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[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Studies in the Terpene Series. XIX.[1] Hydroisomerization and Hydrogenolysis of Cyclohexene, Methylcyclohexene and *p*-Menthene in the Presence of Hydrogenation Catalysts

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The effect of hydrogen pressure and temperature was studied upon cyclohexene, 4-methylcyclohexene and *p*-menthene (1-methyl-4-isopropylcyclohexene) in the presence of a nickel-Kieselguhr catalyst. At lower pressures and higher temperatures the cyclohexenes undergo hydrogenation and hydrogenolysis accompanied by a skeletal isomerization. A similar reaction occurred when nickel-alumina or copper-alumina were used as catalysts.

The hydrogenolysis of pinane in a flow type apparatus in the presence of hydrogenation catalysts, such as nickel-Kieselguhr, nickel-alumina, copper-alumina and nickel, yielded tetramethylcyclohexanes, *o*- and *p*-menthane and a substantial amount of alkylcyclopentanes admixed with bicyclic dihydroterpenes.[5] The formation of the latter two types of compounds indicated that skeletal isomerization accompanied the hydrogenolysis of pinane. The formation of alkylcyclopentanes could have occurred through the isomerization of alkylcyclohexanes during the hydrogenolysis of pinane. In order to test this hypothesis the reactions of several monocyclic hydrocarbons were investigated under experimental conditions similar to those used in the study of the hydrogenolysis pinane. A more detailed study was made of cyclohexane since it was possible to determine the products of the reaction quantitatively by means of a mass spectrograph.

Experimental Results

TABLE I

HYDROISOMERIZATION AND HYDROGENOLYSIS OF CYCLOHEXENE OVER NICKEL-KIESELGUHR CATALYST

The molal ratio of hydrogen to olefins used in the experiments was 4.5(±0.3):1. The hourly liquid space velocity (ml. liquid per hour per ml. catalyst) was 0.49(±0.05). The product withdrawn during the period of 1.5-3 hours was submitted for analysis. Values given in parentheses represent the composition of hydrogenolyzed and hydroisomerized product. They were calculated on benzene and cyclohexane free basis.

Experiment	1	2	3	4	5	6	7	8
Temp., °C.	235	265	293	268	230	275	293	262
Pressure, atm.	2	1.7	1.5	5.5	10.5	10.5	10	45.5
Product composition, mole %[a]								
Cyclohexane	95.8	88.5	73.1	96.0	99.1	98.2	97.4	99.8
Benzene	1.7	5.4	18.4	1.7	...	0.1	0.3	...
Cyclopentane	0.7(28)	1.6(26)	1.2(14)	0.4	...	.2	.2(9)	...
Methylcyclopentane	.6(24)	1.7(28)	2.2(26)	.8	.1	.7	.7(30)	...
n-Hexane	....	0.4(7)	0.5(6)	.1	.2	...	.6(26)	...
2-Methylpentane	.4(16)	0.6(10)	1.7(20)	.4	...	.1	.2(9)	...
3-Methylpentane	.5(20)	1.1(18)	1.5(18)	.5	.3	.5	.3(13)	0.1
2,3-Dimethylbutane	.3(12)	0.7(11)	1.0(12)	.1	.3	.2	.3(13)	.1

[a] Analyzed by means of a mass spectrograph.

1. Cyclohexene and Cyclohexane.—The experimental conditions and the composition of the product obtained from the interaction of cyclohexene and hydrogen over nickel-Kieselguhr catalyst are summarized in Table I. The extent of hydroisomerization decreases sharply with the increase of pressure (Fig. 1), and increases with the temperature of reaction (Fig. 2). The formation of cyclopentane most probably from methylcyclopentane, during hydrogenolysis is of interest in view of the work of Haensel and Ipatieff,[6,7] who found that a methyl group linked to a tertiary carbon atom is removed less readily than a methyl group on a secondary carbon. Thus the paraffins, namely, *n*-hexane and methylcyclopentanes found in the reaction product would be expected to lose a methyl

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[1] For Paper XVIII of this series see H. Pines, E. F. Jenkins and V. N. Ipatieff, THIS JOURNAL, **75**, 6226 (1953).

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[5] V. N. Ipatieff, F. J. Pavlik and H. Pines, THIS JOURNAL, **75**, 5179 (1953).

[6] V. Haensel and V. N. Ipatieff, *ibid.*, **68**, 345 (1946).

[7] V. Haensel and V. N. Ipatieff, *Ind. Eng. Chem.*, **39**, 853 (1947).

group with more facility than methylcyclopentane, and yield *n*- and isopentane, respectively, none of which was found. The results obtained presently cannot be accounted for without the assumption of skeletal rearrangement; this is significant since in the study reported by Haensel and Ipatieff none of the hydrogenolyzed hydrocarbons underwent rearrangement. At atmospheric pressure part of the cyclohexene undergoes dehydrogenation to benzene.

In all the experiments listed previously unused catalyst was used and the sample was withdrawn during the period of 1.5–3.5 hours although it was found that the activity of the nickel–Kieselguhr catalyst did not change much over a period of 12 hours. Duplicate runs were made in many instances and it was found that the results were reproducible.

In order to determine whether the hydroisomerization reaction applies also to saturated hydrocarbons, the effect of hydrogen upon cyclohexane was investigated under conditions described for experiment 4. The results were identical with these obtained with cyclohexene.

The effect of copper–alumina and nickel–alumina upon the hydrogenolysis and hydroisomerization of cyclohexene was studied (Table II). The extent of isomerization in the presence of nickel–alumina catalyst was more pronounced than in the case of the copper catalyst. It was found that the prevailing reactions were general for all the three hydrogenation catalysts, although the extent of the various reactions were different.

TABLE II

HYDROISOMERIZATION AND HYDROGENOLYSIS OF CYCLOHEXENE IN THE PRESENCE OF COPPER–ALUMINA AND NICKEL–ALUMINA CATALYST

The experiments were made at 290° and at 5.5 atmospheres of pressure. The molal ratio of hydrogen to cyclohexane used was 4.4 and the hourly liquid space velocity was 0.45.

Experiment	9	10
Catalyst	Cu–Al$_2$O$_3$	Ni–Al$_2$O$_3$
Product composition, mole %		
Cyclohexane	90.7	94.9
Benzene	8.6	1.5
Cyclopentane	. .	0.5
3-Methylpentane	0.1	.8
2,3-Dimethylbutane	.1	.5
Methylcyclopentane	.5	1.6
n-Hexane	. .	0.1
2-Methylpentane	. .	0.1

2. **Methylcyclohexene.**—The experimental conditions and the composition of the products obtained from the interaction of methylcyclohexene and hydrogen over nickel–Kieselguhr catalyst are summarized in Table III. The composition of the product was determined by selective dehydrogenation and chromatographic separation as described previously.[5] The product which did not undergo dehydrogenation consisted of alkylcyclopentanes which resulted from hydroisomerization and of paraffins which were formed by the hydrogenolysis of the cycloparaffins. The composition of these hydrocarbons was determined by means of infrared spectral analyses.[8] The data obtained indicate that the extent of hydrogenolysis and hydroisomerization is greater in the case of methylcyclohexene than in the case of cyclohexene.

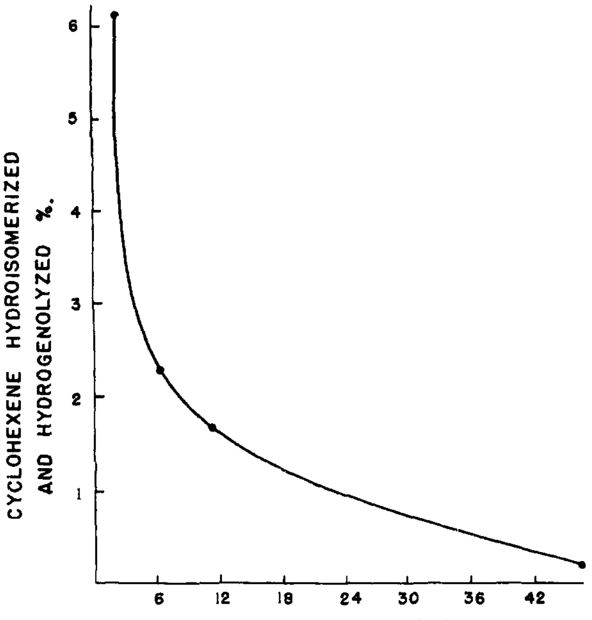

Fig. 1.—Effect of pressure upon hydroisomerization and hydrogenolysis of cyclohexane in presence of nickel–Kieselguhr at 270 (±5°).

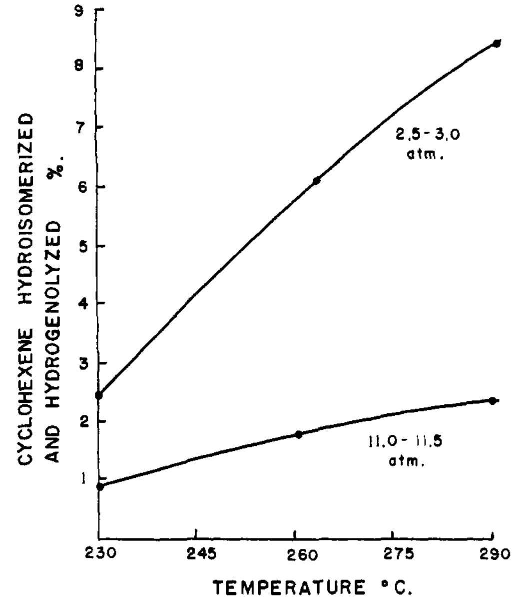

Fig. 2.—Effect of temperature upon hydroisomerization and hydrogenolysis of cyclohexene in presence of nickel–Kieselguhr.

3. ***p*-Menthene (1-Methyl-4-isopropylcyclohexene).**—The extent of hydroisomerization and hydrogenolysis of *p*-menthene (Table IV) was about the same as that of methylcyclohexene.

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[8] The authors are indebted to Mr. Edmond Baclawski of the Physics Department, Universal Oil Products Company, for the infrared spectral analyses.

TABLE III

HYDROISOMERIZATION AND HYDROGENOLYSIS OF METHYLCYCLOHEXENE OVER NICKEL–KIESELGUHR CATALYST AT 265° AND UNDER 6 ATMOSPHERES PRESSURE

The experiment was made at 266° and 5.5 atmospheres of pressure. The molal ratio of hydrogen to methylcyclohexene used was 4, and the hourly liquid space velocity was 0.50.

Experiment	11
Product composition, %	
1. Toluene	4
2. Methylcyclohexane	88
3. Saturated C_7 hydrocarbons other than methylcyclohexane	8
Composition of fraction 3,[a] %	
trans-1,2-Dimethylcyclopentane	0–5
cis- and *trans*-1,3-dimethylcyclopentane	25–30
Ethylcyclopentane	0–5
n-Heptane	15–20
3-Methylhexane	15–20
2-Methylhexane	0–6
2,3-Dimethylpentane	0–4

[a] The composition of fraction 3 was determined by means of infrared analysis.

TABLE IV

HYDROISOMERIZATION AND HYDROGENOLYSIS OF *p*-MENTHENE (1-METHYL-4-ISOPROPYLCYCLOHEXENE)

Experiment[a]	12	13	14	15
Catalyst	Ni(K)	Ni(K)	Ni–Al_2O_3	Cu–Al_2O_3
Temp., °C.	262	262	290	289
Pressure, atm.	5.5	15.5	7.5	6.5
Product composition, wt. %:	5	..	7	26
1. Aromatics[b]	5	..	7	26
2. *p*-Menthane	88	98	88.5	70
3. Paraffins and alkylcyclopentanes[c]	8	2	4.5	4
Anal. and composition of 3, %				
Carbon	85.30	85.24	85.34	85.58
Hydrogen	14.72	14.90	14.62	14.68
Refractive index, $n^{20}{}_D$	1.4215	1.4227	1.4332	1.4311
Alkylcyclopentanes[d]	72	60	80	80
Paraffins[d]	28	40	20	20
Paraffins[d]	28			

[a] The molal ratio of hydrogen *p*-menthane = 5.5. [b] Composed of over 90% *p*-cymene. [c] Hydrocarbons which did not undergo dehydrogenation when passed over platinum–alumina catalyst at 290°. [d] Calculated from the carbon and hydrogen analysis with % C and % H corrected to 100.0%.

Discussion of Results

The hydrogenation of cyclohexene and alkylcyclohexenes in the presence of nickel–Kieselguhr catalyst is accompanied, especially at the lower hydrogen pressures, by a skeletal isomerization. This type of isomerization was not noticed during the selective demethanation of paraffinic hydrocarbons.[6,7] The difference in the behavior of nickel–Kieselguhr catalyst could probably be attributed to the fact that Haensel and Ipatieff in their studies partially deactivated the catalyst by heating it in a stream of hydrogen at 538° for 12 hours prior to its use, and thereby probably destroying the acidic properties of the catalyst.

The skeletal isomerization accompanying the hydrogenation and hydrogenolysis of cyclohexenes implies that the reaction proceeds probably *via* an ionic mechanism. This may occur either through a presence of source of protons on the nickel–Kieselguhr catalyst or through a formation of a polar bond between the hydrocarbon and the catalyst.

The extent of hydroisomerization of *p*-menthene is much less than that observed for pinane.[5] It appears therefore that the hydroisomerization of pinane does not proceed through alkylcyclohexanes but probably through the formation of bicyclic hydrocarbons of the type of bornylane. These hydrocarbons on hydrogenolysis would form alkylcyclopentanes. The presence of bicyclic hydrocarbons, others than pinane, was observed in the reaction products obtained from pinane.

Materials

Cyclohexene was prepared by dehydration of cyclohexanol over activated alumina at 420°. It distilled at 82.2° at 750 mm., $n^{24}{}_D$ 1.4462°.

4-Methylcyclohexene was prepared by dehydration of 4-methylcyclohexanol.[9]

***p*-Menthene (1-Methyl-4-isopropyl-x-cyclohexene).**—1-Menthol (Eastman Kodak Company) was dissolved in equal volume of *n*-hexane and dehydrated at 425° by passing it over activated alumina. The *p*-menthene distilled at 167–169°, $n^{21}{}_D$ 1.4518, $[\alpha]^{25.5}{}_D$ 57°.

Nickel–Kieselguhr was obtained from Universal Oil Products Company.[10]

Copper–alumina contained 13 parts by weight of copper oxide per 100 parts of alumina.[5]

Nickel–alumina was composed of 75% nickel and 25% by weight of alumina.[5]

Apparatus and procedure were the same as described previously.[5]

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(9) V. N. Ipatieff, E. E. Meisinger and H. Pines, THIS JOURNAL, **72**, 2772 (1950).

(10) V. N. Ipatieff and B. B. Corson, *Ind. Eng. Chem.*, **26**, 1838 (1934).