical Industry] of the UkSSR during these years the output of consumer goods has grown by 22 percent. There has been notable increase in the production of inflatable mattresses, rubber and textile boats, fins and masks for skin diving.

There have been introduced and are successfully operating at the enterprises complex systems for controlling product quality. The amount of production with the Emblem of Quality has grown in overall volume from 33.3 percent to 46.3 percent for mineral fertilizer since 1980, and as a whole at the enterprises of Minkhimprom during the same period from 28.1 to 35.9 percent.

There are important tasks facing the republic's chemists in the final year of the five-year plan. They must begin construction on huge complexes for mineral fertilizer production at PO "Sera" in Rozdol and at the Zagaypol'skiy sulfur mine in Ivano-Frankovsk Oblast, and new facility for varnish production at the Borislav Chemical Plant.

Work will continue for increasing production of chemical products at the Kaluga PO "Khlorvinil", the Shostka PO "Svema", the Pervomayskiy Chemical Plant in Kharkov Oblast, and at petrochemical enterprises in Sumy, Belaya Tserkov, and Gorlovka.

In the work collectives there is fervent acceptance of the call from the party to work for two days on saved resources. Concrete measures were developed, and increased socialist obligations were accepted. For example, the workers of the leading organization of the chemical industry, the Severodonetsk PO "Azot" have accepted an obligation to conserve 42,500,000 kiloWatt hours of power, and to increase labor productivity by 1.2 percent above the plan, and to decrease the cost of this supplementary production by 0.6 percent due to widespread use in production of the achievements of scientific and technical progress and the proposals of efficiency experts to obtain savings amounting to 3,600,000 rubles.

Important factors in accelerating the development of the branch, improving its technical and economic indicators are Socialist competition and progressive initiatives of production leaders.

For their victory in the All-Union Socialist Competition for 1984 totals the work collectives of the Kiev PO "Krasnyy Rezinshchik", the Severodonetsk PO's "Stekloplastik" and "Azot", the Sumy PO "Khimprom", the Shostka PO "Svema", and the Dnepropetrovsk Varnish and Paint Plant have been named Challenge Red Banner by the CPSU Central Committee, the USSR Council of Ministers, the VTsSPS [All-Union Central Council of trade Unions], and the Central Committee of the Komsomol and were listed on the Honor Roll at the USSR VDNKh [Exhibition of the Achievements of the National Economy of the USSR].

With each year the number of leaders and innovators of production grows. At their head are such shock workers of the five-year plan as a "Krutil'shchitsa" [presumably winding machine operator] at the Berdyansk Artificial Fibers Plant, the Hero of Socialist Labor G. D. Usatenko, who is already working on the 1989 account; an operator at the Chernigov PO "Khimvolokno", Laureate of the USSR State Prize A. N. Yakimenko, who has finished his task with "the 11th Five Year Plan as eleven annual norms"; a vulcanizing machine operator at the Belaya Tserkov PO for Tires and Rubber and Asbestos Articles A. N. Ponomarev, whose portrait hangs in the Hall of Honor at the UkSSR-VDNKh; a shift leader at the Severodonetsk PO "Azot" whose shift won the title "Best shift in the Ministry in fertilizer production", V. S. Serdyukov; and a machine operator at this same association, the USSR Honored Chemical Worker M. N. Ryzhkov.

Preparing to meet the 27th CPSU Party Congress, the 40th Anniversary of the Great Victory, and the 50th Anniversary of the Stakhanovite Movement, the chemical workers of the republic have given their word to exceed the planned tasks for this year by 41,000 tons of mineral fertilizer and 60,000 automobile tires, and many other products, and together with the construction workers and installers they promise to bring new facilities on-line earlier than tasked. The forced rhythmic work in months just past attests that they will keep their word with honor.

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9016 CSO: 1841/286

UDC 533.6.001

EFFECT OF ACOUSTIC VIBRATIONS OF VARIOUS FREQUENCIES ON GAS MIXING PROCESS

Kiev KHIMICHESKAYA TEKHNOLOGIYA in Russian No 3, May-Jun 85 (manuscript received 20 May 84) pp 7-9

PARKHOMENKO, V. D., SUKHOY, M. P., SIDOROV, A. V. and MYSOV, O. P., Dnepropetrovsk Chemical-Technological Institute

[Abstract] The product yield of high temperature gas phase processes being a direct function of the mixing rate, a study was made of the effects of sonic treatment at various frequencies and intensities on a methane-air mixture at 1-8 meters/sec throughput velocity and $2 \cdot 10^3 - 35 \cdot 10^3$ Reynolds numbers. Analysis of the results shows that the second and fifth harmonics are most effective for changing gas concentration, the third and especially the first being least effective. Specifically, frequencies of 190, 350 and 600 Hz may be considered as the second, third and fifth harmonics, respectively. The results show that acoustic treatment can be effectively used to control gas mixing processes in high velocity chemical processes. Figures 3; references 6 (Russian). [293-12765]

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COMBUSTION

UDC 541.126:542.942:547.21

MECHANISM OF FORMING COLD FLAME BY OXIDATION AND SPONTANEOUS COMBUSTION BY PARAFFIN HYDROCARBONS

Kiev DOKLADY AKADEMII NAUK UKRAINSKOY SSR: SERIYA B. GEOLOGICHESKIYE, KHIMICHESKIYE I BIOLOGICHESKIYE NAUKI in Russian No 4, Apr 85 (manuscript received 17 Sep 84) pp 56-69

MULYAVA, M. P., SHCHEMELEV, G. V., and KUCHER, R. V., academician, UkSSR Academy of Sciences, Borislav Branch of State Scientific Research Institute of Chlorine Industry

[Abstract] Oxidation and self-ignition of hydrocarbons and other organic compounds in the range 250-350° C can result in cold flame. Spectral analysis indicates excited formaldehyde is involved, but the minimum energy of excitation indicates that there must be a reaction between two radicals. Peroxide radicals are known to be directly involved, particularly the CH₃0·₂ radical. Energy considerations indicate that the cold flame originating in a central portion of a reaction vessel produces a temperature rise which leads to its extinction at the point of origin and a spread toward the vessel walls. The reaction CH₃0· + RO[•](R⁺COO·) = ROH(R⁺COOH) + CH₂O* appears to be the critical one. References 13: 10 Russian, 3 Western. [271-12672]

FREE RADICALS

UDC 543.422.27:547.567.5

ELECTROCHEMICAL GENERATION OF FREE N-ARYLQUINONEIMINE RADICALS IN ACETONITRILE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 4, Apr 85 (manuscript received 5 Jun 84) pp 871-877

STRADYN', Ya. P., BAYDER, L. M., GAVAR, R. A., BAUMANE, L. Kh., GLEZER, V. T., MEDYNYA, B. A., FREYMANIS, Ya. F. and MARKAVA, E. Ya., Institute of Organic Synthesis, Latvian SSR Academy of Sciences, Riga

[Abstract] ESR studies were conducted on the free radicals of N-arylquinoneimines generated electrochemically in acetonitrile. Generation was by means of a mercury drop electrode, with the first reduction wave recorded at -0.4to -0.9 V reflecting a reversible single-electron transfer. A second wave was recorded at -0.8 to -1.3 V and corresponded to further irreversible reduction of products formed in the first stage of the process. ESR analysis of the anion radicals indicated that the total electron density on the O=C and C=N-C fragments of N-phenylquinoneimine does not exceed 0.3 electrons, with a total of ca. 0.6 electrons on the two fragments of p-benzoquinone anion radical. The electrophilic nature of the quinoneimine group for the first vacant molecular orbital was 1.5-fold greater than that of the nitro group. Figures 2; references 13: 5 Russian, 8 Western. [282-12172]

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UDC 541.515:541.138.3:547.673.6

RADICAL INTERMEDIATES IN ELECTROCHEMICAL REDUCTION OF ALIZARIN

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 5, May 85 (manuscript received 24 Feb 84) pp 983-988

BULATOV, A. V., SOSONKIN, I. M., NIKITAYEV, A. I., KALB, G. A. and KHIDEKEL', M. L., Department of the Institute of Chemical Physics, USSR Academy of Sciences, Chernogolovka

[Abstract] Study of the nature of intermediates arising during electroreduction of alizarin (1,2-dihydroxyanthraquinone) by electrochemical methods and by use of electron paramagnetic resonance was performed to obtain data which may serve as a basis for more precise description of the mechanism of catalytic reduction of aromatic nitrocompounds. Electroreduction of alizarin in an aprotic medium is accompanied by a stepped formation of the anion-radical and then the corresponding dianion. In a prolonged process, the anion radical disproportionates and is converted into a stable dianion-radical via intermediate stages of deprotonation and reduction. Figures 3; references 9: 8 Russian, 1 Western. [1841-2791]

ION EXCHANGE PHENOMENA

UDC 543.544.42:546.42:546.41

SIMULATION AND CALCULATION OF STRONTIUM AND CALCIUM ION-EXCHANGE SEPARATION BY CARBOXYLIC CATION EXCHANGER KB-4P2 FROM HIGHLY MINERALIZED SOLUTIONS

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 5, May 85 (manuscript received 9 Jan 84) pp 969-973

NIKASHINA, V. A., NIKULICHEVA, T. A., SENKEVICH, I. B. and YEVZHANOV, Kh. N., Institute of Geochemistry and Analytical Chemistry imeni V. I. Vernadskiy, USSR Academy of Sciences, Moscow; Institute of Chemistry, TSSR Academy of Sciences, Ashkhabad

[Abstract] A search for conditions of separation of strontium and calcium on the basis of mathematical modelling which permits rapid determination of conditions of separation of the elements while making possible future use of the model obtained to optimize the extraction process as a whole is described and discussed. The ion-exchange system studied represented a solution of a mixture of 3 components--SrCl₂ (0.01N), CaCl₂ (0.07N) and NaCl(2.5N) and cationite KB-4 P2. The composition of the solution corresponds to that of one of the stages of treating iodine-bromine production effluents. The possibility of using a layer-by-layer model to calculate the frontal dynamics of adsorption of strontium, calcium and sodium on cationite KB-4 P2 in sodium form was demonstrated. This model is used to calculate adsorption of these elements on columns with different layer length and from solutions of different composition. The possibility, in principle, of quantitative separation of strontium and calcium, under frontal conditions, on cationite KB-4 P2 in Na form on long columns, 2M and more, is demonstrated. Concentrations of strontium in the filtrate during frontal separation of these elements may increase 3-10 times in comparison with the starting concentration, depending upon the starting solution. Figures 4; references 7 (Russian). [299-2791]

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ORGANOMETALLIC COMPOUNDS

UDC 542.91:547.1'118

REACTIONS OF COPPER SALTS OF DIALKYLTHIOPHOSPHORIC ACIDS AND PROPARGYL TYPE HALO DERIVATIVES

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 5, May 85 (manuscript received 30 May 84) pp 1181-1183

VIKHREVA, L. A., PUDOVA, T. A., GODOVIKOV, N. N. and KABACHNIK, M. I., Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow

[Abstract] Study of reactions of copper dialkylthiophosphates with some propargyl type halides is described and discussed. In contrast to haloalkyls, these compounds react readily with copper dialkylmonothiophosphates. Copper salts of dialkylthiophosphoric acids interact with propargylhalides with formation of 0,0-dialkyl-S-propargylthiophosphates. Sterically-hindered halides of the propargyl type readily react with copper salts of dialkylthiophosphoric acids and do not react with potassium salts of these acids. References 2: 1 Russian, 1 Western. [1841-2791]

UDC 542.92:541.57:546.811:546.22

CLEAVAGE OF Sn-S BOND BY LITHIUM ALUMINUM HYDRIDE

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 5, May 85 (manuscript received 26 Dec 84) pp 1211-1212

GORSHUNOV, I. Yu., SINYASHIN, O. G., IVASYUK, N. V., BATYYEVA, E. S. and PUDOVIK, A. N., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] It is shown for the first time that ethylmercaptides of trialkylols, under the effect of lithium aluminum hydride in an ether medium, are transformed into corresponding hydrides of trialkylols. Reduction of tialkylol mercaptides is realized readily by lithium aluminum hydride under conditions of interphase catalysis (benzene, dibenzo-18-crown-6). References 2: 1 Russian, 1 Western. [299-2791]

ORGANOPHOSPHORUS COMPOUNDS

UDC 546.18

CHEMICAL PROPERTIES OF BISTRIIODIC HEXAALKYLPHOSPHONIUMS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 5, May 85 (manuscript received 3 Oct 84) pp 1003-1006

MAKOVETSKIY, Yu. P. and FESHCHENKO, N. G., Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Bistriiodic hexaalkylphosphoniums (I) were derived by alkylation of red phosphorus in the presence of catalytic quantities of iodide, and presently studied for reactivity with a variety of chemicals. I react readily at room temperature with primary and secondary alphatic, aromatic and silylated amines with the formation of trialkyl(amido)phosphonium iodides in high yields. Reaction with the silylated amines is markedly exothermic, with the released elemental iodine reacting with the amine to form a variety of additional products. Reactions between Grignard reagents and I also proceed easily with the formation of quaternary phosphonium salts in high yields. Reactions between elemental sulfur and I also proceed readily with the formation of Alk3PS and iodine, while reaction with dibutyl ether or tetrahydrofuran yields, respectively, butyl iodide or 1,4-diiodobutane along with an iodide complex of triethylphosphine oxide. I compounds appear to be easily derived reagents for the synthesis of various phosphonium and quasiphosphonium salts. References 4: 3 Russian, 1 Western. [283-12172]

UDC 547.26'118

REACTION OF 0,0-DIISOPROPYLTHIOPHOSPHORYLSULFENYL CHLORIDE AND-PHOSPHORUS THIOACIDS WITH 1-VINYLSILATRANE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 5, May 85 (manuscript received 28 Oct 84) pp 1030-1033

KUTYREV, G. A., KAPURA, A. A., SOROKIN, M. S., CHERKASOV, R. A., VORONKOV, M. G. and PUDOVIK, A. N., Kazan State University imeni V. I. Ul'yanov-Lenin; Irkutsk Institute of Organic Chemistry, Siberian Department, USSR Academy of Sciences

[Abstract] 0,0-Diisopropylthiophosphorylsulfenyl chloride was found to react readily with 1-vinylsilatrane with the formation of 0,0-diisopropyl-S-(1-silatrany1-2-chloroethy1)dithiophosphate (I). I underwent fragmentation along two pathways: one pathway leads to the formation of 0-isopropy1-0silatranyl-S-vinyl dithiophosphate and isopropyl chloride, and the other to 0,0-diisopropyl-S-vinyl dithiophosphate and 1-chlorosilatrane. The phosphorus dithioacids add to 1-vinylsilatrane double bond with the formation of heat-stable (140°C) adducts in a manner that contradicts the Markownikow rule, indicating that the electronic influence of the silatranyl group on the direction of addition of the dithiophosphates is analogous to the effects of triorganylsilyl groups in vinyl trialkyl- and vinyl trialkoxysilanes. Reaction of 0,0-dimethyldithiophosphoric acid with vinyl trimethoxysilane led exclusively to the synthesis of 0,0-dimethyl-S-(2trimethoxysilylethyl)-dithiophosphate. References 7: 4 Russian, 3 Western. [283-12172]

UDC 547.26'118

REACTION OF P(III) THIOACID AMIDES WITH CC14

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 5, May 85 (manuscript received 16 Jul 84) pp 1183-1184

KOSTIN, V. P., SINYASHIN, O. G., BATYYEVA, E. S. and PUDOVIK, A. N., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] S-Alkyl-N,N-tetraethyldiamidothiophosphites react with CCl₄ at room temperature to form tetraethyldiaminochlorophosphine and the corresponding alkyltrichloromethyl sulfide. Amides of dialkyldithiophosphorous acids react with CCl₄ in the presence of catalytic concentrations of Lewis acids (ZnCl₂, AlCl₃, SnCl₂) to give S-alkyl-N-diethylamidochlorothiophosphites. The latter reactions do not take place in the absence of the Lewis bases even at 140°C. References 5: 3 Russian, 2 Western. [283-12172]

UDC 547.26'118

REACTION OF 4,5-BENZO-1,3,2-OXAZAPHOSPHOLANE OLIGOMER WITH PROTON DONORS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 5, May 85 (manuscript received 16 Jul 84) pp 1184-1185

PUDOVIK, M. A., MIKHAYLOV, Yu. B. and PUDOVIK, A. AN., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] The oligomer 4,5-benzo-1,3,2-oxaphosphol readily undergoes aminolysis on reaction with secondary amines, yielding 2-diethylamino-4,5benzo-1,3,2-oxaphospholane on reaction with diethylamine. On reaction with trimethylsilyldiethylamine the latter was transformed into 2-diethylamino-3-trimethylsilyl-4,5-benzo-1,3,2-oxaphospholane. Under analogous conditions, phenolysis occurs at room temperature with the formation of 2-phenoxy-4,5-benzo-1,3,2-oxaphospholane. References 2: 1 Russian, 1 Western.

[283-12172]

UDC 547.26'118

ADDITION OF OXAZAPHOSPHOLANES AND OXAZAPHOSPHORINANES TO COMPOUNDS WITH ACTIVATED MULTIPLE BONDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 5, May 85 (manuscript received 25 Sep 84) pp 1185-1186

PUDOVIK, M. A., MIRONOVA, T. A. and PUDOVIK, A. N., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] Oxazaphospholanes and oxazaphosphorinanes were found to react readily with compounds with activated multiple bonds, e. g., acrylonitrile (CH₂:CHCN), to yield six-membered imidophosphinates in the crystalline state. In highly polar solvents (dimethylsulfoxide), NMR data indicated that the products exist as monomers, whereas in less polar solvents (acetonitrile) a monomer-dimer equilibrium prevails. 2-Phenyl-1,3,2-oxazaphospholane adds to vinyl phosphonates on heating with the formation of oxazaphospholines. The latter exist as monomers in polar solvents, but as monomers and dimers in benzene.

[283-12172]

UDC 541.138.2

TRIMESITYLPHOSPHINE CATION RADICAL PERCHLORATE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 5, May 85 (manuscript received 18 Jul 84) pp 1186-1187

PARAKIN, O. V., NIKITIN, Ye. V., IGNAT'YEV, Yu. A., ROMAKHIN, A. S., KARGIN, Yu. M., IL'YASOV, A. V., VAFINA, A. A., ROMANOV, G. V. and PUDOVIK, A. N., Kazan State University imeni V. I. Ul'yanov-Lenin

[Abstract] Electrochemical oxidation of trimesitylphosphine on a Pt electrode in acetonitrile and tetrahydrofuran (2:1) with sodium perchlorate yielded cation radical salts of trimesitylphosphine. The salt is isolated as dark-purple crystals that rapidly become colorless in air due to reaction with oxygen. ESR spectroscopy indicated that the radical is a monomeric cation radical with an unpaired electron in the sigma orbital of the phosphorus atom. References 2: 1 Russian, 1 Western. [283-12172]

UDC 547.26'118

REACTION OF UNSATURATED KETIMINES WITH HYDROPHOSPHORYL COMPOUNDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 5, May 85 (manuscript received 6 Aug 84) pp 1187-1188

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

[Abstract] Various spectroscopic modalities were used to follow the reaction of 4-cyclohexylimino-2-methyl-2-pentene, 4-phenyl-imino-2-methyl-2and 1,3-diphenyl-3-phenyliminopropene with dimethyl phosphite or dibutylphosphine oxide in ether or pentane at room temperature. Addition of the hydrophosphoryl compounds to the unsaturated ketimines occurs at the 1,4position of the double bonds, with the products subsequently undergoing prototropic transformations. References 1 (Russian). [283-12172]

UDC 547.18'241

ISOMERIZATION OF P-TRIMETHYLSILYLPHOSPHINOMETHYLENEPHOSPHINE INTO C-TRIMETHYLSILYLMETHYLDIPHOSPHINE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 5, May 85 (manuscript received 25 Sep 84) pp 1190-1191

RUBAN, A. V., POLYACHENKO, L. K., ROMANENKO, V. D. and MARKOVSKIY, L. N., Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Previous observations that P-[2,4,6-tris(tert-butyl)-phenylphosphine]-C,C-bis(trimethylsilyl)methylenephosphine (I) undergoes slow isomerization (7-9 days at 25°C in THF) to P-2,4,6-tris(tert-butyl)phenyl-Pbis(trimethylsilyl)methylenediphosphene, were followed up with observations on a P-trimethylsilyl substituted analog of I. The methylenephosphine derivative of I was found to isomerize instantaneously (ether, -78°C) into the diphosphene (P-2,4,6-tris(tert-butyl)phenyl-P-tris(trimethylsilyl)methyldiphosphene. References 4 (Western). [283-12172]

UDC 547.185

SYNTHESIS AND ISOMERIZATION OF P-PV IMIDOPHOSPHATES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 5, May 85 (manuscript received 11 Jun 84) pp 1191-1193

TUPCHIYENKO, S. K., DUDCHENKO, T. N. and SINITSA, A. D., Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Imidophosphates with a phosphoranyl group on the P atom were synthesized by the action of amidophosphites on dipyrocatecholchlorophosphoranes in the presence of triethylamine. Stability of the imidophosphates as phosphazo compounds with a P-PV bond is determined by the substituents present and the nucleophilicity of the nitrogen atom of the phosphazo group. P-Dipyrocatecholphosphoranyl-0,0-diethyl-N-(p-nitrophenyl)imidophosphate was found to be the most stable of these compounds for a period of several months. References 2: 1 Russian, 1 Western. [283-12172]

UDC 547.341

DIMERIZATION OF BENZYLIDENE AMIDOPHOSPHITES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 5, May 85 (manuscript received 16 Jul 84) pp 1193-1194

NESTEROVA, L. I. and SINITSA, A. D., Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Novel benzylidene amidophosphites were prepared by the action of an imine on chlorophosphites at 0-5°C. The benzylidene amidophosphites readily underwent head-to-tail dimerization, with dimerization facilitated by a decrease in the steric volume of the substituent on the phosphorus atom. Greatest stability of the monomer was shown by a compound with two ethoxyl groups on the phosphorus atom. References 3: 1 Russian, 2 Western. [283-12172]

UDC 547.241

REARRANGEMENT IN C- AND N-PHOSPHORUS SUBSTITUTED AZOMETHINE ISOMERS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 5, May 85 (manuscript received 7 Sep 84) pp 1198-1199

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

[Abstract] N-Tert-butyl-N-propenylamidodichlorophosphite (I) was synthesized by the reaction of phosphorus trichloride with N-tert-butylpropioalimine at -20 to -30°C in absolute pentane. Reaction of I with methylmagnesium iodide led to a mixture of C-phosphorus substituted derivatives of azomethine, consisting of C-substituted aldimine and C-phosphorylated enamine. This indicates the migration of the P(III)-containing group from the nitrogen atom of N-phosphorus(III) substituted enamine to the C atom. References 3 (Russian). [283-12172]

UDC 547.241

SYNTHESIS OF 1-TERT-BUTYL-2,4-DICHLORO-1, $2\lambda^3$, $4\lambda^3$ -AZADIPHOSPHETIDINE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 5, May 85 (manuscript received 7 Sep 84) pp 1199-1201

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

[Abstract] 1-Tert-butyl-2,4-dichloro-1, $2\lambda^3$, $4\lambda^3$ -azadiphosphetidine (I) was synthesized at -40°C by the reaction of 1,2,4-azadiphosphetidines with acetyl chloride in ether. Reaction of I with diethylamine at -78°C led to the formation of 1-tert-butyl-2,4-bis(diethylamido)-1, $2\lambda^3$, $4\lambda^3$ -azadiphosphetidine (II) in the trans form. Over a period of 3 days at 20°C ca. 20% of II underwent rearrangement into the cis form, with no further change in the isomeric composition for over a month. References 3 (Russian). [283-12172]

UDC 547.241

SYNTHESIS AND CHELATING CHARACTERISTICS OF 1,2-PHENYLENEDIOXYMETHYLENE-DIPHOSPHONIC ACID

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 4, Apr 85 (manuscript received 4 May 84) pp 734-738

GROSS, G., MEDVED', T. Ya., NOVAK, S., BEL'SKIY, F. I., KEITEL, I. and KABACHNIK, M. I., Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow; Central Institute of Organic Chemistry, GDR Academy of Sciences, Berlin

[Abstract] A novel chelating agent, 1,2-phenylenedioxymethylenediphosphonic acid (I), was synthesized by the reaction of 1,2-phenylenedioxydichloromethane with triethyl phosphite for 5 h and subsequent acid hydrolysis. I was recrystallized from water in a 87% yield as a colorless crystalline substance with an M.P. of 165-167°C. I acts as a chelating agent for various cations, forming insoluble chelates with Cd^{++} , Hg^{++} , Pb^{++} , La^{++} , Nd^{+++} , Sm^{+++} , Er^{+++} and Yb^{+++} . Complexes with other cations are soluble, including those with the rare earth elements Eu^{+++} , Gd^{+++} , Tb^{+++} , Dy^{+++} and Ho^{+++} . In distinction to the standard stability ranking in which complexes with Mn^{++} are less stable than those formed with Co^{++} and Ni^{++} , the stability of chelates with Mn^{++} are on the same order of magnitude as those formed with Co^{++} or Ni^{++} . In the agent under study, the 1,2-phenylenedioxy substituent group appears to exert only an electronic effect on complex formation. Figures 2; references 18: 9 Russian, 9 Western. [282-12172]

UDC 547.241

SYNTHESIS AND CHARACTERISTICS OF 1,3,4,2-OXADIAZAPHOSPHOLINE IMIDES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 4, Apr 85 (manuscript received 27 Sep 83) pp 748-751

RAZHABOV, A. and YUSUPOV, M. M., Institute of Plant Substance Chemistry, Uzbek SSR Academy of Sciences, Tashkent

[Abstract] Imides of 1,3,4,2-oxadiazaphospholine were synthesized by the reaction of the amides with phenylazide, with the resultant imides undergoing hydrolysis to asymmetric diamido-beta-acetyl-alpha-phenylhydrazido-phosphates. The imides reacted with CS_2 on boiling for 10 h to form the corresponding thioamidophosphates and phenylisothiocyanate. In reactions with pyrocatechol, the reaction proceeded past imide substitution to yield tris(o-phenylenedioxy)phosphate alkylammonium. Neither 1,3,4,2-oxadiaza-phospholine nor the imide react with methyl iodide. References 3 (Western). [282-12172]

UDC 547.558.1

SYNTHESIS AND CHARACTERISTICS OF p-BROMOBENZOYL BROMIDE BISPHOSPHONIUM SALT

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 4, Apr 85 (manuscript received 22 Feb 84) pp 752-756

BUKACHUK, O. M. and SHEVCHUK, M. I., Chernovtsy State University

[Abstract] The bisphosphonium salt acetophenone (p-triphenylphosphonium- ω -triphenylphosphonium)dibromide (I) was synthesized by heating p-bromophenacetyl bromide with triphenylphosphine at 270-275°C for 3 h, using a reactant ratio of 1:3. I was isolated in the form of small crystals and characterized by IR and UV spectroscopies. Reaction of I with basic reagents results in the transformation of one of the phosphonium groups into phosphorus ylide, which reacts with aldehydes according to the Wittig reaction to give phosphonium analogs of stilbene. The ylide also enters into electrophilic additions with halogens and alkyl halides. The reactivity of the carbonyl group in I is retained, making possible the synthesis of novel phosphonium hydrazones and azobisphosphorus ylides. References 3 (Russian). [282-12172]

UDC 547.673+547.558.1'547.241

PHOSPHORUS YLIDES IN QUINONE SERIES: ANTHRAQUINONE DERIVATIVES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 4, Apr 85 (manuscript received 30 Jul 84) pp 756-762

LISTVAN, V. N. and STASYUK, A. P., Zhitomir Pedagogic Institute

[Abstract] Previously described approaches were utilized in the synthesis of phosphorus ylides containing anthraquinone rings, consisting of intensily emerald-green compounds stable over a period of several hours in anhydrous solvents [Listvan, VN, A. Ye. Arbuzov Jubilee Conf. on Organophosphorus Chemistry, Kiev, 1974, p 214]. The Wittig reaction for the preparation of unsaturated derivatives of anthraquinone can be conducted in biphasic CHCl₃ or CH₂Cl₂-50% NaOH system. In addition, with the most reactive aldehydes, the reaction can also be carried out with Et_3N in homogenous solutions, e.g., dimethylsulfoxide, ethanol, CH_2Cl_2 , etc. In the biphasic systems the anthraquinonylmethylenephosphoranes undergo C-acylation with benzoyl chloride. The formation of the emerald-green color can be used in a qualitative paper test for phosphonium salts by the addition of a drop of base to a drop of the chemical. References 9: 5 Russian, 4 Western. [282-12172]

UDC 547.241

STUDIES ON PHOSPHONIC AND PHOSPHONOUS ACID DERIVATIVES, PART 110. REACTION OF HYDROXYLAMINE WITH ARYL(ALKYL)ALKOXYPHOSPHONYL ACETATES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 4, Apr 85 (manuscript received 9 Jul 84) pp 773-776

MUKHACHEVA, O. A., SHCHELKUNOVA, M. A. and RAZUMOV, A. I., Kazan Institute of Chemical Technology imeni S. M. Kirov

[Abstract] Phosphorylated hydroxamic acids were prepared by the reaction of aryl(alkyl)alkoxyphosphonyl acetic acid esters with hydroxylamine. The hydroxamic structure was obtained from the alkoxycarbonyl group when 2 moles of hydroxylamine were used, with concurrent hydrolysis of the alkoxyl group on the phosphorus atom. In the presence of 3 moles of potassium methylate all three acid hydrogen atoms are replaced by potassium, yielding the tripotassium salts of aryl(alkyl)(beta-N-Hydroxy-imino-betahydroxyethyl) phosphonic acid. The tripotassium salts are white amorphous substances that are highly soluble in water and lower alcohols, but insoluble in apolar solvents. References 3: 2 Russian, 1 Western. [282-12172]

UDC 547.234.1+547.241+541.128

CATALYTIC EFFECTS OF PYRIDINE BASES ON REACTION OF DIPHENYL PHOSPHONIC ACID HYDRAZIDE WITH PHENYL ISOTHIOCYANATE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 4, Apr 85 (manuscript received 20 Aug 84) pp 824-829

YANCHUK, N. I. and BALUKH, V. M., Ternopol State Pedagogic Institute imeni Ya. A. Galan

[Abstract] The catalytic effects of various pyridine bases (3-cyanopyridine, 3-bromopyridine, 3-methylpyridine, 2-methylpyridine, 4-methylpyridine, 2,6-dimethylpyridine) on the reaction of diphenyl phosphonic acid hydrazide with phenyl isothiocyanate were studied with reaction conducted at 25°C in benzene. The pyridines were found to exert a catalytic effect on the reaction producing phosphorus-containing thiosemicarbazides. A linear relationship prevailed between the basicity of the base and the velocity constants. Highest catalytic activities--expressed as ratios of catalyzed to uncatalyzed rate constants--were exhibited by 4-methylpyridine (7688), 3-methylpyridine (3187), and pyridine (2309). The lowest catalytic efficiency was possessed by 3-cyanopyridine (19). Figures 2; references 18: 15 Russian, 3 Western. [282-12172]

UDC 541.49:547.26'118.787+546.814'131

2-ARYL-3,3-DIPHENYL-5-OXO-1,4,3-OXAPHOSPHOL-3-INES: COMPLEX FORMATION WITH TIN CHLORIDE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 4, Apr 85 (manuscript received 11 Jul 84) pp 829-833

TARASOVA, R. I., DVOYNISHNIKOVA, T. A. and ALPAROVA, M. V., Kazan Institute of Chemical Technology imeni S. M. Kirov

[Abstract] 2-Aryl-3,3-diphenyl-5-oxo-1,4,3-oxaphosphol-3-ines (I) were synthesized by cycloaddition between derivatized benzaldehydes and isocyanatodiphenyl phosphonite at 0-3°C in ether or methylene chloride. In air, the I compounds rapidly underwent hydrolysis to yield C-(diphenylphosphinylaryl)methyl carbamates (II). On mixing with tin chloride, I formed 1:1 complexes which, on neutral hydrolysis, yielded II compounds. References 6: 4 Russian, 2 Western. [282-12172]

UDC 547.1'118

PHOSPHORYLATION OF THIOACETIC ACID WITH P(III) ACID CHLORIDES -

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 4, Apr 85 (manuscript received 31 May 84) pp 932-933

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

[Abstract] Triacetyltrithiophosphite was prepared by the reaction of phosphorus trichloride with thioacetic acid. Phosphorylation of thioacetic acid with diphenylchlorophosphine in the presence of Et₃N leads to the formation of S-acetyldiphenylthiophosphinite (I). I is thermally unstable and undergoes fragmentation to diphenylacetylphosphine and tetraphenyldithionepyrophosphinate. References 4: 2 Russian, 2 Western. [282-12172]

UDC 546.183+647.55.1

N-PHOSPHORYLATED DIAZAPHOSPHOLANES DERIVED FROM N-METHYL-0-PHENYLENEDIAMINE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 4, Apr 85 (manuscript received 14 Jun 84) pp 933-934

AKHMEDZADE, D. A., MOSKVA, V. V., KULIYEV, A. K., PUDOVIK, M. A. and SAKHNOVSKAYA, Ye. B., Institute of Petrochemical Processes, Azerbaijan SSR Academy of Sciences, Baku; Kazan Institute of Chemical Technology; Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] 1-Methyl-2-diethylamido-3-tetraethyldiamidophosphito-4,5-benzo-1,3,2-diazaphospholane (I) was prepared by the action of hexaethyltriamidophosphite on N-methyl-o-phenylenediamine (II). I can also be prepared by reacting II with an excess of PCl₃ and subsequent amidation of the product, 1-methyl-2-chloro-3-dichlorophosphito-4,5-benzo-1,3,2-diazaphospholane, to I.

[282-12172]

UDC 546.183+547.55.1

N,N'-DIPHOSPHORYLATED 1,3,2-DIAZAPHOSPHOLANES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 4, Apr 85 (manuscript received 16 Jul 84) pp 935-936

MOSKVA, V. V., KULIYEV, A. K., AKHMEDZADE, D. A., PUDOVIK, M. A. and SAKHNOVSKAYA, Ye. B., Institute of Petrochemical Processes, Azerbaijan SSR Academy of Sciences, Baku; Kazan Institute of Chemical Technology; Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] Reaction of o-phenylenediamine with an excess of PCl₃ or hexaethyltriamidophosphite lead to the synthesis of 1,3-bis(dichlorophosphino)-2-chloro-4,5-benzo-1,3,2-diazaphospholane (I) and 1,3-bis(tetraethyldiamidophosphito)-2-diethyl-amido-4,5-benzo-1,3,2-diazaphospholane (II), respectively. Treatment of I with ethanol leads to the formation of the corresponding amide accompanied by the appearance of large quantities of triethyl phosphite, indicating the ease of alcoholysis of the exocyclic P-N bond. Action of diethylamine on I results in the formation of II via ammonolysis. References 1 (Russian). [282-12172]

UDC 546.183+547.587.11

OXAZAPHOSPHORINANES DERIVED FROM SALICYLAMIDE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 4, Apr 85 (manuscript received 16 Jul 84) pp 936-937

KULIYEV, A. K., MOSKVA, V. V., AKHMEDZADE, D. A., SAKHNOVSKAYA, Ye. B., ZYKOVA, T. V., SHAGVALEYEV, F. Sh. and GUSEYNOVA, M. M., Institute of Petrochemical Processes, Azerbaijan SSR Academy of Sciences, Baku; Kazan Institute of Chemical Technology

[Abstract] Depending on reactant proportions, the action of PCl₃ on salicylamide leads to the formation of 2-chloro-5,6-benzo-1,3,2-oxazaphosphorinan-4-one (I) and 2-chloro-3-dichlorophosphino-5,6-benzo-1,3,2-oxazaphosphorinan-4-one (II). The latter compound represents phosphorylation of I on the nitrogen atom. Treatment of I with PCl₃ also gives II. Amidation of I with diethylamine led to the synthesis of 2-diethylamido-5,6-benzo-1,3,2-oxazaphosphorinan-4-one. [282-12172]

UDC 547.341

REACTION OF PYROSULFUROUS ACID SALTS WITH CHLOROPHOSPHONIUM COMPOUNDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 4, Apr 85 (manuscript received 18 Sep 84) pp 938-939

MITRASOV, Yu. N. and KORMACHEV, V. V., Chuvash State University imeni I. N. Ul'yanov, Cheboksary

[Abstract] The use of sodium or potassium pyrosulfites for reaction with styryltrichlorophosphoniumhexachlorophosphonate led to the synthesis of pure styrylphosphonic dichloroanhydride. The reactions were carried out either in benzene or CCl_4 at 70-80°C. The effectiveness of the pyrosulfites was apparently due to their decomposition at this temperature range to sulfur dioxide. References 3 (Russian). [282-12172]

UDC 542.91:547.1'127'118

SYNTHESIS OF CYCLIC BORYLHYDROXYALKYLPHOSPHINES WITH ELECTRON-ACCEPTOR SUBSTITUENTS

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 5, May 85 (manuscript received 28 Feb 84) pp 1102-1106

IGNAT'YEVA, S. N., NIKONOV, G. N., YERASTOV, O. A. and ARBUZOV, B. A., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] Paramagnetic resonance and nuclear magnetic resonance study of the reaction of hydroxyalkylphosphines with electron-acceptor substituents for carbon atoms in the presence of phosphorus showed that reaction of hydroxyalkylphosphines with ethers or anhydrides of boric acids is the common method of producing borylhydroxyalkylphosphines. Hydroxyalkyl derivatives of phosphine, primary and secondary phosphines both with donor and acceptor substituents for carbon atoms in the presence of phosphorus and all types of boric acids may be introduced into it. Reaction of hydroxyalkylphosphines with electron-acceptor substituents with boric acid ethers and anhydrides and boric acid leads to formation of substituted 1,3-dioxa-5-phospha-boranyl-2-oxides. References 9: 7 Russian, 2 Western. [1841-2791]

UDC 542.91:547.1'118

INTERACTION OF OXOCHLORALKENES AND ETHERS OF PHOSPHOROUS ACID

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 5, May 85 (manuscript received 4 Apr 84) pp 1106-1108

MUKMENEVA, N. A., CHEREZOVA, Ye. N., YAMALIYEVA, L. N., KOLESOV, S. V., MINSKER, K. S. and KIRPICHNIKOV, P. A., Kazan Chemico-technological Institute imeni S. M. Kirov; Bashkir State University imeni 40th Anniversary of the October Revolution, Ufa

[Abstract] 2-oxo-5-chloroheptene-3 and 2-oxo-3-methyl-5-chlorohexene were synthesized and their reactions with tributylphosphite, a stabilizer of chlorine-containing polymers (3-120 hours, 20-80°) were studied, described and discussed. Tributylphosphite reacts with these model compounds through the oxovinylene fragment via the stage of formation of intermediate phosphoran structures which are converted into stable ketophosphonates. References 13: 5 Russian, 8 Western. [1841-2791]

UDC 542.91:547.1'118

TRANSFORMATION OF OXYALKYL ETHERS OF THIOPHOSPHONIC ACIDS, CONTAINING PHENOXY OR DIALKYLAMINO GROUPS OF PHOSPHORUS

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 5, May 85 (manuscript received 10 Jul 84) pp 1197-1200

NURETDINOVA, O. N. and NOVIKOVA, V. G., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] Ethers of alkyl(phenyl)thiophosphonic acids containing a phenoxy-or a dialkylamidogroup in the presence of a P atom were synthesized in a continuation of a study of the influence of the surroundings of the P atom in oxyalkyl.ethers on their transformation. It was found that 3-oxyalkyl ethers of ethyl(phenyl)-O-dialkylamido)thiophosphonic acids have less inclination twoard cyclization than do analogous ethers of diphenylthiophosphoric acid. References 2 (Russian). [299-2791]

PHARMACOLOGY AND TOXICOLOGY

UDC 547.458.61(088.8)

DESTRUCTION OF CARBOXYMETHYL STARCH UNDER ACTION OF gamma-RADIATION

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 1, Jan-Feb 85 (manuscript received 19 Dec 83) pp 12-14

FEDOROVA, G. A. and PETROV, P. T., Institute of Physical-Organic Chemistry BSSR Academy of Sciences, Minsk

[Abstract] Aqueous solutions of sodium carboxymethyl starches were subjected to gamma-radiation for the purpose of obtaining products having various molecular weight and hydrodynamic parameters for further study as possible polymer-carriers for medications. The study shows that, by varying the degree of carboxymethyl starch substitution and the radiation dosage, it is possible to obtain starch products having pre-assigned physical chemical and biological factors. Medical biological study indicates that they are sterile, non-toxic and totally compatible with animal bodies. Figures 2; references 6: 4 Russian, 2 Western. [288-12765]

UDC 547.92/.93;547.94

ALKALOID CARDENOLIDES

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 2, Mar-Apr 85 (manuscript received 25 Apr 84) pp 239-244

MAKAREVICH, I. F., IVANOV, L. V., KHADZHAY, Ya. I., BELOKON', V. F., PAVLOVA, V. V., KLIMENKO, O. I., BONDAR', N. Ya. and URYUPINA, Ye. V., All-Union Scientific-Technical Institute of Chemistry and Technology of Medicines, Khar'kov

[Abstract] Some new cardenolide derivatives were synthesized from the alkaloids ajmaline (rauwolfine), hyoscyamine and scopolamine and from 4aminoanthracine. The ajmaline cardenolides have both antiarrhythmic and cardiotonic activity with low to moderate toxicity, while hyoscyamine and scopolamine-strophanthidin are highly toxic compounds. Ajmolinestrophanthidin bromide has an affinity towards phospholipid membranes that is characteristic of many antiarrhythmic agents. The presence of a cardenolide group in this compound evidently enhances the binding of calcium ions to lipose membranes. Figure 1; references 6: 4 Ruwsian, 2 Western. [289-12765]

UDC 547.993

PHOSPHOLIPASE ACTIVITY OF ECHIS MULTISQUAMATUS VENOM

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 2, Mar-Apr 85 (manuscript received 25 Jan 84) pp 261-264

YUKEL'SON, L. Ya., ATAKUZIYEV, B. U. and SAKHIBOV, D. N., Institute of Biochemistry UzSSR Academy of Sciences, Tashkent

[Abstract] Most snake venoms contain A_2 phospholipases which differ markedly one from another in physical chemical properties and in biological activity. In the present work pure A_2 phospholipase of 15 kD molecular weight was obtained from snake venom by gel filtration over sephadex G-75 followed by chromatography over SP-sephadex G-25. During the gel filtration a second A_2 phospholipase of 10 kD molecular weight was obtained in pure form. Figure 1; references 8: 3 Russian, 5 Western. [289-12765]

UDC 547.964.4

PREPARATION AND PROPERTIES OF NEW STRUCTURAL ANALOG OF HUMAN INSULIN-- ASPARAGIN-B³⁰-INSULIN

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 2, Mar-Apr 85 (manuscript received 3 Jul 84) pp 279-280

SHVACHKIN, Yu. P., NIKITINA, A. M., FUNTOVA, S. M., KRASNOSHCHEKOVA, S. P., FEDOTOV, V. P. and IVANOVA, A. I., Institute of Experimental Endocrinology and Hormone Chemistry, USSR Academy of Medical Sciences, Moscow

[Abstract] A previously unknown human insulin analog was prepared by enzymatic transamidization of swine insulin by splitting off of protective groups by chemical means. The new analog differs from the natural hormone by having an L-asparagine group in the B^{30} position instead of L-threonine. Tests for spasmolytic effect on mice show that the compound has 85% activity as compared to that of an international standard. References 3: 2 Russian, 1 Western. [289-12765]

UDC 547.964+547.854

PREPARATION AND PROPERTIES OF METHYL ESTER OF HUMAN VILLARDIINE-B³⁰-INSULIN

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 2, Mar-Apr 85 (manuscript received 10 Nov 85) pp 280-281

SHVACHKIN, Yu. P., NIKITINA, A. M., FUNTOVA, S. M., KRASNOSHCHEKOVA, S. P., VOSKOVA, N. A., RYABTSEVA, O. N., FEDOTOV, V. P. and IVANOVA, A. I., Institute of Experimental Endocrinology and Hormone Chemistry, USSR Academy of Medical Sciences, Moscow; Moscow Order of Lenin and Order of Labor Red Banner State University imeni M. V. Lomonosov

[Abstract] Methyl ester of human villardiine-B³⁰-insulin was prepared by trypsin catalyzed transformation of swine insulin with methyl ester of Lbeta-(uracilyl-N')-alpha-alanine. This analog of human insulin has intense UV-absorption, making it suitable for study of molecular reaction mechanisms of human insulin. Tests on mice show that it has 95% biological activity (spasmolytic effect) as compared with an international standard. References 6: 5 Russian, 1 Western. [289-12765]

POLYMERS AND POLYMERIZATION

UDC 541.64:539.2

HYDROSTATIC EXTRUSION OF POLYMERS. CHANGE OF PROPERTIES AND STRUCTURE

Kiev DOKLADY AKADEMII NAUK UKRAINSKOY SSR: SERIYA B. GEOLOGICHESKIYE, KHIMICHESKIYE I BIOLOGICHESKIYE NAUKI in Russian No 4, Apr 85 (manuscript received 26 Oct 84) pp 47-49

BERESNEV, B. I., corresponding member, UkSSR Academy of Sciences, YENIKOLOPOV, N. S., academician, TSYGANKOV, S. A. and SHISHKOVA, N. V., Donets Physico-Technological Institute of UkSSR Academy of Sciences; Institute of Chemical Physics of USSR Academy of Sciences, Moscow; Scientific Production Association "Plastopolimer," Leningrad.

[Abstract] Solid-phase polyolefins, fluorinated plastics and ABS plastics were hydrostatically extruded at temperatures of 20-70° C below the melting point of crystalline polymers and 10-30° C below the vitrification point of amorphous plastics using pressures of 5-250 MPa. Extruded samples were noticeably transparent and rigid. These properties increased with the degree of deformation (R). Some polyolefins reached an R = 25 and a modulus of elasticity comparable to fiberglass. Improvements were somewhat less for amorphous plastics, but these did show a significant increase in toughness. Fluorinated plastics did not reach an R > 4, but showed the same regular increases in stiffness and elasticity as the polyolefins. Analysis showed that these changes were due to orientational effects, specifically, crystal orientation parallel to the drawing axis for the polyolefins and fluorinated plastics. For high degrees of deformation, intrafibrillar amorphous layers were practically absent and the submolecular structure showed alternating sinuous layers. Solid-phase extrusion can produce finely dimensioned, highly elastic shapes and can be applied to a much wider range of products than in the past. Figures 2; references 4: 2 Russian, 2 Western. [271-12672]

UDC 541.64:539.2

EFFECT OF MORPHOLOGY OF POLYTETRAFLUOROETHYLENE ON CHANGE IN DEGREE OF CRYSTALLINITY DURING TREATMENT WITH ELECTRONS. EFFECTS OF ANNEALING AND QUENCHING

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 27, No 5, May 85 (manuscript received 5 Aug 83) pp 914-920

KOCHERVINSKIY, V. V., GLUKHOV, V. A., LEONT'YEV, V. P. and DANILYUK, T. Ye., Moscow Textile Institute imeni A. N. Kosygin

[Abstract] The effect of morphology of polytetrafluoroethylene film on the extent of change in crystallinity due to electron treatment was studied acoustically by changing the thermal past history of oriented and nonoriented films. Annealing and quenching changes both the morphology and the radiation resistance. This is apparently due to the appearance of skeletal bonds and imperfections in the form of microfissures as well as an increase in the concentration of conformational defects with higher energy. All of these factors should tend to lower the potential carrier required for bond rupture during irradiation. Figures 6; references 35: 9 Russian, 26 Western. [290-12765]

UDC 541.64:547.239.1

REACTIVITY OF 2,4-TOLUYLENEDIISOCYANATE DURING REACTION WITH OLIGOBUTADIENEDIOL

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 27, No 5, May 85 (manuscript received 10 Aug 83) pp 921-926

LODYGINA, V. P., STOVBUN, Ye. V. and BATURIN, S. M., Department of Institute of Chemical Physics, USSR Academy of Sciences

[Abstract] A study was made of the reactivity of the NCO-groups in 2,4toluylenediisocyanate in reactions with hydroxyl groups of oligobutadienediol at various temperatures. The rate constants for individual stages of urethane formation were determined both experimentally and by mathematical modeling on a computer. Allophanate formation reactions were observed to occur at temperatures above 50° and [NCO]:[OH] ratios of 2:1. Figures 3; references 12: 7 Russian, 5 Western. [290-12765]

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UDC 541.64:547.1'128

SYNTHESIS AND STUDY OF THERMOOXIDATIVE BREAKDOWN OF SILICON-ORGANIC URETHANES

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 27, No 5, May 85 (manuscript received 27 Aug 83) pp 931-937

KUZ'MENKO, N. Ya. and BUGRYM, V. V., Dnepropetrovsk Chemical-Technological Institute imeni F. E. Dzerzhinskiy

[Abstract] Silicon-organic urethanes were synthesized from silicon-organic hydroxyl compounds having various length carbofunctional groups and the resistance of these compounds to thermooxidative breakdown was studied. Infra-red spectroscopy and derivatographic analysis data are presented which are used to evaluate quantitatively the effects of such factors as length of the carbofunctional group from the silicon atom and the nature of the isocyanate group on the resistance of the urethane bond to thermooxidative breakdown. Figures 4; references 18: 16 Russian, 2 Western. [290-12765]

UDC 541.64:542.954

PREPARATION AND PROPERTIES OF FREE FILMS BASED ON EPOXYDIANE AND PHENOLOFORMALDEHYDE OLIGOMERS

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 27, No 5, May 85 (manuscript received 5 Sep 83) pp 1000-1007

MARKEVICH, M. A., KUZAYEV, A. I., VLADIMIROV, L. V., SHASHKIN, D. P., KISELEV, M. R. and CHURAKOV, V. V., Institute of Chemical Physics, USSR Academy of Sciences

[Abstract] A study was made of the conditions under which structuring and shaping of free films of epoxydiane and resol phenolformaldehyde oligomers, hardened with o-phosphoric acid, take place. Chromatography shows that after heating the above oligomers at 120° for 5 hours, no reaction takes place. Infra-red spectroscopy shows that hardening the compositions at 200° results in a change in absorption of the C-O bond in the aliphatic alcohols and ester bridges and in the C=C bonds of the benzene ring due to crosslinking of the oligomers. IR-spectra also indicate that the chemical composition and structures of the surface and bulk layers of the polymers are identical. Both the original oligomers and films made from them are X-ray amorphous. The hypomolecular structure of the films is globular and the size of the globules increases slightly with molecular weight. Figrues 6; references 22: 19 Russian, 3 Western. [290-12765]

UDC 541.64:539.2

SYNTHESIS AND STUDY OF POROUS STRUCTURE OF NEW ACRYLATE BASED NITROGEN-PHOSPHORUS-CONTAINING CROSSLINKED POLYMERS

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 27, No 5, May 85 (manuscript received 12 Sep 83) pp 1035-1039

BALAKIN, V. M., TSILIPOTKINA, M. V., TESLER, A. G., GEORGIYEVSKAYA, M. I. and VYDRINA, T. S., Urals Forestry Institute imeni Leninskiy Komsomol; Urals State University imeni A. M. Gor'kiy

[Abstract] A method is described for the synthesis of some new nitrogen and phosphorus-containing crosslinked polymers based on methyl acrylate and divinyl benzene. The sorption capacities some of them with respect to uranyl, copper and trivalent iron ions was studied. Tracing the porous structure genesis of crosslinked methylacrylate-divinyl benzene copolymers during aminolysis and phosphorylation showed that a general tendency towards lower porosity exists during these reactions. The magnitude of these changes depends on the content of crosslinking agent in the copolymer and the nature of the aminolyzing agent. Figures 3; references 11 (Russian). [290-12765]

UDC 541.64:539.2

STRUCTURAL FEATURES AND PROPERTIES OF HIGH AND LOW DENSITY POLYETHYLENE COMPOSITIONS AND HIGHLY ORIENTED SYSTEMS BASED ON THEM

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 27, No 5, May 85 (manuscript received 17 Sep 83) pp 1047-1054

ARTEM'YEV, V. A., GOL'DMAN, A. Ya., MYASNIKOV, G. D. and SUL'ZHENKO, L. L., Scientific-Production Association "Plastpolimer"

[Abstract] Using a mixture of high and low density polyethylenes as an example, the structure and properties of both a polymer-polymer and a highly oriented system based on them were studied. The physical-mechanical properties of the substances are shown to be a complex function of the composition of the mixture, determined mainly by the non-uniformity of the system. This is supported by the rheological characteristics of melts over a wide range of compositions and shear stress. Experiments show that mixtures containing 80% high density polyethylene result in pressed and oriented samples having higher orders of mechanical properties than those of the initial polymers. Figures 4; references 12: 9 Russian, 3 Western. [290-12765]

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UDC 66.095.678.76

VINYLATION KINETICS OF METHYLATED BENZENE SERIES BY ACETYLENE OVER CATIONIC CATALYST

Baku AZERBAYDZHANSKIY KHIMICHESKIY ZHURNAL in Russian No 1, Jan-Feb 85 pp 62-67

NASIROV, F. M., ASLANOVA, N. F. and KULIYEVA, V. G., Institute of Theoretical Problems of Chemical Technology, Azerbaijan SSR Academy of Sciences

[Abstract] Reaction kinetics were analyzed for the vinylation of methylated derivatives of benzene by acetylene on ethyl aluminum dichloride. Studies conducted over the temperature range of 0 to 40°C demonstrated that the benzene derivative ranked as follows in terms of reactivity: toluene< o-xylene<m-xylene<mesitylene. This form of ranking indicates that the contribution of steric factors to vinylation in this case were less significant than the electron donor characteristics. Under the most favorable conditions the polymer yield at 30°C ranged from 8-24% after 40 min to 15-45% after 3 h. Acetylene conversion was 100% in all cases, regardless of the benzene derivative and reaction conditions. Figures 4; references 14: 10 Russian, 4 Western. [303-12172]

UDC 678.017

CHEMICAL MODIFICATION OF FILLED POLYETHYLENE

Baku AZERBAYDZHANSKIY KHIMICHESKIY ZHURNAL in Russian No 1, Jan-Feb 85 pp 68-72

KAKHRAMANOV, N. T., ZAIDOVA, R. R., BURDZHALIYEV, D. A. and ISMAILOV, Kh. M., Azerbaijan Institute of National Economy imeni D. Buniat-zade

[Abstract] Physicomechanical characteristics of chalk- or quartz fluorinetreated polyethylene were analyzed in relation to the degree of filling and the effects of peroxide-mediated cross-linking. In the case of linear polyethylene optimal results were obtained when either filler was used to 10-15 wt% extent. Polymers filled with 20 wt% filler exhibited crystallinity and friability. Filling and subsequent cross-linking showed that the concentration of filler could be raised to 25-30 wt% with retention of optimal physicomechanical properties. Chemical cross-linking significantly increased the elasticity of filled polyethylene. Figure 1; references 3 (Russian). [303-12172]

RADIATION CHEMISTRY

UDC 678.742.2.046.7:678-952

RADIOTHERMOLUMINESCENCE OF RADIATION-MODIFIED POLYETHYLENE

Riga IZVESTIYA AKADEMII NAUK LATVIYSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 2, Mar-Apr 85 (manuscript received 20 Oct 84) pp 179-184

TILTINYA, I. I., VAYNSHTEYN, A. B., MILLERS, D. K., GRIGOR'YEVA, L. G. and KARLIVAN, V. P., Riga Polytechnical Institute imeni A. Ya. Pel'she; Scientific Research Institute of Physics of Solid Bodies of Latvian State University imeni P. Stuchki.

[Abstract] Radiothermoluminescence of high-molecular-weight compounds is indicative of molecular movement and structural transformations; spectral analysis can provide some of the details of these changes. Films of polyethylene with and without 4% hexabromodiphenyl oxide tetracarboxylic acid tetraalyl ester were degassed, cooled, subjected to x-ray radiation at 77° K, and their radiothermoluminescence measured. The constant of the speed of recombination was significantly higher for polyethylene with the additive than without it. Spectral composition changed noticeably with temperature and produced a characteristically asymmetric curve with a maximum in the region 440-480 nm, corresponding to phosphorescence. Spectral composition also changed with the time of irradiation and was quite different for polyethylene with the additive--often indistinguishable from background at short irradiation times but showing a higher intensity at longer irradiation times. Thus, the additive is structurally active with polyolefins, changing the spectral output and the ratios of intensities of individual spectral bands. Figures 5; references 7 (Russian). [287-12672]

UDC 541.64:15+543.42.062

RADIATION POLYMERIZATION OF OLIGOCARBONATEMETHACRYLATES OF LEVOGLUCOSANS

Riga IZVESTIYA AKADEMII NAUK LATVIYSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 2, Mar-Apr 85 (manuscript received 18 Oct 84) pp 185-189

PERNIKIS, R. Ya., ZAKS, I. N. and KRONBERGA, V. Zh., Institute of Wood Chemistry, LaSSR Academy of Sciences

[Abstract] Thin layers of three standard levoglucosan oligocarbonatemethacrylates on KBr tablets were subjected to radiation from Co^{60} . Even small radiation doses led to rapid conversion to reticular polymers. Infrared spectroscopy showed significant decreases in the intensity of extinction bands at 1640, 1420 and 820 cm⁻¹, indicating polymerization proceeded by opening of double bonds. Increasing radiation doses also produced infrared spectral changes indicating oxidative and destructive reactions within the samples. The maximum amount of transformation (70-80%) was reached at an irradiation level of 20 kGR with subsequent thermal conditioning for 24 hours at 120° C. Figures 3; references 11 (Russian). [287-12672]

WATER TREATMENT

UDC 628.3:543.2

CHEMICAL ANALYSIS OF WASTE WATERS FROM DRY CLEANING AND DYEING PLANT

Baku AZERBAYDZHANSKIY KHIMICHESKIY ZHURNAL in Russian No 1, Jan-Feb 85 pp 119-121

IL'YAYEV, D. V., SHIKHALIZADE, P. D., GANIYEVA, T. F. and SALIMOVA, N. A., Azerbaijan Institute of Oil and Chemistry imeni M. Azizbekov

[Abstract] Chemical analysis of the waste waters from a dry cleaning and clothes dyeing plant yielded the following data: 290-350 mg/L petroproducts, 2000-2500 mg/L detergents, 400-450 mg/L soaps, 290-370 mg/L fats, 30-40 mg/L phosphorus, 690-760 mg/L sulfate, and 300-390 mg/L Cl⁻. The pH of the samples varied from, 7 to 7.5, and the biochemical oxygen supply was calculated at 590-850 mg/L. Rinse water had lower concentrations of the chemicals of interest, with the biochemical oxygen supply reduced to 280-300 mg O₂/L. References 4 (Russian). [303-12172]

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