ZAVGORODNIY, N.S.; MCHEDLOV-PETROSYAN, O.P.; SIDOCHENKO, I.M.; STRELKOVA, I.S.

Termographic characteristics of marls from the Amvrosiyevka deposits. (MIRA 13:11)
TSement 26 no.4:8-10 Jl-Ag '60.
(Marl)

SIDOCHENKO, I.M.; ZAVGORODNIY, N.S.

Producing "700" and "800" types of portland cement. TSement 27 no.3:19-20 My-Je '61. (MIRA 14:7)
(Portland cement)

ZAVGORODNIY, N.S., inzh.; SIDOCHENKO, I.M., inzh.

Production of high-strength cement at the Amvrosievka cement combine. Nauch. soob. NIITSementa no.12:24-27 '61. (MIRA 15:7)

1. Amvrosiyevskiy tsementnyy kombinat.
(Amvrosievka--Cement)

SIDOCHENKO, I.M., inzh.; ZAVGORODNIY, N.S., inzh.; ROS', N.A., inzh.

System of open-pit mining of wet marl. Gor.zhur. no.5:20-22 My '61. (MIRA 14:6)

1. Amvrosiyevskiy tsementnyy kombinat, Amvrosiyevka, Stalinskoy oblasti.
(Strip mining--Cold weather conditions) (Marl)

ZAVGORODNIY, N.S.; MCHEDLOV-PETROSYAN, O.P.; SIDOCHENKO, I.M.; STRELKOVA, I.S.

Determination of slags and gypsum in cements by the thermographic method. TSement 28 no.2:13-15 Mr-Ap '62. (MIRA 15:8)
(Cement)

SIDOCHENKO, I.M.; ZAVGORODNIY, N.S.; REYGAUZEN, L.V.

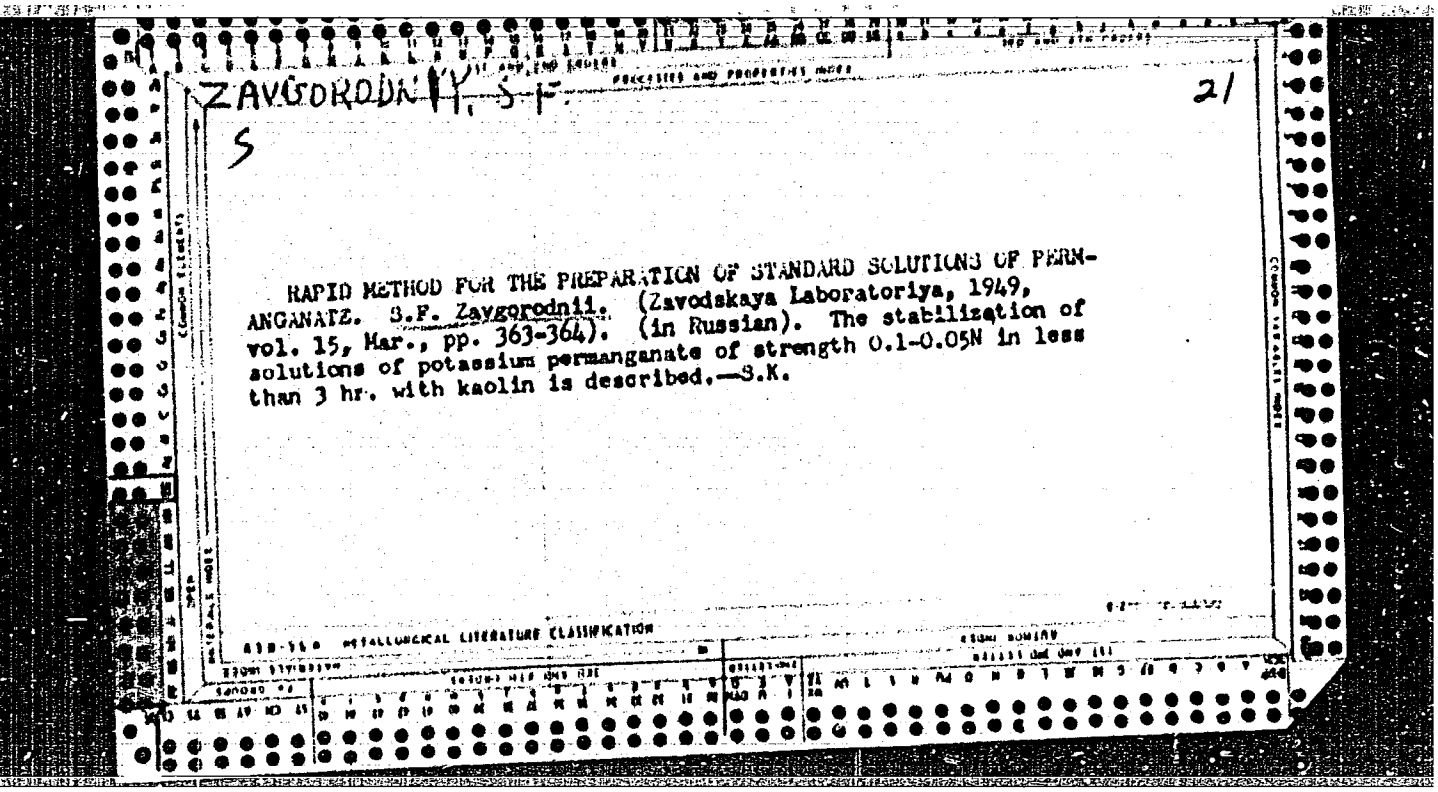
Some defects in design. TSement 27 no.4:13-14 Jl-Ag '61. (MIRA 14:8)

(Cement plants)

SIDOCHENKO, I.M., inzh.; ZAVGORODNIY, N.S., inzh.; MASHKOVICH, M.I., inzh.; REYNGAUZEN, L.V., inzh.; RIVKIN, V.D., inzh.; SHTEYNMAN, Ye.Ye., inzh.

Introduce the system of the automatic control of clinker firing. TSement 30 no. 2:15-17 Mr-Ap '64. (MIRA 17:5)

1. Amvrosiyevskiy tsementnyy kombinat i LSPNU tresta "Sevzapmontazhavtomatika".



ZAVGORODNYY, S.F.

S

21

RAPID METHOD FOR THE PREPARATION OF STANDARD SOLUTIONS OF PERMANGANATE. S.F. Zavgorodnii. (Zavodskaya Laboratoriya, 1949, vol. 15, Mar., pp. 363-364). (in Russian). The stabilization of solutions of potassium permanganate of strength 0.1-0.05N in less than 3 hr. with kaolin is described.—S.K.

ZAVGORODNY, S. F. (Serafim Fedorovich)

Analytical Abst.
Vol. 1 1.
Jan. 1954
General Analytical Chemistry

16. Analytical use of the reaction of hydrolysis of potassium manganate. S. F. Zavgorodny U. Anal. Chem., U.S.S.R., 1953, 8, 172-174).—The determination of manganate by hydrolysis to MnO_2 by means of CO_2, $KHSO_4$, etc., gives low results except in the presence of at least 10 mol. of $KMnO_4$ to each mol. of K_2MnO_4. G. S. SMITH

4 D Chem

MF 9-22-54

GALKINA, Ye.I.; ZAVGORODNIY, S.F.

Use of sodium tripolyphosphate for determining the calcium and magnesium content in river and mineral waters. Lab.delo 7 no.11:36-38 N '61. (MIRA 14:10)

1. Kafedra neorganicheskoy i analiticheskoy khimii Rostovskogo-na-Donu meditsinskogo instituta.
(SODIUM TRIPHOSPHATES) (WATER--ANALYSIS)

GAIKINA, Ye.I.; ZAVGORODNIY, S.F.

Determination of calcium and magnesium in the blood serum using sodium tripolyphosphate. Vop. med. khim. 9 no.2:207-209 Mr-Ap '63. (MIRA 17:8)

1. Kafedra neorganicheskoy i analiticheskoy khimii Rostovskogo-na-Donu meditsinskogo instituta.

ACCESSION NR: AP4033426 Z/0055/64/014/004/0271/0274

AUTHOR: Zavetova, M.

TITLE: The refractive index of CdSb in the neighborhood of the absorption edge

SOURCE: Chekhoslovatskiy fizicheskiy zhurnal, v. 14, no. 4, 1964, 271-274

TOPIC TAGS: cadmium antimonide, refractive index, absorption edge, prism, frequency dependence

ABSTRACT: Fig. 1 of the Enclosure summarizes the results of an experiment in which the prism method was exploited to measure the refractive index of cadmium antimonide at room temperature in the region of the absorption edge (2.3 to 3.1 μ). The index was determined through measurement of the angle δ by which a beam of parallel rays was deflected from its original direction after passing through the prism and through calculation according to Snell's law

$$n = \frac{\sin(\alpha + \delta)}{\sin \alpha},$$

Card 1/4

ACCESSION NR: AP4033426

where α is the angle of refraction of the prism. Three prisms, each of whose refractive edges were parallel to one of the crystallographic axes, were cut from the same p-type CdSb monocrystal (impurity concentration $n = 3 \times 10^{16}$ cm^{-3}) and then ground and optically polished. A surface of 10 x 8 mm was irradiated, with $\alpha = 10$ deg. The radiation source was a Nernst filament chopped with a frequency of 200 cps. The detecting equipment, attached to the moving arm of a Zeiss SGO 1.1 goniometer, consisted of a Glan-Thompson polarizer and an LiF lens. The PbS cell, located below the diaphragm slit into which the lens focused the beam, was connected to an amplifier with a synchronous detector. The angle δ was read by a microscope from the sectioned circle of the goniometer. The small maximum observed near the absorption edge for all three axes harmonizes with the theoretical work of B. Velicky (Thesis, Mat.-Phys. Fac., Charles University, 1960). From the measured values the coefficient of reflection R was calculated according to the relationship

$$R = \frac{(n-1)^2}{(n+1)^2},$$

Card 2/4

ACCESSION NR: AP4033426

The values of R for the a, b, and c axes at hν = 400 to 540 ev range between 40.5 and 43.3%. This is in good agreement with the value of 42% found in two previous papers by the author employing a different method with an error of ±5%. It does not agree with the value of 21% (n = 2.7) found by F. Ermanis and E. Miller (J. El-chem. Soc., 108, 1961, 1048), but the discrepancy is explained by the effect of surface layers present on the samples employed in that previous study. Values for the dielectric constant over the same energy range varied from 20.22 to 23.51.

ASSOCIATION: Institute of Solid State Physics, Czechosl. Acad. Sci., Prague

SUBMITTED: 190ct63 DATE ACQ: 01May64 ENCL: 01

SUB CODE: GP NO REF SOV: 000 OTHER: 008

Card 3/4

ACCESSION NR: AP4033426

ENCLOSURE: 01

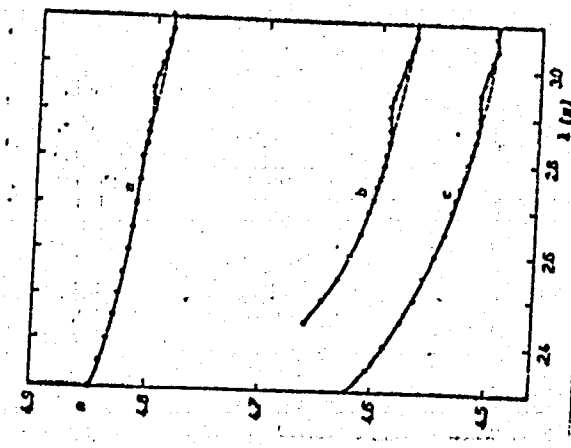


Fig. 1. Frequency dependence of the refractive index of CdSb in the neighbourhood of the absorption region. The letters *a*, *b* and *c* denote the cases of $\vec{E}$ parallel to the crystallographic axis *a*, *b* and *c* respectively.

Card 4/4

KLEYMENOV, Vladimir Vasil'yevich, inzh.; BOLYAYEV, Ivan Pavlovich, kand.-tekhn.nauk, dotsent; NAZIKYAN, Artem Georgiyevich, kand.tekhn.nauk; ZAVEZEN, Aleksandra Fedorovna

Simultaneous use of analog and digital computers in studying processes in electrical machines. Izv. vys. ucheb. zav.; elektromekh. 6 no.1: 11-24 '63. (MIRA 16:5)

1. Nachal'nik laboratorii elektronnykh vychislitel'nykh mashin Novocherkasskogo nauchno-issledovatel'skogo instituta elektrovozostroyeniya (for Kleymenov). 2. Kafedra elektricheskikh mashin, apparatov, matematicheskikh i schetnoreshayushchikh priborov i ustroystv Novocherkasskogo politekhnicheskogo instituta (for Bolyayev, Nazikyan). 3. Starshiy inzhener laboratorii vychislitel'nykh mashin Novocherkasskogo politekhnicheskogo instituta (for Zavezen).
(Electric machinery)
(Electric machinery--Electromechanical analogies)

ZAVFORODNYY, P.Ye.; LEBEDEV, L.V. (Leningrad, Botkinskaya ul., d. 21. komn. 107)

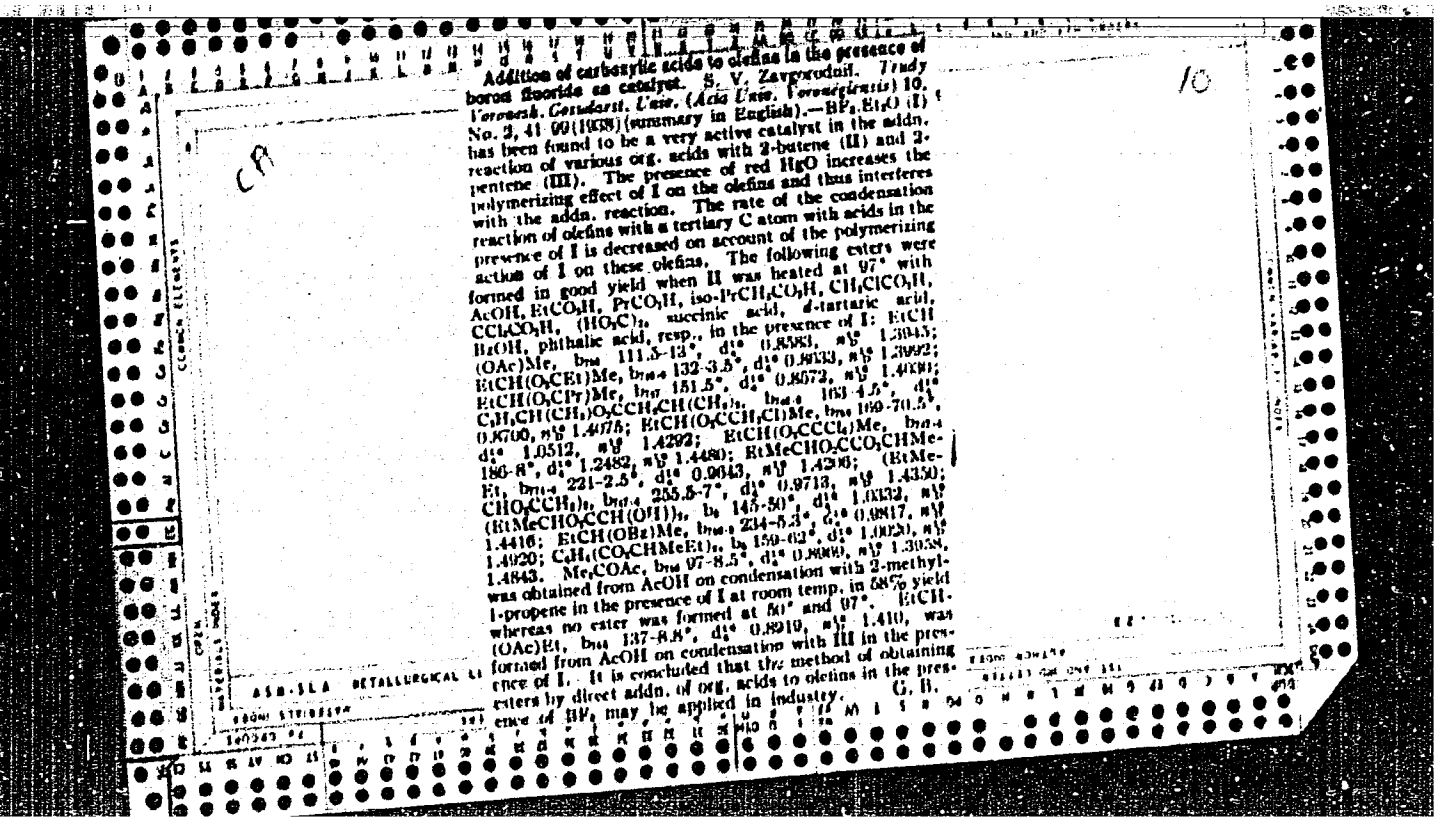
Plastic surgery of the axillary artery using a lavsan prosthesis. Vest. khir. 91 no.7:72-73 Jl'63 (MIRA 16:12)

1. Iz fakul'tetskoy khirurgicheskoy kliniki (nachal'nik - prof. V.M.Sitenk) Voyenno-meditsinskoy ordena Lenina akademii imeni S.M.Kirova.

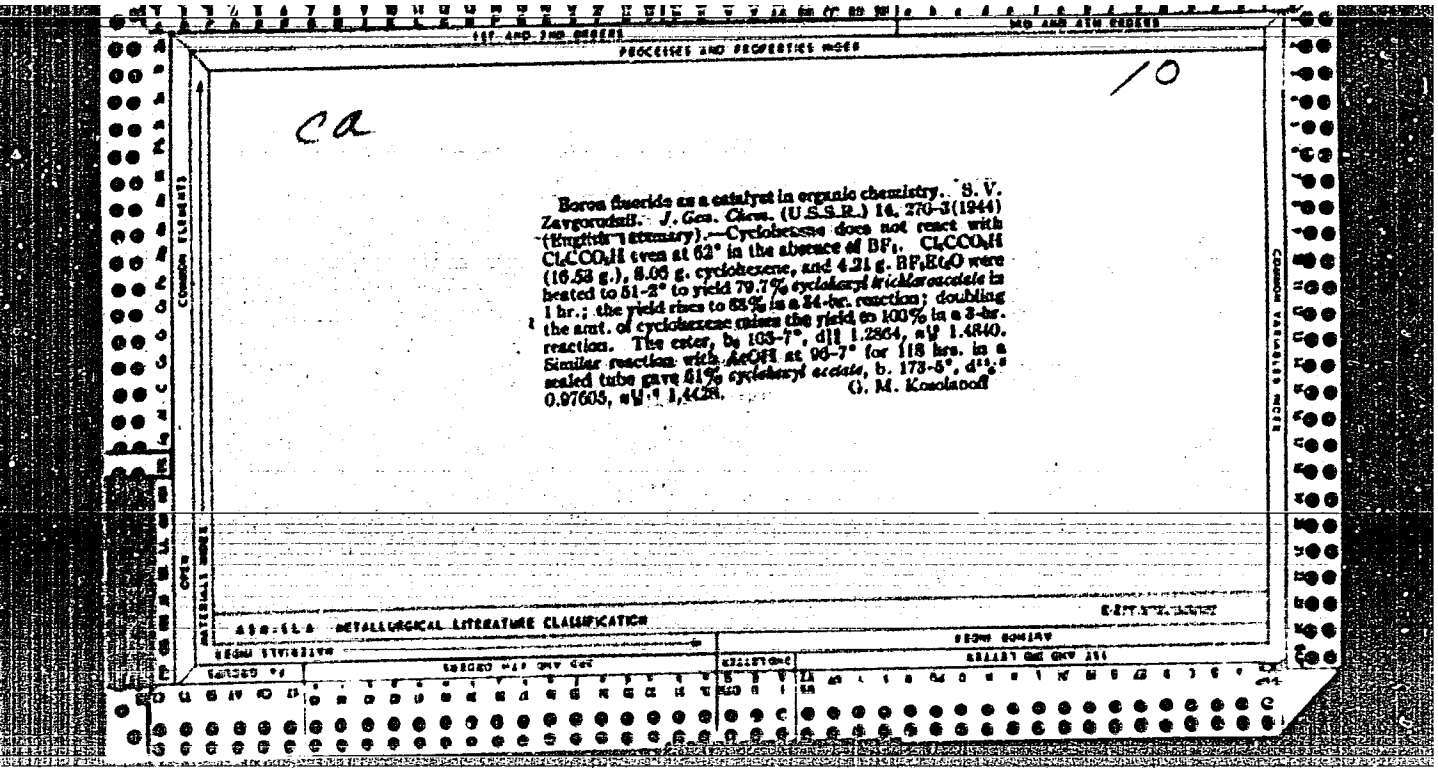
GALUSHKO, V.P.; ZAVGORODNYAYA, Ye.F.; RODAK, Yu.P.

Cathodic reduction of some sparingly soluble cobalt compounds. Zhur. prikl. khim. 38 no. 10:2349-2351 O '65. (MIRA 18:12)

1. Dnepropetrovskiy gosudarstvennyy universitet imeni 300-letiya vossoyedineniya Ukrainy s Rossiyey. Submitted Nov. 12, 1963.



Addition of carboxylic acids to olefins in the presence of boron fluoride as catalyst. S. V. Zavgorodnii. *Trudy Voronezh. Gosudarst. Univ. (Acta Univ. Voronegiensis)* 10, No. 2, 41-99(1938)(summary in English).—$BF_3.Et_2O$ (I) has been found to be a very active catalyst in the addn. reaction of various org. acids with 2-butene (II) and 2-pentene (III). The presence of red HgO increases the polymerizing effect of I on the olefins and thus interferes with the addn. reaction. The rate of the condensation reaction of olefins with a tertiary C atom with acids in the presence of I is decreased on account of the polymerizing action of I on these olefins. The following esters were formed in good yield when II was heated at 97° with AcOH, $EtCO_2H$, $PrCO_2H$, iso-$PrCH_2CO_2H$, CH_2ClCO_2H, CCl_3CO_2H, $(HO_2C)_2$, succinic acid, *d*-tartaric acid, $BzOH$, phthalic acid, resp., in the presence of I: $EtCH(O_2CMe)Me$, b_{760} 111.5-13°, d_4^{20} 0.8383, n_D^{20} 1.3845; $EtCH(O_2CEt)Me$, b_{760} 132-3.5°, d_4^{20} 0.8933, n_D^{20} 1.3992; $EtCH(O_2CPr)Me$, b_{760} 151.5°, d_4^{20} 0.8672, n_D^{20} 1.4080; $C_5H_{11}CH(CH_3)O_2CCH_2CH(CH_3)_2$, b_{760} 163-4.5°, d_4^{20} 0.8700, n_D^{20} 1.4078; $EtCH(O_2CCH_2Cl)Me$, b_{760} 169-70.5°, d_4^{20} 1.0512, n_D^{20} 1.4292; $EtCH(O_2CCCl_3)Me$, b_{760} 180-8°, d_4^{20} 1.2482, n_D^{20} 1.4480; $EtMeCHO_2CCO_2CHMeEt$, b_{760} 221-2.5°, d_4^{20} 0.9043, n_D^{20} 1.4296; $(EtMeCHO_2C)_2CH_2$, b_{760} 255.5-7°, d_4^{20} 0.9713, n_D^{20} 1.4350; $(EtMeCHO_2CCH(OH))_2$, b_5 145-50°, d_4^{20} 1.0332, n_D^{20} 1.4416; $EtCH(OBz)Me$, b_{760} 234-5.5°, d_4^{20} 0.9817, n_D^{20} 1.4920; $C_6H_4(CO_2CHMeEt)_2$, b_5 159-62°, d_4^{20} 1.0020, n_D^{20} 1.4843. Me_2COAc, b_{760} 97-8.5°, d_4^{20} 0.8880, n_D^{20} 1.3958, was obtained from AcOH on condensation with 2-methyl-1-propene in the presence of I at room temp. in 58% yield whereas no ester was formed at 50° and 97°. $EtCH(OAc)Et$, b_{760} 137-8.8°, d_4^{20} 0.8919, n_D^{20} 1.410, was formed from AcOH on condensation with III in the presence of I. It is concluded that the method of obtaining esters by direct addn. of org. acids to olefins in the presence of BF_3 may be applied in industry. G. B.



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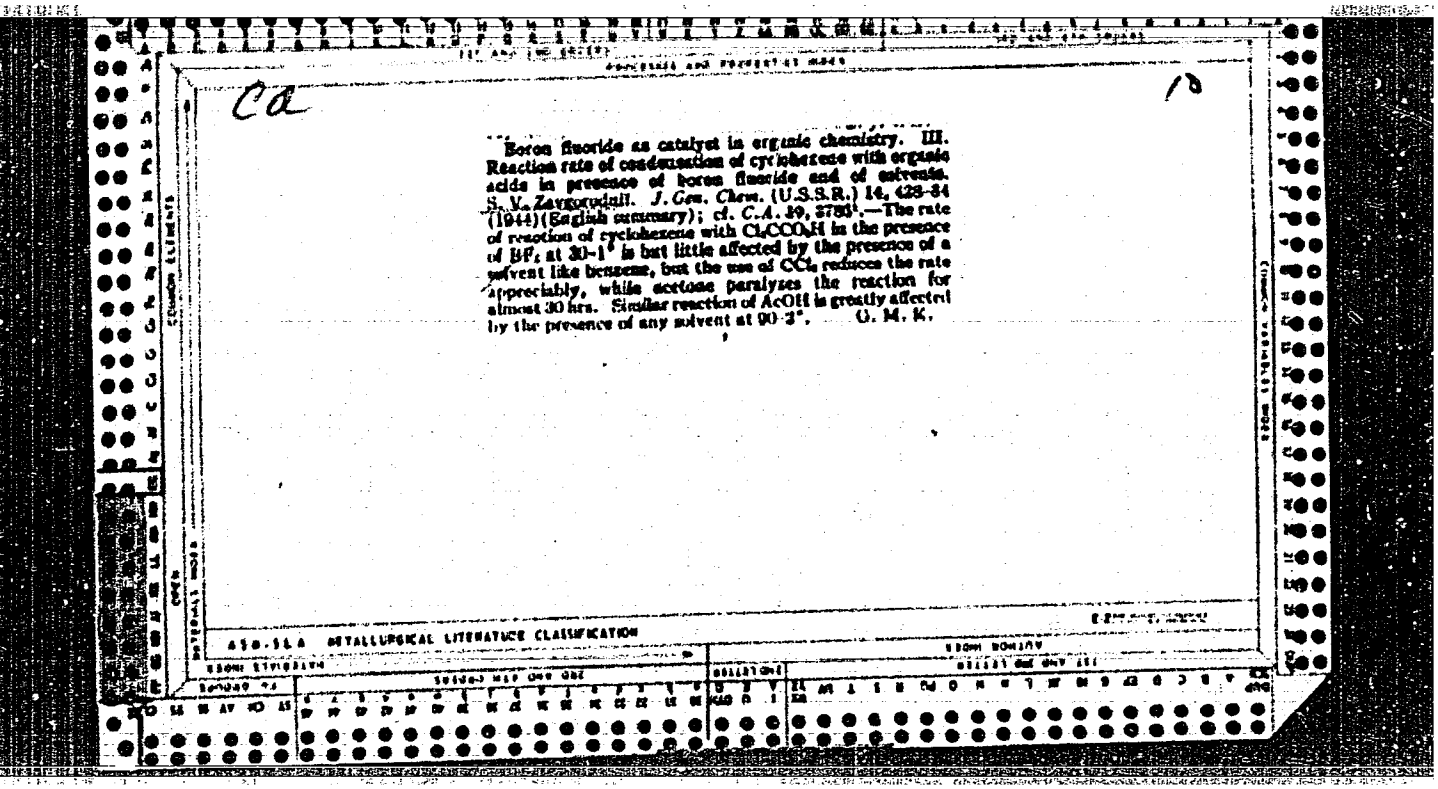
Boron fluoride as a catalyst in organic chemistry. S. V. Zavgorodnii. *J. Gen. Chem.* (U.S.S.R.) 14, 270-3(1944) (English translation). —Cyclohexene does not react with Cl_3CCO_2H even at 62° in the absence of BF_3. Cl_3CCO_2H (16.53 g.), 8.05 g. cyclohexene, and 4.21 g. BF_3Et_2O were heated to 51-2° to yield 79.7% *cyclohexyl trichloroacetate* in 1 hr.; the yield rises to 88% in a 24-hr. reaction; doubling the amt. of cyclohexene raises the yield to 100% in a 3-hr. reaction. The ester, b$_{13}$ 103-7°, d_4^{11} 1.2864, n_D^{11} 1.4840. Similar reaction with AcOH at 96-7° for 118 hrs. in a sealed tube gave 61% *cyclohexyl acetate*, b. 173-5°, $d_4^{15.6}$ 0.97605, $n_D^{15.6}$ 1.4428. G. M. Kosolapoff



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Boron fluoride as catalyst in organic chemistry. III. Reaction rate of condensation of cyclohexene with organic acids in presence of boron fluoride and of ortvents. S. V. Zavgorodnii. *J. Gen. Chem.* (U.S.S.R.) 14, 423-34 (1944)(English summary); cf. *C.A.* 39, 3785⁵.—The rate of reaction of cyclohexene with Cl_3CCO_2H in the presence of BF_3 at 30-1° is but little affected by the presence of a solvent like benzene, but the use of CCl_4 reduces the rate appreciably, while acetone paralyzes the reaction for almost 30 hrs. Similar reaction of AcOH is greatly affected by the presence of any solvent at 90-3°. G. M. K.

A50-51A METALLURGICAL LITERATURE CLASSIFICATION

L 13600-66 EWT(m)

ACC NR: AP6001016 (A) SOURCE CODE: UR/0286/65/000/022/0101/0101

AUTHORS: Isidorov, V. V.; Akunov, V. I.; Dubinskiy, M. G.; Zavadskiy, G. V.; Inshakov, Yu. T.; Lur'ye, M. Yu.; Myasin, N. I.; Nosenko, N. Ye.; Plavako, A. N.; Rybin, V. N.; Sidochenko, I. M.; Sominskiy, D. S.; Titov, P. P.; Khalov, G. G.; Shchevel', A. S.; Zavgorodniy, N. S.

ORG: none

TITLE: A reactor for combined pulverizing and burning of a material, such as cement, in a high temperature gas stream. Class 80, No. 145469

SOURCE: Byulleten' izobreteniy i tovarnykh znakov, no. 22, 1965, 101

TOPIC TAGS: cement, thermal reactor

ABSTRACT: This Author Certificate presents a reactor for combined pulverizing and burning of a material, such as cement, in a high temperature gas stream. To provide automatic regulation of the burning and calcification time for the material in the reactor, the latter is made in the shape of a flat, lenticular chamber. Nozzles of the combustion chambers are built into the peripheral circle of the lenticular chamber and at an angle to its radii. An opening in the center of the chamber bottom is used to discharge the finished burned product.

SUB CODE: 18,13/ SUBM DATE: 24May61

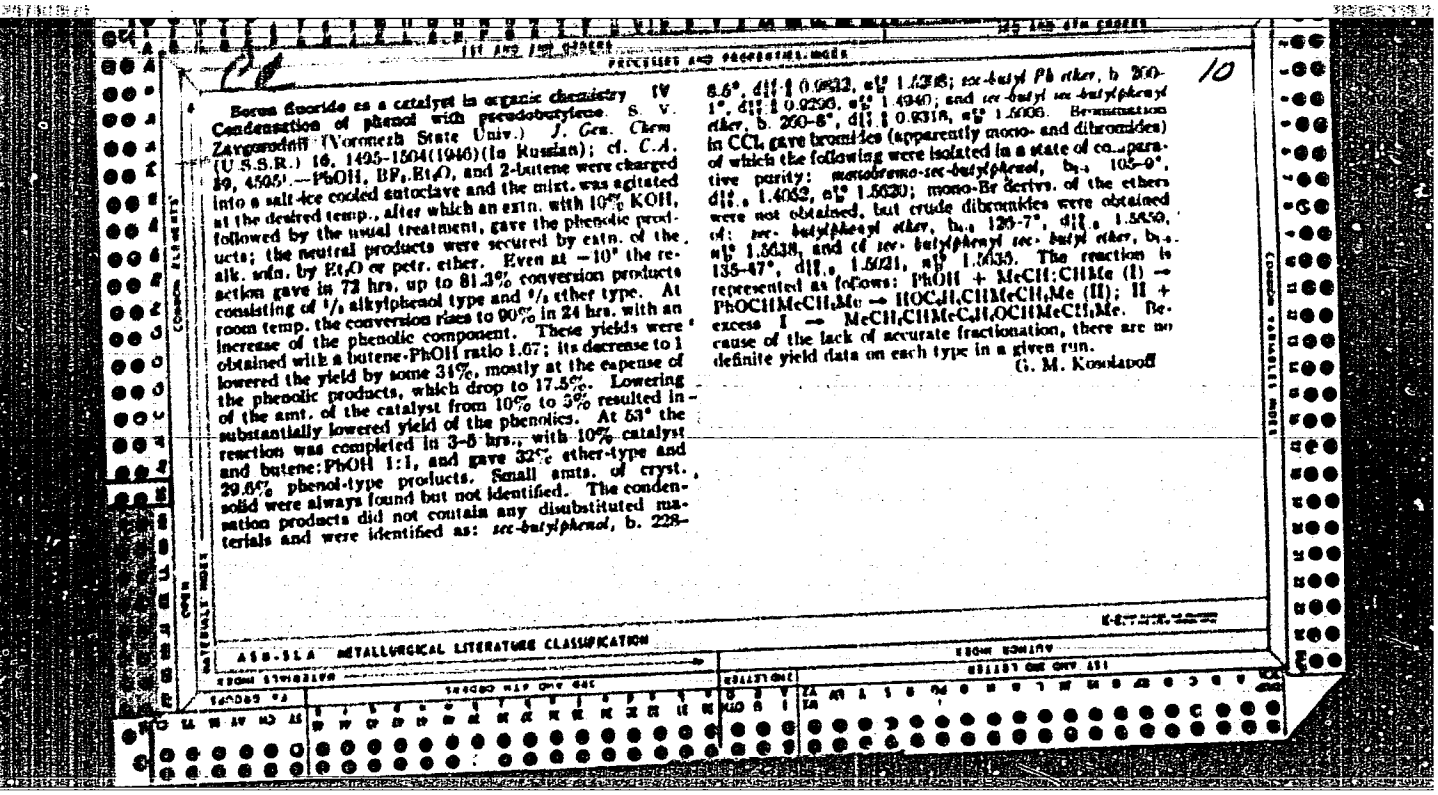
Card 1/1

Zavgorodnii, S. V.

Boron fluoride as a catalyst in organic chemistry. IV. Condensation of phenol with pseudobutylene

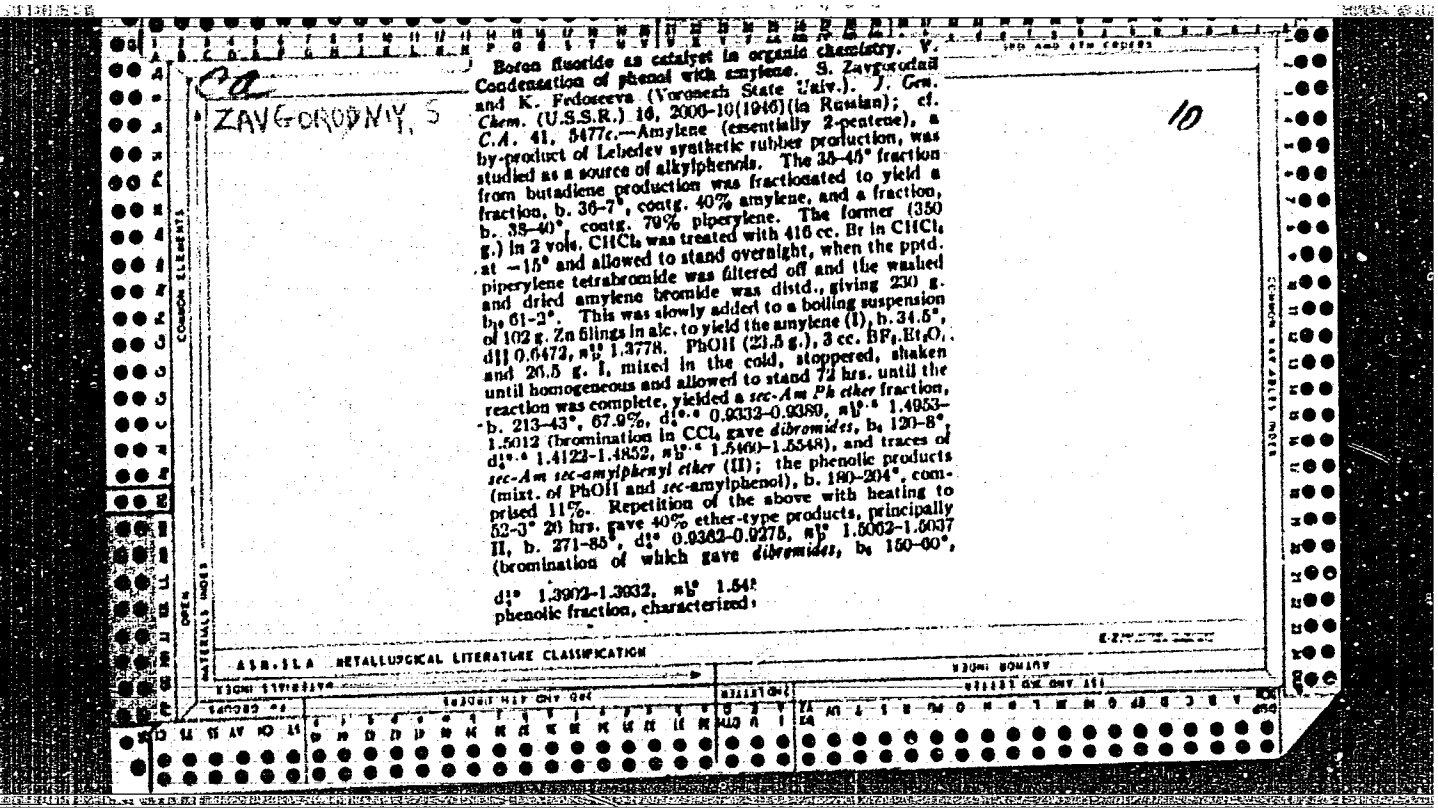
J. Gen. Chem., (USSR), Vol. 16, 1945, pp. 1495-1504

Chem. Abs., Vol. 41, p. 5477-c



Boron fluoride as a catalyst in organic chemistry. IV. Condensation of phenol with pseudobutylene. S. V. Zavgorodnii (Voronezh State Univ.). *J. Gen. Chem.* (U.S.S.R.) 16, 1495–1504(1946)(In Russian); cf. *C.A.* 39, 4505⁵.—PhOH, $BF_3.Et_2O$, and 2-butene were charged into a salt-ice cooled autoclave and the mixt. was agitated at the desired temp., after which an extn. with 10% KOH, followed by the usual treatment, gave the phenolic products; the neutral products were secured by extn. of the alk. soln. by Et_2O or petr. ether. Even at −10° the reaction gave in 72 hrs. up to 81.3% conversion products consisting of ⅓ alkylphenol type and ⅔ ether type. At room temp. the conversion rises to 90% in 24 hrs. with an increase of the phenolic component. These yields were obtained with a butene-PhOH ratio 1.67; its decrease to 1 lowered the yield by some 34%, mostly at the expense of the phenolic products, which drop to 17.5%. Lowering of the amt. of the catalyst from 10% to 5% resulted in substantially lowered yield of the phenolics. At 53° the reaction was completed in 3–5 hrs., with 10% catalyst and butene:PhOH 1:1, and gave 32% ether-type and 29.6% phenol-type products. Small amts. of cryst. solid were always found but not identified. The condensation products did not contain any disubstituted materials and were identified as: *sec-butylphenol*, b. 228–8.6°, d_4^{15} 0.9832, n_D^{15} 1.5238; *sec-butyl Ph ether*, b. 260–1°, d_4^{15} 0.9256, n_D^{15} 1.4940; and *sec-butyl sec-butylphenyl ether*, b. 266–8°, d_4^{15} 0.9318, n_D^{15} 1.5006. Bromination in CCl_4 gave bromides (apparently mono- and dibromides) of which the following were isolated in a state of comparative purity: *monobromo-sec-butylphenol*, $b_{4.5}$ 105–9°, d_4^{15} 1.4052, n_D^{15} 1.5020; mono-Br derivs. of the ethers were not obtained, but crude dibromides were obtained of: *sec-butylphenyl ether*, $b_{4.5}$ 126–7°, d_4^{15} 1.3850, n_D^{15} 1.5038, and of *sec-butylphenyl sec-butyl ether*, $b_{4.5}$ 135–47°, d_4^{15} 1.5021, n_D^{15} 1.5035. The reaction is represented as follows: PhOH + MeCH:CHMe (I) → PhOCHMeCH₂Me (II); II + PhOCHMeCH₂Me → HOC₆H₄CHMeCH₂Me (III); II + excess I → MeCH₂CHMeC₆H₄OCHMeCH₂Me. Because of the lack of accurate fractionation, there are no definite yield data on each type in a given run.

G. M. Kosolapoff



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ZAVGORODNIY, S

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Boron fluoride as catalyst in organic chemistry. V. Condensation of phenol with amylene. S. Zavgorodnii and K. Fedoseeva (Voronezh State Univ.). *J. Gen. Chem.* (U.S.S.R.) 16, 2000-10(1946)(in Russian); cf. *C.A.* 41, 5477c.—Amylene (essentially 2-pentene), a by-product of Lebedev synthetic rubber production, was studied as a source of alkylphenols. The 35–45° fraction from butadiene production was fractionated to yield a fraction, b. 36–7°, contg. 40% amylene, and a fraction, b. 38–40°, contg. 70% piperylene. The former (350 g.) in 2 vols. $CHCl_3$ was treated with 416 cc. Br in $CHCl_3$ at −15° and allowed to stand overnight, when the pptd. piperylene tetrabromide was filtered off and the washed and dried amylene bromide was distd., giving 230 g. b_{10} 61–2°. This was slowly added to a boiling suspension of 102 g. Zn filings in alc. to yield the amylene (I), b. 34.5°, d_4^{11} 0.6472, n_D^{19} 1.3778. PhOH (23.5 g.), 3 cc. $BF_3.Et_2O$, and 26.5 g. I, mixed in the cold, stoppered, shaken until homogeneous and allowed to stand 72 hrs. until the reaction was complete, yielded a *sec-Am Ph ether* fraction, b. 213–43°, 67.9%, $d_4^{20.6}$ 0.9332–0.9380, $n_D^{20.6}$ 1.4953–1.5012 (bromination in CCl_4 gave *dibromides*, b_4 120–8°, $d_4^{20.6}$ 1.4122–1.4852, $n_D^{20.6}$ 1.5469–1.5548), and traces of *sec-Am sec-amylphenyl ether* (II); the phenolic products (mixt. of PhOH and *sec*-amylphenol), b. 180–204°, comprised 11%. Repetition of the above with heating to 52–3° 20 hrs. gave 40% ether-type products, principally II, b. 271–85°, d_4^{20} 0.9362–0.9275, n_D^{20} 1.5062–1.5037 (bromination of which gave *dibromides*, b_4 150–60°, d_4^{20} 1.3992–1.3932, n_D^{20} 1.54[illegible] phenolic fraction, characterized

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

ZAVGORODNIY, S. V.

USSR/Chemistry - Boron Fluoride . May/Jun '49
Chemistry - Catalysis

"Utilization of Boron Fluoride as a Catalytic Agent in Organic Chemistry," S. V. Zavgorodniy, Voronezh, 29 pp

"Uspekh Khim" Vol XVIII, No 3

Review literature on the application of the BF_3 catalyst in organic chemistry, expressing the opinion that this is a universal catalyst which will find a much wider application in the near future.

58/49T20

ZAVGORODNIY, S. V.

INST OF ORGANIC CHEMISTRY, ACAD SCI USSR

ZAVGORODNIY, S. V. - "Investigation in the Field of Reactions of Unsaturated Compounds in the Presence of a Boron Fluoride Catalyst." Sub 25 Nov 52, Inst of Organic Chemistry, Acad Sci USSR. (Dissertation for the Degree of Doctorates in Chemical Sciences).

SO: Vechernaya Moskva January-December 1952

ZAVGORODNYY, S. V., TOPCHIYEV, A. V. and PAUSHKIN, Ya. M.

"Present Trends in Using Boron Fluoride in Catalytic Transformation of Hydrocarbons," Usp. khim., 21, No.4, 1952

ZAVGORODNII, S. V.

"Interaction of ethyl etherate of boron fluoride with organic carboxylic acids and with phenol." (p. 1781)

SO: Journal of General Chemistry, (Zhurnal Obshchei Khimii), 1952, Vol. 22, No. 10

ZAVGORODNIY S. V.

238T30

USSR/Chemistry - Germicides Insecticides — Nov 52

"Boron Fluoride as a Catalyst in Organic Chemistry: VI. The Reaction of o-Chloro Phenol With Cyclohexene," S. V. Zavgorodniy, Voronezh State U, Lab of Org Chem

"Zhur Obshch Khim" Vol 22, No 11, pp 1995-1997

Alkylhalogenophenols and alkyl ethers of halogenophenols have strong germicidal and insecticidal properties and therefore are of definite interest. They are usually obtained by the halogenation of alkyl phenols or alkylphenyl ethers and more rarely by the action of alcs or alkyl

238T30

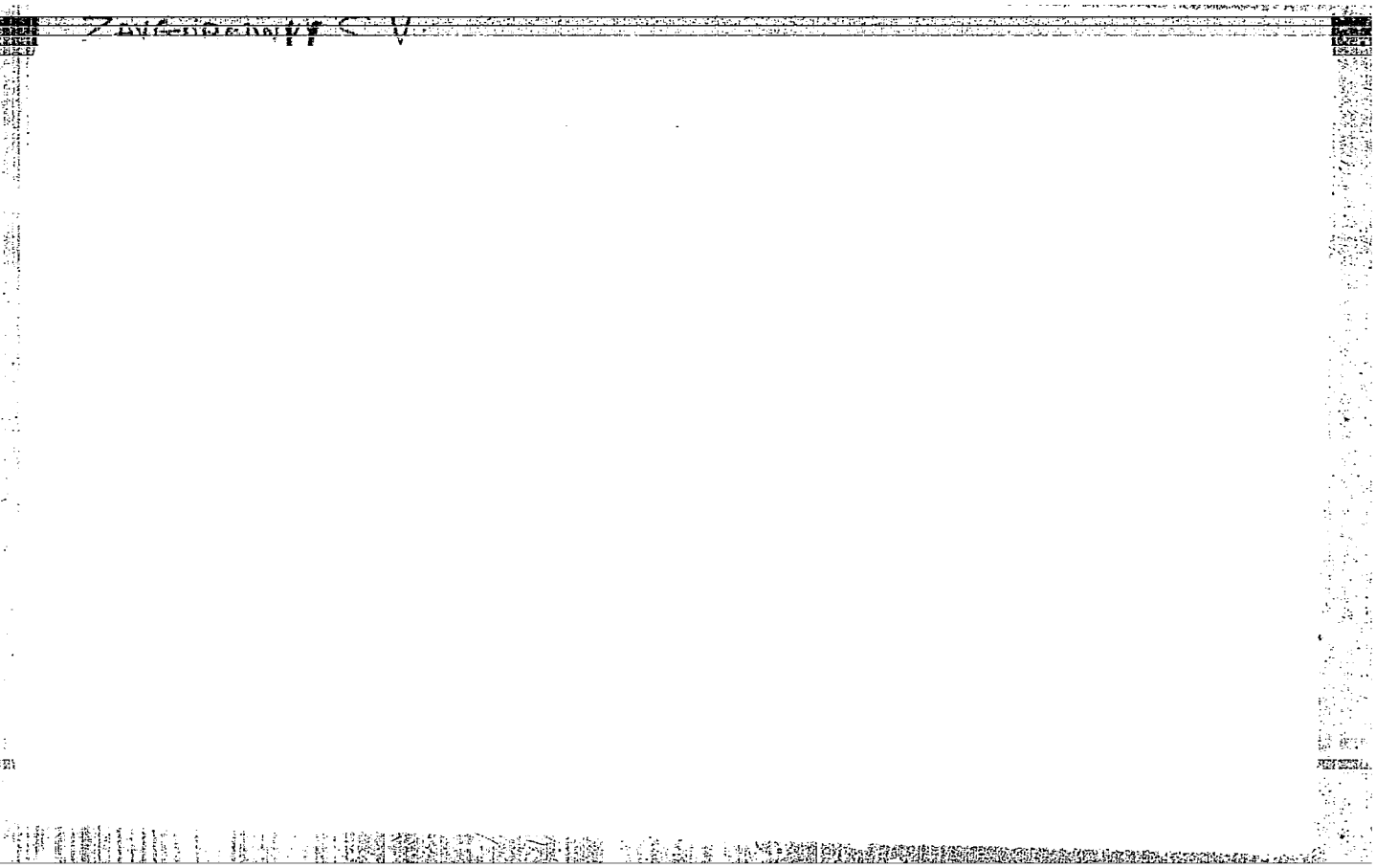
halides on halogenophenols. The direct alkylation of halogenophenols with olefins has hardly been investigated. The reaction of o-chloro phenol with cyclohexene at room temp, and in the presence of the catalyst, boron fluoride ethyl ether adduct, results only in the formation of the cyclohexyl ether of o-chloro phenol. There is significant polymerization of cyclohexene at the temp of a boiling water bath. Cyclohexyl ether of o-chloro phenol is quite stable and is not isomerized in the presence of boron fluoride ethyl ether adduct when heated for 8 hrs at 120-140°

238T30

ZAVGORODNYI, S. V.

Chemical Abst.
Vol. 48 No. 9
May 10, 1954
OrganicChemistry

Boron trifluoride as a catalyst in organic chemistry. VI. Reaction of o-chlorophenol with cyclohexane. S. V. Zavgorodnii. *J. Gen. Chem. U.S.S.R.* 22, 2045–7 (1952) (Engl. translation).—See *C.A.* 47, 8667*b*. H. L. H.



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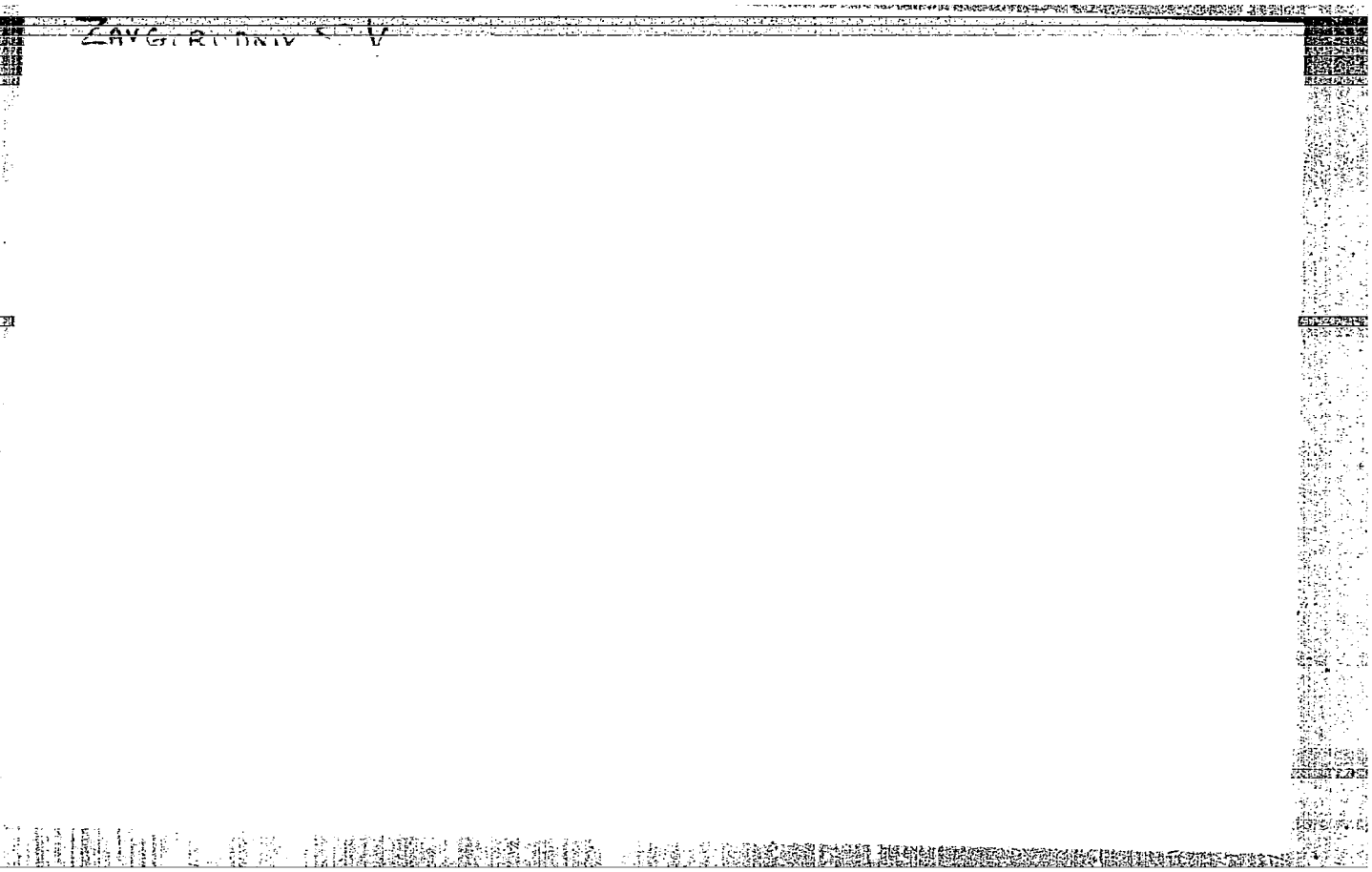


TOPCHIYEV,A.V.; ZAVGORODNIY,S.V.; PAUSHKIN,Ya.M.; SHUYKIN,N.I., redaktor; STRUCHKOV,Yu.T., redaktor; ZELENKOVA,Ye.V., tekhnicheskiy redaktor

[Boron fluoride and its compounds as catalyzers in organic chemistry] Ftoristyi bor i ego soedineniia kak katalizatory v organicheskoi khimii. Moskva, Izd-vo Akademii nauk SSSR, 1956. 356 p. (MLRA 9:4)

1. Chlen-korrespondent AN SSSR (for Shuykin)
(Boron fluoride)

ZAVGORODNIY, S. V

E-2

USSR/ Organic Chemistry - Synthetic organic chemistry

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11684

Author : Zavgorodniy S.V., Vakhtin V.G.
Inst : Voronezh University
Title : Alkylation of Anisole with Beta-Amylene in the Presence of Catalysts Ethyletherate of Boron Trifluoride and Boron Fluoride Compound of Ortho-Phosphoric Acid

Orig Pub : Tr. Voronezhsk. un-ta, 1956, 42, No 2, 37-39

Abstract : On alkylation of anisole (I) with beta-amylene (II) in presence of $BF_3 \cdot H_3PO_4$ were obtained 4-sec-amylanisole (III) as principal reaction product, 2-sec-amylanisole (IV) and diamylanisoles (V). Alkylation in the presence of BF_3 etherate results in lower yields. To 9.5g H_3PO_4 saturated with 5.2 g BF_3, are added 27 g I, and at ~20°, are added, within 1.5 hours, 35 g II. After 14-16 hours washed with water, 5% Na_2CO_3, dried (to 170° driving off I and II), yield of

Card 1/2

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11684

alkylate 62%; contains 80% III, BP 104-106°/5 mm, $n^{20}D$ 1.5164, d_4^{20} 0.9584; 16% unpurified IV, BP 95-98°/5 mm, $n^{20}D$ 1.5012, d_4^{20} 0.9330, and ~4% V. On oxidation of III with 5% HNO_3 there was obtained 4-$CH_3OC_6H_4COOH$, and on oxidation of IV an acid of MP 105-107°.

ZAVGORODNIY, S.V.

79-2-12/58

AUTHORS: Zavgorodniy, S. V., and Kryuchkova, V. G.

TITLE: Boron Fluoride as a Catalyst in Organic Chemistry. Part 13. Alkylation of 2- and 4-Bromophenols with Pseudo-Butylene and Cyclohexene in the Presence of BF_3. H_3PO_4 and BF_3. $O(C_2H_5)_2$ Catalysts (Ftoristyy bor kak katalizator v organicheskoy khimii. XIII. Alkilirovaniye 2- i 4-bromofenolovpsevdobutilenom i tsiklogeksenom v prisutstvii katalizatorov $BF_3.H_3PO_4$ i $BF_3.O(C_2H_5)_2$)

PERIODICAL: Zhurnal Obshchey Khimii, 1957, vol 27, No 2, pp. 330-333 (U.S.S.R.)

ABSTRACT: Investigation was conducted to determine the alkylation of 2- and 4-bromo phenols with pseudobutylene and cyclohexene in the presence of two boron fluoride catalysts. It is shown that the alkylation of 2-bromophenol with pseudobutylene leads to the formation of phenol products or mixture of ether and phenol products. In all other cases the authors obtained only ester type compounds. The alkylation products derived are identified as: secondary-butyl-2-bromophenol, secondary-butyl ether of 2-bromophenol, secondary-butyl ether of secondary-butyl-2-bromophenol, cyclohexyl ester of 2-bromophenol, secondary-butyl ether of 4-bromophenol, secondary butyl ether, 2-secondary-butyl-4-bromophenol and cyclohexyl ester of 4-bromo-phenol. The effect of the molar ratios of reagents and catalysts, and

Card 1/2

Boron Fluoride as a Catalyst in Organic Chemistry, Part 13. 79-2-12/58

effect of time and temperature on the total yield of ether and phenol base compounds is described in a table.

1 table. There are 4 Slavic references.

ASSOCIATION: The Voronezh State University

PRESENTED BY:

SUBMITTED: March 1, 1956

AVAILABLE: Library of Congress

Card 2/2

ZAVGORODNIY, S.V

AUTHOR VDOVTSOVA YE.A., ZAVGORODNIY S.V. PA - 3152

TITLE Alkylation of Aromatic Compounds By Diene Hydrocarbons.Alkenylation of Anisole By Piperylene.
(Alkilirovaniye aromaticheskikh soyedineniy diyenovymi uglevodorodami. Alkenilirovaniye anizola piperilenom. -Russian)

PERIODICAL Doklady Akademii Nauk SSSR,1957,Vol 113,Nr 3,pp 590-593 (U.S.S.R.)
Received 6/1957 Reviewed 7/1957

ABSTRACT A systematic investigation of the reaction on the occasion of the alkylation of the aromatic core with pyperilene (a by-product obtained when producing synthetic rubber by the Lebedev method) was carried out for the purpose of determining the reactivity of pierylene from a double-functional combination. By the example of anisol it is shown to be possible to alkylize the aromatic core with piperylene, viz. with a yield of 56 - 92% of the theoretical quantities of pentenil anisole. The anisole was selected as the first experimental object because it represents those substances which have a sufficient amount of movable hydrogens in order in this way to avoid the use of energetic catalyzers and thus also a polymerization of the pierylene. Molecular compounds of boron fluoride were tried out as catalyzers. With all these catalyzers the alkylation process suppresses the polymerization of the pierylene. Results are shown together in form of a table. The structure of the pentenile anisoles was proved. Pentenilanisole was obtained in the presence of $BF_3.O(C_2H_5)_2$ and is in

Card 1/2

Alkylation of Aromatic Compounds By Diene Hydrocarbons. PA - 3152
Alkenylation of Anisole By Piperylene.

its basic mass a 4-(n-methoxyphanyl)-penten-2(XI) which is mentioned in publications as an intermediate product in the synthesis 2,3-to-(n-oxyphenyl)-pentane. The products obtained by alkylation in the presence of BF_3, H_3PO_4, $BF_3 \cdot H_3PO_4$ apparently consist essentially of 4-(n-methoxyphenyl)-penten-2. The experiments are described.
(With 1 table and 7 Slavic references).

ASSOCIATION State University of Voronesh
PRESENTED BY TOPCHIYEV A.V., Member of the Academy
SUBMITTED 15.11.1956
AVAILABLE Library of Congress
Card 2/2

79-28-5-37/69

AUTHORS: Zavgorodniy, S. V., Sigov, O. V., Bayev, I. F.

TITLE: Synthesis of 1,4-Diisopropylbenzene and Some of its Conversions (Sintez 1,4-diizopropilbenzola i nekotoryye yego prevrashcheniya)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol. 28, Nr 5, pp. 1279 - 1284 (USSR)

ABSTRACT: In the present work the alkylation of the isopropylbenzene with propylene in the presence of $BF_3 \cdot H_3PO_4$ was dealt with. When using these three compounds at equimolar ratios (4 : 1 : o,26) at 98 - 1oo°C the 1,4-diisopropylbenzene was obtained in a yield of 73% (at 52 to 55°C - 19%). The oxidation of the 1,4-diisopropylbenzene (in liquid phase) with atmospheric oxygen in the presence of various stimulators in mono- and dihydrogen peroxide was investigated. During some time of this oxidation an accumulation of peroxide to a certain maximum takes place, on which the decomposition begins and the amount decreases. At 11o°C such a maximum is reached after 12-14 hours,

Card 1/3

Synthesis of 1,4-Diisopropylbenzene and Some of its Conversions

at 85°C after 2o-4o hours, depending on the stimulators. The stimulator mixture, consisting of manganese resinate and cobalt acetate with an addition of calcium hydrogen peroxide stimulates oxidation much more than the first two, taken singly. The addition of sodium stearate to the mixture accelerates the oxidation and makes it possible to obtain 51% hydrogen-peroxide at 85°C during 17 hours, whereas without stearate only 33% result at 11o°C during 16 hours, on which the decom-position of the peroxide starts. Calcium-hydrogen-peroxide also accelerates the oxidation and strengthens the hydrogenperoxide which leads to a deeper oxidation. The oxidation is mainly directed to the formation of monohydrogen peroxide of the diisopropylbenzene in the cleavage of which in acidous medium the 4-isopropylphenol forms in a yield of 9o%. Partially also dihydrogen peroxide of the diisopropylbenzene forms which then splits into hydroquinone. There are 2 figures, 1 table and 5 references, 4 of which are Soviet.

Card 2/3

ASSOCIATION: Voronezh State University

SOV/79-28-10-8/60

AUTHORS: Zavgorodniy, S. V., Shvetsova, L. S.

TITLE: Alkylation of Isopropyl Benzene With Pseudobutylene in the Presence of $BF_3 \cdot H_3PO_4$ (Alkilirovaniye izopropilbenzola psevdobutilenom v prisutstvii $BF_3 \cdot H_3PO_4$)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 10, pp 2668 - 2670 (USSR)

ABSTRACT: In an earlier paper the authors already showed that the molecular compound $BF_3 \cdot H_3PO_4$ proves to be a highly active catalyst in the alkylation of benzene with pseudobutylene. In connection herewith they also attempted to alkylate isopropyl benzene in this way. In this case the reaction took place with more difficulty; also the yields of the alkylation products were smaller. A mixture of isopropyl-sec.-butyl benzenes was formed which consisted of about 91% para and 9% ortho isomers. The most favorable conditions with the highest yields of isopropyl-sec.-butyl benzenes are offered by the molar ratios of isopropyl benzene, pseudo butylene and catalyst of 3-3,5:1:0,2-0,3, the temperature of 50-60°, and the

Card 1/2

Alkylation of Isopropyl Benzene With Pseudobutylene in the Presence of $BF_3 \cdot H_3PO_4$ SOV/79-28-10-8/60

introduction velocity of pseudo butylene of 1,6-2,5 ℓ/hour. In the case of a larger amount of the catalyst, the yield of isopropyl-sec.-butyl benzenes decreases; it also decreases if there are more than 3 mole isopropyl benzene per 1 mole pseudo butylene, even with a larger quantity of the catalyst. A considerable role is also played by the reaction temperature. The yield of isopropyl-sec.-butyl benzenes is, for instance, 18% at 20°, 47% at 30°-35° and 55% at 50-60°. At 100° the pseudo butylene is not readily absorbed by the mixture, with the catalyst also gradually losing its activity, which again causes a small yield. There are 1 table and 2 references, 2 of which are Soviet.

ASSOCIATION: Voronezhskiy gosudarstvennyy universitet (Voronezh State University)

SUBMITTED: July 12, 1957

Card 2/2

ZAVGORODNIY, S. V.

20-1-27/58

AUTHORS: Zavgorodniy, S. V., and Sidel'nikova, V. I.

TITLE: The Alkylation of Diphenyl by Pseudobutylene in the Presence of the Catalyst $BF_3 \cdot H_3PO_4$ (Alkilirovaniye difenila psevdobutilenom v prisutstvii katalizatora $HF_3 \cdot H_3PO_4$).

PERIODICAL: Doklady AN SSSR, 1958, Vol. 118, Nr 1, pp. 96-98 (USSR).

ABSTRACT: The authors studied this reaction in different molar ratios of the two substances and the catalyst, without solvent and dissolved in CCl_4, at 50-100°C. It was proved that this reaction takes place in molar ratios 1 - 4 : 1 : 0,2 - 0,3 and yields monobutyldiphenyls as main products. Besides at 70°C and above an isomerization of pseudobutylene to isobutylene takes place and a mixture of p-second.-butyldiphenyl develops. Their relative quantities depend on the temperature and on other factors. When the ratio of the two reacting substances and of the catalyst is 2 : 1 : 0,2 and when the temperature is 90°C the total yield of monobutyldiphenyl amounts to 38,8% of the theoretically possible. The relative content of p-second.-butyldiphenyl and p-tert.-butyldiphenyl is 74% and 26% respectively. The most favorable conditions under which monobutyldiphenyls with a 58-60% yield form and amount up to 92% in the result of alkylation, are:

Card 1/2

The Alkylation of Diphenyl by Pseudobutylene in the Presence of the Catalyst $BF_3 \cdot H_3PO_4$. 20-1-27/58

the ratio of diphenyl : pseudobutylene : catalyst = 1,75 : 1 : 0,25, a temperature of 90°C and the speed of the introduction of pseudobutylene 2,5-3 liters per hour. The reduction of the quantity of catalyst to 0,13 Mol under the last-mentioned conditions diminishes the yield of monobutyldiphenyls to 32 %. The increase in the quantity of diphenyl to 3 and 4 Mol per 1 Mol pseudobutylene reduces the yield of monobutyldiphenyls to 19-29%. But now the polybutyldiphenyls are absent in the result of alkylation. The ratio of the reacting substances and the catalyst 1 : 1 : 0,2 leads to a 43-45 % yield of monobutyldiphenyls and a 7-8% yield of polybutyldiphenyls of the theoretically possible yields. In a CCl_4-solution the alkylation proceeds very slowly and in molar ratios of the reacting substances and the catalyst of 1 : 1 : 0,15, 1 : 1 : 0,3, 3 : 1 : 0,3 it gives yields of monobutyldiphenyls 12, 14 and 18% of the theoretically ones. An experimental part with the usual data follows. The constants and yields of the monobromides of the two above-mentioned p-butyldiphenyls and the self-oxidation as well as the splitting up of the hydroperoxide of p-second.-butyldiphenyl are described.
There are 1 table, and 4 references, 3 of which are Slavic.

Card 2/2 VORONEZH State Univ.

ALISOVA, E.V.; ZAVGORODNIY, S.V.

Alkylation of anisole and phenetole by isobutylene in the presence of $BF_3 \cdot H_3PO_4$. Zhur.ob.khim. 32 no.11:3502-3505 N '62. (MIRA 15:11)

1. Kiyevskiy politekhnicheskiy institut.
(Anisole) (Phenetole) (Propene)

NOVIKOV, I.N.; ANTONOVA, A.M.; ZHILINA, R.I.; FURTICHEVA, R.P.; SHATALOV, V.P.; ZAVGORODNIY, S.V.

Synthesis and autoxidation of isopropylcyclohexylbenzene. Zhur.ob.khim. 32 no.9:2954-2957 S '62. (MIRA 15:9)

1. Kiyevskiy politekhnicheskiy institut.
(Cumene) (Oxidation)

NOVIKOV, I.N.; ZAVGORODNIY, S.V.

Autoxidation of p-dicyclohexylbenzene. Dokl.AN SSSR 148 no.4:853-855 F '63. (MIRA 16:4)

1. Kiyevskiy politekhnicheskiy institut. Predstavleno akademikom A.V.Topchiyevym.

(Benzene) (Oxidation)

ZAVGORODNIY, S.V.; FEDOSEYEVA, T.G.; SHUMAKHER, A.Ya.

Boron fluoride as a catalyst in organic chemistry. Part 14: Alkylation of toluene and ethylbenzene by pseudobutylene. Trudy VGU 57:107-116 '59. (MIRA 13:5)
(Butene) (Toluene) (Benzene)

ZAVGORODNIY, S.V.

Boron fluoride as a catalyst in organic chemistry. Part 15: Alkylation of naphthalene by olefins from by-products of the synthetic rubber industry. Trudy VGU 57:117-131 '59. (MIRA 13:5)

(Naphthalene) (Olefins)

ZAVGORODNIY, S.V.

Boron fluorids as a catalyst in organic chemistry. Part 16: Alkylation of guaiacol and phenetole by pseudobutylene. Trudy VGU 57:133-140 '59. (MIRA 13:5)
(Guaiacol) (Phenetole) (Butene)

5 (3)
AUTHORS: Zavgorodniy, S. V., Kryuchkova, V. G. SOV/79-29-4-64/77

TITLE: Alkylation of 4-Bromophenol With Propylene and β-Amylene in the Presence of the Catalysts BF_3 HPO_4 and BF_3 $O(C_2H_5)_2$
[Alkilirovaniye 4-bromfenola propilenom i β-amilenom v prisutstvii katalizatorov BF_3 H_3PO_4 i BF_3 $O(C_2H_5)_2$]

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 4, pp 1340 - 1343 (USSR)

ABSTRACT: This is a continuation of earlier investigations (Refs 1-5). In the present paper the authors investigated the alkylation of 4-bromophenol with propylene in the presence of BF_3 HPO_4 and with β-amylene in the presence of BF_3 $O(C_2H_5)_2$ and BF_3 HPO_4 in carbon tetrachloride without solvents. It was found that 4-bromophenol yields with propylene and β-amylene in the presence of BF_3 H_3PO_4 and BF_3 $O(C_2H_5)_2$ only ether products. Two compounds, the isopropyl ether of 4-bromophenol (I) and the isopropyl ether of isopropyl-4-bromophenol (II) are obtained with propylene. A secondary amyl ether of 4-bromophenol (III) was obtained with

Card 1/3

Alkylation of 4-Bromophenol With Propylene and β-Amylene in the Presence of the Catalysts BF_3 HPO_4 and BF_3 $O(C_2H_5)_2$

30V/79-29-4-64/77

β-amylene. The molar conditions of the reacting compounds and the catalyst 2:1:0,2 are for the alkylation of 4-bromophenol with propylene in the presence of BF_3 H_3PO_4 the best at 30° and in the case of slow addition of propylene (yields of (I) and (II), 48 and 14% respectively). These products resulted in the same total yield (62%) in the molar ratio 1:2:0,15 of 4-bromophenol, propylene, and catalyst. In this case, however, considerable quantities of resin are produced and the yields in (I) and (II) amount to 37 and 25% respectively. The temperature rise up to 50° increases the resin formation and reduces considerably the yield in alkylation products. The application of CCl_4 as solvent reduces the resin formation as well as the yield in (I) and (II). Further data are given in table 1. The alkylation of 4-bromophenol with β-amylene in the presence of BF_3 HPO_4 in a carbon tetrachloride solution is at room temperature accompanied by a polymerization. The yield in ether (III) is here not higher than 40%. In the presence of BF_3 $O(C_2H_5)_2$ in the same

Card 2/3

Alkylation of 4-Bromophenol With Propylene and β-Amylene in the Presence of the Catalysts BF_3 HPO_4 and BF_3 $O(C_2H_5)_2$

solution the reaction proceeds more smoothly and the yield can be increased up to 75% under a certain optimum molar ratio. An intensive resin formation takes place without solvent. The influence of the reaction duration and other conditions of the reacting compounds and the catalyst is illustrated in table 2. There are 2 tables and 6 Soviet references.

ASSOCIATION: Voronezhskiy gosudarstvennyy universitet (Voronezh State University)

SUBMITTED: February 5, 1958

SOV/79-29-5-8/75

5(3)
AUTHORS: Zavgorodniy, S. V., Volkov, R. N.

TITLE: Alkylation of p-Diisopropyl Benzene With Propylene in the Presence of the Catalyst $BF_3 \cdot H_3PO_4$ (Alkilirovaniye p-diizopropilbenzola propilenom v prisutstvii katalizatora $BF_3 \cdot H_3PO_4$)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 5, pp 1447 - 1449 (USSR)

ABSTRACT: In the present paper the alkylation of p-diisopropyl benzene with propylene in the presence of the catalyst $BF_3 \cdot H_3PO_4$ in the temperature range 3 - 105° and at a ratio of p-diisopropyl benzene, propylene and catalyst 1-5: 1: 0.1 - 0.5 was investigated. Triisopropyl benzenes and tetraisopropyl benzene were found to be formed. Triisopropyl benzenes represent a mixture of 1,2,4- and 1,3,5-triisopropyl benzenes. Their relative content in the mixture is 80-82 and 18 - 20%, respectively. According to the conditions the total yield is 53-84%. The yield in 1,2,4,5-tetraisopropyl benzene is 5-29%. Optimum conditions for the alkylation were determined as follows: the molar ratio of n-diisopropyl benzene - propylene - catalyst 3 : 1 : 0.3,

Card 1/2

temperature 60°, rate of propylene introduction 1.5 l/h and subsequent mixing of the reaction mixture for 40 minutes. Under these conditions 81% triisopropyl benzenes and 15% 1,2,4,5-tetraisopropyl benzene are obtained. In this case other products are formed to practically no extent. As can be seen from the table the yield is considerably influenced by the quantity of the catalyst. There are 1 table and 2 references, 1 of which is Soviet.

ASSOCIATION: Voronezhskiy gosudarstvennyy universitet (Voronezh State University)

SUBMITTED: April 11, 1958

S/153/60/003/005/005/016
B013 /B058

AUTHORS: Zavgorodniy, S.V., Novikov, I.N.

TITLE: Autooxidation of p-Diisopropyl Benzene

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, 1960, Vol. 3, No. 5, pp. 863 - 867

TEXT: The possibility of oxidation of p-diisopropyl benzene, forming in the alkylation of benzene with a propane - propylene mixture in the presence of $BF_3 \cdot H_3PO_4$ into hydrogen peroxides, and subsequent cleavage of the monohydrogen peroxide into p-isopropyl phenol, and of the dihydrogen peroxide into hydroquinone, was studied in this paper. Autooxidation of p-diisopropyl benzene at 85°, 110°, and 130°C in the presence of diisopropyl benzene hydrogen peroxide and manganese resinate with alkaline additions, as well as cleavage of the hydrogen peroxides into corresponding phenols, was studied for this purpose. It was shown that the rate of oxidation of industrial p-diisopropyl benzene depends on its purity. NaOH, KOH, $Ca(OH)_2$ and Na_2CO_3 were used as additions. These materials are

Card 1/3

only little effective in themselves, and have all about the same effect. Their addition (0.5 -1 g per 1 mole of diisopropyl benzene) to the manganese resinate, however, initiates the autooxidation process, and permits a deep-reaching oxidation of the hydrocarbon up to the hydrogen peroxide. Autooxidation becomes specially intensive if p-diisopropyl benzene is preoxidized in the presence of alkaline additions up to a content of 2 - 3% hydrogen peroxide in the solution. Manganese resinate or diisopropyl benzene hydrogen peroxide is subsequently added, and oxidation is continued with the blowing-through of air. Under such conditions, a maximum hydrogen peroxide concentration of 78% was obtained within 44 hours at 110 ± 2°C. The experiments showed that p-diisopropyl benzene dihydrogen peroxide is only precipitated if the hydrogen peroxide concentration in the hydrocarbon solution is higher than 40%. It may be assumed that in the oxidation of p-diisopropyl benzene, monohydrogen peroxide is formed first. Not until this has reached a certain concentration does it begin to oxidize into p-diisopropyl benzene dihydrogen peroxide. The cleavage of the dihydrogen peroxide proceeds most smoothly with concentrated sulfuric acid in ether, the highest hydroquinone yield being obtained here. Strong resinification can be observed with dilute

Autooxidation of p-Diisopropyl Benzene

S/153/60/003/005/005/016
B013/B058

sulfuric acid. By reproduction of pure dihydrogen peroxide, 96% of p-di-(α,α'-oxy-isopropyl)-benzene was obtained in the form of white needles with a melting point of 140°C. Figs.1 - 3 show the effect of the purity of diisopropyl benzene, temperature, and various admixtures on the rate of oxidation. B.D. Kruzhalov and V.V. Fedorova are mentioned. There are 3 figures, 2 tables and 5 Soviet references.

ASSOCIATION: Voronezhskiy gosudarstvennyy universitet. Kafedra organicheskoy khimii (Voronezh State University. Department of Organic Chemistry)

SUBMITTED: February 17,1959

Card 3/3

KRYUCHKOVA, V.G.; ZAVGORODNIY, S.V.

Alkylhalophenoxyacetic acids. Zhur.ob.khim. 30 no.5: 1747-1748 My '60. (MIRA 13:5)

1. Voronezhskiy gosudarstvennyy universitet.
(Acetic acid)

KRYUCHKOVA, V.G.; ZAVGORODNIY, S.V.

Alkylation of 4-bromoanisole by propylene, pseudobutylene, and cyclohexene in the presence of $BF_3 \cdot H_3PO_4$. Zhur.ob.khim. 30 no.6:1929-1932 Je '60. (MIRA 13:6)

1. Voronezhskiy gosudarstvennyy universitet.
(Anisole) (Alkylation)

85610

S/079/60/030/007/026/039/XX
B001/B066

5.3400 2209, 1153, 1321

AUTHORS: Zavgorodniy, S. V., Zaytsev, B. A., Yel'chinov, D. P.

TITLE: Aryl-alkylation of Phenol With Styrene and α-Methyl Styrene

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 7, pp. 2196-2199

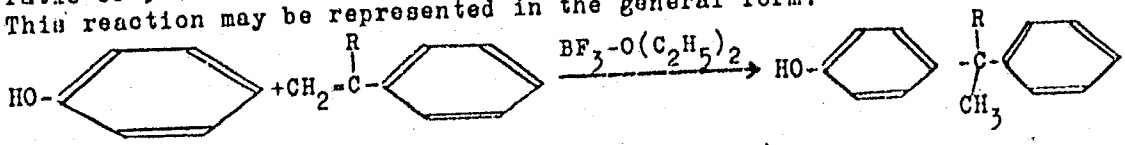
TEXT: The aryl-alkylation of phenols with aryl olefins has so far been given little attention, in spite of the practical importance of its reaction products (Ref. 1). The authors studied the reaction of phenol with styrene and α-methyl styrene, using the ethyl etherate of boron fluoride (BF_3-$(C_2H_5)_2O$) and boron fluoride with 75% orthophosphoric acid as catalysts. In both cases aryl alkyl phenols resulted. Styrene gave a mixture of mono- aryl and diaryl alkyl phenols (32 - 60% yield, according to conditions), α-methyl styrene p-hydroxy-diphenyl-dimethyl methane (60%), and a small quantity of resinous products whose composition could not be determined. In both cases, aryl-alkylation is accompanied by polymerization of the aryl olefins, which is the main reaction in the case of styrene. α-methyl styrene is more stable to polymerization, and is partially dimerized (in

Card 1/2

Aryl-alkylation of Phenol With Styrene and α-Methyl Styrene

S/079/60/030/007/026/039/XX
B001/B066

addition to the formation of resinous polymerization products) to give the crystalline 1,1,3-trimethyl-3-phenyl indan which distills over together with p-hydroxy-diphenyl-dimethyl methane. The best yield of hydroxy-diphenyl-methyl methane was obtained at a molar ratio of 2 : 1 : 0.06 between phenol, styrene, and the ethyl etherate of boron fluoride, at a temperature of 95-97° and with a reaction time of two hours. In the reaction of phenol with α-methyl styrene in the presence of the above etherate, the best yield (60%) of p-hydroxy-diphenyl-dimethyl methane results at a molar ratio of 3 : 1 : 0.15, at 80-83° and with a reaction time of nine hours. This reaction may be represented in the general form:



(R = H or CH_3).

There are 2 tables and 2 references: 1 Soviet and 1 German.

ASSOCIATION: Voronezhskiy gosudarstvennyy universitet (Voronezh State University)

SUBMITTED: July 6, 1959

Card 2/2

ZAVGORODNIY, S.V.; SHALGANOVA, V.G.

Autooxidation of *P*-ethyl- sec.butylbenzene. Zhur.ob.khim. 30 no.7:2402-2406 Jl '60. (MIRA 13:7)

1. Voronezhskiy gosudarstvennyy universitet.
(Benzene)

84874

S/079/60/030/010/010/030
B001/B075

11.1210

AUTHORS: Shalganova, V. G. and Zavgorodniy, S. V.

TITLE: Autooxidation of Secondary p-Butyltoluene

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 10, pp. 3223-3226

TEXT: The authors studied the autooxidation of p-sec-butyltoluene and carried out a quantitative determination of the products of acid splitting of hydrogen peroxide, as well as of the products obtained from a complete oxidation of p-sec-butyltoluene. The oxidation took place at different temperatures. Autooxidation carried out by means of atmospheric oxygen in the presence of manganese resinate, caustic soda, and other additions, proceeds most conveniently at 110°C. It was shown that in the presence of manganese resinate and alkali the oxidation of the secondary butyl radical proceeds 1.8 times more easily than that of the primary methyl group, and 1.2 times more easily than on the addition of sodium stearate or cobalt acetate. The main products of oxidation are p-methyl acetophenone, p-tolylmethylethyl carbinol, and p-sec-butyl benzoic acid. It was found

Card 1/2

Autooxidation of Secondary p-Butyltoluene S/079/60/030/010/010/030
B001/B075

that p-sec-butyl benzoic acid can be oxidized with atmospheric oxygen to form p-acetyl benzoic acid in a 30.5% yield. The oxidation rate of p-sec-butyltoluene at 110°C under different conditions is illustrated in a figure. Experimental data are given in Tables 1 and 2. There are 1 figure, 2 tables, and 11 references: 9 Soviet, 1 US, and 1 German.

ASSOCIATION: Voronezhskiy gosudarstvennyy universitet
(Voronezh State University)

SUBMITTED: November 4, 1959

Card 2/2

87523
S/079/60/030/012/003/027
B001/B064

53600 2209

AUTHORS: Kryuchkova, V. G. and Zavgorodniy, S. V.

TITLE: Alkylation of 2- and 4-Anisole Chloride With Pentene-1 in the Presence of $BF_3 \cdot H_3PO_4$ as Catalyst

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 12, pp. 3869-3871

TEXT: For several years the authors have studied the alkylation of phenol halides and anisole halides with olefins in the presence of boron fluoride catalysts. Alkylation is a very convenient method of synthesizing interesting alkyl halide phenols which have hitherto been hardly accessible in laboratory. This is a continuation of previous studies describing the results of alkylating 2- and 4-anisole chloride with pentene-1 in the presence of $BF_3 \cdot H_3PO_4$ as catalyst. In contrast to the reaction of 4-anisole chloride with propylene, pseudobutylene, cyclohexene and 4-anisole bromide with propylene, and cyclohexene (Ref. 1), only mono-sec.-amyl anisole chlorides are obtained. 2-anisole chloride alkylates with pentene-1 1.5 times more readily than 4-anisole chloride under similar conditions. The molar ratios 3:1:0.1 between 2-phenol chloride, pentene and the catalyst.

Card 1/2

87523

Alkylation of 2- and 4-Anisole Chloride With Pentene-1 in the Presence of $BF_3 \cdot H_3PO_4$ as Catalyst

S/079/60/030/012/003/027
B001/B064

and a temperature of 40°C proved to be the optimum conditions under which the 4-sec.-amyl-2-anisole chloride yield was 86%. To synthesize 2-sec.-amyl-4-anisole chloride in a 54% yield, the molar ratio of the reagents and the catalyst must be 4:1:0.2, and the temperature 40°C. A temperature between 20 and 60°C has no essential effect upon the yield in alkylation products. The ratios of the reagents of 4:1 to 2:1, and the amounts of catalyst between 0.1 - 0.3 per 1 mole pentene-1 bear also no influence upon the yields. The best results are obtained when the calculated amount of anisole chloride is at once added to the catalyst and when pentene-1 is slowly added to this mixture. When pentene-1 is mixed with a part of anisole chloride, the yield in alkylation products is lower. There are 2 tables and 3 Soviet references.

ASSOCIATION: Voronezhskiy gosudarstvennyy universitet (Voronezh State University)

SUBMITTED: February 4, 1960

Card 2/2

87524

S/079/60/030/012/004/027
B001/B064

53600

AUTHORS: Kryuchkova, V. G. and Zavgorodniy, S. V.

TITLE: Demethylation of Alkyl Halide Anisoles

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 12, pp. 3872-3873

TEXT: The authors demethylated several alkyl halide anisoles hitherto little investigated. This paper does not discuss the rate of demethylation and the finding of the best reaction conditions, but the synthesis of alkyl halide phenols. Nevertheless, the results obtained lead to interesting conclusions on the behavior of the anisole group toward hydriodic acid and hydrobromic acid. It was found that all monoalkyl substituted o- and p-fluoro anisoles and o- and p-chloro anisoles can be demethylated into the corresponding alkyl halide phenols when heated with HI or HBr for a longer time; this demethylation, is, however, not quantitative. 4-alkyl-2-anisole halides demethylate more readily. Among the 14 alkyl halide anisoles, 4-sec.-amyl-2-fluoro anisole demethylate most readily to 4-sec.-amyl-2-fluoro phenol (88% yield) (Table), 2,6-dialkyl-4-anisole halides do not demethylate with

Card 1/2

Demethylation of Alkyl Halide Anisoles

87524
S/079/60/030/012/004/027
B001/B064

HI and HBr under ordinary conditions; the reason is the blocking of the methoxy group by the two alkyl radicals which are in ortho position to it. At continuous heating of 2-cyclohexyl-4-chloro anisole with HI, besides demethylation also a splitting off of the chlorine atom takes place, which instead of the expected 2-cyclohexyl-4-chloro phenol leads to 2-cyclohexyl phenol. There are 1 table and 3 references: 2 Soviet and 1 British.

ASSOCIATION: Voronezhskiy gosudarstvennyy universitet
(Voronezh State University)

SUBMITTED: February 4, 1960

Card 2/2

S/079/60/030/012/011/027
B001/B064

AUTHORS: Shalganova, V. G. and Zavgorodniy, S. V.

TITLE: Autooxidation of 4-sec.-butyl-o-xylene

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 12, pp. 3964-3967

TEXT: The authors investigated the autooxidation of 4-sec.-butyl-o-xylene (I) with atmospheric oxygen at 110°C in the presence of manganese resinate, combined with $Ca(OH)_2$, NaOH, Na_2CO_3, sodium stearate, cobalt acetate. The compound was oxidized up to the maximum concentration of the hydroperoxide or the complete vanishing of the latter from the reaction mass. The maximum concentration of hydroperoxide was found to depend on the type of the admixture and the amounts of manganese resinate. The maximum concentration of hydroperoxide (13 %) is caused by the autooxidation of butyl xylene (I) in the presence of resinate and soda with the following products forming from the reaction mass until the complete vanishing of hydroperoxide: 3,4-dimethyl acetophenone (II); o-xylenol-(1,2,4) (III); 1,2-dimethyl-phenyl-methyl-ethyl carbinol (IV); 2-methyl-4-sec.-butyl- and 2-methyl-

Card 1/3

Autooxidation of 4-sec.-butyl-o-xylene

S/079/60/030/012/011/027
B001/B064

5-sec.-butyl benzoic acid (V); 2-methyl-4-sec.-butyl- and 2-methyl-5-sec.-butyl benzyl alcohol (VI). The oxidation of (4-sec.-butyl-o-xylene) in the presence of manganese resinate, sodium stearate, and calcium hydroxide with atmospheric oxygen (18 l/h) in a time of 60 h gave a 25.8 % yield of oxidation products. The products (II-VI) form at a molar ratio of 3.75 : 1 : 3 : 5.65 : 2.5. The yield of the oxidation product was 32.3 % in the presence of resinate, cobalt acetate, sodium stearate, caustic soda, and calcium hydroxide. The products (II-VI) were obtained in a molar ratio of 7.5 : 1 : 3 : 26 : 4. From the composition of the oxidation products it may be concluded that in the oxidation of 4-sec.-butyl-o-xylene all three radicals are oxidized, under the formation of a hydroperoxide mixture: 2-methyl-4-sec.-butyl benzyl (VII), 2-methyl-5-sec.-butyl benzyl (VIII), and 3,4-dimethyl-α-methyl-α-ethyl benzyl (IX) which were all identified by their reduction to alcohols. The time of oxidation of all three alkyl radicals depends on the character of the additions. Among two methyl groups, the one in para position to the sec.-butyl group oxidizes more readily than the other. The sec.-butyl radical oxidizes in the presence of manganese resinate, sodium stearate, and calcium hydroxide twice as rapidly as the methyl radical. There are 2 tables and

Card 2/3

Autooxidation of 4-sec.-butyl-o-xylene

S/079/60/030/012/011/027
B001/B064

8 Soviet references.

ASSOCIATION: Voronezhskiy gosudarstvennyy universitet (Voronezh State University)

SUBMITTED: January 11, 1960

Card 3/3

5.3600

68991

S/020/60/131/02/033/071
B011/B005

AUTHORS: Topchiyev, A. V., Academician, Kryuchkova, V. G., Zavgorodniy, S. V.

TITLE: Alkylation of 4-Fluorophenol With Propylene and Cyclohexene in the Presence of the Catalysts $BF_3 \cdot H_3PO_4$ and $BF_3 \cdot O(C_2H_5)_2$

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol 131, Nr 2, pp 329-331 (USSR)

ABSTRACT: As the reaction of fluorophenols with olefins had been neglected in publications, the authors studied the reaction mentioned in the title in continuation of their previous papers. 4-fluorophenol reacts more intensely than chloro- and bromophenols. Together with olefins (with propylene) it forms a rather complex mixture of products. Isopropylfluorophenolisopropyl ether is always, isopropylfluorophenol sometimes, formed besides the 4-fluorophenolisopropyl ether. The yields in individual products depend on the nature and quantity of the catalyst, the temperature, and the molar ratios of the reagents. Thus, only ethers are formed in the presence of $BF_3 \cdot O(C_2H_5)_2$ at 60° whereas phenol products are missing, at least in noticeable quantities. In the presence of $BF_3 \cdot H_3PO_4$, the yields in phenol compounds are the higher, the higher the temperature between 40 and 70°. The best conditions for a formation of 4-fluorophenolisopropyl ether (54% yield) are: molar ratio of fluorophenol,

Card 1/2

68992

Alkylation of 4-Fluorophenol With Propylene and Cyclohexene in the Presence of the Catalysts $BF_3 \cdot H_3PO_4$ and $BF_3 \cdot O(C_2H_5)_2$

S/020/60/131/02/033/071
B011/B005

propylene and $BF_3 \cdot H_3PO_4$ = 3:1:0.4 and 40°; the same for isopropyl-4-fluorophenolisopropyl ether is: 5:1:0.3 and 60° (36% yield), and for isopropyl-4-fluorophenol 3:1:0.2 and 70° (38% yield). Table 1 lists these results. One product only - 4-fluorophenolcyclohexyl ether - is formed from 4-fluorophenol with cyclohexane in the presence of $BF_3 \cdot H_3PO_4$ with a yield of 70.7% of the theoretical one. Already after the 1st distillation of the alkylate, the product has a boiling limit of 2-3° (Table 2). The compounds of the ether type were identified by splitting into corresponding phenols and transformation of the phenols into phenoxy acetic acids. Table 3 shows the physical and chemical constants of the products obtained. There are 3 tables and 8 references, 6 of which are Soviet.

4

ASSOCIATION: Voronezhskiy gosudarstvennyy universitet (Voronezh State University)

SUBMITTED: November 19, 1959

Card 2/2

S/020/60/132/03/28/066
B011/B008

5.3200

AUTHORS: Volkov, R. N., Zavgorodniy, S. V.

TITLE: Kinetic Peculiarities of the Isopropyl Xylene Autoxidation in the Liquid Phase

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 3, pp. 591-594

TEXT: In this paper the authors continued the previous investigations (Ref. 1). They now studied the problem mentioned in the title on polyalkyl benzenes with neighboring substituents. o-xylene (I), 4-isopropyl-o-xylene (II), 3-isopropyl-o-xylene (III), 2-isopropyl-p-xylene (IV), 4-isopropyl-m-xylene (V), 2,5-di-isopropyl-p-xylene (VI) and o-cymene (VII) were investigated. It was determined that γ-lactones (phthalide-derivatives) also develop during the autoxidation of these substances, besides alcohols, ketones, acids etc. From (I) there forms in the presence of 0.6 Mol-% cobalt acetate: o-toluic acid, 5-8% of phthalide, and 2-5% mixture from toluyl aldehyde and tolyl carbinol. The highest concentration of hydroperoxide does not exceed 1-1.5%.

Card 1/3

Kinetic Peculiarities of the Isopropyl Xylene Autoxidation in the Liquid Phase

S/020/60/132/03/28/066
B011/B008

A rather complex mixture develops from (II) at the oxidation. It can be seen from Table 1 that the yield of lactones amounts to approximately 5% of the oxidized hydrocarbon. Other products with two oxidized groups develop in noticeable quantities at an intensity of the oxidation of over 30%. (III)-(V) are very slowly oxidized in the presence of manganese resinate. Cobalt acetate and cobalt isopropyl toluylene accelerate the process considerably. It was not possible to direct the process by these two catalysts towards the predominant formation of hydro peroxides, since these decompose very quickly in the presence of cobalt salts. (VI) could oxidize at 110°C within 7 hours with 6 mg/Mol manganese resinate and 10 mg/Mol soda up to a 10% concentration of hydro peroxides. The isopropyl-group can be oxidized in (II) almost 4 times more easily than the CH_3-group, but in (IV) and (V) the total rate of oxidation of the groups placed side by side is only 1.3-1.7 times greater than that of the individually placed groups, owing to steric hindrance. Fig. 1 shows the kinetics of the oxidation products of (V) at 130°C in the presence of 1 Mol-% cobalt isopropyl toluylate, as well as of (IV) at 160°C. The rate of the introduction of air was

Card 2/3

Kinetic Peculiarities of the Isopropyl Xylene Autoxidation in the Liquid Phase

S/020/60/132/03/28/066
B011/B008

1 l/min. The composition of the oxidation products of (IV) and (V) is given in Table 2. It follows therefrom that lactones develop at a considerable rate already in the earliest phases. More than 50% lactones develop at the oxidation of (VI), (III) and (VII) give also high yields. Based on the results, the authors come to the conclusion that the main cause of the high yield of lactones lies in the isomerization of the free radical (see Scheme). There are 1 figure, 2 tables, and 5 references, 3 of which are Soviet.

ASSOCIATION: Voronezhskiy gosudarstvennyy universitet (Voronezh State University)

PRESENTED: January 8, 1960, by A. V. Topchiyev, Academician

SUBMITTED: January 8, 1960

Card 3/3

TOPCHIYEV, A.V., akademik; KHYUCHKOVA, V.G.; ZAVGORODNIY, S.V.

Alkylation of 2-chloroanisole by propylene, 2-butene, and cyclohexene in the presence of $BF_3.H_3PO_4$. Dokl.AN SSSR 133 no.3:617-619 Jl '60. (MIRA 13:7)

1. Institut neftekhimicheskogo sinteza Akademii nauk SSSR i Voronezhskiy gosudarstvennyy universitet.
(Anisole) (Alkylation)

86465

S/020/60/133/004/037/040XX
B016/B054

5.3300

AUTHORS: Volkov, R. N., and Zavgorodniy, S. V.

TITLE: The Character of Alkylation of Aromatic Hydrocarbons by Olefins in the Presence of $BF_3 \cdot H_3PO_4$

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 133, No. 4, pp. 843-846

TEXT: The authors report on the investigation of the following alkylation reactions in the presence of the catalyst $BF_3 \cdot H_3PO_4$: of benzene by propylene, cyclohexene, as well as α- and β-isobutylene; of binary mixtures of toluene and benzene, ethyl benzene, cumene, as well as o-, m-, and p-xylene by the same olefins; of a mixture of benzene and cyclohexene; of a mixture of cumene, and the xylenes by butylenes and ethyl benzene, m-xylene with secondary and tertiary butyl benzene by propylene and β-butylene; of benzene mixed with tert.-butyl benzene; of cumene, diisopropyl benzene, and a mixture of the latter with benzene, by

Card 1/4

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S/020/60/133/004/037/040XX
B016/B054

- The Character of Alkylation of Aromatic Hydrocarbons by Olefins in the Presence of $BF_3 \cdot H_3PO_4$

propylene. These experiments were made to check the assumption saying that the presence of alkyl groups in the benzene ring strongly activates the substitution reaction only if the attacking agent has a considerable positive charge. The authors performed the alkylation as it is described in Ref. 8. They made special experiments to determine the effect of dealkylation on the composition of the alkylate. They proved that only hydrocarbons with tertiary butyl groups are noticeably dealkylated. The rate of this process only depends on the concentration of the substance to be dealkylated, and on temperature. Table 1 shows the alkylation results of the benzene - toluene mixture. Hence, the authors conclude that neither the reaction conditions nor the ratio of the reagents can strongly influence the reaction rate of toluene. The same applies to the alkylation of other hydrocarbons by propylene, n-butylene, and cyclohexene. Only in the reaction of benzene and its homologues with isobutylene, temperature and duration of the experiment exerted some influence in the above sense. Table 2 gives the relative reactivities of benzene homologues to various

Card 2/4

86465

The Character of Alkylation of Aromatic Hydrocarbons by Olefins in the Presence of $BF_3 \cdot H_3PO_4$

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olefins. The catalyst $BF_3 \cdot H_3PO_4$ does not produce a strong disproportionation of primary and secondary alkyl radicals, nor does it form any "special complexes" during alkylation. Table 3 shows the composition of the alkylation products. Hence, the authors conclude that the relations of the rate constants of successive reactions do not depend on the intensity of alkylation of an aromatic hydrocarbon. Therefore, it is possible to forecast the composition of the alkylate with relative accuracy. The authors mention the phenomenon of hyperconjugation, but do not discuss it. For an interpretation of several rules observed by them, they must assume that the alkyl groups are an obstacle not only in ortho-, but also in meta- and para-substitutions. Generally speaking, alkyl benzenes can react faster (than with benzene) only with such olefins that are polarized by the catalyst, and form ions with a highly effective charge, which are concentrated on the reacting carbon atom. Finally, the authors point out that the rupture of the π-bond proceeds gradually during the formation of a bond with the aromatic ring. This is confirmed by the difference in

Card 3/4

The Character of Alkylation of Aromatic Hydrocarbons by Olefins in the Presence of $BF_3 \cdot H_3PO_4$

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B016/B054

relative reactivities of alkyl benzenes and α- and β-butylene. There are 3 tables and 9 references: 8 Soviet and 1 US.

ASSOCIATION: Voronezhskiy gosudarstvennyy universitet (Voronezh State University)

PRESENTED: March 19, 1960, by A. V. Topchiyev, Academician

SUBMITTED: March 19, 1960

Card 4/4

84690

S/020/60/134/004/015/023
B016/B060

5.3300 2209, 1153 only

AUTHORS: Topchiyev, A. V., Academician, Volkov, R. N., and Zavgorodniy, S. V.

TITLE: A Study of the Rules Governing the Alkylation of Xylenes With Propylene in Presence of $BF_3 \cdot H_3PO_4$

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 134, No. 4, pp. 844 - 847

TEXT: The rules governing the alkylation of o- (I), m- (II), and p-xylene (III) with propylene in the presence of $BF_3 \cdot H_3PO_4$ have not been studied by previous researchers (Ref. 2), nor have their yields of isopropyl xylene been higher than 52%. The authors of the present paper made a systematic study of the effects of catalyst concentration, temperature, time of reaction, and molar ratio of reagents upon the yield and the composition of the alkylation product of (I) - (III). In doing so, they established the conditions under which it is possible to obtain a 90% yield in

Card 1/4

A Study of the Rules Governing the Alkylation of Xylenes With Propylene in Presence of $BF_3 \cdot H_3PO_4$

S/020/60/134/004/015/023
B016/B060

isopropyl xylenes, and clarified the kinetic characteristics of the reaction. Alkylation and fractional distillation were performed in the same way as shown in Ref. 3. The propylation of (I) gives rise to 4-isopropyl-o-xylene (IV), 3-isopropyl-o-xylene (V), and 4,5-diisopropyl-o-xylene (VI), while (II) yields 4-isopropyl-m-xylene (VII), 5-isopropyl-m-xylene (VIII), 2-isopropyl-m-xylene (IX), 4,6-diisopropyl-m-xylene (X), and 2,5-diisopropyl-m-xylene (XI). The monoalkylate of (III) exclusively consists of 2-isopropyl-p-xylene (XII), while its dialkylate mainly consists of 2,5-diisopropyl-p-xylene (XIII). Table 1 contains the principal constants of the resulting compounds and the xylenes employed in the process. Heretofore, there was no description of (V) and (VI) to be found in publications. The authors describe the methods of identifying the isomers. They were oxidized to form benzene polycarboxylic acid, and examined both refractometrically and by means of infrared absorption spectra. The authors further describe the separation of benzene tricarboxylic acids, and that of their esters. The dilactone of 2,5-di-(α-oxy-isopropyl)-terephthalic acid was obtained from (XIII) by oxidation.

Card 2/4

A Study of the Rules Governing the Alkylation of Xylenes With Propylene in Presence of $BF_3 \cdot H_3PO_4$

S/020/60/134/004/015/023
B016/B060

Moreover, isopropyl xylenes were also identified by self-oxidation. Results obtained from some experiments on xylene propylation are shown in Table 2 and include composition of reaction mass, yields, ratio of apparent rate constants of the alkylation of isopropyl xylenes and initial xylene ($r = k_2/k_1$). It may be seen from Table 2 that an increase in temperature and in the concentration of $BF_3 \cdot H_3PO_4$ reduces the relative formation rate of products resulting from secondary alkylation, as had already been established previously by the first-named author jointly with N. V. Kuranhev and Ya. M. Paushkin (Ref. 7). The rules governing the isomerization of polyalkyl benzenes are formulated as follows: the migration of the isopropyl group has an inner-molecular character, and chiefly occurs whenever there are alkyl radicals in the positions 2,3, 2,4, or 2,3,5 relative thereto. These rules, in addition to explaining the character of the orientation of substituents, allow the process to be controlled in such a way that the substances desired can be obtained with highest yields. There are 1 figure, 2 tables, and 9 references: 8 Soviet and 1 US.

A Study of the Rules Governing the Alkylation of Xylenes With Propylene in Presence of $BF_3 \cdot H_3PO_4$

S/020/60/134/004/015/023
B016/B060

ASSOCIATION: Voronezhskiy gosudarstvennyy universitet (Voronezh State University)

SUBMITTED: April 29, 1960

Card 4/4

26288
S/190/61/003/008/001/019
B110/B220

15.8100

AUTHORS: Rayevskiy, A. B., Kryuchkova, V. G., Zavgorodniy, S. V.

TITLE: Effect of alkyl halophenols on the polymerization of styrene

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 8, 1961, 1121-1124

TEXT: The inhibiting effect of phenol derivatives on the polymerization of styrene and its dependence on the structure of the phenol derivatives were studied. The compounds mentioned in the legend of the figure were synthesized to this end. Anisole halides were alkylated by olefins in the presence of $BF_3 \cdot H_3PO_4$ and $BF_3 \cdot O(C_2H_5)_2$ at 60°C. Demethylation of the anisole alkyl halides obtained was performed in the presence of HI, HBr, and acetic anhydride. Commercial styrene was purified from hydroquinone by treatment with 20% KOH, dried over Al_2O_3 and distilled in a nitrogen flow. The molar ratio of styrene to inhibitor was $5 \cdot 10^3$:1. For comparison, styrene was polymerized without inhibitor. The polymer content P was calculated from the refractive index: $P = (2.05 \cdot n_D^{20} - 3.17) \cdot 10^3$. Results: 1) The nature

Card 1/4

Effect of alkyl halophenols on ... S/190/61/003/008/001/019
B110/B220

of the halogens and their position influences the inhibiting effect; 2) 2-alkyl-4-halophenols are stronger inhibitors than 2-halogen-4-alkyl phenols; 3) fluorine derivatives are stronger inhibitors than chlorine derivatives; 4) 4-fluorophenols show an increasing inhibiting effect in the sequence: 2-sec-butyl-; 2-cyclohexyl-; 2-sec-amyl-; 2-isopropyl-4-fluorophenol; 5) the inhibiting effect of 4-chlorine derivatives increases conversely; 6) the nature of the alkyl radical has no essential effect in the case of 4-alkyl-2-halophenols; 7) Since phenol derivatives have an inhibiting effect only in the presence of O_2, the compounds studied did not show such an effect in the polymerization of styrene in a nitrogen atmosphere. There are 1 figure, 2 tables, and 7 references: 3 Soviet and 4 non-Soviet. The most important references to English-language publications read as follows: Ref. 1: E. G. Edwards, G. F. P. Harris, Chem. Ind., 1955, 625; Ref. 2: S. G. Food, J. chem. Soc., 1940, 48. Ref. 6: USA Patent 2, 221 809, 1940.

ASSOCIATION: Zavod sinteticheskogo kauchuka im. S. M. Kirova (Synthetic Rubber Works imeni S. M. Kirov). Voronezhskiy gosudarstvennyy universitet (Voronezh State University)

Card 2/4

KRYUCHKOVA, V.G.; ZAVGORODNIY, S.V.

Alkylation of 4-chloroanisole by propylene, pseudobutylene, and cyclohexene in the presence of the catalyst $HF_3 \cdot H_3PO_4$. Izv.vys. ucheb.zav.; khim.i khim.tekh. 4 no.1:92-95 '61. (MIRA 14:6)

1. Voronezhskiy gosudarstvennyy universitet, kafedra organicheskoy khimii.

(Anisole) (Alkylation)

B/153/61/004/001/004/009
B110/B203

AUTHORS: Zavgorodniy, S. V., Sigova, V. I.

TITLE: Synthesis of 1-ethyl-4-isopropyl benzene and some of its conversions

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, v. 4, no. 1, 1961, 99-101

TEXT: In the alkylation of ethyl benzene with propylene (I) and isopropyl alcohol (II) in the presence of $BF_3 \cdot H_3PO_4$, mainly 1-ethyl-4-isopropyl benzene is formed (polyalkyl benzenes 7% maximum). With (I), 0.2-0.3 moles of $BF_3 \cdot H_3PO_4$ are required per mole of propylene; the optimum yield (69% of the theory) is obtained with the ratio: 3 moles of ethyl benzene : 1 mole of propylene : 0.3 moles of catalyst. With (II), 0.5-1 moles of $BF_3 \cdot H_3PO_4$ are required per mole of isopropyl alcohol; the optimum yield (61% of the theory) is obtained with the ratio: 2 moles of ethyl benzene : 1 mole of isopropyl alcohol : 1 mole of catalyst, and at

Card 1/5

Synthesis of 1-ethyl-4-isopropyl ...

88-90°C. Alkylation with propylene and $BF_3 \cdot H_3PO_4$ at the molar ratios 4 : 1 : 0.3 and 1 : 1 : 0.2 proceeds slowly at 53-55°C (yield 20% of the theory). At 100°C, the reaction proceeds vigorously, the catalyst being thrown out of the reaction mixture. 0.5 and more than 2 moles of ethyl benzene per mole of isopropyl alcohol gives only 50% of the theoretical yield. Nitration of 1-ethyl-4-isopropyl benzene proceeds readily. Excess bromine gives pentabromo ethyl benzene. Nitric acid oxidizes to terephthalic acid. In autooxidation with atmospheric oxygen in the presence of manganese resinate, cobalt acetate, and calcium hydroxide, mainly the α-carbon of the ethyl radical is affected, and the hydroperoxide of α-methyl-p-isopropyl benzyl is formed. Maximum hydroperoxide concentration is attained after 2-4 hr (Fig. 1), then decomposition sets in. With the use of proper amounts of suitable alkali additions, the authors obtained up to 37% of hydroperoxides in the reaction mass after 20 hr. Then, decomposition by H_2SO_4 mainly gives p-isopropyl phenol. Initial substances were: industrial ethyl benzene (boiling point = 135-136.5°C, $d_4^{20} = 0.8655$, $n_D^{20} = 1.4950$); propylene produced by dehydration of

Card 2/5

Synthesis of 1-ethyl-4-isopropyl ...

isopropyl alcohol; and freshly prepared $BF_3 \cdot H_3PO_4$. Alkylation was performed by the method earlier described by the first author (Ref. 1: S. V. Zavgorodniy et. al.: Zh. obshchey khimii, 26, 2180 (1956)). Results are tabulated. 1-Ethyl-4-isopropyl benzene is formed almost exclusively (values obtained: boiling point = 193-194°C; d_4^{20} = 0.8626; n_D^{20} = 1.4927, MR_D = 49.8; calculated: 49.4; published data: boiling point = 1.94°C; d_4^{20} = 0.8625; n_D^{20} = 1.4927). The following derivatives were prepared: (1). Pentabromo ethyl benzene by bromination with Br_2 in the presence of Al chips at 0°C (white powder, mp = 137-138.5°C). (2) Mononitro-ethyl isopropyl benzene (34.5% yield) by nitration with mixed acid. Highly viscous liquid, mp = 136-137°C at 3 mm Hg; d_4^{20} = 1.0535; d_D^{20} = 1.5338. Found: M = 192.5 $C_{11}H_{15}NO_2$; calculated: M = 193.0. Oxidation with HNO_3 gives nitro-terephthalic acid (yellow platelets, mp = 263-265°C (from alcohol)). (3) Terephthalic acid by prolonged heating with 25% HNO_3 to weak boiling, identified by

Card 3/5

B/153/61/004/001/004/009
B110/B203

conversion with CH_3OH and concentrated H_2SO_4 to the dimethyl ester of terephthalic acid (mp = 139-140°C). Autooxidation of 1-ethyl-4-isopropyl benzene with atmospheric oxygen proceeded in the presence of manganese resinate and alkali additions to a decrease of the hydroperoxide concentration in the reaction mass. The concentration was iodometrically determined every 2-4 hr (Fig. 1). On decomposition with H_2SO_4, the hydroperoxide of any concentration yielded p-isopropyl phenol (long, white needles, mp = 57.5°C (from petroleum ether)) besides considerable amounts of resin. With $CH_2ClCOOH$, p-isopropyl phenoxy acetic acid is formed (small, white needles, mp = 80°C, published: mp = 81°C). There are 2 figures, 1 table, and 5 references: 3 Soviet-bloc and 2 non-Soviet-bloc. The reference to the English-language publication reads as follows: C. E. Welsh, G. F. Hennion, J. Amer. Chem. Soc., 63, 2603 (1941).

Synthesis of 1-ethyl-4-isopropyl ...

S/153/61/004/001/004/009
B110/B203

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Card 5/5

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AUTHORS: Zavgorodniy, S.V., Gonsovskaya, T.B.

TITLE: Benzene alkylation with olefins of scrubber exhaust gases in the divinyl production by the Lebedev method

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, v. 4, no. 1, 1961, 128 - 131

TEXT: In contrast to the alkylation of aromatics with individual olefins, the alkylation with olefin mixtures has only been dealt with in the book by M.A. Dalin (Ref. 9: Alkilirovaniye benzola olefinami, Goskhimizdat, M., 1957). It is of special interest since olefin mixtures are obtained in the chemical industry, e.g., 13-15% of ethylene and propylene in the scrubber exhaust gas in the divinyl production according to S.V. Lebedev during rubber synthesis. They could be used for the production of large quantities of valuable for synthesis ethyl and isopropyl benzenes instead of fuels. For this purpose, the authors studied the benzene alkylation with ethylene and propylene of the scrubber exhaust gas in the presence of $AlCl_2 \cdot H_2PO_4$, $AlCl_3$, $AlCl_2 \cdot HSO_4$ and $BF_3 \cdot H_3PO_4$. Favorable conditions

Card 1/4

Benzene alkylation with ...

yielded a quantitative utilization of olefins (mainly ethylene and isopropylene). $AlCl_3$ is the most efficient catalyst. Optimum ratio benzene/olefin/catalyst = 2.5/1/0.05. Optimum temperature = 78-80°C, gas velocity = 4.5-5 l/hr. Here, the yield of isopropyl benzene (I) is 90%, that of ethyl benzene (II) 70%, referred to propylene or ethylene absorption. The fraction of (I) in the alkylate is 32%, that of (II) 51%. Ethylene conversion = 77%, propylene conversion = 89%. The efficiency of $AlCl_2 \cdot H_2PO_4$ and $AlCl_2 \cdot HSO_4$ is worse than that of $AlCl_3$. With the use of $BF_3 \cdot H_3PO_4$, benzene was only propylated (Tables 1 and 2). With 0.05 moles of $AlCl_2 \cdot HSO_4$ and 0.10 moles of $AlCl_2 \cdot H_2PO_4$ per mole of olefin, the propylation rate is high up to 35°C, isopropyl benzene being mainly formed. In the ethylation, hexaethyl benzene is also formed (8-26% in the alkylate). Higher amounts of catalyst and increase in temperature to 50 - 80°C increase the ethyl benzene formation, and reduce slightly the isopropyl formation. Here, almost no hexaethyl benzene is formed. Thiophene-free benzene was used. After divinyl adsorption with ethyl alcohol, the scrubber exhaust gas (3-6 % of the alcohol passing through) contained 12-15% of

Card 2/7