Thermal Isomerization of 2-Methyl-4.5-dihydrofuran to Methyl-cyclopropyl Ketone SOV/20-125-5-27/61

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences,USSR)

SUBMITTED: February 5, 1959

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5(2)

AUTHORS: Timofeyeva, Ye. A., Shuykin, ~~N. I.,~~ SOV/20-125-6-27/61
Corresponding Member, AS USSR,
Plotnikov, Yu. N., Kleymenova, V. M.

TITLE: Dehydrogenation of n-Hexane on an Aluminochromium Catalyst (Degidrogenizatsiya n-geksana na alyumokhromovom katalizatore)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 125, Nr 6, pp 1272-1274 (USSR)

ABSTRACT: A survey of publications on the reaction mentioned in the title (Refs 1-2) shows that neither the instructions concerning the reaction nor the yield of hexenes nor the formation of aromatic hydrocarbons under the given conditions have been hitherto discussed. Papers on the afore-mentioned reaction on oxide catalysts lack. Further references follow (3-6). Table 1 shows the data given in the publications concerning the reaction mentioned in the title in the presence of chromium and with the aromatization of n-heptane. This shows that catalyzates have hitherto been obtained by various research workers which contained considerably less unsaturated hydrocarbons than aromatic ones. On the strength of their investigations carried out in the last years the authors drew the conclusion that it is possible to

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change considerably the ratios of the yields of the two aforementioned hydrocarbon types, i.e. from 0.14 to 2.11 by changing the production of the catalysts mentioned in the title, furthermore, by the introduction of oxides of alkali metals, finally by changing the instructions concerning the reaction. The catalyst without alkaline additions was the best of all catalysts investigated, as far as the maximum yields of unsaturated hydrocarbons are concerned. It was produced by the saturation of aluminum oxide with ammonium bichromate solution. Unsaturated hydrocarbons with a yield of 20% and not more than 14% benzene were obtained from n-hexane at 500° and a rate of passage of 0.5 h^{-1}. It was the authors' object to suppress the aromatization even more in this investigation. All factors were investigated for this purpose: temperature, rate of passage, and individual parts of the catalyzate were analyzed etc. Table 2 and figure 1 show the results. The gas produced by the transformations of n-hexane at 475 and 500° contained 90.6-95.3% hydrogen, up to 1.8% unsaturated hydrocarbons, and 2.7-7.5% alkanes. The temperature rise within the afore-mentioned range increases the yield of hexenes only by 2%, that of benzene, Dehydrogenation of n-Hexane on an Aluminochromium Catalyst SOV/20-125-6-27/61

however, by 9-13%. Thus, it was found that the dehydrocyclization of n-hexane practically does not take place under the given conditions, whereas hexenes are produced in rather considerable quantities. The result is of general importance since the authors succeeded in suppressing the aromatization of an n-alkane which is capable of immediate dehydrocyclization in the presence of an aluminochromium catalyst. The dehydrogenation of n-hexane is rather considerable. There are 1 figure, 2 tables, and 8 references, 6 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: January 30, 1959

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5 (3)

AUTHORS: Shuykin, N. I., Corresponding Member SOV/20-126-1-28/62
AS USSR, Bekauri, N. G.

TITLE: Catalytic Polycyclization of Higher Alkanes (Kataliticheskaya politsiklizatsiya vysshikh alkanov)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 126, Nr 1, pp 103 - 106 (USSR)

ABSTRACT: A group of scientists detected at the same time (Refs 1-3) the reaction of the catalytic dehydrocyclization of alkanes which have a chain of carbon atoms in the molecule (not less than 6). This reaction was investigated mainly in the case of hydrocarbons of simple composition. They gave as final yield benzene, toluene, and xylenes. According to the multiplet theory of A. A. Balandin and other theories it could, however, be expected, that higher alkanes of normal structure (beginning with the n-decane) are bound to yield condensed systems of naphthalene, phenanthrene, and still more complicated polycycles under conditions which favor dehydrocyclization. This is in fact the case (Ref 4) (see scheme). α-Naphthalenes can be partly or completely isomerized into the β-form in this reaction. This formation is, however, possible with an intermediate stage of

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a substituted benzene with a subsequent closing of the side chain (see scheme). This is based upon a previous paper of the first author (Ref 5, see scheme). In the present paper transformations of n-heptadecane and n-octodecane were investigated in the presence of 0.5% platinum precipitated on aluminum oxide and on "gumbrine" (bleaching earth), or palladium precipitated at 450° and a hydrogen pressure of 30 atm (Ref 6). The initial alkanes were isolated from the fraction 190-350° of the Sokolovogorskaya and Mirzaanskaya petroleum (Ref 7) and carefully cleaned. 8 liquid catalyzates were obtained as the result of the experiments which were thoroughly investigated according to an earlier described (Ref 4) method. These catalyzates contained products of the polymerization, of hydrocracking, and of the dehydrocyclization of the initial alkanes. After a small fraction which boils out up to 100° has been distilled off, aromatic hydrocarbons were isolated from the rest of the individual catalyzates by means of the chromatographic adsorption on silica gel of the type ASM. By means of further fractionating in a nitrogen atmosphere a greater content of toluene and xylene and platinum was obtained on "gumbrine" in fractions which boil out up to 150°. Therefore, "gumbrine" is able to initiate aromatization reactions. Figure 1 shows the properties of the aromatic hydrocarbons which boil above 150°. They have a blue-green fluorescence. The mixture was divided into 5, 6 zones respectively by ultraviolet illumination with a luminescence of different intensity and color (wave length 360 mμ). The comparison of the spectra showed that the fraction II (Figs 1:1 cursive) is in this connection most similar to phenanthrene and its homologues. The spectrum of the fraction IV (Figs 1:2 cursive) is similar to that of α-methyl-naphthalene (Figs 1:4 cursive), although the two spectra did not agree. Thus alkyl phenanthrenes with the side groups $C_3 - C_4$ exist in the fraction II. They represent probably a mixture of n-propyl- and n-butyl phenanthrenes with a chrysene admixture (see scheme). The investigations are continued. There are 1 figure, 1 table, and 7 Soviet references.

Catalytic Polycyclization of Higher Alkanes SOV/20-126-1-28/62

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR). Institut khimii im. P. G. Melikishvili Akademii nauk GruzSSR (Institute of Chemistry imeni P. G. Melikishvili of the Academy of Sciences, Gruzinskaya SSR)

SUBMITTED: February 21, 1959

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SOV/20-127-1-23/65

5(3)

AUTHORS: Bel'skiy, I. F., Shuykin, N. I., Corresponding Member, AS USSR

TITLE: Catalytic Isomerization of δ-Oxides (Tetrahydropyrans) to Aliphatic Carbonyl Compounds (Kataliticheskaya izomerizatsiya δ-okisey (tetragidropiranov) v alifaticheskiye karbonil'nyye soyedineniya)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 1, pp 91-92 (USSR)

ABSTRACT: Hitherto it has been assumed that the γ- and δ-oxides cannot be isomerized by the opening of the ring to the compounds mentioned in the title, in contrast to the α-oxides. The authors proved, however, (Ref 1) that this is possible as well in the case of the δ-oxides (tetrahydrofuran and its homologs) in the vapor phase on platinized charcoal at 250°. They are transformed mainly into aliphatic ketones. The reaction of the δ-oxides mentioned in the title could be carried out as well with an alkyl substituent in an α-position at 300-350°, as was expected. The corresponding aliphatic ketones (yield 70-80 %) and alkanes (20-30 %) are formed also in this case (see Scheme). This speaks in favor of the fact that the isomerization of

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Catalytic Isomerization of δ-Oxides (Tetrahydropyrans) to Aliphatic Carbonyl Compounds SOV/20-127-1-23/65

α-alkyl-tetrahydropyrans proceeds like in the case of the γ-oxides, mainly by the opening of the ring of the C—O bond which is farthest away from the alkyl substituent (bond 1—6). The reaction proceeds as smoothly as that of the γ-oxides; the reaction products are the same. An analogy with the γ-oxides exists with respect to the easiness of opening (raskrytiye) of the ring as well. The transformation degree of the δ-oxides into ketone and aldehydes was higher than that of the γ-oxides (50-60 % per passage over the catalyst), since their isomerization was carried out at a higher temperature. There are 2 references, 1 of which is Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: April 18, 1959

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5.(3) SOV/20-127-2-34/70

AUTHORS: Shuykin, N. I., Corresponding Member AS USSR, Bel'skiy, I. F.

TITLE: Hydrogenolysis of Carbonyl-containing Furan Compounds. Transformation of Alkyl-acyl-furans Into Six-membered Carbocyclic Compounds

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 2, pp 359-361 (USSR)

ABSTRACT: The direction of the hydrogenolysis of the furan ring depends on various factors, in the first place on the nature of the catalyst and on the properties of the lateral substitutents (Refs 1-5). Strict conclusions on the influence of the latter on the mentioned direction of the ring cleavage are possible only on the strength of the comparison of experimental results obtained under equal conditions of phase state and pressure. In a previous paper (Ref 5) the authors found a ring aperture in the α-alkyl-furans on Pt-C only at the C—O-bond at normal pressure which is not adjacent to the alkyl radical. Aliphatic ketones are formed here. In the present paper the hydration reaction of pyromucic acid-methyl-ester and 2-methyl-5-acetyl-furan was investigated under conditions completely analogous to the last mentioned ones. In this case the carbonyl-containing groups influence decisively

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the direction of the aperture of the furan ring. The effect of these groups is opposed to that of the alkyl radical. The hydrogenolysis mentioned in the title proceeds in all substances investigated easily and only at the C—O-bond adjacent to carbonyl-containing groups. The primary products produced by this are subjected to further changes in the vapor phase under the hydration conditions. This hydration is interesting not only from the theoretical point of view, but also opens new ways of catalytic synthesis of valuable compounds on the furfurol base. The mentioned ester forms methyl butyrate with a yield of 95 % in the hydration on Pt-C at 275°. This is a decarbonylization product of the esters of the corresponding aldehyde acid produced meanwhile (see Scheme). 3-methyl-cyclohexanone, 3-methyl-cyclohexanol as well as metacresol are produced as main products from 2-methyl-5-acetyl-furan under the mentioned hydration conditions. This formation of carbocyclic compounds is based upon profound structural changes in the molecule of this heterocyclic ketone (2-methyl-5-acetyl-furan) and is certainly a result of several subsequent reactions (see Scheme). Thus a hydrogenolysis of the furan ring at the C—O-bond adjacent to the

Hydrogenolysis of Carbonyl-containing Furan Compounds. SOV/20-127-2-34/70
Transformation of Alkyl-acyl-furans Into Six-membered Carbocyclic Compounds

carbonyl group proceeds first on Pt-C (in contrast to Ni catalysts). This leads to the formation of carbocyclic compounds. A primary reduction of the carbonyl group in 2-methyl-5-acetylfuran takes as well place on Pt-C, however, to a much lower extent than on Ni catalysts. An immediate transformation of I into IV and V (see Scheme) has obviously a general importance and may serve as a catalytic synthesis method of the alkylcyclohexanones and alkyl-phenols from 2-alkyl-5-acyl-furans. Finally the hydration apparatus, the reaction conditions, and the physical constants of the obtained substances are described. There are 6 references, 3 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: April 18, 1959

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SOV/20-127-4-24/60

5(3)

AUTHORS: Shuykin, N. I., Corresponding Member, AS USSR, Bel'skiy, I. F., Karakhanov, R. A.

TITLE: Isomerization of γ-Oxides to Aliphatic Carbonyl Compounds. Effect of the Temperature and Structure of These Compounds

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 4, pp 815-817 (USSR)

ABSTRACT: Four problems are solved in this article: (1) What is the action exercised by the length of the carbon chain of the alkyl radicals placed in α-position on the capacity of the tetrahydrofuran cycle to isomerize: Does this action proceed in the direction I (splitting of the 1,5-bond), or in the direction II (splitting of the 1,2-bond, Scheme)? (2) What is the effect of temperature on the relative capacity of the 1,2- and 1,5-bonds to be split by the isomerization of α-alkyl tetrahydrofurans ? (3) How does the isomerization of 2,5-dialkyl tetrahydrofurans develop, which possess alkyl radicals with different numbers of carbon atoms ? (4) What is the direction in which the isomerization of 2,2-dialkyl tetrahydrofurans takes place ? Table 1 shows experimental results. Solutions:

(1) The isomerization of α-n-propyl-, α-n-butyl-, and α-n-amyl tetrahydrofuran was investigated under equal conditions in the vapor phase on platinized coal at 350°. Table 1 indicates

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that the increasing number of carbon atoms in the side chain of α-alkyl tetrahydrofurans increases the capacity of the C-O bond to be split in the cycle isomerization. On the other hand, the tendency of the C-O bond 1,5 towards splitting decreases. The yields of the isomerization products are given. In this case, a pronounced dependence of the capacity of the tetrahydrofuran cycle to isomerize on the length of the alkyl side radical is noticeable in direction I or II. (2) This problem was solved by results obtained from the isomerization of α-n-propyl tetrahydrofuran at 250, 350, and 400°. The relative quantities of n-hexane and dipropyl ketone show an orientation of the isomerization of the tetrahydrofuran cycle on the C-O 1,2- and 1,5-bond in the dependence on temperature. Table 1 further shows that the relative capacity to isomerize under the action of the ring splitting at the C-O bond in the vicinity of the alkyl radical increases with rising temperature. (3) In so far as the difference of the C-O bonds 1,2 and 1,5 in their capacity to be split by the isomerization of the substituted tetrahydrofuran ring depends on the length of the alkyl radical in α-position, it may be expected that this difference also exists in 2,5-dialkyl tetrahydrofurans containing various numbers of C-atoms. This was

Isomerization of γ-Oxides to Aliphatic Carbonyl SOV/20-127-4-24/60
Compounds. Effect of the Temperature and Structure of These Compounds

twice confirmed. (4) In the isomerization of dialkyl tetrahydrofurans containing both alkyl radicals in α-position on one and the same C-atom, the rings are always split at the C-O bond which is adjacent to the alkyl side radical. After the decarbonylization of the aldehyde formed in the meantime, this leads to the formation of corresponding aliphatic hydrocarbons. There are 1 table and 3 references, 2 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: May 21, 1959

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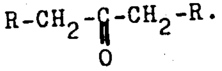
SOV/20-128-5-22/67

~~5(3)~~ 5.3400

AUTHORS: Bel'skiy, I. F., Shuykin, N. I., Corresponding Member, AS USSR

TITLE: A New Method for the Synthesis of Tetrahydrofuran Homologs

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 5, pp 945-947 (USSR)

ABSTRACT: The authors recall the methods used so far for the above synthesis (Refs 1-3). The new method worked out by the authors is described. It is based on a direct transformation of 1-furyl-alkanols-3 into tetrahydrofurans of varying structure. This depends on intermediate formation of 1,4-diols due to hydrogenolysis of the furan cycle in the molecule of the 1-furyl-alkanols-3. In hydrogenation in the vapor phase 1,4-diols are easily cyclized. They separate water and form corresponding tetrahydrofurans. Two cases are to be discussed with regard to the possibility of synthesizing various homologs (mentioned in the title) due to furfurol and aliphatic ketones: 1) Condensation of furfurol with methylalkyl ketones. 2-n-propyl-5-alkyl-tetrahydrofurans (III) are formed (see Diagram). 2) Condensation of furfurol with ketones of the type  $R-CH_2-\underset{\underset{O}{\|}}{C}-CH_2-R$. 2-n-propyl-4,5-dialkyl-tetrahydrofurans (VI) are formed (see Diagram). The reaction

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A New Method for the Synthesis of Tetrahydrofuran Homologs SOV/20-128-5-22/67

mechanism mentioned above is proved by the structure of di- and trialkyl-tetrahydrofurans formed by hydrogenation of 1-furyl-alkanols-3 in the vapor phase. This is a peculiar case of hydrogenolysis of the furan cycle and of simultaneous closure of the new tetrahydrofuran cycle by carbon atoms, three of them having formed a side chain in the initial substance. This fact offers many possibilities of synthesizing various homologs of tetrahydrofuran since the side chain may vary in dependence on the structure of the carbonyl-containing group of the furan compound as well as the structure of the aliphatic ketone. The structure of this side chain of 1-furyl-alkanols-3 is decisive for the structure of the new substituted tetrahydrofuran cycle being formed. Hydrogenolysis of the furan cycle readily proceeds on various catalysts containing metals of group VIII, e.g. on Pt-C and skeleton Ni-Zn, as well as on a skeleton Cu-Al catalyst. The most important side reactions on Pt-C are: a) isomerization of the homologs of tetrahydrofuran to aliphatic ketones (Ref 4). b) Formation of 1,4-dions. c) Hydrogenation of 1-furyl-alkanols-3 to 1-tetrahydrofuryl-alkanols-3. The authors obtained furfurylidene-

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A New Method for the Synthesis of Tetrahydrofuran Homologs SOV/20-128-5-22/67

methyl-alkyl-ketones (I) by condensation of furfurol with acetone, methylethyl ketone, and methyl-propyl ketone in the presence of an NaOH solution. The yield was 70-80%. Condensation with diethylketone was less satisfactory: only 50-55% of the corresponding furfurylidene ketone (IV) was formed. Hydrogenation of the latter substances to 1-furyl-alkanols-3 (II,V) gave a yield of up to 95%. Four of these substances are mentioned together with their constants. There are 4 references, 3 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: June 25, 1959

Card 3/3

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~~5(3)~~ 5.3300

SOV/20-129-1-35/64

AUTHORS: Timofeyeva, Ye. A., Shuykin, N. I., Corresponding Member AS USSR, Plotnikov, Yu. N., Kleymenova, V. M.

TITLE: Dehydrogenation of n-Nonane on an Aluminum-Chromium Catalyst

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 129, Nr 1, pp 128-130 (USSR)

ABSTRACT: In connection with previous investigations (Refs 1, 2) the authors wanted to dehydrogenate n-alkanes with higher molecular weight on the catalyst mentioned in the title. Data from publications are very scarce (Ref 3). The investigations were carried out at various temperatures and volume rates. The method described earlier (Ref 2) was applied. The gas formed due to reaction contained 92-97% hydrogen, 1.5 - 3.5% unsaturated and 1.0 - 4.5% saturated hydrocarbons. Table 1 and figure 1 show the results. Table 1 shows that with a volume rate of 2.1 h^{-1} the olefin content is increased from 8% to not more than 14-15% if the temperature increases from 400 to 475°. At the same time the content of aromatic hydrocarbons increases considerably, namely from traces to 15-16%. Thus a temperature of 400° is optimum with regard to the selective reaction progress of dehydrogenation.

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MINACHEV, Kh.M.; SHUYKIN, N.I.; MARKOV, M.A.

Effect of the specific surface area of platinized aluminosilicate on the degree of n.nonane conversions. Report No.2: Change in the catalytic activity of platinized aluminosilicate in the course of the carrier treatment by water vapors. Izv.AN SSSR Otd. khim.nauk no.8:1466-1470 Ag '60. (MIRA 15:5)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
(Nonane) (Aluminosilicates) (Catalysis)

USSR

BALANDIN, Aleksey A. - "On the theory of contact catalysis of hydrogenation and dehydrogenation reactions" (Section I)

BORESKOV, Georgiy K., and VASILEVICH, A. A. - "Mechanism of isotope exchange of hydrogen on platinum" (Section I)

EYDUS, T. (probably Yakov T. EYDUS) - "On the role of intermediate surface forms in some heterogeneous-catalytic reactions of carbon monoxide and olefines" (Section I)

FREYDLIN, Lev Kh, and GORSHKOV, V. I. - "Catalytic transformation of cyclohexene and copper and the multiplet theory" (Section II)

MAMEDALIYEV, Yusuf G., and GUSEYNOV, M. M. - "Chlorocarbons manufacture by chlorination of alkanes in the fluid bed of a catalyst" (Section III)

NIKOLAYEV, L. A. - "Specific aspects of the mechanism of catalysis by complex compounds" (Section II)

PECHERSKAYA, Yu. I., KAZANSKIY, V. B. and VOYEVODSKIY, V.V. - "Investigation of heterogeneous catalysts by electron spin resonance" (Section II)

PETROV, A. D. - "On the catalytic synthesis of organosilica compounds" (Section III)

ROGINSKIY, Simon Z. - "Electronic effects in catalysis" (Section I or II)

RUBINSHTEYN, A. M. - "The structure and texture of Chromia-alumina-potassium oxide catalysts" (Section II)

SHUYKIN, N. I., and BEL'SKIY, I. P. - "Catalytic transformations in the furannic compound group" (Section III)

SOKOL'SKIY, D. V., and SIMONINA, V. P. - "Kinetic and mechanism of catalytic reduction in aromatic nitro derivatives" (Section I)

TERENIN, A. N. and ROYEV, A. - "Active sites on transition metal catalysts, revealed in the infrared spectrum of adsorbed NO." (Section II)

TOPCHIYEVA, K. V., ANTIPINA, T. V., and **LEE HEH SHENG** (Possibly LI Ho-seng, Moscow Textile Institute) - "The effects of structural characteristics of porous catalysts on activity and kinetic behavior of heterogenous-catalytic reactions" (Section I)

VOL'KENSHTEYN, F. - "General ideas on the electronic theory in catalysis on semiconductors" (Section I)

YEROFEYEV, B. V., and NIKIFOROVA, N. F. - "Catalytic transformation of cyclohexene and copper and the multiplot theory" (Section II)

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reports to be presented at the 2nd Intl Congress on Catalysis, Paris, France, 4-9 Jul '60.

PHASE I BOOK EXPLOITATION SOV/4941

Mezhvuzovskoye soveshchaniye po khimii nefti, Moscow, 1956.

Sbornik trudov Mezhvuzovskogo soveshchaniya po khimii nefti (Collection of Transactions of the Inter-University Conference on Petroleum Chemistry) [Moscow] Izd-vo Mosk. univ., 1960. 313 p. Errata slip inserted. 1,600 copies printed.

Organizing Committee of the Conference: Chairman: B. A. Kazanskiy, Academician; Vice-Chairman: S. I. Khromov, Docent; G. M. Panchenkov, Professor; A. F. Plate, Professor; Secretary: Ye. S. Balenkova, Scientific Worker. Editorial Board: Resp. Ed.: A. F. Plate; I. V. Gostunskaya, I. N. Tits-Skvortsova, L. A. Erivanskaya.

PURPOSE: This collection of articles is intended for the teaching staff of universities and schools of higher education training specialists for the petroleum and petroleum-refining industries.

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COVERAGE: The collection includes articles dealing with the present state of the petroleum industry, the scientific research problems in petroleum chemistry, the chemistry of petroleum, the composition of petroleum and petroleum products, the scientific principles of refining petroleum into motor fuels and lubricants, and the manufacture of synthetic products from hydrocarbon gases and petroleum. One article discusses the effect of chemical composition and additives on fuel combustion in jet engines. The material was presented at the Inter-University Conference on Petroleum Chemistry, held at the Moscow State University imeni M. V. Lomonosov November 26-28, 1956. No personalities are mentioned. References accompany most of the articles.

TABLE OF CONTENTS: None given

The authors and the titles of articles are as follows:

Introduction by B. A. Kazanskiy, Academician

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SHuykin, N. I.

S/595/60/000/000/011/014
E040/E435

AUTHORS: Shuykin, N.I., Naryshkina, T.I.

TITLE: Catalytic synthesis of cyclopentadiene series of hydrocarbons

SOURCE: Vsesoyuznoye soveshchaniye po khimicheskoy pererabotke neftyanykh uglevodorodov v poluprodukty dlya sinteza volokon i plasticheskikh mass. Baku, 1957. Baku, Izd-vo AN Azerb, SSR, 1960. 249-259

TEXT: In view of the importance of hydrocarbons of the cyclopentadiene series because of their high reactivity, the present authors studied their production 1) by catalytic dehydrocyclization of diolefinic hydrocarbons and 2) by catalytic dehydrogenation of five-member cyclanes into cyclenes. The optimum dehydrocyclization conditions for piperylene were found to be at 600°C under reduced pressure (20 to 25 mm Hg). Alumino-chrome-potassium catalyst was found to give the highest yield of (I) and to have a useful active life of up to 80 hours. A much higher yield of 47% was obtained under the same reaction conditions in dehydrocyclization of piperylene-3-methylpentadiene-1,3 to methylcyclopentadiene. 2-ethylbutadiene formed easily methylcyclopentadiene with

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38% yield. The reaction is sensitive to pressure. Dehydrocyclization of piperylene under a slightly reduced pressure leads to some isomerization to isoprene and pentadiene-1,4 and to hydrogenation giving pentenes and 2-methylbutene-1. A considerable quantity of aromatic hydrocarbons is formed if the reaction is carried out under atmospheric pressure: at 600°C and atm pressure piperylene gives a 50% yield of benzole, toluol and xylol. By carrying out the reaction at reduced pressure and re-cycling the non-reacted piperylene, the yield of (I) is raised to 40%. The two methods of (I) preparation were studied on pentadiene-1,3, 3-methylpentadiene-1,3 and 2-ethylbutadiene-1,3 (dehydrocyclization method) and on cyclopentene, methylcyclopentene and cyclopentane (dehydrogenation method). The reactions were carried out in a quartz tube, 18 mm in diameter at 500 to 600°C, the pressure being varied from atmospheric to 20 to 25 mm Hg. The yield of (I) in the reaction products was determined using B.N.Afanas'yev's method (Ref.1: Zavodskaya laboratoriya, no.12, 1948, 1493). The catalysate was fractionated and analysed by optical and chemical methods. Evaluation was made of a number of catalysts but a mixture of Al_2O_3 (84%) + Cr_2O_3 (14%) + K_2O (2%) ground to a specific surface of 97.9 cm²/g was found to be the most efficient. Complete results are reported including data for the composition of all catalysts tried and the reaction products identified in the catalysate. It is concluded that cyclopentadiene and its homologues can be obtained by dehydrocyclization of diene hydrocarbons of the aliphatic series and dehydrogenation of five-member cyclanes and cyclenes, the yield of (I) in dehydrocyclization of alkadienes being 18 to 47%. Dehydrogenation of cyclenes gives up to 58% of (I). Under the same conditions, cyclopentane and methylcyclopentane are dehydrogenated in 14 to 31% yield. The optimum conditions for cycloalkadiene formation from the above hydrocarbons are at 600°C and 20 to 25 mm Hg. Acknowledgments are expressed to Yu.P.Yegorov for his assistance. Academician S.V.Lebedev is mentioned in connection with his method for the production of divinyl. There are 1 figure, 5 tables and 41 references: 14 Soviet-bloc, 1 English translation from Soviet publication and 26 non-Soviet-bloc. The four most recent references to English language publications read as follows:

Ref 26: Jones T.G., US Patent 2,636,066, 1953; C.A., 47, 6645, 1953

S/595/60/000/000/011/014
E040/E435

Catalytic synthesis of ...

Ref.27 Kennedy R.M., Hetzel S.J. Industr. Engng. Chem., 42, 1959
547 Ref.28 Lodge W.V., Walters W.D. J. Am. Chem. Soc., 74, 1952,
451. Ref.29: Mundy C.W. J. Oil Colour. Chemist. Assoc. 38, 1955
219.

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S/595/60/000/000/012/014
E196/E485

AUTHORS: Shuykin, N.I., Timofeyeva, Ye.A., Dobrynina, T.P.

TITLE: Contact-catalytic dehydrogenation of pentanes

SOURCE: Vsesoyuznoye soveshchaniye po khimicheskoy pererabotke neftyanykh uglevodorodov v poluprodukty dlya sinteza volokon i plasticheskikh mass. Baku, 1957. Baku, Izd-vo AN Azerb. SSR, 1960. 261-265

TEXT: In earlier published work, the authors found that dehydrogenation of n-pentane using catalyst composed of oxides of Al, Cr and Mg in molar ratio 45:30:25 at 500 to 550°C with space velocity of 1.2 hr^{-1} gave condensate containing 21 to 26% pentenes, i.e. 18 to 19% of the transformed pentane. A more effective catalyst of the composition Al_2O_3, Cr_2O_3, K_2O (90.7:5.6:3.7 mol %) gave from isopentane at 527°C an 87% yield of catalysate with an olefin content of 38%, consisting of all isomeric isopentenes, mainly 2-methyl-2-butene and also n-pentane (3%), isoprene (2%) and small quantities of pentene-1, pentene-2 and toluene. Under identical conditions, n-pentane was dehydrogenated in 88% yield to a product containing 31% of olefins including: pentene-2 (28%),

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Contact-catalytic dehydrogenation ... E196/E485

pentene-1 (3%), also isopentane (3%) and pentadienes (<1%). The yield is increased by 3 to 4% if the catalyst is reactivated with hydrogen. The same catalyst was used to study the effect of temperature, space velocity and the duration of working cycles. The catalyst's activity is claimed to be such that reaction equilibrium is reached at 500 to 550°C with a space velocity of 0.3 to 0.5 hr^{-1}. The effect of space velocity on the yield of pentenes varies with temperature. At 500°C the yield of isopentenes is reduced from 39 to 27 mol % when space velocity rises from 0.5 to 1.1 hr^{-1}. The corresponding reduction in the yield of isopentenes is 46 to 42% at 527°C and none at 550°C. At 575°C space velocity can be varied from 0.3 to 1.7 hr^{-1} without effect on the yield. The catalyst's active life decreases with increase in reaction temperature. In order to obtain maximum quantity of isopentenes without regard to the usage of raw materials, high reaction temperature (550°C) and high space velocity (1.1 to 1.7 hr^{-1}) are recommended. If, however, the object is to get the highest conversion of isopentane to isopentene, then the lower temperatures may give more economical operation. There are

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S/595/60/000/000/012/014
Contact-catalytic dehydrogenation ... E196/E485

2 figures, 2 tables and 5 references: 4 Soviet-bloc and 1 non Soviet-bloc.

Card 3/3

5(0)

AUTHOR: Shuykin, N.I., Corresponding Member of the Academy of Sciences USSR S/030/60/000/01/026/067
B015/B008

TITLE: Scientific Conference Devoted to Petroleum- and Coal Chemistry

PERIODICAL: Vestnik Akademii nauk SSSR, 1960, Nr 1, pp 73-74 (USSR)

ABSTRACT: The Conference was held at the Technical School of Higher Education for Chemistry Leuna-Merseburg (Eastern Germany) from October 1 to 5, 1959. K. Winkler, Minister for the Chemical Industry of Eastern Germany, reported on the chemical industry in the Republic and the establishment of a number of new productions which are based mainly on the chemical processing of petroleum. V. Blauhut described the essential problems which resulted in connection with the further development of petroleum- and coal chemistry. He underlined the utility of a scientific-technical cooperation with the USSR and the people's democracies. Reports of scientists from Eastern Germany are mentioned further. The author jointly with I.F. Bel'skiy on behalf of the Soviet scientists reported on the catalytic hydrogenolysis in the series of the furfuran

Card 1/2

Scientific Conference Devoted to Petroleum- and Coal Chemistry

S/030/60/000/01/026/067
B015/B008

compounds. The delegates visited the Chemical Kombinat "Leuna" ✓ after the conclusion of the Conference.

Card 2/2

[illegible]

AUTHORS: Bragin, O. V., [illegible], V. I.

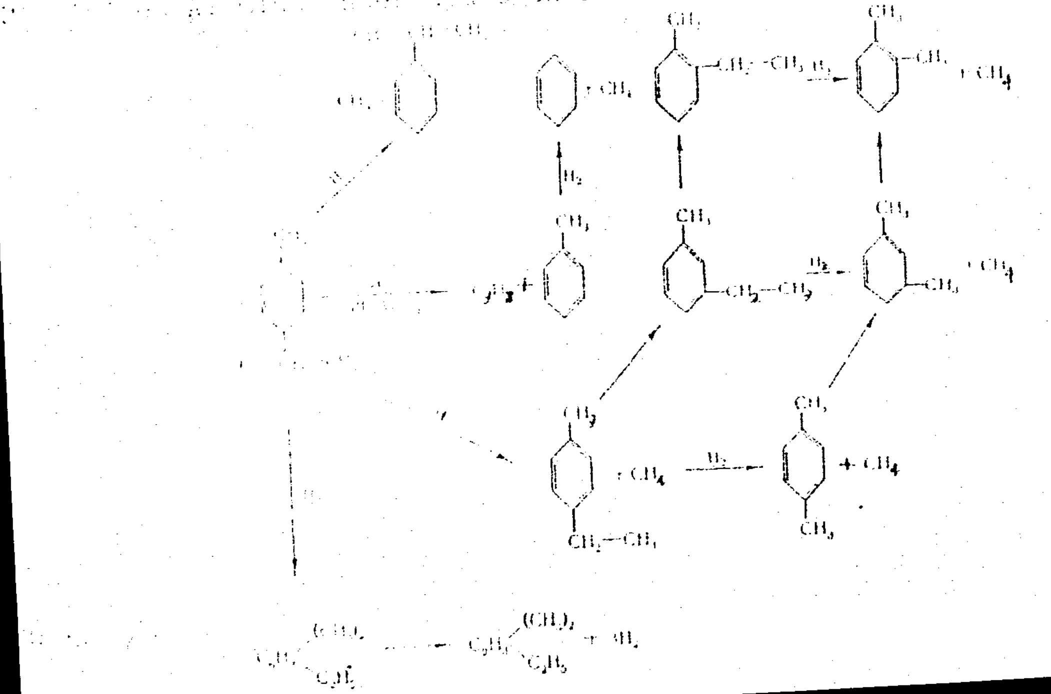
TITLE: Catalytic Conversions of p-Cymene Over Platinized Alumina Under Hydrogen Pressure

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, [illegible], Nr 1, pp [illegible] (USSR)

ABSTRACT: The major part of the catalytic products of p-cymene consist of toluene, xylenes, methylethylbenzenes, and dimethylethylbenzenes. p-Cymene undergoes dealkylation more easily than 1-methyl-4-isopropylcyclohexane. The yield of the dealkylation products in the case of p-cymene at [illegible] and [illegible]° is [illegible] and 64%, respectively, and in the case of 1-methyl-4-isopropylcyclohexane, only [illegible] and ~[illegible]%. The chemical conversion of 1-methyl-4-isopropylbenzene occurs in the following manner:

Card 1/[illegible]

[illegible]


CH3
CH2-CH3
H2
+ CH4
C2H6

Catalytic Conversions of p-Cymene Over Platinized Alumina Under Hydrogen Pressure

78070
SOV/62-60-1-16/37

There are 9 references, 6 Soviet, 3 U.S. The 3 U.S. references are: Haensel, V., Donaldson, G. R., Industr. and Engng. Chem., 42, 582 (1950); Pitts, P. M., Connor, J. E., Leum, L. M., Industr. and Engng. Chem., 47, 770 (1955); Szwarc, M., Chem. Rev., 47, 171 (1950).

ASSOCIATION: N. D. Zelinskiy Institute of Organic Chemistry of the Academy of Sciences of the USSR (Institut organicheskoy khimii imeni N. D. Zelinskogo Akademii nauk SSSR)

SUBMITTED: June 6, 1950

Card 3/3

5.3400

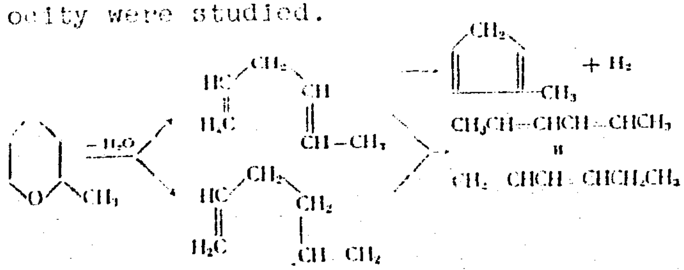
75076
SOV/62-60-1-24/37

AUTHORS: Shuykin, N. I., An, V. V

TITLE: Brief Communications. Dehydration of α-Methyltetrahydropyran Over TiO_2-Al_2O_3 Catalyst

PERIODICAL: Izvestiya akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960. Nr 1, pp 127-129 (USSR)

ABSTRACT: Conversions of α-methyltetrahydropyran (I) under the conditions of its dehydration over TiO_2-Al_2O_3 catalyst at 450, 500, 600°; 25-30 mm pressure; and 0.2-0.3 $hour^{-1}$ space velocity were studied.



Card 1/4

The results of the investigations are given in Fig. 1 and in the Table.

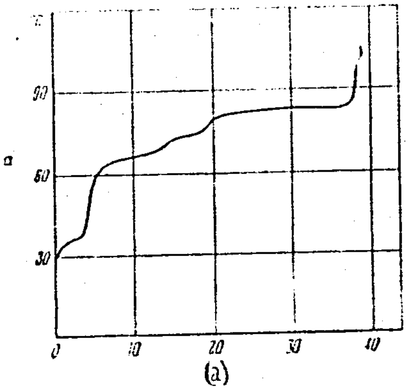


Fig. 1. Fractional distillation curve of the products of catalysis of experiment 1, conducted at 450°; (a) amount, g.

[illegible] of [illegible] [illegible] [illegible]
1-Methyltetrahydropyran Over
TiO$_2$-Al$_2$O$_3$ Catalyst

[illegible]

Conversion of 1-methyltetrahydropyran over TiO$_2$-Al$_2$O$_3$

a	b	c	d	e	f						
					g	h	i	j	k	m	n
1	450	30	0,2	87,6	9,8	5,1	15,4	9,7	33,9	5,3	~0,5
2	500	30	0,2	77,3	10,4	16,6		10,3	23,3	9,7	1,0
3	600	90	0,3	58,6	12,1	4,8	5,9	3,3	21,6	27,6	2,3

Key to Table: (a) Experiment Nr; (b) temperature of experiment, in °C; (c) pressure in mm Hg; (d) space velocity, hours^{-1}; (e) yield of the products of catalysis in %; (f) content in the products of catalysis (%); (g) pentane, pentenes, penta-1,3-diene, and cyclopentadiene; (h) hexenes; (i) 1,4- and 1,5-hexadienes; (j) 1,3-hexadiene; (k) 2,4-hexadiene; (m) benzene; (n) methylcyclopentadiene.

Card 3/4

There is 1 figure; 1 table; and 10 references, 3 U.S., 1 German, 6 Soviet. The 3 U.S. references are: C. L. Wilson, J. Am. Chem. Soc., 70, 1311, (1948); C. L. Wilson, J. Am. Chem. Soc., 69, 3004 (1947); S. F. Burch, W. D. Skott, Industr. and Engng. Chem., 24, 49 (1932).

ASSOCIATION: N. D. Zelinskiy Institute of Organic Chemistry Academy of Sciences USSR (Institut organicheskoy khimii imeni N. D. Zelinskogo Akademii nauk SSSR)

SUBMITTED: May 25, 1959

Card 4/4

S/062/60/000/03/05/007
B008/B006

AUTHORS: Shuykin, N. I., Tulupova, Ye. D.

TITLE: Preparation of Aromatic Hydrocarbons From Tuymazy Gasoline by Two-stage Aromatization

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 3, pp. 490-494

TEXT: The possibility of preparation of toluene and xylenes from Tuymazy gasoline with a low anti-knock value was investigated. The two-stage aromatization method was applied for the heptane-methyl cyclohexane fraction (boiling point 91 - 103°C) and the octane-dimethyl cyclohexane fraction (boiling point 117 - 127°C). The fractions investigated were obtained by rectification. The properties of the initial material and the fractions obtained are listed in Table 1. The results obtained by two-stage aromatization of the heptane-methyl cyclohexane- and octane-dimethyl cyclohexane fractions, as well as of Tuymazy unrectified gasoline and the residue remaining after distillation of the fraction boiling at 91 - 103°C

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Preparation of Aromatic Hydrocarbons From Tuymazy Gasoline by Two-stage Aromatization

S/062/60/000/03/05/007
B008/B006

are tabulated in Table 2. Changes in the activity of the catalyst during long-time dehydration are illustrated in Figs. 1 and 2. Platinized carbon containing 10% finely dispersed platinum and nickel - copper - aluminum oxide (67.5% Ni + 2.5% Cu + 30% Al_2O_3) were used as catalysts. Tests showed that the toluene content of the heptane-methyl cyclohexane fraction can be increased from 5 to 30% by volume by two-stage aromatization in the presence of 10% platinized carbon. A Ni-Cu-Al_2O_3 catalyst can also be used for dehydrogenizing hexamethylene hydrocarbons. It is less stable than the platinized carbon catalyst, but can be regenerated in situ. In the case of the octane-dimethyl cyclohexane fraction (boiling point 117 - 127°C) of the Tuymazy gasoline, the content of aromatic hydrocarbons, particularly that of xylenes, can be increased from 8 to 33% by volume by two-stage aromatization. The xylene content alone is increased by 17% owing to isomerization of 5-membered cycloparaffins to form 6-membered cycloparaffins. Removal of the fraction boiling at 91-103°C does not lower the anti-knock value of the residual Tuymazy gasoline. There are 2 figures, 2 tables, and 15 references, 12 of which are Soviet.

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Preparation of Aromatic Hydrocarbons From Tuymazy Gasoline by Two-stage Aromatization

S/062/60/000/03/05/007
B008/B006

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR) ✓

SUBMITTED: July 18, 1958

Card 3/3

MINACHEV, Kh.M.; SHUYKIN, N.I.; MARKOV, M.A.

Effect of the specific surface of a platinized aluminosilicate on the degree of n-nonane conversion. Report No.1: Change in the activity of platinized aluminosilicate in the course of the treatment of the carrier with hydrogen. Izv.AN SSSR Otd.khim. nauk no.5:907-912 My '60. (MIRA 13:6)

1. Institut organicheskoy khimii imeni N.D. Zelinskogo Akademii nauk SSSR.
(Aluminosilicates) (Platinum) (Nonane)

SALIMOV, M.A.; VIKTOROVA, Ye.A.; ERIVANSKAYA, L.A.; SHUYKIN, N.I

Infrared spectra of alkylphenols and their simple ethers. Azerb. khim.zhur, no.6:99-105 '60. (MIRA 14:8)

(Phenol--Spectra)

SHUYKIN, N.I.; POZDNYAK, N.A.

Catalytic alkylation of tetralin. Report No.1: Alkylation of tetralin with amylenes. Izv.AN SSSR.Otd.khim.nauk no.6: 1094-1097 Jl '60. (MIRA 13:7)

1. Institut organicheskoy khimii imeni N.D.Zelinskogo Akademii nauk SSSR.
(Naphthalene) (Pentene) (Alkylation)

Shuykin, N.

5.3200

82102
S/062/60/000/07/06/007
B015/B054

AUTHORS: Shuykin, N. I., Pozdnyak, N. A., Shlyapochnikov, V. A.

TITLE: Catalytic Alkylation of Tetralin. Information 2. Alkylation of Tetralin With Heptene-1

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 7, pp. 1254-1257

TEXT: The authors alkylated Tetralin with heptene-1 in a continuous-flow apparatus using two types of catalysts. In one series of experiments they used an aluminum oxide treated with hydrofluoric acid (10% and 20% HF), in the other series an aluminosilicate catalyst; the experiments were carried out at atmospheric and increased pressure and at different temperatures (Tables 1-3, influence of different test conditions). In the catalytic alkylation, a mixture of β-heptyl Tetralin and β,β'-diheptyl Tetralin was obtained. The given data show that with the aluminosilicate catalyst the following optimum conditions exist: volume velocity 0.25 hours^{-1}, temperature 200°C, pressure 10 atm, molar ratio Tetralin : heptene-1 = = 2 : 1. Under these conditions, the yield in β-heptyl Tetralin is 48.7%

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4H

82102

Catalytic Alkylation of Tetralin. Information 2. S/062/60/000/07/06/007
Alkylation of Tetralin With Heptene-1 B015/B054

with respect to heptene-1, and 24.3% with respect to Tetralin. The infrared spectra of the heptyl Tetralin synthesized showed that the heptyl group lies in the β-position. B. A. Kazanskiy, G. A. Tarasova, and O. D. Sterligov are mentioned in the paper. There are 3 tables and 6 references: 3 Soviet and 3 American.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: December 10, 195

Card 2/2

86413
S/062/60/000/008/021/033/XX
B013/B055

5.3610
1153
2209
1375

AUTHORS: Popov, M. A. and Shuykin, N. I.

TITLE: Catalytic Synthesis of Nitriles. Communication 3. Preparation of Aromatic Nitriles

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 8, pp. 1451-1456

TEXT: The present paper deals with the catalytic synthesis of nitriles from aromatic alcohols and ammonia in the presence of nickel/aluminum-oxide catalysts. The investigation was undertaken with a view to finding the most suitable conditions of synthesis, and to study the effect of the phenyl radical on the composition of the reaction products. Experiments were performed with benzyl alcohol, β-phenyl ethanol and γ-phenyl propanol. The reaction was carried out at 270-390°C and atmospheric pressure in a continuous system. The catalysts contained 3, 7.5 and 15% reduced nickel precipitated on aluminum oxide. Catalyst preparation and experimental apparatus have been described in Ref. 7. Systematic experiments showed that at 390°C, benzonitrile is formed from ammonia and benzyl alcohol on a 3% nickel/aluminum-oxide catalyst in 51.7% theoretical yield. The

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Catalytic Synthesis of Nitriles. Communication 3. Preparation of Aromatic Nitriles

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B013/B055

reaction of β-phenyl ethanol with ammonia at 300°C and of γ-phenyl propanol with ammonia at 330°C over 7.5% nickel/aluminum-oxide catalysts also lead to the formation of the corresponding phenyl acetonitrile (44.8% yield) and β-phenyl propionitrile (50.8% yield). The authors describe the reaction conditions given above as optimal. The following reaction mechanism is assumed to explain the formation of small quantities of amines and aromatic hydrocarbons as by-products in the cyanation of aromatic and aliphatic (Ref. 7) alcohols. The experiments showed that the amine formation is independent of the amount of nitrile formed. The first step is therefore assumed to be the conversion of alcohol to the primary amine. Formation of secondary and tertiary amines can then proceed according to the scheme: $2ArCH_2NH_2 \longrightarrow (ArCH_2)_2NH + NH_3$. Part of the ammonia is decomposed to nitrogen and hydrogen on the catalyst surface: $2NH_3 \longrightarrow N_2 + 3H_2$. The hydrogen so formed, together with the hydrogen formed in the main reaction, reduces a certain amount of the final nitrile to the aromatic hydrocarbon. There are 4 tables and 24 references: 6 Soviet, 8 US, 6 German, 6 French, 3 British, and 1 Belgian.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

Card 2/3

86413

Catalytic Synthesis of Nitriles. Communication 3. S/062/60/000/008/021/033/XX
Preparation of Aromatic Nitriles B013/B055

SUBMITTED: February 2, 1959

Card 3/3

86414
S/062/60/000/008/022/033/XX
B013/B055

11.1210

AUTHORS: Shuykin, N. I., Timofeyeva, Ye. A., Dobrynina, T. P., Plotnikov, Yu. N., Petryayeva, G. S., and Gayvoronskaya, G. K.

TITLE: Catalytic Dehydrogenation of Isohexanes

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 8, pp. 1457-1465

TEXT: The present paper is a continuation of the investigation into the dehydrogenation of hydrocarbons of different structures over an aluminum-chromium-potassium catalyst. The catalyst is discussed in detail in Ref.1. The 2-methyl pentane, 3-methyl pentane, and 2,3-dimethyl butane used in this investigation were prepared by the Grignard reaction. 2,2-dimethyl butane was obtained by pyrolysis of pinacoline alcohol acetate (Ref. 2). The experiments were carried out in a continuous system, at 500°C and atmospheric pressure and a flow rate of 0.5 h^{-1}. The catalyst was regenerated after every experiment by oxidation in air at 700°C. The properties of the isohexane catalyzates are listed in Table 1 and the

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Catalytic Dehydrogenation of Isohexanes S/062/60/000/008/022/033/XX
B013/B055

composition of the gases formed in Table 2. For comparison, the corresponding data for n-hexane are also given. As is shown, dehydrogenation of 2-methyl pentane, 3-methyl pentane and 2,3-dimethyl butane yields 34-40% unsaturated hydrocarbons. Isohexanes form up to 2% and n-hexane up to 43% aromatic hydrocarbons. 2,2-dimethyl butane was found to form 15% unsaturated hydrocarbons. Formation of aromatic hydrocarbons was not observed. The gaseous products formed from 2-methyl pentane, 3-methyl pentane and 2,3-dimethyl butane contained 84 - 90% hydrogen, 9 - 12% methane, ethane, and propane, and 1 - 4% of other alkenes and alkanes. The gas obtained from 2,2-dimethyl butane contained 72.6% hydrogen, 21.2% C_1-C_3 alkanes and 6.2% of other hydrocarbons. These data show that 2,2-dimethyl butane is less stable under the given conditions than all other isohexanes. This conclusion was confirmed by the examination of the liquid catalyzates. Analytical data on the catalyzate composition allow the conclusion that, in hydrogenation under the given conditions, all the isohexanes form alkenes containing essentially 6 carbon atoms. Isomerization was not observed in dehydrogenation of 3-methyl pentane. Slight isomerization occurred during dehydrogenation of 2-methyl pentane and 2,3-dimethyl butane. 2,2-dimethyl butane formed alkenes during the catalytic reaction. Approximately half of these alkenes were isomerization products: 4-methyl 2-pentene,

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Catalytic Dehydrogenation of Isohexanes

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B013/B055

2-methyl 2-pentene and 2,3-dimethyl 1,3-butadiene. Finally, a thermodynamic calculation of the reaction isohexanes $\rightleftarrows$ isohexenes was carried out (Table 8, Fig. 2). It is evident from the results obtained that the experimental yields of isohexenes approach the equilibrium yields. Fig. 1 represents chromatograms of an artificial hydrocarbon mixture and several fractions of isohexane catalyzates. The authors thank R. N. Shafran for carrying out the analysis of the gases. There are 2 figures, 9 tables, and 9 references: 7 Soviet, 1 US, and 2 British.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR
(Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: February 17, 1959

Card 3/3

S/062/60/000/008/023/033/XX
B013/B055

AUTHORS: Minachev, Kh. M., Shuykin, N. I., and Markov, M. A.

TITLE: Investigation of the Effect of the Specific Surface of Platinized Alumosilicate on the Degree of n-Nonane Conversion

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 8, pp. 1466-1470

TEXT: This paper is a continuation of the studies on the effect of the specific surface of catalysts on the degree of hydrocarbon conversion. For this purpose, the authors studied the conversion of n-nonane on alumosilicate catalysts with widely varying specific surfaces. Two 0.5% platinum/alumosilicate catalysts with specific surfaces of 320 m^2/g (K-1) and 60 m^2/g (K-2) were used. A standard alumosilicate catalyst for the cracking process was used as carrier for the preparation of the platinum catalysts. To prepare the latter, the carrier was saturated with a dilute H_2PtCl_6 solution. The data of the n-nonane used were in agreement with those given in Ref. 4. Infrared spectra showed the n-nonane to be free

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Investigation of the Effect of the Specific Surface of Platinized Alumosilicate on the Degree of n-Nonane Conversion

S/062/60/000/008/023/033/XX
B013/B055

of isomers. The experimental apparatus has been described in Ref. 1. The experiments were carried out in a continuous system at 360 to 450°C, a hydrogen pressure of 10 atm and a flow rate of 1 h^{-1}. The molar ratio of hydrocarbon and hydrogen was 1:5. A fresh catalyst was used for each experiment. The results of the examination of the catalyzates are listed in Tables 1 and 2 and graphically represented in Figs. 1 - 3. These data show that the degree of hydrocracking of hydrocarbons considerably decreases with decreasing specific catalyst surface. This is in agreement with data given in Ref. 2. The yields of hydrocracking products on K-1 catalysts were found to increase more rapidly with a temperature rise than on K-2 catalysts. At temperatures of 420° - 450°C, hydrocracking on K-2 is insignificant, which enables C_9-isoalkanes to be obtained in comparatively high yields (54% at 450°C). On K-1, the maximum yield of isononanes is obtained at 380°C (53%). Since aromatization occurs to a noticeable degree only at 400°C, aromatic hydrocarbons can be obtained over K-2 before C_9 isoalkane yields are reduced. The total yield of hydrocracking products under the experimental conditions was 45.7% over K-1, and 25.3% over K-2. The experiments have thus shown that by decreasing the specific surface

Card 2/3

Investigation of the Effect of the Specific Surface of Platinized Alumosilicate on the Degree of n-Nonane Conversion

S/062/60/000/008/023/033/XX
B013/B055

of the catalyst the process can be carried out at higher temperatures without the occurrence of hydrocracking. There are 3 figures, 2 tables, and 4 Soviet references.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR
(Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: February 18, 1959

Card 3/3

S/062/60/000/008/026/033/XX
B013/B055

AUTHORS: Shuykin, N. I. and An, V. V.

TITLE: Dehydration of Tetrahydropyran on TiO_2 - Al_2O_3

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 8, pp. 1508-1510

TEXT: In this brief publication, the authors describe a study of the dehydration of tetrahydropyrans on TiO_2 - Al_2O_3 (8 mole% Al_2O_3) and the dependence of the yields in cyclopentadiene and pentadienes on the flow rate and temperature. The experimental technique and preparation of the catalyst were described in Ref. 3. The relation between tetrahydropyran transformation to cyclopentadiene and piperylene and the flow rate at 600°C was found to be the same as in the case of tetrahydrosylvan. The maximum yields of cyclopentadiene and piperylene, however, were lower, i.e., 10.2 and 36.6% respectively at 600°C and a flow rate of 1 h^{-1}. The maximum cyclopentadiene yields are obtained at comparatively low temperatures, around 400°C, a fact which deserves attention. Piperylene yields increase with rising temperature and at high temperatures attain a practically constant value. Thermodynamic equilibrium calculations carried out

Card 1/2

Dehydration of Tetrahydropyran on $TiO_2 - Al_2O_3$ S/062/60/000/008/026/033/XX
B013/B055

by Kilpatrick and collaborators (Ref. 2) showed that 1,4-pentadiene can be transformed to piperylene in yields of 90 to 95% in the temperature range investigated (350° - 600°C). The low 1,4-pentadiene content in the catalyzate proves that its transformation to piperylene proceeds at a remarkable rate. It was found that the isomerization of the primarily formed 1,4-pentadiene is accompanied by a number of other reactions: hydrogenation, polymerization, cracking and charring. As a result, the catalyzate contains up to 18.5% (at 600°C) 1-pentene and 2-pentene, and traces of isoprene, isoamylenes, n-pentane and isopentane. There are 2 figures and 4 references: 3 Soviet and 1 US.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR
(Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: January 7, 1960

Card 2/2

S/062/60/000/008/027/033/XX
B013/B055

AUTHORS: Viktorova, Ye. A., Shuykin, N. I., and Korosteleva, G. S.

TITLE: Catalytic Synthesis of 2,4-Di-tert-amyl Phenol

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 8, p. 1510

TEXT: This is a brief communication on the catalytic synthesis of 2,4-di-tert-amyl phenol. The latter was synthesized by alkylating phenol with trimethyl ethylene in the presence of a KU-1 cationite, a sulfonated phenol-formaldehyde resin. The yield of pure 2,4-di-tert-amyl phenol was 30% of the theory. 2,4-di-tert-amyl phenol was then transformed to the corresponding phenoxy acetic acid derivative. This was then precipitated with hydrochloric acid and recrystallized from 20% alcohol. The yield was 30 to 35%. Amyl phenols, including 2,4-di-tert-amyl phenol, was used as antioxidants and as intermediates for the synthesis of insecticides and herbicides. There is 1 non-Soviet reference.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

~~Card 1/2~~

S/062/60/000/009/015/021
B023/B064

AUTHORS: Shuykin, N. I. and Vasilevskaya, G. K.

TITLE: Catalytic Dehydration of Alpha Isobutyl Tetrahydrofurane

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 9, pp. 1664-1667

TEXT: N. I. Shuykin, V. A. Tulupov, and I. F. Bel'skiy referred in their paper (Ref. 3) on the dehydration of tetrahydrosylvane on a titanium-alumina catalyst at $500-600^{\circ}C$ and a pressure of 20-30 mm to the fact that this catalyst leads to the formation of both open and cyclic dienes. The authors studied the dehydration of a more complex tetrahydrofurane homolog, viz. α-isobutyl tetrahydrofurane. They carried out this reaction on the same catalyst and expected to obtain 6-methyl pentadiene-1,3 in the mixture with its dehydrocyclization products. At 600 and 550°, and a pressure of 20-30 mm, and a volume rate of 0.1 h^{-1}, α-isobutyl tetrahydrofurane underwent strong cracking, and, consequently, liquid catalyzates were obtained in a yield of 25-30% only. It was a complex mixture of rapidly resinifying hydrocarbons with a high boiling point. After the

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Catalytic Dehydration of Alpha Isobutyl Tetrahydrofurane

S/062/60/000/009/013/021
B023/B064

dehydration temperature had been reduced to 400°C and the contact time shortened, a liquid catalyzate was obtained in a yield of 95%. In individual fractions, with boiling points between 121.7-136°C, it contained between 81.0 and 92% diene hydrocarbons. Summing up: Considerable amounts of unsaturated hydrocarbons, especially dienes, may be obtained on the basis of a pentosan-containing initial substance and furfurole, furane homologs, and their tetrahydro derivatives. The finding of conditions for the catalytic dehydration of tetrahydrofurane homologs under the formation of complicated mixtures of dienes and alkenes is regarded as a further task; in this connection it is possible to isolate individual hydrocarbons. A formula of Ye. A. Timofeyeva, T. P. Dobrynina, and V. M. Kleymenova is mentioned. A determination method developed by G.P.Kaufman and G. D. Gal'pern is applied. There are 1 table and 9 references: 6 Soviet, 4 French, 1 US, 2 British, and 1 German.

ASSOCIATION: Institut organicheskoy khimii im. N.D.Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: March 18, 1959

Card 2/2

S/062/60/000/010/011/018
B015/B064

AUTHORS: Minachev, Kh. M., Ryashentseva, M. A., and Shuykin, N. I.

TITLE: Catalytic Transformations of Cyclohexane, Methyl Cyclopentane, and n-Hexane on a Palladium Alumina Catalyst at Increased Temperature and Increased Hydrogen Pressure

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 10, pp. 1844 - 1847

TEXT: In previous papers (Refs. 1-4), the authors investigated the catalytic properties of 0.5% palladium alumina catalysts in the re-forming of small gasoline fractions of petroleum from the Il'skiy, Khadyzhenskiy, Ural, and Volga deposits. To confirm the results obtained, the authors studied the transformation of cyclohexane, methyl cyclopentane, and n-hexane on 0.5% palladium-containing alumina catalysts under the optimum conditions of re-forming gasoline fractions (480°C, 20 atm, H_2:HC = 5, v = 1.0 hours^{-1}). The experiments were carried out in a continuous-flow apparatus. The catalyzate obtained from cyclohexane

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Catalytic Transformations of Cyclohexane, Methyl Cyclopentane, and n-Hexane on a Palladium Alumina Catalyst at Increased Temperature and Increased Hydrogen Pressure

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contained 50% benzene, while C_6 paraffin hydrocarbons with approximately 8% and five-membered cyclanes with approximately 43% were detected in the naphthene paraffin component (Table 1, composition), i.e., a dehydrogenation to benzene, an isomerization with a contraction of the cycle, and a slight hydrogenolysis under the formation of alkanes took place. Approximately 9.5% aromatic hydrocarbons and, besides unchanged n-hexane, approximately 5% paraffin hydrocarbons with iso-structure were obtained from the transformation of n-hexane. Besides unchanged methyl cyclopentane, methyl cyclopentane (Table 2) yielded approximately 11% 2,3-dimethyl butane, 3-methyl pentane, n-hexane, n-pentane (approximately 3.8%), and approximately 1.2% cyclohexane of the paraffin components, and 33% benzene as the aromatic component of the catalyzate. Thus, methyl cyclopentane undergoes an isomerization to cyclohexane and subsequent dehydrogenation to benzene, as well as hydrogenolysis and hydrocracking under the formation of n-pentane. A Scheme is given on the basis of the results obtained, and it is stated that the present

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Catalytic Transformations of Cyclohexane, Methyl Cyclopentane, and n-Hexane on a Palladium Alumina Catalyst at Increased Temperature and Increased Hydrogen Pressure

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experiments confirm the formation mechanism of aromatic hydrocarbons in re-forming the above gasoline fractions. There are 2 tables and 6 Soviet references.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: May 14, 1959

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Card 3/3

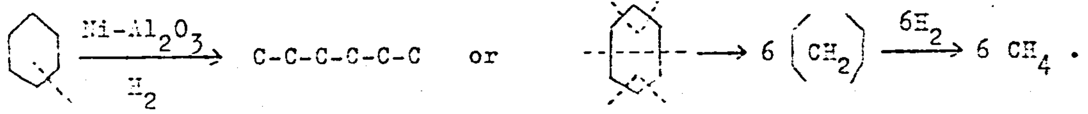
S/062/60/000/010/031/031
B002/B060

AUTHORS: Shuykin, N. I., Tyan' Sin-khua

TITLE: Some Problems Concerning the Mechanism of Conversion of Methyl Cyclohexane on a Nickel - Alumina Catalyst at Increased Hydrogen Pressure

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 10, pp. 1891-1894

TEXT: The authors studied the reaction of cyclohexane, methyl cyclohexane, methyl cyclopentane, and toluene at 360°C and 20 atm hydrogen pressure on a 10% Ni-Al_2O_3 catalyst, volume velocity 0.2 h^{-1}, and molar ratio hydrogen: hydrocarbon = 4:1. Benzene, methyl cyclopentane, n-pentane, n-hexane, and 2-methyl pentane are chiefly formed from cyclohexane under these conditions. Cyclohexane may decompose by two mechanisms:

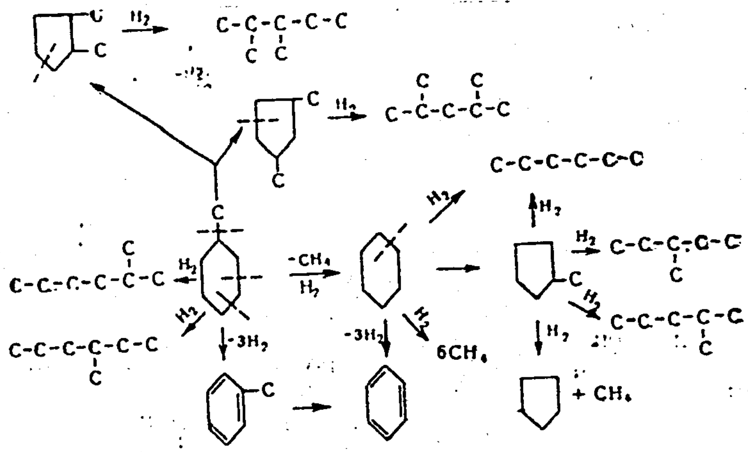


Card 1/3

Some Problems Concerning the Mechanism of Conversion of Methyl Cyclohexane on a Nickel - Alumina Catalyst at Increased Hydrogen Pressure

S/062/60/000/010/031/031
B002/B060

Cyclohexane, toluene, and benzene are chiefly formed from methyl cyclohexane. Moreover, also 3-methyl hexane, 2-methyl hexane, and others, are formed. The following scheme is suggested for these reactions:



Card 2/3

Some Problems Concerning the Mechanism of Conversion of Methyl Cyclohexane on a Nickel - Alumina Catalyst at Increased Hydrogen Pressure

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B002/B060

The reaction of methyl cyclopentane mainly yielded 2-methyl pentane, 3-methyl pentane, and benzene. The toluene reaction yielded methyl cyclohexane, cyclohexane, benzene, and others. There are 2 tables and 7 Soviet references.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR
(Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: March 25, 1960

Card 3/3

S/062/60/000/011/008/016
B013/B078

AUTHORS: Shuykin, N. I., Tyan' Sin-Khua

TITLE: Demethylization of Methyl Cyclohexane in Contact With Nickel Catalysts Under Hydrogen Pressure

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 11, pp. 2014 - 2018

TEXT: In this paper the catalytic demethylization of methyl cyclohexane on nickel catalysts was investigated in a continuous system under hydrogen pressure of 20 at and at temperatures of 330°-360°C. Industrially produced silica gels served as carriers with a granulation of 1.5-2 mm, aluminum oxide of the type A-2 (A-2) and alumosilicate from GrozNII (Groznyy Petroleum Scientific Research Institute) which were pre-treated by the dynamic method (Refs. 9 and 10). Nickel aluminum oxide, nickel silica gel, and nickel-aluminum silicate catalysts were obtained by impregnation of the respective carriers with a nickel nitrate solution, by calculating 10% nickel per catalyst. A second specimen of the 10% nickel silica gel catalyst was obtained by simultaneous precipitation of

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Demethylization of Methyl Cyclohexane in Contact S/062/60/000/011/008/016
With Nickel Catalysts Under Hydrogen Pressure B013/B078

appropriate nitrate solutions, and a third specimen by pre-treatment of the carrier with hydrofluoric acid. Results obtained by catalysis of methyl cyclohexane are shown in Tables 1-5. It was found that the catalyst treated with hydrofluoric acid is best suited for the demethylization of methyl cyclohexane. The yield of cyclohexane in the presence of this catalyst amounted, after one passage, to 30.1% of the converted methyl cyclohexane. Moreover, this catalyst shows a larger selectivity than the non-treated one. The demethylization of methyl cyclohexane with nickel catalysts is complicated by the fact that part of the resulting cyclohexane is isomerized to methyl cyclopentane, and next, the hydrogenolysis of the latter takes place under formation of alkanes.
Ye. I. Sil'chenko is mentioned. There are 5 tables and 11 references: 9 Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: Jun. 20, 1959

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S/062/60/000/011/011/016
B013/B078

AUTHORS: Shuykin, N. I., Tyan' Sin-Khua

TITLE: Hydrogenolysis of C_7 Alkanes in the Presence of a Nickel Aluminum Oxide Catalyst Under Hydrogen Pressure

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 11, pp. 2046 - 2048

TEXT: This is a brief report on the hydrogenolysis of n-heptane, 3-methyl hexane, 2,4-dimethyl pentane, and 2,2-dimethyl pentane with a $Ni-Al_2O_3$ catalyst in the continuous-flow system at 360°C and at a hydrogen pressure of 20 atm. The molar ratio of hydrogen to hydrocarbon was 4:1. The volume velocity amounted to 0.2 h^{-1}. The composition of the liquid catalyzate was determined by chromatography. The waste gases were examined with a chromatographic gas analyzer. Results are tabulated. The table shows that, under the present conditions, the alkanes considered undergo hydrogenolysis, but isomerization does not take place.

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Hydrogenolysis of C_7 Alkanes in the Presence of a Nickel Aluminum Oxide Catalyst Under Hydrogen Pressure

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Methylcyclohexane and cyclohexane are partially isomerized under the same conditions. Here, the rings are compressed into pentamethylene hydrocarbons. The composition of the gases thus obtained and of the liquid catalyzates indicates that the hydrogenolysis of the alkanes proceeds according to the mechanism of a systematic demethylation. The authors propose the following systems for the catalytic hydrogenolysis of C_7 alkanes with varying structure:

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Hydrogenolysis of C_7 Alkanes in the Presence of a Nickel Aluminum Oxide Catalyst Under Hydrogen Pressure

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It was found that, under the present conditions, the tertiary carbon atom in the 3-methylhexane atom not only inhibits the hydrogenolysis of the group directly bound to it, but also the relatively easy hydrogenolysis of the neighboring C-C bonds. The hydrogenolysis of the groups being most distant from the tertiary carbon atom proceeds with great rapidity. This hydrogenolysis is even more distinct in the case of 2,2-dimethylpentane which contains a quaternary carbon atom. D. M. Tilicheyev and A. A. Polyakova are mentioned. There are 1 table and 9 references: 5 Soviet, 3 US, and 1 German.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR).

SUBMITTED: April 18, 1960

Card 4/4

VIKTOROVA, Ye.A.; SHUYKIN, N.I.; POLYANSKAYA, E.I.

Cycloalkenylation of phenol by 1,3-cyclohexadiene. Izv. AN SSSR. Otd. khim. nauk no.11:2048-2049 N '60. (MIRA 13:11)

1. Moskovskiy gosudarstvennyy universitet im.M.V.Lomonosova. (Cyclohexadiene) (Phenols) (Alkenylation)

S/062/60/000/012/010/020
B013/B055

AUTHORS: Shuykin, N. I., Timofeyeva, Ye. A., Plotnikov, Yu. N., and Andreyev, N. S.

TITLE: Composition of the Products of Dehydration of $C_6 - C_9$ n-Alkanes Over Aluminum-chromium-potassium Catalyst

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 12, pp. 2173-2177

TEXT: In the present paper the authors studied the structure of unsaturated and aromatic hydrocarbons, but above all the composition of alkenes formed from n-alkanes at 500°C over an aluminum-chromium-potassium catalyst and a volume velocity of 0.5 h^{-1}. n-hexane, n-heptane, n-octane and n-nonane were used for this reaction. The unsaturated hydrocarbons formed were found to consist mainly of alkenes. As regards number of carbon atoms, they correspond to the initial alkanes and have double bonds in the positions 2, 3 or 4. The catalyzate of n-hexane was found to contain 1-hexene also, but in much smaller amounts than 2- and 3-hexenes. The catalyzates of n-heptane, n-octane, and n-nonane possibly contain other alkenes in addition to the 2-heptene, 4-octene, and 4-nonene actually found. The quantities contained, however, are so small that they were not detectable in the Raman spectra.

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Composition of the Products of Dehydration of C_6 - C_9 n-Alkanes Over Aluminum-chromium-potassium Catalyst

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B013/B055

All catalyzates were found to contain dienes, the structures of which could not yet be established exactly. The structure of the aromatic hydrocarbons formed from n-alkanes becomes more complicated as the molecular weight of the initial alkane increases. n-hexane forms benzene, n-heptane toluene, n-octane mainly xylenes and ethyl benzene as well as lower-boiling aromatic hydrocarbons, benzene and toluene. The aromatic hydrocarbons formed from n-nonane consist mainly of methyl ethyl benzene, trimethyl benzene, and n-propyl- and isopropyl benzenes. Apart from these, the catalyzate contains lower-boiling hydrocarbons, benzene, toluene, and ethyl benzene. There are 5 tables and 5 references: 3 Soviet and 2 British.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR
(Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: July 10, 1959

Card 2/2

VIKTOROVA, Ye.A.; SHUYKIN, N.I.; POPOVA, G.V.

Contact catalytic conversions of phenols. Part 5: Alkylation of m-cresol by piperylene. Vest. Mosk. un. Ser. 2: Khim. 15 no.6: 62-65 N-D '60. (MIRA 14:2)

1. Kafedra khimii nefti Moskovskogo universiteta.
(Cresol) (Piperylene)

BEKAURI, N.G.; SHUYKIN, N.I.; SHAKARASHVILI, T.S.

Catalytic transformations of N tridecane, N tetradecane and N pentadecane under hydrogen pressure in a flow system. Soob.AN Gruz. SSR 24 no.6:655-662 Je '60. (MIRA 13:9)

1. AN GruzSSR, Institut khimii im. P.G. Melikashvili, Tbilisi i AN SSSR, Institut organicheskoy khimii im.N.D. Zelinskogo, Moskva Predstavleno chlenom-korrespondentom Akademii G.V. TSitsishvili.
2. Chlen-korrespondent AN SSSR (for Shuykin).
(Decane)

BEKAURI, N.G.; SHUYKIN, N.I.; SHKARASHVILI, T.S.

Improving the motor characteristics of a normal undecane and dodecane. Soob.AN Gruz.SSR 25 no.5:525-531 N '60. (MIRA 14:1)

1. Akademiya nauk GruzSSR, Institut khimii imeni P.G.Melikishvili, Tbilisi i AN SSSR, Institut organicheskoy khimii imeni N.Zelinskogo, Moskva. Predstavleno chlenom-korrespondentom Akademii G.V.TSitsishvili.

(Dodecane) (Undecane)

SHUYKIN, N.I.; ERIVANSKAYA, L.A.

Catalytic hydrogenation of phenols. Usp.khim. 29 no.5:648-668 My '60. (MIRA 13:7)

1. Khimicheskiy fakul'tet Moskovskogo gosudarstvennogo universiteta im. M.V.Lomonosova.
(Phenols) (Hydrogenation)

80732

S/074/60/029/05/03/005
B008/B006

5.3200

AUTHORS: Shuykin, N. I., Erivanskaya, L. A.

TITLE: Catalytic Hydrogenation of Phenols

PERIODICAL: Uspekhi khimii, 1960, Vol.29, No. 5, pp. 648-668

TEXT: An investigation of catalytic transformations occurring in the hydrogenation of phenols separated from higher fractions of primary resins, and in the hydrogenation of narrow fractions enriched in one or the other component was carried out. Sharp rectification- or chromatographic methods can be applied for separating these fractions. Previous research in the field of phenol transformation in hydrogenation is described in Refs. 1-8. Hydrogenation of phenols to hydroaromatic alcohols is discussed in Refs. 1, 9-91. Hydrogenations on platinum-, palladium-, copper-, and nickel catalysts are described. Hydrogenation of pure phenols can be carried out at comparatively low temperatures (up to 200°C) as well as at high- or atmospheric pressures in the presence of nickel- or platinum catalysts. Hydrogenation of industrial phenol mixtures is more difficult, owing to catalyst poisoning by sulfur-containing compounds. The reaction order of phenol hydrogenation is probably between zero and one. Which of the possible geometric isomers of the correspond-

X

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Catalytic Hydrogenation of Phenols

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B008/B006

ing alcohol is formed, depends on hydrogenation conditions. Published data on the properties of cis- and trans-methyl cyclohexanols and melting points of their derivatives are given in Table 1. Hydrogenation of phenols to hydroaromatic ketones is described in Refs. 29, 66, 78, 92-101. In general, alicyclic ketones can be prepared by hydrogenating the corresponding phenols. Yields of these ketones, however, depend not only on hydrogenation conditions, the nature of the catalyst, and the amount of hydrogen adsorbed, but also on the structure of the initial phenol. The reduction of phenols to aromatic hydrocarbons is discussed in Refs. 5, 102-154. Catalysts based on molybdenum are generally applied. Experimental- and thermodynamic data indicate that a pressure drop during the hydrogenation of phenols in the presence of molybdenum catalysts increases the yields of aromatic hydrocarbons. The reaction, however, is slower and accompanied by considerable charring. At higher temperatures, phenols tend to give various condensation reactions. The formation of alicyclic hydrocarbons in the hydrogenation of phenols to the corresponding alcohols was observed by many investigators (Refs. 27, 28, 31, 66, 113, 118, 137, 140, 141, 149, 155-160). These hydroaromatic hydrocarbons, however, were only formed in small quantities as by-products of hydroaromatic alcohols. In order to obtain alicyclic hydrocarbons

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as main reaction product, the hydrogenation temperature must be chosen high enough to ensure dehydration of the alcohols. The behavior of polynuclear phenols in hydrogenation reactions has not been investigated widely (Refs. 107, 128, 136, 141, 158, 161-168). High-pressure hydrogenation of these compounds in the presence of molybdenum catalysts yields hydrocarbon mixtures containing aromatic-, hydroaromatic-, and various other hydrocarbons. Phenol formation is also observed. Refs. 6, 169-213 deal with the destructive hydrogenation of higher phenols, by which lower phenols are obtained. Thermodynamically, dealkylation of phenols is also possible. It can be effected by cracking higher phenols, or, by reacting higher phenols, without a catalyst at higher temperatures. Yields of lower phenols, however, are small. Several patents (Refs. 199-204) recommend destructive transformations of phenols to be carried out not only in the presence of metal oxides and metal sulfides, but also in contact with cracking catalysts. The direction of the reaction can be determined by choosing appropriate conditions and catalyst admixtures. The following persons are mentioned: V. V. Tishchenko, M. A. Belopol'skiy, B. L., Moldavskiy, I. B. Rapoport, S. Ye. Lifshits, A. V. Lozovoy, M. K. D'yakova, V. N. Ipat'yev, N. A. Orlov, M. F. Shostakovskiy, V. V. Shabarov, Ye. A. Viktorova, I. Ye. Pokrovskaya, A. I.

Catalytic Hydrogenation of Phenols

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B008/B006

Afanas'yeva, V. F. Polozov, Ye. I. Sil'chenko, A. Bag, T. Yegupov, D. Volokitin, S. A. Deryabin, A. M. Yasnyy, A. P. Terent'yev, A. N. Guseva, I. N. Nazarov, Ye. N. Zil'berman, F. Fisher, N. Prokopchuk, Ye. I. Prokopets, I. I. Yeru, B. K. Klimov, I. F. Bogdanov, V. I. Bobyshev, M. P. Minchenkov, V. P. Konov, K. A. Alekseyeva, T. Gritsevich, V. Ilomanov, G. Z. Koshel', V. A. Lanin, M. V. Pronina, M. S. Knyazeva, V. I. Zabavin, M. I. Kuznetsov, K. A. Belov, N. P. Masina, I. V. Kalechits, F. G. Salimgareyeva, N. N. Vorozhtsov junior , and V. N. Lisitsyn. There are 1 table and 213 references, 58 of which are Soviet.

ASSOCIATION: Khimicheskiy fakul'tet MGU im. M. V. Lomonosova (Chemical Department of the MSU (Moscow State University) imeni M. V. Lomonosov)

Card 4/4

S/074/60/029/010/002/004
B013/B075

AUTHORS: Shuykin, N. I. and Viktorova, Ye. A.

TITLE: Catalytic Synthesis of Alkyl Phenols

PERIODICAL: Uspekhi khimii, 1960, Vol. 29, No. 10, pp. 1229-1259

TEXT: The authors give a survey of studies made on the catalytic synthesis of alkyl phenols. The available publications were systematized according to the character of the alkylating substances. Papers are mentioned referring to some catalysts, on the character of which the structure and the ratio of alkylation products are dependent. The subject of the first chapter is the alkylation of phenols with unsaturated hydrocarbons. The application of the following catalysts is described: Acids as alkylation catalysts (Refs. 32-108); metal chlorides in alkylating phenols with alkenes (Refs. 63, 109-128); borofluoride (Refs. 129-168). Data obtained show that sulfuric acid is the most frequently used catalyst. It is preferred due to its accessibility and its sufficiently high yields of alkyl phenols. Also alkylation in the presence of resin - ion exchangers seems to be promising. The use of borofluoride and of some of its molecular com-

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Catalytic Synthesis of Alkyl Phenols

S/074/60/029/010/002/004
B013/B075

pounds requires further study. The use of aluminum phenoxide seems to open new possibilities in the synthesis of o-alkyl phenols. The second chapter deals with the alkylation of phenols with alcohols (Refs. 36, 65, 80, 81, 99, 173-277). As was proved by the mentioned data, the structure and the yield of alkyl phenols are dependent on the reaction conditions. These, in turn, depend on the structure of the alcohols employed, on the temperature, as well as on the nature of the catalyst. In some cases, phase state and pressure factor play an essential part. In spite of the high yields, alkylation of phenols with alcohols is rather inexpedient for industrial purposes; in laboratory practice, however, it offers a number of advantages. In the third chapter, alkylation of phenols with alkyl halogens is discussed (Refs. 109, 278-335). Data available on alkylation with alkyl halogens show that the reaction in the presence of aluminum chloride is most thoroughly investigated. However, it has to be taken into consideration that the isomerization of the radical entering into the phenol molecule does not always take place. Alkylation with ternary alkyl halogens in the presence of halogen hydracid is extremely easy, especially if the alkyl halogen forms during the synthesis. By this means, the possibility of using more easily accessible alkenes is given.

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Catalytic Synthesis of Alkyl Phenols S/074/60/029/010/002/004
B013/B075

Yu. G. Mamedaliyev, V. N. Ipat'yev, V. I. Isagulyants, A. V. Topchiyev, I. Tsukervanik, V. Tambovtseva, B. M. Dubinin, A. Ye. Chichibabin, A. S. Abdurasuleva, N. G. Sidorova, Z. N. Nazarova, I. N. Samsonova, Z. P. Aleksandrova, A. B. Kuchkarev, and P. P. Bagryantseva are mentioned. There are 335 references: 40 Soviet, 188 US, 1 Austrian, 1 Belgian, 29 British, 1 Canadian, 1 Czechoslovakian, 1 Danish, 1 Dutch, 20 French, 38 German, 3 Italian, 1 Rumanian, 6 Japanese, and 1 Swiss.

ASSOCIATION: Khimicheskiy fakul'tet MGU im. M. V. Lomonosova (Department of Chemistry of the Moscow State University imeni M. V. Lomonosov)

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5.3300,5.1190

77864
SOV/79-30-2-15/78

AUTHORS: Shuykin, N. I., Kashkovskaya, L. K., Kononov, N. F.

TITLE: Catalytic Hydrodealkylation of Polyalkylbenzenes. II. Demethylation of Toluene over 10% Nickel-Alumina Catalyst. Effect of Temperature and of the Rate of Feed of Toluene

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, Nr 2, pp 424-430 (USSR)

ABSTRACT: The authors studied the effect of temperature and feed rate of toluene upon the degree of hydrogenolysis of toluene over 10% nickel-alumina, in the temperature range 430-510°. It was found earlier (Zhur. Obshchey Khim., 29, 2230, (1959) that the following reactions can take place under conditions of hydrogenolysis ($Ni-Al_2O_3$, 460°, 5 atm):

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Catalytic Hydrodealkylation of Polyalkylbenzenes. II. Demethylation of Toluene over 10% Nickel-Alumina Catalyst. Effect of Temperature and of the Rate of Feed of Toluene

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The experimental results show that in the temperature range 430-460°, reactions (2), (3), and (4) do not take place to any appreciable extent. (Hydrogenation was performed in apparatus which was described earlier (loc. cit.); the products of catalysis were fractionated and identified by their Raman spectra (optical analysis was performed by Yu. P. Yegorov); in all experiments the hydrogen:toluene ratio equaled 5). Increase of pressure speeds up reactions (3) and (4) (from 0.6 to 35% for toluene-methylcyclohexane conversion and from 1

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Catalytic Hydrodealkylation of Polyalkyl-
benzenes II. Demethylation of Toluene
over 10% Nickel-Alumina Catalyst. Effect
of Temperature and of the Rate of Feed of
Toluene

to 49% for benzene-cyclohexane conversion with an increase in pressure from 5 to 25 atm), while raising the temperature above 460° increases destruction of the aromatic ring: reaction (2). It was found that a change of temperature from 430 to 510° does not essentially affect the yield of the catalysis products (85-90%), nor the content of benzene (30-35%). The "life" of the catalyst under conditions of steadily rising temperature is over 120 hours, which is longer than at constant temperature (at 460° it was found to be only 50 hours (loc.cit.). Increase in the feed rate of toluene from 0.5 to 1 hr^{-1} leads to a considerable (from 30-35 to 15-20%) decrease in benzene content in the products of catalysis (but on the other hand destruction. reaction (2), is inhibited by higher flow rate of toluene). There are 3 tables; and 8 references, 7 Soviet, 1 U.S. The U.S. reference is: Selected Values of Physical and Thermodynamic Properties of

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Catalytic Hydrodealkylation of Polyalkylbenzenes. II. Demethylation of Toluene over 10% Nickel-Alumina Catalyst. Effect of Temperature and of the Rate of Feed of Toluene

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SOV/79-30-2-15/78

Hydrocarbons and Related Compounds, Pittsburgh, Pennsylvania (1953).

ASSOCIATION: Institute of Organic Chemistry of the Academy of Sciences, USSR (Institut organicheskoy khimii Akademii nauk SSSR)

SUBMITTED: February 17, 1959

S/079/60/030/006/033/033/XX
B001/B055

AUTHORS: Shuykin, N. I., Bel'skiy, I. F., and Karakhanov, R. A.

TITLE: Hydrogenolysis of Tetrahydrofurans

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 6, pp. 1933 - 1937

TEXT: Since all the investigations of Refs. 1 - 4 on the reaction mechanism of the catalytic hydrogenation of the furan ring were mainly carried out to establish only this mechanism, it sufficed to determine that the furan- and the tetrahydrofuran ring behaved differently in hydrogenolysis, without investigating possible transformations of tetrahydrofurans during hydrogenolysis in greater detail. In an investigation of the hydrogenolysis of tetrahydrofurans, however, everything indicating the difference between the furan and the tetrahydrofuran rings and their behavior in hydrogenolysis is of importance. For this reason the authors of the present work investigated the hydrogenolysis of tetrahydrofurans. They studied the hydrogenolysis of

Hydrogenolysis of Tetrahydrofurans

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2-alkyl-, 2,2-dialkyl-, and 2,5-dialkyl-tetrahydrofurans in the vapor phase at atmospheric pressure, using platinized carbon and a nickel - aluminum skeleton catalyst. The hydrogenolysis of tetrahydrofuran homologs requires higher temperatures and takes an entirely different course than the hydrogenolysis of furan compounds. Hydrogenolysis of tetrahydrofurans on platinized carbon at 350°C, besides causing isomerization to aliphatic carbonyl compounds, occurs simultaneously at both C-O bonds. This leads to paraffin hydrocarbons with the same number of carbon atoms as the initial tetrahydrofurans. On the nickel - aluminum skeleton catalyst, hydrogenolysis of 2-alkyl- and 2,2-dialkyl - tetrahydrofurans occurs at the C-O bond adjacent to the alkyl groups. Primary alcohols and aldehydes forming as intermediates react to give paraffin hydrocarbons, the carbon chains of which contain one carbon atom less than the initial tetrahydrofuran derivative. The nickel - aluminum skeleton catalyst also causes a more radical decomposition of tetrahydrofurans, thus forming water and gaseous products. The hydrogenolysis of furans has definite advantages over that of tetrahydrofurans, since in the first case aliphatic alcohols and ketones

Card 2/3

Oxidation of β-Ketoacetals by Means of Lead Tetraacetate

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B001/B055

A reaction mechanism is suggested involving intermediate formation of α alkoxy vinyl ketone and subsequent acetoxylation with lead tetraacetate. A method was developed for the synthesis of α-hydroxy-β-ketoacetals by treating α acetoxy-β-ketoacylal compounds with a methanolic solution of hydrogen chloride (Scheme 5) (yield 35 - 65%). It was shown that α-acetoxy-β-ketoacylals react with polyhydric phenols or β-naphthol forming 3-acetoxy substituted benzo- or naphtho-pyrylium salts. The data given show that α-acetoxy-β-ketoacylals are now accessible and may prove important for the synthesis of several hitherto inaccessible heterocyclic compounds. There are 14 references: 7 Soviet, 4 US, 3 German

ASSOCIATION: Moskovskiy gosudarstvennyy universitet (Moscow State University)

SUBMITTED: June 11, 1959

Card 3/3

SHUYKIN, N.I.; BEL'SKIY, I.F.; SHOSTAKOVSKIY, V.M.

Catalytic isomerization of γ-oxides. Conversion of alkyl tetrahydrofuryl carbinols into aliphatic ketones. Zhur.ob.khim. 30 no.8:2757-2759 Ag '60. (MIRA 13:8)

1. Institut organicheskoy khimii Akademii nauk SSSR.
(Ketones) (Methanol)

84869

S/079/60/030/010/005/030
B001/B075

11.1210

AUTHORS: Naryshkina, T. I. and Shuykin, N. I.

TITLE: Synthesis of New Homologs of Cyclopentadiene 7

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 10, pp. 3205-3207

TEXT: Due to its difficult production, the chemistry of highly active cyclopentadiene homologs - unlike the cyclopentadiene itself - has hitherto not been thoroughly investigated. The synthesis of cyclopentadiene homologs described in Refs. 1 and 2 is reliable but somewhat complicated. The synthesis mentioned in Ref. 3 has to be improved in order to reach a higher purity and yield of the final products, cyclopentadiene and methyl cyclopentadiene. As cyclopentadiene yields organometallic derivatives (e.g., cyclopentadiene potassium), alkyl or aryl radicals can be introduced into its ring. However, this method only leads to cyclopentadiene hydrocarbons having substituents in the CH_2 group. Thus, homologs of cyclopentadiene having C_1-C_4 substituents (Refs. 5, 6) in position 5 were synthesized, as well as gem-substituted cyclopentadienes

Card 1/2

S/080/60/033/008/012/013
A003/A001

AUTHORS: Shuykin, N.I., Pozdnyak, N.A.

TITLE: The Catalytic Methylation of Benzene by Methanol

PERIODICAL: Zhurnal prikladnoy khimii, 1960, Vol. 33, No. 8, pp. 1904-1906

TEXT: The article is a continuation of the work published in Ref. 3. A special apparatus was designed for the continuous methylation of benzene by methanol and also for the methylation under a pressure of 20-60 atm. This apparatus makes it possible to obtain catalyzates containing 92-95% alkylate with at least 60% toluene. The apparatus comprises an electric furnace with the alumosilicate catalyst, in which the reaction takes place at 450 and 500°C. The ratio of benzene:methanol is 4:1. The alkylate obtained at 500°C consists of 60.5% toluene, 20.3% xylenes and 19.2% polymethylbenzenes. The methylation under pressure was investigated at 400, 450 and 475°C and pressures from 20 to 60 atm. An increase in pressure as well as in temperature promotes the formation of methylbenzenes, among them also xylenes. The yield of the toluene fraction increases very slowly in the pressure range from 20 to 40 atm and decreases with a further pressure increase. The effect of an excess of methyl alcohol in the reaction mix-

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S/076/60/034/04/31/042
B010/B009

AUTHORS: Yegorov, Yu. P., Romadan, I. A., Shlyapochnikov, V. A., Shuykin, N. I. (Moscow)

TITLE: Investigation of the Structure of the Radicals of Substances Obtained by Alkylation of Aromatic Hydrocarbons by Means of Alcohols in the Presence of Boron Trifluoride

PERIODICAL: Zhurnal fizicheskoy khimii, 1960, Vol. 34, No. 4, pp. 888 - 893

TEXT: In a number of earlier papers (Refs. 1-6) I. A. Romadan described a method for the alkylation of aromatic hydrocarbons with molecular alcohol compounds of boron trifluoride at 165-170° in an autoclave, or at a pressure of 1 atmosphere. The results obtained do not agree with those given by other authors, and it is assumed that a different reaction mechanism prevails under such conditions (without activator and at 165-170°). For instance, in the alkylation of naphthalene with n-butyl, n-amyl, and n-propyl alcohol alkyl naphthalenes with normal radicals were obtained. The structure of n-butylnaphthalene was confirmed spectroscopically (Ref. 13) and by a special method of deuterium exchange at the fiziko-khimicheskiy institut im. L. Ya. Karpova (Physicochemical Institute imeni L. Ya. Karpov) in the

Card 1/2

Investigation of the Structure of the Radicals of Substances Obtained by Alkylation of Aromatic Hydrocarbons by Means of Alcohols in the Presence of Boron Trifluoride

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B010/B009

laboratory of A. I. Shatenshteyn. The reaction mechanism can hardly be explained by means of the data concerning the alkylation with iso-alcohols; however, the reaction might take place via an intermediate stage during which olefines are formed. The structure of the alkylation products obtained was determined from infrared spectra; particular attention was paid to the structure of the side chain, which was investigated on the basis of the frequency of CH oscillations (2800-3000 cm^{-1}). The spectra of the alkyl naphthalenes and diphenyls (Figs. 1,2), the constants of which are given in a table, were recorded by means of an IKS-11 infrared spectrometer with the aid of an FEOU-15 amplifier. The assumption was confirmed that there is a weak interaction between the alkyl radicals and aromatic rings. The investigation results given in the paper show that in the way described the structures of the radicals in compounds of the type Ar-R (Ar = phenyl, diphenyl, naphthyl, and R = alkyl groups from C_3 to C_5) may be determined. Papers by A. V. Topchiyev, Ya. M. Paushkin, and M. V. Kurashev are mentioned in the paper. There are 2 figures, 1 table, and 22 references, 13 of which are Soviet.

SUBMITTED: September 17, 1958

Card 2/2

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68816
S/020/60/131/01/030/060
B011/B006

AUTHORS: Shuykin, N. I., Corresponding Member, AS USSR, Bel'skiy, I. F.

TITLE: Hydrogenation of Furan Compounds on a Skeleton Cu-Al Catalyst

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol 131, Nr 1, pp 109-112 (USSR)

ABSTRACT: The authors investigated the effects of pressure and temperature on the sequence of the reduction of unsaturated bonds in various compounds of the furan series. 1) The pressure determines the direction of hydrogenolysis of the furan ring. In the presence of skeleton Cu-Al catalyst and under normal pressure, the silvan ring is cleaved at the C-O bond not adjacent to the methyl group. Methyl propyl ketone is formed (see scheme: reference 3). Furan ring cleavage, however, is possible in both directions (C-O bonds 1,2 and 1,5) if silvan is hydrogenated in the vapor phase as before, but with pressurized hydrogen. The quantities obtained of pentanol-1 and pentanol-2 vary considerably with the pressure applied. Higher temperatures promote both the dehydration of pentanol-2 to methyl propyl ketone, and the cleavage of silvan under formation of n-pentane and

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Hydrogenation of Furan Compounds on a
Skeleton Cu-Al Catalyst

water. Five to eight percent tetrahydrofuran was formed in all reactions involving pressurized hydrogen. 2) The primary reaction in the hydrogenation of alkylfurylcarbinols on skeleton Cu-Al catalyst under normal or increased hydrogen pressure is the reduction of the hydroxyl group, yielding the corresponding α-alkylfurans. Under normal pressure and at 230-250° yields of up to 95% are obtained. Further hydrogenolysis of the ring (at higher temperatures) leads to aliphatic ketones. Under these conditions hydrogenolysis of the ring is much more in- 4
tense in both directions. Aliphatic alcohols and small quantities of α-alkyltetrahydrofurans are also contained in the reaction products. 3) In the case of alkyl-α-furyl ketones and alkyl-α-furylcarbinols selective reduction of the carbonyl group under retention of the furan ring is possible in the vapor phase. As a catalyst for this reaction, e.g., nickel, deposited on zinc- or cadmium oxide can be used (Ref 4). However, the sequence of the reactions may also be different (on platinized carbon). The effect of skeleton Cu-Al catalyst on the hydrogenation of alkylfuryl ketones at normal pressure in

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