CA

Contact catalytic transformations of 1,1-dimethylcyclohexane in the presence of platinized carbon. B. A. Kazanskiĭ and A. L. Liberman (Acad. Sci. U.S.S.R., Moscow). *Bull. acad. sci. U.R.S.S., Classe sci. chim.* 1947, 265-75 (in Russian).—In connection with the problem of the mechanism of the catalytic aromatization of dimethylhexanes, in particular of 3,3-dimethylhexane which, at 307-346°, on platinized C, reacts in the main according to $MeCH_2CH_2CMe_2CH_2Me \rightarrow CH_4 + 3H_2 + PhMe$, failure to detect intermediate formation of 1,1-dimethylcyclohexane (I) led to the investigation of the transformations of the latter on the same catalyst; its activity was characterized by 95% hydrogenation of C_6H_6 at 151° and a space velocity $v = 0.48$, and 87% dehydrogenation of cyclohexane at 300°, $v = 0.40$, in a very slow stream of H_2. (1) Without carrier gas, 24.3 g. I at 300°, $v = 0.10$, time of contact $\tau = 68$ sec., on 75 ml. catalyst, gave 18.6 g. catalyzate and 2.6 g. (10.4 l.) gas, H_2 60.1, CH_4 26.2, N_2 3.0, O_2 1.5, CO_2 0.1%. The catalyzate was fractionated into b_{748} 103.2-10.3° (18.6%), 110.3-13.1° (39.3), 113.1-22.0° (26.2), residue 12.0%, losses 3.9%. By nitration, the contents of aromatic hydrocarbons in the 3 fractions and in the residue were 74.5, 70.5, 16, and 79%, i.e., with respect to the catalyzate, 14, 28, 4, and 10%, and in % of the theory with respect to the amt. of I used, 13, 26, 4, and 8%; the aromatic hydrocarbon of the 1st 3 fractions is PhMe (total yield 43%), those of the residue *o*- and *m*-$C_6H_4Me_2$, in the approx. ratio ortho:meta = 5:1; the ratio of PhMe:$C_6H_4Me_2$ = 5.4:1. There is no *p*-$C_6H_4Me_2$. (2) In a strong stream of H_2, 4 l./hr. (300% excess), 12.25 g. I, at 300°, on 100 ml. catalyst, rate of flow 5 ml./hr., $v = 0.05$, $\tau = 34$ sec., gave 12.1 g. catalyzate and 25 l. gas, H_2 91.3, CH_4 5.1, CO_2 1.8, N_2 1.2, O_2 0.9%. The catalyzate was fractionated into b_{748} 97.8-111.5° (30.6%), 111.5-19.3° (51.5%), residue 12.2%, losses 5.7%. Contents of aromatic hydrocarbons in the 2 fractions and in the residue, 62.5, 9.5, and 38%, i.e., with respect to the catalyzate, 19, 5, and 5%, or, in % of the theory with respect to the amt. of I, 18, 5, and 4%; the hydrocarbon of the two fractions being PhMe, that of the residue $C_6H_4Me_2$, the ratio is 5.7:1, i.e., practically the same as in the absence of H_2. (3) On a catalyst previously used for hydrogenation of C_6H_6 at 151° and then twice for dehydrogenation of cyclohexane at 300°, I at 300°, without carrier gas, at a rate of flow of 2.2 ml./hr./15 ml. catalyst, $v = 0.15$, $\tau = 50$ sec., gave about 40% aromatic hydrocarbons. (4) The ratios of PhMe:$C_6H_4Me_2$ approx. 5:1 and *o*-$C_6H_4Me_2$:*m*-$C_6H_4Me_2$ approx. 5:1 are independent of the absence or presence of H_2 as carrier gas. The total yield of aromatic hydrocarbons is, within the interval studied, a linear function of τ, being 27, 40, and 50% at $\tau = 34$, 50, and 68 sec., resp. No ring opening takes place in the reaction. The rate of the aromatization of I is halfway between that of dehydrogenation of cyclohexane and that of aromatization of paraffins on the same catalyst.

N. Thon

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ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

LIBERMAN, A. L.

"The Contact Transformations of 1,1-Dimethyl-Cyclohexane in the Presence of Platinized Charcoal," ibid. Khim. Nauk, No. 3, 1947.

Inst. of Organic Chem., Acad. Sci. USSR, -1947-.

CA

Synthesis and properties of some 1-alkenes. B. A.
Kazanskii, A. L. Liberman, A. F. Plate, M. I. Rosengart,
and G. A. Tarasova. *J. Gen. Chem.* (U.S.S.R.) 17, 1503-10
(1947)(in Russian).—The literature on the prepn. of 1-
alkenes is reviewed (29 references) and the divergences
ascribed to impurities, primarily isomers. Pure 1-alkenes
were prepd. for standards in the work of the Soviet oil
industry. Mg (48 g.) and 150 cc. Bu_2O were treated with
240 g. EtBr in 250 cc. Bu_2O (the mixt. being dild. with 250
cc. Bu_2O when the reaction began); after 2 hrs. and then
heating 15 min. to 50°, the Grignard reagent was treated
at 18-20° over 6-7 hrs. with 153 g. allyl chloride in 250
cc. Bu_2O, the cooling moderated, and the temp. allowed
to rise to 50°; after standing overnight, the mixt. was
distd. up to 110°; fractionation (40-plate column) gave a
pentene fraction, b. 29-31.5°, which, shaken 8 hrs. with
0.5 vol. $H_2NCH_2CH_2OH$, washed with acid, and distd.,
gave pure *1-pentene* (40-5%), b_{760} 29.2°, n_D^{20} 1.3719,
d_4^{20} 0.6411. Purification by heating to 110° with NaOPr
in PrOH led to high losses and was less satisfactory. The
entire Grignard reaction is best conducted in a slow stream
of N. The Grignard reagent from 52 g. Mg and 246 g.
EtBr in 500 cc. Et_2O was decanted from the solid ppt.
and added over 6 hrs. at 14-18° to a stirred soln. of 153
g. allyl chloride in 250 cc. Et_2O in a N atm.; after stand-
ing overnight, the mixt. was decompd. with 1 kg. ice-1.5
kg. H_2O, the org. layer sepd., the aq. layer satd. with NH_4-
Cl, and the sepd. oil added to the Et_2O soln.; distn. gave a
crude hexene fraction (b. 61.5-64°) which, boiled 20 hrs.
with NaOMe or shaken with $H_2NCH_2CH_2OH$, gave 40-5%
1-hexene, b_{760} 63.4-3.6°, n_D^{20} 1.3880, d_4^{20} 0.6748. Mg (50
g.) and 250 cc. Et_2O were treated with 3-5 cc. BuBr and
a crystal of iodine; upon the beginning of a reaction, 275 g.
BuBr in 250 cc. Et_2O was added over 30-5 min. with cool-
ing; after standing 20-5 min. the soln. was warmed 0.5
hr., cooled to 13-14°, and treated with 153 g. allyl chlo-
ride in 250 cc. Et_2O over 6-7 hrs.; then, after allowing the
temp. to rise to 30-2° and letting the mixt. stand over-
night, working up as above gave 47% *1-heptene*, b_{760} 92.8-
3.1°, n_D^{20} 1.4005, d_4^{20} 0.6975. n-$C_8H_{17}OH$ (b_{760} 106°, n_D^{20}
1.4305) (325 g.) and 10 cc. concd. H_2SO_4, slowly treated
with 255 g. Ac_2O and heated 2 hrs. on a steam bath, gave
70% Ac deriv., b_{10} 101-2.5°, n_D^{20} 1.4190, d_4^{20} 0.8705; this
was passed at 18 cc./hr. through a 26-mm. diam. tube
filled with glass wool and kept at 500-15° to give, after
washing, rough distn., and a 2nd pyrolysis pass, 63.5%
1-octene, b_{760} 120.9-1.5°, n_D^{20} 1.4094, d_4^{20} 0.7160. Mg
(24.5 g.) in 100 cc. Et_2O in a N atm. was treated with 193
g. n-$C_8H_{17}Br$ (b. 201°, n_D^{20} 1.4507, d_4^{20} 1.0832) in 175 cc.
Et_2O at 36° over 15-30 min.; after stirring 0.5 hr. and
standing 1 hr., the soln. was treated below 36° with 76.5
g. allyl chloride in 80 cc. Et_2O over 1-1.5 hrs.; after stir-
ring 1.5 hrs. and letting stand overnight, the mixt. was
treated with ice-water, then with dil. HCl; the org. layer,
after washing, gave a crude product, b. 175-200°, which,
boiled 48 hrs. with NaOPr, washed with cold concd. HCl
and H_2O, and distd., gave 51% *1-hendecene*, b_{760} 191.4-
1.7°, n_D^{20} 1.4270, d_4^{20} 0.7506. G. M. Kosolapoff

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ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

1ST AND 2ND ORDERS

3RD AND 4TH ORDERS

AUTHOR INDEX

COMMON VARIABLES INDEX

CH

10

Hydrogenation of cyclopentane with ring opening in the presence of platinized carbon. B. A. Kazanskii, A. L. Liberman, and A. F. Plate (Acad. Sci., U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.S.R.* **57**, 571-4(1947); *Chem. Zentr.* (Russian Zone Ed.) **1948**, II, 825.—Hydrogenation of cyclopentane in the presence of platinized C yielded *n*-pentane (cf. *C.A.* **42**, 4634*e*). No compds. having a fewer no. of C atoms were obtained. In the case of cyclopropane and cyclobutane similar hydrogenation with ring opening can be attributed to inner strains in the ring. However, this assumption cannot be made in the case of cyclopentane. It is assumed that in cyclopentane there are 4 like C—C bonds and a 5th which is less stable and breaks under the influence of activated H atoms.

M. G. Moore

LIBERMAN, A. L.

Tables for computing molecular refractions
Moskva, 1948

1ST AND 2ND ORDERS

3RD AND 4TH ORDERS

PROCESSES AND PROPERTIES INDEX

LIBERMAN, A.L.

2

Some physical properties of acetonitrile-water mixtures and the azeotropic acetonitrile-water mixture. A. L. Liberman, Z. N. Parnes, and D. N. Kursanov (Inst. Org. Chem. Acad. Sci. U.S.S.R., Moscow). *Bull. acad. sci. U.R.S.S., Classe sci. chim.* 1948, 101-6(in Russian).—MeCN and H_2O form an azeotropic mixt. (not previously described), b_{760} 76.70-76.75°, n_D^{20} 1.3437, n_D^{25} 1.3466, d_4^{20} 0.8175, by analysis (Dumas N) MeCN 84.12, H_2O 15.88%. The curves of *n* against the compn. show a peculiar, extended horizontal portion of const. *n*; at 20° this portion extends from about 23 to 46% H_2O, *n* = 1.3473; at 25° from 22 to 55% H_2O, *n* = 1.3450. Actual constancy (within 5×10^{-4}) of *n* in these regions, not simulated by a broad and flat max., was demonstrated directly by a diffraction method on layers having the extreme compns. of the horizontal branch. The azeotropic compn. from the n_D^{20} curve is MeCN 84.23, H_2O 15.77%, i.e., practically the same as by analysis. D. and specific refraction are linear functions of the compn.; sp. vol. and molar refraction are slightly hyperbolic.

N. Thon

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

MATERIALS INDEX

AUTHOR INDEX

LIBERMAN, A. L.

USSR/Chemistry - Acetonitrile Jan/Feb 1948
Chemistry - Mixtures

"Some Physical Qualities of a Mixture of Acetonitrile With Water, and the Azeotropic Mixture of Acetonitrile - Water," A. L. Liberman, Z. N. Parnes, D. N. Kursanov, Inst of Org Chem, Acad Sci USSR, 5 pp

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 1

Describes experiments and research that show the nature of the azeotropic mixture of acetonitrile with water at atmospheric pressure, and establish its composition and physical qualities.

66T30

1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

CA

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Cyclization of paraffin hydrocarbons with a quaternary carbon atom, and mechanism of the aromatization of paraffins on platinized carbon. B. A. Kazanskii, A. L. Liberman, and M. I. Batuev. *Doklady Akad. Nauk S.S.S.R.* 61, 67-70(1948).—Proof that the catalytic aromatization of 3,3-dimethylhexane (I) proceeds over the intermediate formation of 1,1-dimethylcyclohexane (II) was afforded through the detection of the latter compd. among the products of the reaction carried out at lower temps., 290-300°, than the usual 306-346°. With a Pt-C catalyst, characterized by 92% dehydrogenation of cyclohexane at 300° and space velocity 0.33, 23.1 g. I, at 300° and space velocity 0.11, gave 850 ml. gas (H_2 85.6, CH_4 9.8%) and 21.2 g. catalyzate, fractionated into b. 99.1-112.1 (26.5%), 112.1-112.4(63.0%), residue 9.0%, losses 1.0%; in the nonsulfonatable part of the residue, II was identified by the Raman line 705 cm.$^{-1}$; its amt. in the catalyzate is estd. ~3%, PhMe ~2%, m-$C_6H_4Me_2$ ~1%. The catalyzate of the reaction at 290° showed the Raman lines of II, 459, 705, 829, 963, and 1020 cm.$^{-1}$, and the 705 line was very distinct from the 715, 724, 732 triplet of I. Under the same conditions, 2,2-dimethylhexane reacted much slower than I, giving about 0.1 as much PhMe and $C_6H_4Me_2$; the amt. of the fraction in which II might be present was insufficient for its identification. N. Thon

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

LIBERMAN, A. L.

PA 35/49T12

USSR/Chemistry - Catalysts, Platinum Sep 48
Chemistry - Ketones, Hydrogenation

"Reasons for the High Catalytic Activity of One Preparation of a Platinum Catalyst," V. V. Patrikeyev, A. L. Liberman, 4 pp

"Dok Ak Nauk SSSR" Vol LXII, No 1

Used active platinum catalyst prepared in authors' laboratory in 1934 for liquid-phase hydrogenation of ketones. Tested components of this catalyst in hydrogenation of dimedone in acetic acid solution. In experiments with H_2PtCl_6 on platinized carbon, H_2PtCl_6 on activated carbon, platinum black and H_2PtCl_6, the latter compound alone, and platinized

[redacted] 35/49T12

USSR/Chemistry - Catalysts, Platinum (Contd) Sep 48

carbon alone, established that hydrogen in presence of platinized carbon rapidly reduced H_2PtCl_6 to the metal, and that the latter coated the highly developed surface of the platinized carbon, creating a very active catalyst. Submitted by Acad B. A. Kazanskiy, 1 Jul 48.

[redacted] 35/49T12

LIBERMAN, A.L.

✓ Contact transformations of 1,1-dimethylcyclohexane and the mechanism of aromatization of paraffin hydrocarbons on platinized carbon. A. L. Liberman. *Problemy Kinetiki i Kataliza Akad. Nauk* ~~S.S.S.R. 6, 2~~45-51(1949).—Examn. of the products of contact of 3,3-dimethylcyclohexane and 1,1-dimethylcyclohexane with Pt-C at 300° showed that aromatization of the paraffin hydrocarbons over this catalyst is a 2-phase event; the hydrocarbon is transformed into a hexamethylene radical, which then aromatizes. This corresponds to the data obtained on the kinetics of aromatization of diisobutyl and dehydrogenation of cyclohexane over Pt-C. The 1st stage involves a 6-point adsorption on the catalyst. G. M. Kosolapoff

LIBERMAN, A. L.

"A Complex Method of Detailed Investigation of the Indidual'nogo Sostava Benzinov), G. S. Landsberg, B. A. Kazanskiy, P. A. Bazhulin, M. I. Batuyev, A. L. Liberman, A. S. Plate, and G. A. Tarasova, edited by V. S. Fedorov, Gostoptekhizdat, Moscow/ Leningrad, 1949, 68 pages, 3 rubles.

Subject Method is based on spectral analysis.

SO: Uspekhi Khimii , Vol 18, #6, 1949; Vol 19, #1, 1950, (W-10083)

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CA

A laboratory method for rapid hydrogenation of olefins at atmospheric pressure. B. A. Kazanskii, A. L. Liberman, A. F. Plate, M. I. Rozengart, and O. D. Sterligov. *Doklady Akad. Nauk S.S.S.R.* 71, 477-80(1950).—Platinized C activated by a small amt. of $PdCl_2$ or H_2PtCl_6 is a very active, rapidly acting catalyst for atm.-pressure hydrogenation of olefins even without added solvents. A considerable economy in the amts. of catalysts needed is one of the results. Reductions of MeCCH:CHEt and octene were performed in a rocking flask with a 50-200 ml. charge and platinized charcoal contg. 0.01-0.05 g. Pt to which was added 1-2.85 ml. of the activator soln. (either 0.03 g. Pt/ml. of H_2PtCl_6 or 0.018 g. Pd/ml. of $PdCl_2$ soln.); the reduction was complete in 3-8 hrs. (usually 97%) and after filtration the products were distd. G. M. Kosolapoff

LIBERMAN, A. L.

USSR/Chemistry - Hydrocarbons
Isotopes

Aug 52

"Hydrogen Exchange in Saturated Hydrocarbons Resulting From the Action Of Sulfuric Acid," V. N. Setkina, D. N. Kirsanov, O. D. Sterlingov, and A. L. Liberman, Inst of Org Chem Acad Sci USSR

"DAN SSSR" Vol 85, No 5, pp 1045-1048

The exchange of H in a no of hydrocarbons was studied with the aid of sulfuric acid having an atom of heavy H. It was found that the reaction passes through the following stages. Radicals or carbonium ions are formed by oxidation. They are capable of exchanging their H atoms for deuterium. H exchange continues from one radical to the next in a chain reaction. The final stage is breaking off of the chain taking place in the usual manner. Submitted by Acad b. A. Kazanskiy 3 Jun 52

PA 239T16

USSR.

✓Preparation of 1,2-dialkylcyclanes. Synthesis of stereoisomeric 1-methyl-2-butylcyclopentanes. A. F. Plate, A. L. Liberman, and N. A. Momma. *Bull. Acad. Sci. U.S.~~S.R.~~, ~~Div. Chem.~~ Sci.* 1953, 617-24 (Engl. translation).—See C.A. 48, 12685c H. L. H.

1

USSR/Chemistry - Hydrocarbons Jul/Aug 53

"Preparation of Dialkylcyclanes. Synthesis of Stereoisomeric 1-Methyl-2-n-Butylcyclopentanes," A. F. Plate, A. L. Liberman, N. A. Momma, Moscow State U im M. V. Lomonosov: Inst of Org Chem, Acad Sci USSR

Iz Ak Nauk SSSR OKhN, No 4, pp 689-696

Proposed a method for the prepn of 2-methylcyclopentanone-1 (I) by the dehydration of the glycel obtained by the oxidation of 1-methylcyclopentane-1 with a mixt of hydrogen peroxide and fermic acid. Starting with I, synthesized 1-methyl-2-n-butylcyclopentane, which was separated into the cis- and trans-isomers.

270T3

Chemical Abst.
Vol. 48 No. 6
Mar. 25. 1954
Organic Chemistry

The possibility of determination of the number and position of side chains in benzene homologs by the spectral method. V. L. Broude, A. I. Liberman, [illegible] hotko. [illegible]

It was shown that within the limits of [illegible] alkylated benzenes can be identified [illegible] The spectra of some of the [illegible] photographically. The [illegible] [illegible] given. [illegible] PrPh, cryst. [illegible] PrPh amorphous, 37,231; cumene [illegible] n-C_4H_9Ph, cryst. high temp. form 37,3[illegible] [illegible]xylene, cryst., 38,815; p-EtC_6H_4Me, cryst. high temp. form 38,390; p-cymene, cryst. 38,567; m-xylene, cryst. high temp. form 36,578; o-EtC_6H_4Me, cryst. [illegible] tetrahydronaphthalene, cryst., 36,370; o-xylene, cryst. [illegible] temp. form 36,779. In a given series of a type the spectra are similar and chain-branching does not alter the general type of the spectrum.

G. M. Kosolapoff

6

By-products in the Sandmeyer reaction. A. L. Liberman, O. D. Sterligov, T. V. Lapshina, and B. A. Kazanskii (Inst. Org. Chem., Acad. Sci., U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.S.R.* 91, 845-8(1953).—While it is generally assumed that in the Sandmeyer reaction the halogen enters the position previously occupied by the diazonium group, this is not necessarily the case. When extremely pure o-MeC$_6$H$_4$NH$_2$ was converted to the Br analog by the Sandmeyer reaction, and the by-product cresol was carefully examd., it was found that the material sepd. from the main product by means of H_2SO_4 and NaOH washing was not pure o-MeC$_6$H$_4$OH but an equimolar mixt. of this with *5,2-Br(HO)C$_6$H$_3$Me* (I) (each in 13% yield). When pure o-cresol was treated with concd. HBr and $NaNO_2$ under the conditions used in a Sandmeyer reaction the above material was obtained in 74% yield, thus affording a halogenation method for phenols. The Cu_2Br_2 was not essential to this reaction and the same product formed in its absence, in even higher yield. Thus $NaNO_2$ can be used in concd. HBr soln. as an oxidizing agent for bromination by nascent Br. o-MeC$_6$H$_4$NH$_2$ was purified through the Ac deriv. to a constant f.p. (cooling curve of the product is shown) at 110.4°. The free amine, freed by hydrolysis with 25% H_2SO_4, was then diazotized in 162-g. portions in 48% HBr according to Sandmeyer and the product steam-distd., yielding, after the usual treatment, 48% o-MeC$_6$H$_4$Br. Recovery of the org. material from the washings (NaOH) gave o-MeC$_6$H$_4$OH, identified by several derivs. The residue after its distn. solidified and was purified by crystn. from H_2O, yielding I, m. 64.7-5.3°; benzoate, m. 65.9-6.4°. In a quant. expt., 103.4 g. o-MeC$_6$H$_4$NH$_2$ in 470 ml. 47% HBr was diazotized with 77.0 g. dry $NaNO_2$, the diazonium salt decompd. by 29 g. Cu_2Br_2 and 1 g. Cu, and the mixt. distd. with steam, yielding 78.6 g. o-MeC$_6$H$_4$Br from the fore-run of the distn.; the alk. washes gave 13.6 g. o-cresol and 24.7 g. bromocresol, identical with I, b_{14} 131-3°, m. 64.2-4.4°. To 108.1 g. o-cresol in 470 ml. 47% HBr chilled to 0° was added slowly 77.0 g. $NaNO_2$ with shaking, then 29 g. Cu_2Br_2 and 1 g. Cu shavings, the mixt. warmed to 40-5°; the product steam-distd., the distillate extd. with Et_2O, and the ext. distd., giving 69% I. When Cu_2Br_2-Cu was omitted, the yield rose to 74%. To 92 g. MePh in 470 ml. 47% HBr was slowly added over 1 hr. at 0° 77.0 g. $NaNO_2$, the mixt. warmed 1 hr. to 35-43°, cooled, and the upper layer sepd.; distn. gave 13% BrC$_6$H$_4$Me (isomer not identified), b_{21} 180-3.5°, n_D^{20} 1.5532, d_{20} 1.4015. G. M. K.

USSR .

Hydrogen exchange [illegible] in reaction with sulfuric acid. [illegible]

[illegible] H$_2$SO$_4$ was studied. The D-H exchange is restricted to monocyclic hydrocarbons which contain tertiary C atoms (methyl-, 1,[illegible]-dimethyl- and 1-methyl-4-ethylcyclohexane, methylcyclopentane) and the equil. is reached at room temp. in a few hrs. No exchange takes place with cis and trans forms of decahydronaphthalene. In mixts. of hydrocarbons which contain secondary and tertiary C atoms, only the latter react. Substantially no exchange occurs with cyclohexane. 1,1-Dimethylcyclohexane also does not react, neither does cyclopentane. When the exchange takes place, all H atoms are capable of exchange. Isomerization of substituted cyclohexanes is taken into account. G. M. Kosolapoff

Determination of individual hydrocarbon composition of gasolines by the combined method. II. Two gasolines from petroleum of Kazanbulak origin. [illegible] A. F. Plate [illegible] Petrov [illegible] Zhiv[illegible] [illegible] *Izvest. Akad. Nauk S.S.S.R.* [illegible] *Kaza[illegible]* [illegible] 1954 266-77; cf. [illegible] 45, 734[illegible] [illegible] from Kazanbulak area [illegible] optical-distn. method [illegible] hydrocarbons were identified [illegible] for [illegible] of the total [illegible] It is [illegible] despite the [illegible] origin of the specimens geographically, considerable [illegible] differences in compn. are found. III. [illegible]orakhan gasolines. B. A. Kazanskii, G. S. Landsberg, A. F. Plate, A. L. [illegible] [illegible] A. Mikhailova [illegible] M. [illegible] S. A. Ukhol[illegible] F. F. Bulanova [illegible] [illegible] 278-91.—Two specimens of [illegible] gasolines [illegible] examd. by the combined method [illegible] carbons were identified [illegible] of the total compn. [illegible] are listed.

[illegible]

KAZANSKIY, B.A.; LANDSBERG, G.S.; PLATE, A.F.; LIBERMAN, A.L.; MIKHAYLOVA, Ye.A.; BAZHULIN, P.A.; BATUYEV, M.I.; UKHOLIN, S.A.; BULANOVA, T.F.; TARASOVA, G.A.

Composite method for the determination of individual hydrocarbons in gasolines. Part 3. The Surakhany gasolines. Izv.AN SSSR. Otd.khim.nauk no.2:278-291 Mr-Ap '54. (MLRA 7:6)

1. Institut organicheskoy khimii im. N.D.Zelinskogo, Fizicheskiy institut im. P.N.Lebedeva Akademii nauk SSSR.
(Hydrocarbons) (Surakhany--Petroleum) (Petroleum--Surakhany)

LIBERMAN, A.L.

USSR/ Chemistry Fuels

Card : 1/1

Authors : Kazanskiy, B.A., Landsberg, G.S., Plate, A.F., Bazhulin, P.A., Liberman, A.L., Suschinskiy, N.M., Tarasova, G.A., Ukholin, S.A., Voron'ko, S.V.

Title : Combined method for the determination of the individual hydrocarbon composition of gasolines. Part 4.- Gasoline from the Tuymazinsk petroleum.

Periodical : Izv. AN SSSR, Otd. Khim. Nauk., 3, 456 - 469, May - June 1954

Abstract : The results obtained from the study of the individual hydrocarbon composition of gasoline with end point of 150°, derived from low-sulfur Tuymazinsk petroleum (Devonian horizon), are described. The quantitative, individual hydrocarbon composition of Tuymazinsk gasoline and the general losses are presented in percentage by weight values. The structure of paraffin-base gasoline derived from Tuymazinsk petroleum and the aromatic contents of other hydrocarbons are discussed. Toluene and m-xylene were found to be predominant among aromatic hydrocarbons. Four USSR references. Tables, graphs.

Institution : Acad. of Sc. USSR, The P. N. Lebedev Physics Institute

Submitted : July 20, 1953

LIBERMAN, A. L.

USSR/ Chemistry Spectral analysis

Card : 1/1 Pub. 40 - 20/27

Authors : Bashulin, P. A., Koperina, A. V., Liberman, A. L., Ovodova, V. A., and Kazanskiy, B. A.

Title : Optical method of studying hydrocarbons. Part 7.- Combined diffusion spectra of certain naphthenes

Periodical : Isv. AN SSSR. Otd. khim. nauk 4, 709 - 715, July - August 1954

Abstract : Combined diffusion spectra of seven cyclopentane and cyclohexane hydrocarbons, were investigated and the intensities of the spectral lines in the maximum state were determined photometrically. The spatial orientation of side chains in naphthenes and stereoisomers, was determined on the basis of spectroscopic data. Tables, showing the frequency and intensity of spectral lines of the investigated naphthenes, are included. Ten references: 8 USSR and 2 USA (1941 - 1951). Tables; diagrams.

Institution : Acad. of Sc. USSR, The N. D. Zelinskiy Institute of Organic Chemistry

Submitted : August 30, 1953

LIBERMAN, A.L.,

KAZANSKIY, B.A.; LANDSBERG, G.S.; PLATE, A.F.; BAZHULIN, P.A.; LIBERMAN, A.L.; MIKHAILOVA, Ye.A.; SUSHCHINSKIY, M.M.; TARASOVA, ~~G.A.; UKHOLIN;~~ S.A.; VORON'KO, S.V.

Composite determination of the individual hydrocarbon composition of benzins. Report no.5. Gasoline from Emba petroleum. Izv.AN SSSR Otd.khim. nauk no.5: 865-877 S-O '54. (MLRA 8:3)

1. Institut organicheskoy khimii im. N.D.Zelinskogo Akademii nauk SSSR.
(Emba region--Gasoline)

[illegible]

USSR/Chemistry - Analytical chemistry

Card 1/2 Pub. 40 - 16/27

Authors : Kazanskiy, B. A.; Landsberg, G. S.; Plate, A. F.; Liberman, A. L.; Mikhaylova, E. A.; Sterli[illegible], [illegible]; [illegible]va, T. F.; Tarasova, G. A. and Aleksanyan, V. T.

Title : Determination of the individual hydrocarbon composition of gasolines

Periodical : Izv. AN SSSR. Otd. Khim. Nauk 6, 1057-1066, Nov-Dec 1954

Abstract : The individual hydrocarbon composition of straight run gasolines with 150° end point obtained from Karachukhursk crude oil, was investigated by means of a combination method. The content of all individual hydrocarbons found in the gasolines was calculated in percentages by weight with consideration of the initial and end points.

Institution : Acad. of Sc., USSR, The N. D. Zelinskiy Institute of Org. Chemistry

Submitted : December 19, 1953

[illegible] : Izv. [illegible]

[illegible]

[illegible] : [illegible] from the [illegible] of aromatic hydrocarbons [illegible] of the paraffinic hydrocarbons [illegible] structure paraffins. The ratio between cyclopentane and cyclohexane hydrocarbons was set at 0.44. Five USSR references (1951-1954). Tables; graphs.

LIBERMAN, A. L.

USSR/ Physics - Spectral analysis

Card 1/1 Pub. 43 - 36/62

Authors : Kazanskiy, B. A.; Landsberg, G. S.; Aleksanyan, V. T.; Bulanova, T. F.; Liberman, A. L.; Mikhaylova, Ye. A.; Plate, A. F.; Sterin, Kh, Ye.; and Ukholin, S. A.

Title : Analysis of aromatic ligroin parts b the combined diffusion spectra

Periodical : Izv. AN SSSR. Ser. fiz. 18/6, 704-706, Nov-Dec 1954

Abstract : Brief report is presented on the method and some results obtained during individual and close-group analysis of primary and secondary aromatics of ligroin, Analysis of results obtained showed that the basic ligroin (taken front the Embensk Petroleum Scouce) contained alkyl substitutes of benzene and cyclohexane with shotr term substituting radicals. Three references: 1 USA and 2 USSR (1947-1953). Tables.

Institution: Acad. of Sc., USSR., The N. D. Zekinskiy Inst. of Organ. Chem. and the Commission on Spectroscopy

Submitted : .....

USSR.

Catalytic transformations of *n*-heptane and *n*-octane in the presence of platinized carbon. B. A. Kazanskii, A. L. Liberman, T. F. Bulanova, V. T. Aleksan[illegible] [illegible] Kh. E. Sterin. *Doklady Akad. Nauk S.S.S.R.* 95, [illegible] Passage of *n*-heptane over Pt-C at [illegible] gave 85.0[illegible] catalyzate contg. [illegible]% aromatic [illegible] hydrocarbons; the dearomatized [illegible] tained cyclic products, and Raman [illegible] presence of 10% *trans*-1,2-dimethylcyclopentane, PrCH MeEt, possibly BuCHMe$_2$, CHEt$_3$, and PrCHMeCHMe$_2$. Similar treatment of *n*-octane gave analogous results with the catalyzate (88.3%) contg. small amts. of *n*-propylcyclopentane and *cis*-1-methyl-2-ethylcyclopentane.

G. M. Kosolapoff

KAZANSKIY, B.A., akademik; LIBERMAN, A.L.; ALEKSANYAN, B.T.; STERIN, Kh.Ye.

Contact cyclization of isoöctane with the formation of a five-membered ring. Dokl.AN SSSR 95 no.2:281-284 Mr '54. (MLRA 7:3)

1. Institut organicheskoy khimii i Komissiya po spektroskopii Akademii nauk SSSR. (Cyclization) (Pentane)

ALEKSANYAN, V.T.; STERIN, Kh.Ye.; LIBERMAN, A.L.; MIKHAYLOVA, Ye.A.
PRYANISHNIKOVA, M.A.; KAZANSKIY, B.A.

Report no.8. Raman spectra of a few aromatic hydrocarbons.
Izv.AN SSSR.Ser.fiz.19 no.2:225-233 Mr-Ap '55. (MLRA 9:1)

1.Komissiya po spektroskopii i Institut organicheskoy khimii
imeni N.D.Zelinskogo Akademii nauk SSSR.
(Tartu--Spectrum analysis--Congresses)

LIBERMAN A.L.

USSR/Chemistry - Organic chemistry

Card 1/1 Pub. 22 - 24/51

Authors : Kazanskiy, B. A., Academician, and Liberman, A. L.

Title : About stereoisomeric 1-methyl-4-ethylcyclohexanes

Periodical : Dok. AN SSSR 101/5, 877-880, Apr 11, 1955

Abstract : The experimental synthesis of 1-methyl-4-ethylcyclohexane and the splitting of same into stereoisomers through accurate rectification are described. Measures were taken during each phase of the synthesis to obtain possibly pure intermediate substances even at the expense of reducing the total yield of the hexane. It was found that an increase in molecular weight of the stereoisomers was always followed by an approximation of their boiling points, indices of refraction and specific weights. The physico-chemical properties of stereoisomeric 1-methyl-4-ethylcyclohexanes are described. Eighteen references: 7 USSR, 6 USA, 2 English, 2 German and 1 French (1922-1954). Tables; graph.

Institution : Acad. of Sc., USSR, The N. D. Zelinskiy Inst. of Organ. Chem.

Submitted : December 27, 1954

[illegible]

LIBERMAN, A.L.; PRYANISHNIKOVA, M.A.; KAZANSKIY, B.A.

Physical properties of certain isodurol homologs. Izv. AN SSSR. Otd. khim.nauk no.8:1000-1005 Ag '56. (MLRA 9:10)

1. Institut organicheskoy khimii imeni N.D. Zelinskogo Akademii nauk SSSR.

(Benzene)

BAZHULIN, P.A.;SOKOLOVSKAYA, A.I.;BELIKOVA, N.A.;LIBERMAN, A.L.;PLATE, A.F.

Optical method in hydrocarbon research. Part 9. Raman spectra of certain naphthenes. Izv. AN SSSR. Otd khim.nauk no.9:1130-1134 S '56.
(MLRA 9:11)

1. Fizicheskiy institut imeni P.N. Lebedeva i Institut organicheskoy khimii imeni N.D.Zelinskogo Akademii nauk SSSR.
(Naphthenes--Spectra)

Synthesis of triethylcarbinol and 3-ethyl-2-pentene from ethylmagnesium bromide and carbon dioxide. [illegible] Liberman, T. V. Lapshin[illegible] [illegible] Chem., Acad. Sci. [illegible] Khim. 26, 46 [illegible] (Engl. translation).—EtMgBr [illegible] N, treated with CO_2 at below [illegible] H_2O, dil. H_2SO_4, and washed [illegible] $EtCO_2H$ and 30–42.5% Et_3COH [illegible] a dehydration during distn. [illegible] f.p. −12.65°, n_D^{20} 1.43534, n_D^{25} 1.4[illegible] 0.84511, cryoscopic const. 0.0114 [illegible] The best yield of Et_3COH formed when [illegible] CO_2 per mole of EtMgBr was used. The low boiling fraction contained Et_2CO and 3-ethyl-2-pentene which [illegible] sepd. on SiO_2 column using [illegible] pure alc. gave *3-ethyl-2-pentene* [illegible] 1.41488, n_D^{25} 1.41238, d_{25} 0.72[illegible] 36.5%.

- L - MHY, A.L

Auwers Skita rule and [illegible] 1,4-Diisopropylcyclohexanes [illegible] shina, and [illegible] Chem., Akad. [illegible] Nauk S.S.S.R. 107, 93-6 (1956). —Repeated fractiona[illegible] sulfonation and desulfonation of a sample of [illegible] propylbenzene gave pure [illegible] f.p. −17.1°, n_D^{20} 1.4[illegible] hydrogenated over Raney Ni at 190° yielding [illegible] hexane, b... 78.9°, f.p. [illegible] trans isomer, b... 80.4 [illegible] Passage of the cis isomer over [illegible] gave quite pure I, while the trans isomer under these conditions gave somewhat less pure I. Thus [illegible] low-boiling isomer had [illegible] refraction and f.p. The structure [illegible] was further confirmed by Raman [illegible] et al., C.A. 47, 12[illegible]

LIBERMAN, A. L.

d **Catalytic cyclization of n-propylbenzene into indan**. A. L. Liberman, O. V. Bragin, and B. A. Kazanskii (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.S.R.* 111, [illegible] Passage of 270 ml. PrPh [illegible] velocity 0.2 gave a catalyzate [illegible] of indan, confirmed by [illegible] tribromoindan.

LIBERMAN, A.L.

KAZANSKIY, B.A., akademik; LIBERMAN, A.L.; LUKINA, M.Yu.; GOSTUNSKAYA, I.V.

Catalytic conversion of hydrocarbons. Khim. nauka i prom. 2 no.2: 172-180 '57. (MIRA 10:6)

(Hydrocarbons)

LIBERMAN, A.L.

20-6-19/42

AUTHORS: Bragin, O. V., Broude, V. L., Zotova, S. V., Liberman, A. L. Pakhomova, O. S., and Pryanishnikova, M. A.

TITLE: Spectral Method of Determination of the Number and Position of Side Chains in the Molecules of Benzene Homologues (K voprosu o spektral'nom metode ustanovleniya chisla i polozheniya bokovykh tsepey v molekulakh gomologov benzola)

PERIODICAL: Doklady AN SSSR, 1957, Vol. 116, Nr 6, pp. 961 - 964 (USSR)

ABSTRACT: In an earlier work the second author and the fourth one have shown that the ultraviolet absorption spectra of crystals of benzene homologues at 77°K (= temperature of liquid nitrogen) may be used for the purpose mentioned in the title. The result may be obtained quickly and by a small quantity of substance (some hundreth grams). These spectra consist of series of narrow strips which are, in compounds with the same position of the side chains, of the same type, independent of the length and the ramification of these chains. If the spectra of these compounds which have a similar substitution type within the molecules are put together, such as the first absorption strips (corresponding to the pure-electronic transition) lie together, also the following will do the same. Therewith also the relative strip-intensities are reproduced. This phenomenon was proved on a great number of examples of the monoalkylbenzene-order,

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20-6-19/42

Spectral Method of Determination of the Number and Position of Side Chains in the Molecules of Benzene Homologues

as well as for some simplest o- and p-dialkylbenzenes. In the present work further informations on the affirmation of the regularity mentioned are quoted. The physical characters of the hydrocarbons investigated are concentrated in table 1. It has been pointed out that the same spectrum type with the growing side chain length will be preserved. (1, 2, 4-trialkylbenzene - figure 1 A). The correspondence of the spectra of p-di-isopropylbenzene and p-xylene confirms the fact that the state branched out of both chains does not influence the position of the absorption bands. This analogy also is retained for the case that a double-binding, which is not conjugated with the benzene nucleus, is introduced into a side chain. (Comparison of ethyl- and propyl-mesitylenes with allyl-mesitylenes - figure 1 B). Quite another picture will be at an immediate conjugation of the double-binding with the benzene nucleus. So, the absorption spectrum of the 2-methyl--phenylpropene-1 also is interrupted in the temperature of the nitrogen. Here the absorption intensity is much higher, than in the case of all the other investigated substances. In spite of a same symmetry of the spectra of alkyl- and alkylene-mesitylenes (figure 1 B) and of monoalkylbenzenes (figure 1 G) an essentially dif-

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20-6-19/42

Spectral Method of Determination of the Number and Position of Side Chains in the Molecules of Benzene Homologues

ferent construction of the spectra renders possible the spectral identification of the molecules of these substances. Table 2 gives the strip frequency of the pure-electronic transitions within the investigated spectra. All the hydrocarbons investigated have been produced as high-pure compounds at the above mentioned purpose and their purity has been proved. There follows an experimental part with the usual data. There are 1 figure, 2 tables, and 3 Slavic references.

ASSOCIATION:	Institute for Physics AN Ukrainian SSR , Institute for Organic Chemistry imeni N. D. Zelinskiy AN USSR (Institut fiziki Akademii nauk USSR, Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR)
PRESENTED:	May 24, 1957, by B. A. Kazanskiy, Akademician
SUBMITTED:	May 24, 1957
AVAILABLE:	Library of Congress

Card 3/3

20-3-20/52

AUTHORS: Liberman, A. L. , Vasina, T. V., and Kazanskiy, B. A., Academician

TITLE: Cyclization of 3-Ethylpentane to Ethylcyclopentane (Tsiklizatsiya 3-etilpentana v etiltsiklopentan)

PERIODICAL: Doklady AN SSSR, 1957, Vol. 117, Nr 3, pp. 430 - 432 (USSR)

ABSTRACT: From works (references 1, 2, 3) recently published by the authors it became known that the paraffinic hydrocarbons may be cyclized in presence of platinum during the formation of a 5-membered ring. The direct possibility of formation of cyclopentanes from paraffins was reliably proved. For the purpose of comparison the authors intended to investigate another hydrocarbon, which was not so much branched out as isooctane, and the cyclization product of which, however, should have a boiling point suffidently distant from the initial hydrocarbon. By means of that the individual isolation of the cyclization product should be rendered possible. For that purpose 3-ethylpentane was chosen, having only one side chain and yielding to an unique reaction product by cyclization: Ethylcyclopentane. Because the difference of the boiling points amounts to 10°, the separation of both substances does not show any difficulty. The initial substance was filtered through the catalyst hap-

Card 1/2

Cyclization of 3-Ethylpentane to Ethylcyclopentane 20-3-20/52

pening but once at 310° and at a volume velocity of 0,19 - 0,22 per hour. The analysis of the 5 parts of the "catalyzate" showed a content of from 1,2 - 1,9 % of olefins and 0,4 - 0,7 % of aromatic hydrocarbons. After removing of these reaction products by means of the chromatography, the ethylcyclopentane content (12,5 - 5,7 %) decreasing from experiment to experiment, could be stated according to the constants in the "catalyzate". By means of the fractionation of the connected, desaromatized 2 "catalyzate" parts the individual ethylcyclopentane could be isolated (the fractionating curve figure 1). The constants of the fraction V of this fractionating practically do not differ from the constants of the ethylcyclopentane. Follows an experimental part with usual data. There are 1 figure, 2 tables, and 5 references, 4 of which are Slavic.

ASSOCIATION: Institute for Organic Chemistry imeni N. D. Zelinskiy AN USSR (Institut organicheskoy khimii im. N. L. Zelinskogo Akademii nauk SSSR)

SUBMITTED: July 13, 1957

AVAILABLE: Library of Congress

Card 2/2

SOV/51-5-2-3/26

AUTHORS: Broude, V.L., Izrailevich, Ye.A., Liberman, A.L., Onopriyenko, M.I., Pakhomova, O.S., Prikhot'ko, A.F., and Shatenshteyn, A.I.

TITLE: On Electron Spectra of Aromatic Hydrocarbons and their Deuterated Derivatives at 20°K (Ob elektronnykh spektrakh aromaticheskikh uglevodorodov i ikh deyterirovannykh proizvodnykh pri 20°K)

PERIODICAL: Optika i Spektroskopiya, 1958, Vol 5, Nr 2, pp 113-122 (USSR)

ABSTRACT: The present paper is the first of a series on the ultraviolet absorption spectra of deuterated compounds and the changes in the molecular and crystal structure produced by deuteration. To obtain the hyperfine structure and to observe the small isotopic shifts measurements were made at 20°K. The work reported here is also an extension of the application of the deuteration methods based on the isotopic exchange of hydrogen with liquid deuterium bromide or with a solution of KND_2 in liquid ND_3 (Refs 4-10). The results are given in Table 1 which shows that using such methods all atoms of hydrogen in diphenyl, naphthalene, toluene, n-xylene, durene, penta- and hexamethylbenzene may be replaced by deuterium. The preparation followed the method described in Ref 10, which gives the method of

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SOV/51-5-2-6/26

On Electron Spectra of Aromatic Hydrocarbons and their Deuterated Derivatives at 20°K

calculation of the number of replaced hydrogen atoms n in a hydrocarbon molecule. The last column of Table 1 shows that the number n differs only a little from the total number of hydrogen atoms in the hydrocarbon molecule in question. The following hydrocarbons were deuterated: benzene, toluene, m-xylene, n-xylene, mesitylene, durene, hexamethylbenzene, naphthalene, phenanthrene, diphenyl. The constants, such as the boiling point and refractive index, of the original and deuterated substances are given in Table 2. Using polarized light the authors obtained the electron spectra of the crystals listed in Table 2 (both in deuterated and non-deuterated forms). Measurements were made at 20°K and the results are shown in Figs 1-7. The spectral changes produced by deuteration are due, firstly to changes in the energy states of molecules, and secondly to changes in the crystal structure. The first produce spectral shifts towards the short wavelengths by some 100-200 cm^{-1} and a decrease of frequencies of the molecular vibrations by a factor of 1.04-1.15. The crystal structure changes show up in the polarization ratios for the absorption bands and in the change of spacing between strongly polarized bands. A.L. Liberman (Institute of Organic Chemistry, Academy of Sciences of the U.S.S.R.) prepared pure benzene and alkylbenzenes. A.I. Shatenshteyn and Ye.A. Izrailevich

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SOV/51-5-2-3/26

On Electron Spectra of Aromatic Hydrocarbons and their Deuterated Derivatives at 20°K

(Physico-Chemical Institute imeni Karpov) prepared deuterated compounds. V.L. Broude, M.I. Onopriyenko, O.S. Pakhomova and A.F. Prikhot'ko (Institute of Physics, Academy of Science of the Ukrainian S.S.R.) obtained and interpreted the electron spectra. The authors thank Yu. Antonchik for density measurements of the deuterated hydrocarbons and P. Manochkina for help in deuteration of the hydrocarbons. There are 7 figures, 2 tables and 16 references, 14 of which are Soviet, 1 American and 1 English.

ASSOCIATION: Institut fiziki AN UkrSSR; Fiziko-khimicheskiy institut im. Karpova (Institute of Physics, Academy of Sciences of the Ukrainian S.S.R.; Physico-Chemical Institute imeni Karpov)

SUBMITTED: July 16, 1957

Card 3/3

1. Hydrocarbons-d--Spectrographic analysis 2. Ultraviolet spectrum --Applications

AUTHORS: Liberman, A. L., Kuznetsova, I. M., 20-118-5-26/59
Tyun'kina, N. I., Kazanskiy, B. A.,
Member of the Academy.

TITLE: Stereoisomeric 1-Methyl-2-Alkylcyclohexanes (Stereoizomernyye 1-metil-2-alkiltsiklogeksany)

PERIODICAL: Doklady Akademii Nauk SSSR, 1958, Vol. 118, Nr 5, pp. 942-945 (USSR)

ABSTRACT: Data on dialkylcyclohexanes of this kind are rarely found in publications (references 1 - 6). For this reason their investigation is interesting in spite of great experimental difficulties. Certain surprising facts are found: the cis-isomer of 1,4,-di-isopropylcyclohexane boils at a lower temperature than the trans-isomer (reference 5) though according to the rule of Auvers Skit the contrary would have been expected. The reason of this peculiar inversion of the boiling points remains unexplained and still waits for investigation. In order to find out whether such exceptions are found in the series of other dialkylcyclane hydrocarbons, for example among the 1,2-dialkylcyclo-

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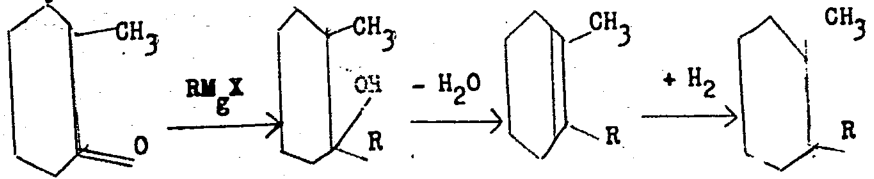
hexanes, the authors synthesized some 1-methyl-2-n-alkylcyclohexanes, and separated them according to the stereoisomers. The syntheses were conducted according to a uniform procedure:



with R representing n-propyl, n-hexane, and n-heptyl. According to the results of the fractional distillation all stereoisomers were obtained in a highly pure form. It was proved that the constants of all hydrocarbons thus produced agree with the Auvers-Skit rule. 1-methyl-2-n-hexylcyclohexane and 1-methyl-2-n-heptylcyclohexane have as yet not been mentioned in publications, whereas 1-methyl-2-n-propylcyclohexane was obtained previously as a mixture of stereoisomers (reference 7) only, and not separated further by the mentioned authors. In the experimental part 7 compounds of the respective group are specified, among them one chloride and two bromides, as well as the usual data, are given.

There are 2 figures, 3 tables, and 11 references, 4 of which are Soviet.

SOV/20-120-4-28/67

AUTHORS: Liberman, A. L., Loza, G. V., Chang Ming-nan , Kazanskiy, B. A., ~~Member,~~ Academy of Sciences, USSR

TITLE: Catalytic Cyclisation of n-Pentane and n-Hexane Under Formation of a Five-Membered Ring (Kataliticheskaya tsiklizatsiva n-pentana i n-geksana s obrazovaniyem pyatichlennogo tsikla)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 120, Nr 4, pp. 789-792 (USSR)

ABSTRACT: In several papers the authors proved that paraffin hydrocarbons can easily be cyclisated into cyclopentane homologues in the presence of platinised coal (Refs 1 - 5). The yields in cyclopentanes depend to a great extent on the structure of the initial substances. n-pentane is particularly interesting since its behavior is quite different from that of all its investigated homologues whereas n-hexane can be cyclisated like n-octane. From the point of view of thermodynamical experience n-pentane is an exception (content 30 - 34 % instead of only 8 % in a thermodynamical system of equilibrium of n-pentane - cyclopentane at 500°K). At 310° n-pentane remains unchanged on a

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SOV/20-120-4-28/67

Catalytic Cyclisation of n-Pentane and n-Hexane Under Formation of a Five-Membered Ring

freshly prepared catalyst. The reaction sets in at 350°, however, still in a small yield. The reaction was carried on tentatively for several days. Strangely in the top fraction of the fractionation 25 - 30 % isopentane (1,7 % of the entire catalysate) was determined. Hitherto reliable proofs for the isomerisation of paraffin hydrocarbons on platinum-plated coal have been lacking. The authors criticize the frequently mentioned paper by Yu. K. Yur'yev and P. Ya. Pavlov (Ref 6) since they believe that the isoparaffins of those 2 authors were secondary products. As far as in hydrogenolysis of cyclopentane only n-pentane can be formed the occurrence of isopentane in the catalysate is due to a direct isomerisation. There are 4 tables and 9 references, 8 of which are Soviet.

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

Card 2/3

Card 3/3

5(3) SOV/20-122-6-19/49

AUTHORS: Kazanskiy, B. A., Academician, Liberman, A. L., Tyun'kina, N. I., Kuznetsova, I. M.

TITLE: On the Limited Applicability of the Auwers-Skita Rule in Stereoisomeric Dialkyl Cyclanes (Ob ogranichennoy primenimosti pravila Auversa-Skita k stereoizomernym dialkiltsiklanam)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 122, Nr 6, pp 1025-1028 (USSR)

ABSTRACT: In recent years it was repeatedly noticed that the rule mentioned in the title cannot be applied to 1,3-dialkyl cyclopentanes and 1,3-dialkyl cyclohexanes. In these latter series the interrelation of the properties of cis-and trans--isomers is reversed. By the example of the stereoisomeric 1,3-dimethyl cyclopentanes and 1,3-dimethyl cyclohexanes this statement was confirmed by thermodynamic data as well as by synthesis. Recently the authors have observed such a case in which a peculiar deviation from the same rule took place (Ref 1) in the 1,4-dialkyl cyclohexane series. In this series the applicability of the rule under consideration was denied by nobody. It became evident that in the case of the

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stereoisomeric 1,4-diisopropyl cyclohexanes the specific weight and the refractive index are higher, the molecular refraction, however, and the melting temperature of the isomer boiling at a lower temperature are lower; the spectroscopic data have shown that the latter isomer is a cis-form. So in this case not the trans- but the cis-form has a lower boiling-point - contrary to the rule mentioned. The observations so far collected make it possible to approach the problem of the relations between the configuration and the physical constants by a new method; the applicability of the rule mentioned is not only restricted by the arrangement of the side chains in the dialkyl-cyclane molecule, but also by the atomic number of carbon in the latter. The authors believe that the deviation described above is a regular phenomenon. The reflections mentioned make it possible to conclude that stereoisomeric 1,4-dialkyl cyclohexanes with 12 or a few more carbon atoms in the molecule must, similar to 1,4-diisopropyl cyclohexane, deviate from the rule under consideration. Thus the Auwers-Skita rule is only applicable to the first members of the series of the 1,4-dialkyl cyclohexanes. By studying own data and those mentioned in publications on boiling temperatures of the stereoisomeric dialkyl cyclanes it can be concluded that the linear character of the dependence between the differences in boiling temperature of the stereoisomers and the atomic number of carbon in the molecule is not confined to the 1,4-dimethyl cyclohexane series, but applies also for the 1,2-dialkyl cyclopentanes (Table 2 and line A of Fig 1). In the stereoisomeric 1,2-dialkyl cyclanes discussed here the boiling temperatures of the trans-form increase more rapidly with increasing molecular weight than in the cis-forms. In these cases, however, the Auwers-Skita rule must have a somewhat wider range of applicability than for 1,4-dialkyl cyclohexanes. There are 1 figure, 3 ables, and 10 references, 5 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)

LIBERMAN, A. L., KAZANSKIY, B. A.

"Catalytic Dehydrocyclization of Paraffinic Hydrocarbons."

Report submitted at the Fifth World Petroleum Congress, 30 May - 5 June 1959. New York.

LIBERMAN, A.L.

21(0),24(0) PHASE I BOOK EXPLOITATIO! SOV/32.?

Akademiya nauk SSSR. Fizicheskiy institut

Issledovaniya po eksperimental'noy i teoreticheskoy fizike; [sbornik] (Studies on Experimental and Theoretical Physics; Collection of Articles) Moscow, Izd-vo AN SSSR, 1959. 304 p. Errata slip inserted. 2,300 copies printed.

Ed.: I. L. Fabelinskiy, Doctor of Physical and Mathematical Sciences; Eds. of Publishing House: A. L. Chernyak and V. G. Berkgaut; Tech. Ed.: Yu. V. Rylina; Commission for Publishing the Collection in Memory of Grigoriya Samuilovich Landsberg: I. Ye. Tamm (Chairman), Academician; M. A. Leontovich, Academician; P. A. Bazhulin, Doctor of Physical and Mathematical Sciences; S. L. Mandel'shtam, Doctor of Physical and Mathematical Sciences; I. L. Fabelinskiy, Doctor of Physical and Mathematical Sciences; F. S. Landsberg-Baryshanskaya, Candidate of Physical and Mathematical Sciences; and G. P. Motulevich (Secretary), Candidate of Physical and Mathematical Sciences.

PURPOSE: This book is intended for physicists and researchers engaged in the study of electromagnetic radiations and their role in investigating the structure and composition of materials.

COVERAGE: The collection contains 30 articles which review investigations in spectroscopy, sonics, molecular optics, semiconductor physics, nuclear physics, and other branches of physics. The introductory chapter gives a biographical profile of G. S. Landsberg, Professor and Head of the Department of Optics of the Division of Physical Technology at Moscow University, and reviews his work in Rayleigh scattering, combat gases, spectral analysis of metals, etc. No personalities are mentioned. References accompany each article.

30

LANDSBERG, Grigoriy Samuilovich, akademik [deceased]; KAZANSKIY, Boris Aleksandrovich, akademik; BAZHULIN, P.A., doktor fiziko-matemat. nauk; BULANOVA, T.F.; LIBERMAN, A.L., MIKHAYLOVA, Ye.A.; PLATE, A.F.; STERIN, Kh.Ue.; SUSHCHINSKIY, M.M.; TARASOVA, G.A.; UKHOLIN, S.A.; BRUSOV, I.I., red.izd-va; KASHINA, P.S., tekhn.red.

[Determination of the individual hydrocarbon composition of straight-run gasolines by the combined method] Opredelenie individual'nogo uglevodorodnogo sostava benzinov priamoi gonki kombinirovannym metodom. Moskva, Izd-vo Akad.nauk SSSR, 1959. 362 p. (MIRA 12:8)

(Gasoline)

LIBERMAN, A. L.(IOKh AS USSR)

A. L. Liberman, and B. A. Kazanskiy, "On the Connection Between the Configurations of Dialkyl Cyclanes and Their Physical Properties."

report presented at the Symposium on Concepts of Conformation in Organic Chemistry which took place in Moscow at the IOKh AN SSSR (Institute of Organic Chemistry, AS USSR) from September 30 to October 2, 1958.

Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1959, No. 3, 561-564

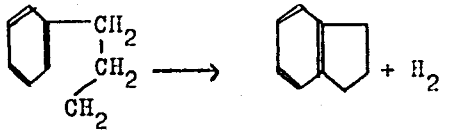
5 (3)

AUTHORS: Liberman, A. L., Bragin, O. V., Kazanskiy, B. A. SOV/62-59-5-17/40

TITLE: Catalytic Cyclization of Some Alkylbenzenes Into Indan and Its Homologues (Kataliticheskaya tsiklizatsiya nekotorykh alkilbenzolov v indan i yego gomologi)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk; 1959, Nr 5, pp 879-887 (USSR)

ABSTRACT: The authors showed in a number of works (Ref 1) that paraffin hydrocarbons cyclize into homologues of cyclopentane by the effect of platinized coal at moderate temperatures (310°) and a throughput rate of 0.2/hr. The cyclization is explained by intermolecular dehydrocondensation. In connection with it, the possibility was considered of cyclizing more complicated compounds, e.g. a secondary chain of a benzene homologue according to the scheme:



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Catalytic Cyclization of Some Alkylbenzenes Into Indan and Its Homologues SOV/62-59-5-17/40

Some data on a similar cyclization are quoted from publications: Orchin (Ref 2), patent date (Ref 3), Zelinskiy and Tits (Ref 4) etc. Table 1 shows a comparison of the constants of the initial products and the cyclized compounds with the corresponding data from publications. The conditions of synthesis were equal to those of the cyclization of paraffins. Indan and 1- and 2-methylindan were obtained from n-butyl-, secondary butyl- and isobutyl benzene. Methylindan was brominated and the compounds 4,5,6,7-tetrabromo-2-methylindan and 2,4,5,6,7-pentabromo-1-methylindan not yet described in the literature were synthesized. The synthesis of the individual compounds is described in the experimental part. The R. and **W. Meyer** method was used in the bromination of tribromoindan (Ref 17). The properties and yield of the various cyclized compounds are summarized in tables 2,3,4,5, 6, and 7. There are 1 figure, 7 tables, and 18 references, 9 of which are Soviet.

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Catalytic Cyclization of Some Alkylbenzenes Into Indan and Its Homologues SOV/62-59-5-17/40

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 30, 1957

Card 3/3

5 (3)

AUTHORS: Kazanskiy, B. A., Liberman, A. L., Loza, G. V., Kuznetsova, I. M., Aleksanyan, V. T., Sterin, Kh. Ye.

SOV/62-59-6-19/36

TITLE: Catalytic Cyclization of n-Octane With Formation of the Homologs of the Cyclopentane (Kataliticheskaya tsiklizatsiya n. oktana s obrazovaniyem gomologov tsiklopentana)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 6, pp 1071 - 1078 (USSR)

ABSTRACT: By the action of a platinum catalyst n-octane forms the cyclic compounds: 1-methyl-2-ethylcyclopentane and n-propylcyclopentane. The present investigation dealt with the cyclization process and the spatial structure of the compounds produced by cyclization. For the purpose of this cyclization n-octane was for five hours passed through platinated coal with a passage rate of 0.2/hour at 310°. Two samples of the catalyst were used in parallel. In contrast to ramificated isomers cyclization of n-octane is fairly difficult. The yield on both catalysts was only 2.2 and 4.5%, respectively. The cyclic product could be enriched by distilling the catalysate. An investigation by means of the Raman spectrum showed that there was trans-1-methyl-2-

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Catalytic Cyclization of n-Octane With Formation of the Homologs of the Cyclopentane SOV/62-59-6-19/36

ethylcyclopentene in the lower boiling fraction, and n-propylcyclopentene in the residue. The cis-form of the first mentioned compound could not be discovered. Apart from the compounds mentioned, there were still small quantities of 4-methylheptane to be observed. Furthermore, a line (762 cm^{-1}) was discovered, which was assigned to the pentalane bicyclo-[0,3,3]-octane. This could, however, not yet be proved owing to the difficulties that arise in the production of the pentalane. Since the Raman spectra of the two cyclic compounds obtained are yet hardly known, the single compounds were synthetized in pure form and plotted separately. The synthesis was carried out according to a method which was worked out in the institute mentioned in the Association, with the only difference that instead of aluminum oxide, silica gel was used for isomerisation. In the experimental part the production of the different substances is described in detail. The properties of and the yield in catalysates, obtained from n-octane, are compiled in table 1. Table 2 gives the data concerning the substances produced by distillation. When analyzing the catalysates, distillates,

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Catalytic Cyclization of n-Octane With Formation of the Homologs of the Cyclopentane SOV/62-59-6-19/36

and residues from n-octane it is shown that about the same portions are obtained for both compounds. There are 2 tables and 12 references, 10 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR i Komissiya po spektroskopii Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR, and Committee for Spectroscopy of the Academy of Sciences, USSR)

SUBMITTED: August 15, 1957

Card 3/3

LIBERMAN, A.L.

5 (4)

AUTHORS: Kazanskiy, B. A., Landsberg, G. S. (Deceased), SOV/62-59-9-15/40
Aleksanyan, V. T., Bulanova, T. A., Liberman, A. L., Mikhaylova, Ye. A., Plate, A. F., Sterin, Kh. Ye., Ukholin, S. A.

TITLE: Investigation of the Composition of the Fraction With a Boiling Point Between 150 and 250° of the Emba Crude Petroleum

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 9, pp 1612 - 1622 (USSR)

ABSTRACT: An attempt is being made to apply the combined investigation method for benzines (Ref 1) to the investigation of the petroleum fraction with a boiling point between 150 and 250° of the Emba crude petroleum. The petroleum investigated came from the Koschagylskoye deposit. It was proved that this fraction contains 12.6% of aromatic and 13.0% of hexahydroaromatic hydrocarbons. In the aromatic fraction 29 different hydrocarbons were identified. The quantitative division in groups of the aromatic hydrocarbons boiling in this range was carried out with characterisation of the arrangement of the side-chains on the benzene ring or the corresponding cyclohexane ring and that for the multicyclic according to the arrangement of the rings. By this method

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the authors succeeded in establishing the composition of the aromatic compounds up to 70% and that of the hydroaromatic compounds up to 46%. In the paraffin-naphthene part of the fraction the presence of naphthene with two different substituents in the same carbon atom of the cyclohexane could be established (mixed substitution). The limiting into narrower fractions was possible at the paraffin-naphthenes by investigating the specific gravities, the refractive index and the aniline point of these fractions. In figures 1 and 2 the paraffin-naphthene fractions are identified and tables 1-6 contain the results of the analysis. Table 7 gives the results of the distillation of the paraffin-cyclopentane fraction of the Ligroin applying the coefficient proposed by P. S. Maslov (Ref 11). There are 2 figures, 7 tables, and 11 references, 10 of which are Soviet.

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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). Komissiya po spektroskopii Akademii nauk SSSR (Committee of Spectroscopy of the Academy of Sciences, USSR)

SUBMITTED: January 4, 1958

Card 3/3

~~5(3)~~ 5.3300 66420

AUTHORS: Kazanskiy, B. A., Academician, SOV/20-128-6-25/63
Liberman, A. L., Loza, G. V., Vasina, T. V.

TITLE: Parallel Formation of Five- and Six-membered Cycles of Paraffins (C_5- and C_6-Dehydrocyclization) on Platinized Charcoal

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 6, pp 1188 - 1191 (USSR)

ABSTRACT: Three different possibilities of cyclization of paraffins have become known: a) Dehydrocyclization with a direct formation of aromatic hydrocarbons (B. A. Kazanskiy and A. F. Plate, Ref 1); b) conversion into a corresponding cyclohexane hydrocarbon; c) aromatization of the compound formed as under b). Since 1954 (Refs 5,6) it has been known that besides aromatic hydrocarbons also the corresponding cyclopentane homologs are formed on platinized charcoal from n-heptane and n-octane. They were particularly formed from branched paraffins with 5 C-atoms in the principal chain (Refs 7-9). The formation mechanism had to be more complicated here: either an isomerization with formation of a longer chain had taken place before, or the aromatization mentioned under c) had occurred. The former assumption is little

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probable, the case c), however, is confirmed by experiment. Thus, one cyclopentane hydrocarbon (Ref 8) - 1,1,3-trimethyl cyclopentane - and 3 aromatic hydrocarbons - m- and p-xylene, and toluene - are formed from the isooctane (see Diagram). The assumption saying that aromatic hydrocarbons are formed by the extension of a five-membered ring is further confirmed by a similar conversion of the 2,2,3-trimethyl pentane. As was expected, there was almost no p-xylene in this case. As there were no publications on direct proofs of such a ring extension in the said simple systems and under mild conditions, the authors carried out a direct experiment with 1,1,3-trimethyl cyclopentane without carrier gas. Here, the same aromatic substances were formed as from isooctane, though in a slightly different proportion. The parallel experiments carried out here with 1,1,3-trimethyl cyclopentane and n-propyl cyclopentane yielded more aromatic substances from the former. This confirms the assumption that the ring is mainly extended at the expense of the geminal methyl groups. Moreover, it was assumed (Refs 13, 14) that aromatic hydrocarbons may develop from paraffins with

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Parallel Formation of Five- and Six-membered Cycles of Paraffins (C_5- and C_6-Dehydrocyclization) on Platinized Charcoal

SOV/20-128-6-25/63

6 and more C-atoms in a straight chain via intermediate products with a 5-membered ring. But this has never been confirmed. The experiment with 2,5-dimethyl hexane delivered 95% p-xylene and 5% m-xylene. Thus, the majority of the aromatic substances developed, in this case, by a direct closing of the paraffin chain to a 6-membered cycle without an intermediate stage of the cyclopentane hydrocarbon. On the strength of this, the authors state that here 2 independent parallel cyclization reactions of paraffins are possible. They designate them as mentioned in the title (in parentheses). There are 16 references, 14 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: July 8, 1959

Card 3/3

5.3300

78069
SOV/62-60-1-15/37

AUTHORS: Aleksanyan, V. T., Sterin, Kh. Ye., Liberman, A. L., Lukina, M. Yu., Tayts, G. S., Tarasova, G. A., Terent'eva, Ye. M.

TITLE: Investigation of Hydrocarbons by Optical Method. XII. Raman Spectra of Some Hydrocarbons of Various Series

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, Nr 1, pp 84-89 (USSR)

ABSTRACT: The Raman spectra of the following hydrocarbons were studied: n-dodecane; 5,5-dimethylundecane; 1,1,2-trimethylcyclopropane; sec-butylcyclopentane, 2-cyclopentyloctane, n-propylcyclohexane, 1-methyl-2-ethylcyclohex-1-ene. Combination of the chemical and spectroscopic data confirm that 1,2-dialkylcyclohexan-1-ol on dehydration yields 1,2-dialkylcyclohexenes with double bond predominantly in position (I).

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Investigation of Hydrocarbons by
Optical Method. XII

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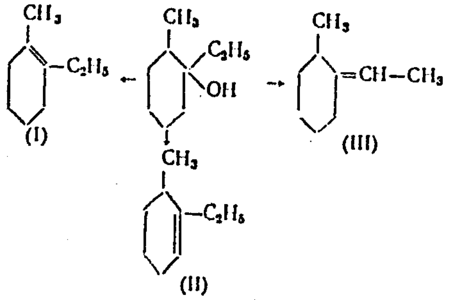
SOV/62-60-1-15/37



There are 26 references, 16 Soviet, 6 U.S., 4 German. The 5 most recent U.S. references are: Mosher, W. A., J. Am. Chem. Soc., 62, 552 (1940); Fenske, M. R., Anal. Chem., 19, 700 (1947); Signaigo, F. K., Cramer, P. L., J. Am. Chem. Soc., 55, 3326 (1933); Foehr, F. G., Fenske, M. R., Industr. and Engng. Chem., 41, 1956 (1949); Kelso, R. G., Greenlee, K. W., Derfer, J. M., Boord, C. E., J. Am. Chem. Soc., 74, 287 (1952).

Card 2/3

Investigation of Hydrocarbons by Optical Method. XII

78069
SOV/62-60-1-15/37

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: May 30, 1958

Card 3/3

LIBERMAN, A.L.; VASINA, T.V.; KAZANSKIY, B.A.

Stereospecificity of the interaction between esters of stereoisomeric 1,4-cyclohexanedicarboxylic acids and a Grignard reagent. Zhur. ob. khim. 30 no.12:3938-3945 D '60. (MIRA 13:12)

1. Institut organicheskoy khimii Akademii nauk SSSR.
(Cyclohexanedicarboxylic acid)
(Grignard reagents)

80060

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5.3100

S/020/60/132/01/34/064
B011/B126

AUTHORS: Liberman, A. L., Vasina, T. V., Kazanskiy, B. A., Academician

TITLE: The Steric Configuration of Stereoisomeric 1,4-Diisopropylcyclohexanes

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 1, pp. 130-133

TEXT: The authors encountered a peculiar deviation from the Auvers-Skit rule, in that the cis-forms of the di-substituted cyclanes have a higher boiling point than the trans-forms. Since several facts of this sort exist, the authors have decided to confirm the said rule in respect of synthetically produced 1,4-diisopropyl-cyclohexanes. By that means the spectroscopic proofs were to be completed. The initial substances used were dimethyl esters of cis- and trans-hexahydroterephthalic acids, whose steric configuration (as of the acids themselves) stands beyond question (Refs. 7, 8). Each of the stereoisomers was to be separately changed into the relevant form of 1,4-diisopropyl-cyclohexane (see scheme). This synthesis succeeded at first in the stereo-specific form only for the trans-forms. The syntheses and properties of the newly obtained stereoisomeric diols, the transdichloride and some other substances are not given in

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The Steric Configuration of Stereoisomeric 1,4-Diisopropylcyclohexanes

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B011/B126

detail here. A detailed publication follows. The original dimethyl-esters of cis- and trans-cyclohexane-1,4-dicarboxylic acids were separated by distillation, and showed the above-mentioned deviation from the Auvers-Skit rule. 1,4-Bis-(α-oxyisopropyl)-cyclohexanes were obtained by reaction of the esters of stereoisomeric acids with the great surplus of methyl-magnesium-chloride or methyl-magnesium-bromide. The appropriate dichlorides were produced by saturation of the diols with anhydrous HCl in a methanolic solution. The trans-isomer was obtained in pure state, while a mixture of inseparable cis- and trans-dichlorides came from the cis-diol. It was very difficult to substitute hydrogen for chlorine. The familiar methods have failed here. The authors have succeeded in finding a suitable solvent, namely ethylacetate. It contains not only dichloride and $CrCl_2$, but also $CrCl_3$ in fairly soluble form. $CrCl_2$ forms directly from the latter in the ethylacetate solution. The required reaction could thus be carried out at room temperature. Table 1 shows the constants of the trans-1,4-diisopropylcyclohexane that was produced. They show that the configurations of the stereoisomers that were determined earlier (Ref. 1), on the basis of the Raman spectra, were right. A certain deviation of the constants of the synthetic preparation from that of the high-purity product separated by distillation (Ref. 1), is explained through the presence of a small admixture of the cis-isomer in the

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KAZANSKIY, B.A., akademik; LIBERMAN, A.L.; KUZNETSOVA, I.M.;
ALEKSANYAN, V.T.; STERIN, Kh.Ye.; LOZA, G.V.

C_5-Dehydrocyclization of alkyl cyclopentanes into bicyclic hydrocarbons. Dokl.AN SSSR 133 no.2:364-366 Jl '60. (MIRA 13:7)

1. Institut organicheskoy khimii im. N.D.Zelinskogo Akademii nauk SSSR i Komissiya po spektroskopii Akademii nauk SSSR.
(Cyclopentane) (Cyclization)

KAZANSKIY, B.A., akademik; LIBERMAN, A.L.; TYUN'KINA, N.I.

Deviation of stereoisomeric 1,4-bis-tert. butylcyclohexanes from the Auwers-Skita rule. Dokl. AN SSSR 134 no.1:93-95 S '60.
(MIRA 13:8)

1. Institut organicheskoy khimii im. N.D. Zelinskogo Akademii nauk SSSR.
(Cyclohexane)

S/020/60/134/003/012/020
B016/B054

AUTHORS: Liberman, A. L., Tyun'kina, N. I., and Kazanskiy, B. A., Academician

TITLE: The Stereoisomeric 1,4-Di-n-Propyl- and 1-Methyl-4^2-metho-4-butyl Cyclohexanes

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 134, No. 3, pp. 603-606

TEXT: After having proved (Refs. 1-3) that the physical properties of some 1,4-dialkyl cyclohexanes deviate from the constants usually holding for this series, the authors expressed the opinion that the differences between the boiling points of the stereoisomers ($\Delta t = t_{cis} - t_{trans}$) are linearly dependent on the molecular weight (Ref. 4). There were, however, several deviations from this rule. This is explained by the fact that the structure of the side chain was not considered. The present paper is to clarify the influence of this structure. For this purpose, the authors synthesized 1,4-di-n-propyl- and 1-methyl-4^2-metho-4-butyl cyclohexanes, and separated them into cis- and trans-isomers. These two compounds are

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The Stereoisomeric 1,4-Di-n-Propyl- and
1-Methyl-4^2-metho-4-butyl Cyclohexanes

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B016/B054

structural isomers of 1,4-di-isopropyl cyclohexane, in whose stereoisomers there occurs an inversion of boiling points. The hydrocarbons were chosen in such a way that in one case their side chains were equal, while being different in another. This should make it clear in how far the asymmetry of radicals can influence the value Δt. It was found that the trans-form of the stereoisomers produced in this investigation boils lower than the cis-form, i.e., Δt has a positive value, whereas the value of 1,4-di-isopropyl cyclohexanes was negative (Refs. 1,4). Thus, the primary, secondary, or tertiary character of the side chain considerably influences the relation of boiling points of the stereoisomeric dialkyl cyclohexanes. The problem of a linear dependence in the series of 1,4-dialkyl cyclohexanes with primary radicals remains unsolved. The authors synthesized the hydrocarbons in such a way that products of maximum possible purity were formed. The hydrogen addition to the double bond of the resulting intermediate product, butenyl toluene, is (in the presence of platinum at room temperature) accompanied by partial hydrogenation of the benzene ring. Nevertheless, it was possible to obtain the hitherto unknown 4^2-metho-4-butyl toluene by distillation in the pure state. Further. 4^2-oxy-4^2-metho-4-butyl toluene was produced for the first time. The

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The Stereoisomeric 1,4-Di-n-Propyl- and
1-Methyl-4^2-metho-4-butyl Cyclohexanes

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B016/B054

configuration, hitherto not described in publications, of the four stereoisomers was determined with the aid of the Raman spectra (taken by V. T. Aleksanyan and Kh. Ye. Sterin, co-workers of the Komissiya po spektroskopii (Commission on Spectroscopy) OFMN AN SSSR (Department of Physical and Mathematical Sciences of the Academy of Sciences, USSR)). Table 1 shows that both the refractive indices and the specific gravities are in all cases higher in the cis-forms, whereas the boiling points of the cis-forms are higher or lower depending on the structure of the side chains. Fig. 1 shows refractive index and specific gravity of the fractions of the hydrocarbons investigated. There are 1 figure, 1 table, and 10 references: 8 Soviet and 2 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: June 6, 1960

Card 3/3

S/020/60/135/002/020/036
B016/B052

AUTHORS: Kazanskiy, B. A., Academician, Khromov, S. I., Liberman, A. L., Balenkova, Ye. S., Vasina, T. V., Aleksanyan, V. T., and Sterin, Kh. Ye.

TITLE: Contact Transformations of Cyclodecane in the Presence of Platinized Charcoal

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 135, No. 2, pp. 327 - 330

TEXT: The authors studied the following problem: Hitherto (Refs.1,2) it has been stated that cyclodecane on platinized charcoal is directly transformed into azulene. In connection with the C_5 dehydrocyclization (Ref.4) which has been discovered in the meantime, the question arose whether the formation of azulene is a secondary process, while decahydroazulene is formed in the main reaction (transannular C_5 dehydrocyclization) and yields azulene by dehydrogenation. To prove this reaction, cyclodecane was catalyzed on platinized charcoal (5 and 20% Pt)

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Contact Transformations of Cyclodecane in the Presence of Platinized Charcoal

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B016/B052

at 300 and 310°C and without tear gas. It was shown that the major part of cyclodecane is transformed. After rectification, the catalyzates were chromatographed on silica gel, and their Raman spectra were studied. The catalyzates proved to be complicated mixtures containing aromatic, paraffin, mono-, and bicyclic naphthene hydrocarbons. Naphthalene and o-diethyl benzene were found to be most important. Small amounts of α-methyl indan, n-butyl benzene, indan, and o-methyl benzene were detected. Approximately equal amounts of n-decane, cis-decahydroazulene, and 1,2-diethylcyclohexane, a small amount of trans-decalin. and a hydrocarbon of unknown spectrum were detected in the paraffin - naphthene part. The formation of decalin and naphthalene is obviously the result of transannular C_6 dehydrocyclization, while decahydroazulene is obtained from cyclodecane by C_5 dehydrocyclization. This indicates that C_5 and C_6 dehydrocyclizations are caused not only by the closure of open chains, but may also occur within a cycle while bicyclic systems are formed. Thus, n-decane can only have formed in the catalyzate by cleavage of the ten-membered cycle. Since hydrogenolysis has been

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Contact Transformations of Cyclodecane in the Presence of Platinized Charcoal

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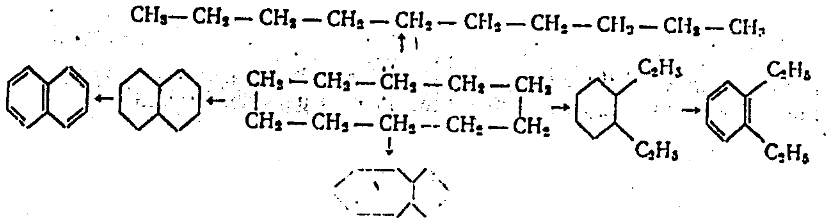
B016/B052

achieved only in cycles with no more than 5 hydrocarbon atoms, this observation is of fundamental importance. Hitherto, the formation of o-diethyl benzene and 1,2-diethyl cyclohexane has not been explained. It is pointed out that none of the traditional reactions can be used to explain this observation. The following reaction scheme is suggested for cyclodecane on platinized charcoal:



The remaining hydrocarbons detected in the catalyzate were probably formed by secondary transformations. There are 4 tables and 9 references: 6 Soviet, 2 US, and 1 Swiss.

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Contact Transformations of Cyclodecane in the Presence of Platinized Charcoal

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B016/B052

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M.V. Lomonosova (Moscow State University imeni M.V. Lomonosov). Komissiya po spektroskopii Akademii nauk SSSR (Commission of Spectroscopy of the Academy of Sciences USSR). 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 28, 1960

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BUTLEROV, A.M.;KEKULE, A.; KUPER, A.S.; MARKOVNIKOV, V.V.; BYKOV, G.V. [translator]; LIBERMAN, A.L.[translator]; RAYTMAN,L.A.[translator]; KAZANSKIY, B.A., red.; GUSEVA, A.P., tekhn. red.; GUS'KOVA, O.M., tekhn. red.

[Centennial of the theory of chemical structure] Stoletie teorii khimicheskogo stroeniia; sbornik statei. By A.M.Butlerov i dr. Moskva, Izd-vo Akad.nauk SSSR, 1961. 146 p. (MIRA 14:12)
(Chemical structure)

LIBERMAN, A.L.; BRAGIN, O.V.; KAZANSKIY, B.A.

Catalytic dehydrocyclization of diethylamine with the formation of a five-membered heterocyclic system. Izv.AN SSSR Otd.khim.nauk no.3: 525-527 Mr '61. (MIRA 14:4)

1. Institut organicheskoy khimii imeni N.D.Zelinskogo AN SSSR.
(Diethylamine) (Pyrrole) (Butylamine)

ALEKSANYAN, V.T.; STERIN, Kh.Ye.; UKHOLIN, S.A.; BRAGIN, O.V.;
LIBERMAN, A.L.; MIKHAYLOVA, Ye.A.; SMIRNOVA, E.N.; TYUN'KINA, N.I.
KAZANSKIY, B.A.

Raman spectra of certain hydrocarbons of the benzene series havong one or two side chains. Izv. AN SSSR. Otd.khim.nauk no.8:1437-1443 Ag '61. (MIRA 14:8)

1. Komissiya po spektroskopii AN SSSR i institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR.
(Hydrocarbons—Spectra)

LIBERMAN, A.L.; SHNABEL', K.Kh.; KAZANSKIY, B.A.

Effect of the method of preparing platinized coal on its activity in C_5 -dehydrocyclization of paraffins and dehydrogenation of cyclohexane hydrocarbons. Part 2: Influence of platinum reduction conditions. Kin.i kat. 2 no.4:547-552 Jl-Ag '61. (MIRA 14:10)

1. Institut organicheskoy khimii imeni N.D.Zelinskogo AN SSSR.
(Platinum) (Catalysis) (Dehydrogenation)

39439
S/081/62/000/012/023/063
B166/B101

5.3300

AUTHORS: Kazanskiy, B. A., Liberman, A. L.

TITLE: Catalytic dehydrocyclization of paraffin hydrocarbons

PERIODICAL: Referativnyy zhurnal. Khimiya, no. 12, 1962, 212, abstract 12Zh92 (Sb. "5-y Mezhdunar. neft. kongress, v. 3, 1959". M., Gostoptekhizdat, 1961, 241-249)

TEXT: In the presence of Pt/C paraffin hydrocarbons having >5 carbon atoms in their longest chain are cyclized into cyclopentane homologues. The process is called C_5 dehydrocyclization as distinct from the reaction of the formation of hexamethylenes from paraffins and their subsequent aromatization which proceeds under the same conditions (and which is called C_6 dehydrocyclization). C_5 dehydrocyclization is a straight process, which proceeds without preliminary or subsequent isomerization of the carbon chain. It is demonstrated by thermodynamic calculations how (with increase in temperature) the concentration of cyclic hydrocarbons increases when they are in equilibrium mixtures with the

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corresponding paraffins [mixtures of n-pentane (I) and cyclopentane (II), n-hexane (III) and methyl cyclopentane (IV), n-heptane (V) and 1,2-dimethyl cyclopentane (VI), (V) and ethylcyclopentane (VII), 2,2-dimethyl pentane and 1,1-dimethyl cyclopentane, 3-ethyl pentane (VIII) and VII]. Hydrocarbons of normal and iso structure were introduced into the C_5 dehydrocyclization reaction (Pt/C, 310°C, volume rate 0.2 hours^{-1}). The aromatic and olefinic hydrocarbons which formed in small quantities were separated by chromatography on silica gel, whilst the paraffin-naphthene part was subjected to precise rectification; the homologues of I were identified by their constants and Raman spectra. The paraffin hydrocarbon, the product of C_5 dehydrocyclization, the yield in %, the yield of aromatic hydrocarbons in % and the yield of olefins in % are given as follows: III, IV, 3 - 4, 1.0 - 1.5, 0.5 - 0.9; V, cis and trans VI and VII, 10, (a triple passing through), 4 - 5, 1 - 2; n-octane, trans-1-methyl-2-ethyl cyclopentane (IX) and n-propyl cyclopentane (X), 3 - 4, 1, 0.5 - 1.5; VIII, VII, 12, 1 - 2, 0.7; 2,2,4-trimethyl pentane (XI), 1,1,3-trimethyl cyclopentane (XII), 25 - 30, 5.5, -; 2,2,3-trimethyl pentane, 1,1,2-trimethyl cyclopentane (XIII), -,

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2,3,3-trimethyl pentane, XIII, -. C_5 dehydrocyclization of I took place only at 350°C, the yield of II was 4-5%. The C_5 dehydrocyclization reaction is also extended to benzene homologues: from n-propyl-, sec-butyl- and isobutyl benzene indan, α- and β-methyl indan were obtained respectively; the yield of indan hydrocarbons was 6%. The possibility of the closing of the second five-member ring under conditions of C_5 dehydrocyclization in IX and X with the formation of pentalane is suggested. It is demonstrated that in the presence of Pd/C, Ni/C, Ni/Al_2O_3, Os/C and Ir/C the C_5 dehydrocyclization reaction will not go. H_2 and N_2 pressure retards C_5 dehydrocyclization over Pt/C. The XII which is formed from XI under conditions of C_5 dehydrocyclization is partially isomerized (mainly with the participation of the gem-group) into 1,3- and 1,4-dimethyl cyclohexanes which form m- and p-xylenes (35 and 50% respectively of the aromatic part of the XI catalysis product). The C_5 dehydrocyclization reaction proceeds

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according to a null order; the value of the apparent activation energy of C_5 dehydrocyclization of III, VIII and XI is 20 kcal/mole, for C_5 dehydrocyclization of alkyl benzenes it is 27.5 kcal/mole. It is suggested that the active (for C_5 dehydrocyclization) conformation for VIII, and particularly XI, is achieved more easily than for normal paraffin hydrocarbons. It is assumed that the C_5 dehydrocyclization reaction proceeds according to a molecular mechanism through a transition state, in addition to which there is a geometric correspondence between the latter and the surface of the catalyst. [Abstracter's note: Complete translation.]

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STERIN, Kh.Ye.; ALEKSANYAN, V.T.; UKHOLIN, S.A.; BRAGIN, O.V.; GAVRILOVA, A.Ye.; ZOTOVA, S.V.; LIBERMAN, A.L.; MIKHAYLOVA, Ye.A. SMIRNOVA, E.N.; STERLIGOV, O.D.; KAZANSKIY, B.A.

Raman spectra of some tri- and tetraalkylbenzenes and condensed aromatic hydrocarbons. Izv. AN SSSR. Otd.khim.nauk no.8:1444-1450 Ag '61. (MIRA 14:8)

1. Komissiya po spektroskopii AN SSSR i Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR.
(Benzene--Spectra)
(Hydrocarbons--Spectra)

LIBERMAN, A.L.; VASINA, T.V.

Physical properties of stereoisomeric 1-methyl-3n.-alkylcyclohexanes. Neftekhimiia 2 no.2:129-136 Mr-Ap '62. (MIRA 15:6)

1. Institut organicheskoy khimii AN SSSR imeni N.D.Zelinskogo.
(Cyclohexane)

S/048/62/026/010/009/013
B117/B186

AUTHORS: Zhizhin, G. N., Barinova, Z. B., Liberman, A. L., Kuznetsova, I. M., and Tyun'kina, N. I.

TITLE: Infrared absorption spectra of cis- and trans-isomers of 1-methyl-2-N-alkyl cyclohexanes

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Seriya fizicheskaya, v. 26, no. 10, 1962, 1263-1266.

TEXT: Infrared absorption spectra of five pairs of cis- and trans-isomers of the 1-methyl-2-alkyl cyclohexane series having alkyl radicals (CH_3, C_2H_5, C_3H_7, C_6H_{13}, and C_7H_{15}) were examined and compared with the corresponding Raman spectra (V. T. Aleksanyan, Kh. Ye. Sterin, A. L. Liberman, I. M. Kuznetsov, N. I. Tyun'kina, B. A. Kazanskiy, Sb.: Issledovaniya po eksperimental'noy i teoreticheskoy fizike. Pamyati akademika G. S. Landsberga (Investigations in the field of experimental and theoretical physics. In memory of Academician G. S. Landsberg), p. 43, Izd. AN SSSR, M., 1959). The cis- and trans-isomers had been synthesized previously (P. A. Bazhulin, S. A. Ukholin,

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T. F. Bulanova, A. V. Koperina, A. F. Plate, B. A. Kazanskiy, Izv. AN SSSR, Otd. khim. nauk, no. 5, 480 (1949); G. S. Landsberg, B. A. Kazanskiy et al. Opredeleniye individual'nogo uglevodorodnogo sostava benzinov pryamoy gonki kombinirovannym metodom (Determination of the pure hydrocarbon composition of direct distillation gasolines by the combined method), Izd. AN SSSR, M., 1959; A. L. Liberman, N. M. Kuznetsova, N. I. Tyun'kina, B. A. Kazanskiy, Dokl. AN SSSR, 118, 942 (1958)). At most frequencies the two spectra were identical. The greatest difference was observed with the infrared spectra of cis- and trans-isomers within the range 585-610 cm^{-1}, wherein cis-isomers show a band with an absorption maximum of not less than 30-35 % while trans-isomers exhibit no marked bands. The lines in the corresponding range of the Raman spectra are very weak. Further differences: Within the ranges 800-810, 842-853, 972-975, 1155-1157 cm^{-1} cis-isomers exhibit distinctly marked bands with absorption maxima of 60-90%, while the corresponding bands of trans-isomers are either weak or absent. Trans-isomers display intense lines between 865 and 871 cm^{-1} and distinct lines between 1350 and 1357 cm^{-1} on the edge of the very intense 1380 cm^{-1} bands. In the spectra of the trans-isomers, the bands of the cis-isomers (972-975 and 1155-1157 cm^{-1}) are shifted into the

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ranges 965-968 and 1159-1163 cm^{-1}, respectively. Despite the identity of most of the frequencies, the characteristics of Raman and infrared absorption spectra very rarely coincide, so the two spectra complement one another. There are 1 figure and 1 table.

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

LIBERMAN, A.L.; GUR'YANOVA, G.K.

New data on the molecular compounds of stereoisomeric ditertiary
glycols of the 1,4-di-(α-hydroxy-sec.alkul)cyclohexane series.
Izv.AN SSSR. Otd.khim.nauk no.11:2092-2093 N '62. (MIRA 15:12)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR.
(Glycols) (Cyclohexane) (Isomerism)

ZHIZHIN, G.N.; BARINOVA, Z.B.; LIBERMAN, A.L.; KUZNETSOVA, I.M.; TYUN'KINA, N.I.

Infrared absorption spectra of cis-trans isomers of 1-methyl-2-n-alkylcyclohexanes. Izv. AN SSSR.Ser.fiz. 26 no.10:1263-1266 O '62. (MIRA 15:10)

1. Komissiya po spektroskopii AN SSSR i Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
(Cyclohexane) (Isomers—Spectra)