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Alumina: Catalyst and Support. XVI.*

Aromatization and Dehydroisomerization of Branched C_6–C_8 Hydrocarbons over "Nonacidic" Chromia-Alumina Catalyst †

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The aromatization and dehydroisomerization has been studied over a "nonacidic" chromia-alumina catalyst in which the alumina was prepared from potassium aluminate. The reactions were carried out at atmospheric pressure and at about 530°C.

2,2,4-Trimethylpentane formed only *p*-xylene over this catalyst while 2,3,4-trimethylpentane produced all the three xylenes and ethylbenzene. The aromatics derived from 2,2,3-trimethylpentane consisted mostly of *m*-xylene and toluene.

2,2-Dimethylbutane dehydroisomerized mainly to 2-methylpentenes and 2-methylpentadienes, while 2,3-dimethylbutane went to 2- and 3-methylpentenes. Neopentane did not undergo a dehydroisomerization reaction.

The dehydrogenation reactions involving branched hydrocarbons were accompanied by a cracking reaction involving the preferential splitting of the bonds between the highly substituted carbon atoms.

Small amounts of 1,1,2-trimethylcyclopropane were observed in the dehydrogenation reaction of 2,2-dimethylbutane.

The mechanism of aromatization and dehydroisomerization has been discussed and the involvement of adsorbed cyclopropane- and cyclobutane-type intermediates in the transition state has been proposed.

INTRODUCTION

It was reported previously that chromia-alumina catalyst, which was prepared by impregnating alumina obtained by the hydrolysis of aluminum isopropoxide with chromic acid, caused skeletal isomerization of cyclic (*2*) and aliphatic (*1*) hydrocarbons. This type of isomerization was considered to be associated with the acidic sites of the alumina (*3*) and was assumed to proceed by means of a carbonium ion mechanism. It was thus found that C_6 and higher hydrocarbons with five or less carbon atoms in a chain underwent isomerization through stepwise methyl shifts before (or after) ring closure to form aromatics (*1*). Such acid-catalyzed, stepwise skeletal isomerization did not occur when the chromia-alumina catalyst was prepared using an alumina which was obtained from potassium aluminate (*1, 2*). The very limited isomerization over this catalyst produced only certain specific isomers and the structures of these isomers were different from the ones formed when the "acidic" chromia-alumina catalyst was used (*4*).

Trimethylpentanes can be converted to

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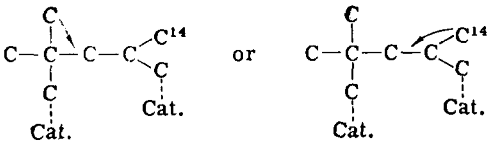
* For paper XV of this series see K. Watanabe, C. N. Pillai and H. Pines, *J. Am. Chem. Soc.* In Press.

† Paper VIII of the series "Aromatization of Hydrocarbons." For previous paper see reference (*1*).

‡ Monsanto Predoctoral Fellow 1960–1961.

aromatic hydrocarbons only if skeletal isomerization steps are involved either before or after the ring closure. Even in the absence of acid-catalyzed isomerization, trimethylpentanes produced xylenes in good yields over nonacidic chromia-alumina catalyst. The aromatization yielded only one or two of the four possible C_8 aromatics. 2,2,4-Trimethylpentane gave almost exclusively *p*-xylene (*5*), and 2,2,3- and 2,3,3-trimethylpentanes were converted to *m*-xylene (*6*) over chromia-alumina catalysts impregnated with potassium and cerium salts. Any other isomers formed could be explained by side reactions such as recombination of cracking products as will be explained later.

Recently Cannings *et al.* (*5*) reported the aromatization of 2,2-dimethyl-4-methyl-C^{14}-pentane over chromia-alumina catalyst promoted with potassium and cerium. *p*-Xylene was the only C_8 aromatic produced and 46–53% of the radioactivity was located in the methyl groups of *p*-xylene. 1,1,3-Trimethylcyclopentane over the same catalyst formed mixed xylenes. From this it was concluded that the adsorbed 2,2,4-trimethylpentane did not desorb as trimethylcyclopentane, but either broke down to form gaseous hydrocarbons or produced *p*-xylene and toluene:



In order to get a better insight into the nature of this isomerization, various model hydrocarbons were dehydrogenated over chromia-alumina catalyst in which the alumina was prepared from potassium aluminate.

EXPERIMENTAL PART

Apparatus and Procedure

The dehydrogenation reactions were performed in a 20 mm OD Pyrex tubular reactor which was placed in a vertical furnace. The catalyst bed was 210 mm long. A thermowell held thermocouples inside the reactor. The temperature was maintained constant by an automatic temperature controller. The catalyst pellets, ⅛ inch in diameter, were diluted with glass pieces of similar sizes to decrease temperature changes during the reaction. The amount of catalyst used was 14.1 ml (10.3 g) mixed with 38.6 g of glass pieces. All the experiments were made at atmospheric pressure. The hydrocarbons were introduced into the reaction tube by means of a stainless steel syringe-type displacement pump of 40 ml capacity. The flow rate could be continuously changed from 0.2 to 40 ml per hour by means of a Zero-Max Model 14 variable speed torque converter (Revco Inc., Minneapolis, Minnesota). The liquid products were condensed either in a Dry Ice-acetone, Dry Ice-carbon tetrachloride or ice-water trap, depending on the freezing points of reactants or products. The gases were trapped in a liquid nitrogen condenser and at the end of each experiment collected and measured over saturated salt-water. Hydrogen was measured by a wet test meter.

Gaseous hydrocarbons, propylene and butylenes, were fed directly from a cylinder, and the flow rate was measured through a calibrated capillary flow meter. The low-boiling reaction products obtained from these experiments were condensed in a Dry Ice-acetone trap and dissolved immediately after withdrawal in *n*-pentane cooled to −78°C.

A dehydrogenation experiment usually consisted of 3–4 cuts. Liquid samples were withdrawn from the Dry Ice–acetone trap at the end of each cut, and analyzed separately.

At the end of each experiment the carbonaceous material which was deposited on the catalyst was burned off at 540°C with an air-nitrogen mixture. Carbon dioxide was absorbed in 0.1 *N* sodium hydroxide solution, and back-titrated with 0.6 *N* hydrochloric acid using phenolphthalein and methyl orange indicators. The difference between the two endpoints is equal to the carbon dioxide absorbed. In certain experiments carbon dioxide was determined gravimetrically as barium carbonate. Equal rate of formation of carbonaceous materials was assumed during each cut within any single experiment. Catalysts were reconditioned under hydrogen flow at 525° before each experiment for at least 2 hours.

Contact times were calculated using the formula:

$$\text{C. T. (sec)} = \frac{(\text{ml Catalyst})(MW)(P)(273°\text{K})(3600\ \text{sec/hr})(0.5)}{(\text{g. Hydrocarbon/hr})(22{,}410\ \text{ml})(760\ \text{mm})(T°\text{K})}$$

where

MW = the molecular weight of the hydrocarbon.

P = the partial pressure of the hydrocarbon at the entrance of the catalyst bed.

$T°\text{K}$ = the average temperature of the catalyst bed.

An arbitrary value of 0.5 as void fraction was assumed to account for the space occupied by the solid catalyst.

Analytical Procedure

Liquid and gaseous reaction products were analyzed by gas chromatography using two Podbielniak Chromacon Vapor Phase Chromatographic Analytical Apparatus (Models No. 9475 3A and 9580) and an F and M Model 300 Programmed Temperature Gas Chromatograph with the following columns:

1. Silica gel "950," 60/200 mesh, 8 ft; for C_1–C_2 compounds.
2. 33% Dimethylsulfolane on 100/120 mesh firebrick, 10 ft; for C_3–C_8 aliphatics.
3. 35% Dimethylsulfolane-dipropylsulfone (ratio 3:7) on 30/60 mesh firebrick, 35 ft; for C_2–C_4 aliphatics.
4. 5% 7,8-Benzoquinoline on 100/120 mesh firebrick, 26 ft; for C_6–C_8 diolefins and aromatics.
5. 15% Carbowax "600" on 80/100 mesh Gas-Chrom P, 14 ft; for aromatics, ketones, and alcohols.
6. 20% Dinonylphthalate ester on 30/60 mesh Celite, 10 ft; for C_6–C_8 aliphatics, cyclic hydrocarbons, and aromatics.
7. 7% Di-*n*-propyl-tetrachlorophthalate on 30/60 mesh Celite, 22 ft; for C_6–C_8 diolefins, aromatics, and ketones.

Chromatograms of each liquid sample were taken injecting 1 μliter sample and using the highest sensitivities. To detect very small amounts of certain components another chromatogram was taken using 10 μliters or even larger samples.

Each sample was hydrogenated on a microhydrogenation apparatus at room temperature and atmospheric pressure, using 5% palladium on charcoal catalyst. The large number of C_7 and C_8 olefins and diolefins makes their accurate identification and correct determination difficult. Some peaks could not be detected in the multitude of larger peaks, if present in small quantities. Hydrogenation reduced the number of peaks, and even minor components were then possible to detect.

Hydrogenation experiments were made with 3-ethylhexenes, 2,2,3-trimethylpentene, and 1-octene to prove that skeletal isomerization and cyclization did not occur during hydrogenation. Aromatic hydrocarbons did not undergo hydrogenation under these conditions.

Catalyst

Nonacidic chromia-alumina catalyst was prepared as described previously (*2*). The alumina was precipitated from potassium aluminate and impregnated with chromic acid. Surface area, measured by the B.E.T. method was 89 m^2/g. Average pellet weight was 0.022 g. The catalyst contained 13.8 wt.% Cr_2O_3.

Hydrocarbons

Most of the hydrocarbons used in the dehydrogenation study or used as VPC standards were pure or research grade commercial products of over 99% purity.

2,2,3-Trimethylpentane

a. 2,2,3-Trimethyl-3-pentanol. Pinacolone, 183 g, was added to a Grignard reagent prepared from 51 g of magnesium and 272 g of ethyl bromide in 1200 ml of ether under a nitrogen stream. The product was poured onto a mixture of ice and 110 g of ammonium chloride. Only enough dilute sulfuric acid was added to the aqueous layer to dissolve all the precipitate, keeping the pH above 7. The aqueous layer was extracted thrice with ether, and the combined fractions were dried over potassium carbonate. The 2,2,3-trimethyl-3-pentanol thus obtained distilled between 154–156°; yield 51.3%, n_D^{30} 1.4314, purity by VPC ~ 99%, the main impurity being pinacolyl alcohol.

b. 3,4,4-Trimethyl-2-pentene and 3,3-Dimethyl-2-ethyl-1-butene. A mixture of one mole of 2,2,3-trimethyl-3-pentanol, 2.1 moles of phenyl isocyanate, and 0.36 moles of pyridine was refluxed for two hours. The material was then distilled at a take-off temperature of 108°. The distillation was stopped when the flask temperature reached 142°, yield 68%.

Five to ten ml of methanol was added to the crude olefin to remove any traces of phenyl isocyanate. After standing overnight, the mixture was washed twice with dilute acetic acid to remove pyridine, aniline, and other nitrogen compounds. Following this treatment the mixture was washed with cold water, dilute potassium carbonate solution, dried over anhydrous potassium carbonate and distilled from calcium oxide through a 12-inch wire-packed column, b.p. 107°–109°. The product was composed of 52.5% 3,3-dimethyl-2-ethyl-1-butene, 47% 3,4,4-trimethyl-2-pentene, and 0.5% 2,3,3-trimethyl-1-pentene.*

c. 2,2,3-Trimethylpentane. This hydrocarbon was prepared by hydrogenating the corresponding olefins in a shaker at room temperature and at 2–3 atmospheres of hydrogen pressure, using 5% palladium on charcoal catalyst. The paraffins distilled at 110° through a 60 cm spinning band column, n_D^{19} 1.4046, purity 99.5% by VPC.

3-Ethylhexane and 3-Ethylhexenes.

3-Ethyl-3-hexanol was prepared from 3-pentanone and propylmagnesium bromide; it distilled at 76.5 – 80° at 35 mm. The alcohol was dehydrated over Harshaw Alumina Al-D104T 1/8† at 312° in the presence of a stream of ammonia to avoid skeletal isomerization (7). The olefins, 73% yield, were composed of 3-ethyl-3-hexene, 24%, and 3-ethyl-2-hexene, 76%. On hydrogenation, under experimental conditions as described for 2,2,3-trimethylpentane, the olefin yielded 3-ethylhexane, b.p. 117° at 744 mm, n_D^{20} 1.4009, purity by VPC 99.4%.

DISCUSSION OF RESULTS

2,2,4-Trimethylpentane and Isobutylene

It was shown previously that the product distribution from the aromatization of hydrocarbons over chromia-alumina catalysts are greatly influenced by the type of alumina used in the preparation of the catalyst (*1*, *2*, *8*). Recently Cannings and co-workers (*5*) reported the aromatization of 2,2-dimethyl-4-methyl-C^{14}-pentane over chromia-alumina catalyst promoted with potassium and cerium. The C^{14} distribution in the produced *p*-xylene supported the proposed mechanism which involved the insertion of a methyl group between the quaternary carbon to which the methyl group is attached and the adjacent secondary carbon atom.

In the present study the aromatization of nonlabeled 2,2,4-trimethylpentane was carried out over a "nonacidic" chromia-alumina catalyst, prepared according to the procedure described previously (*2*). The results obtained (Table 1) are in agreement with those of Cannings' *et al.* (*5*) and do not invalidate their mechanism. The only aromatics produced are *p*-xylene and toluene in a ratio of twelve to one. 2,5-Dimethylhexenes and 2,5-dimethylhexadienes were the only aliphatic products of skeletal isomerization (1.66–1.39 mole % of the over-all conversion in four successive cuts).

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* More skeletal isomerization was observed when less pyridine was used in the reaction. The yield of olefins produced could be raised from 68 to 78% if the distillation is continued until the flask temperature reaches 230°, however the product contains up to 2% skeletal isomers of the title olefins.

† The Harshaw Chemical Company, Cleveland, Ohio. For further characteristics of the catalyst see reference (*3*).

TABLE 1

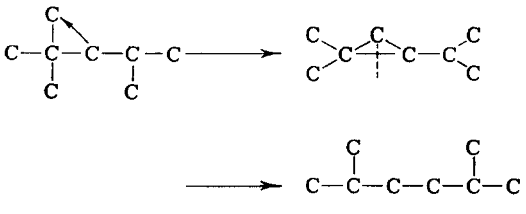
Dehydrogenation of 2,2,4-Trimethylpentane over Cr_2O_3–Al_2O_3 Catalyst at 527° and Contact Time of 3 Seconds[a]

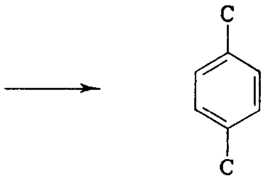
Cut number	1	4
Length of cuts (minutes)[b]	6	12
2,2,4-Trimethylpentane reacted (Mole %)	19.4	25.2
Composition of reaction product (mole %)		
Methane	6.20	6.20
Carbon monoxide	0.30	0.30
Carbon dioxide	0.03	0.03
Ethane	0.16	0.16
Ethylene	0.13	0.13
Propane	1.00	1.01
Propylene	2.21	1.80
Isobutane	9.80	9.40
Isobutylene	41.00	35.40
n-Pentane	0.02	0.02
Isopentane	0.13	0.16
Neopentane	1.69	1.20
Methylbutenes	0.74	0.73
Isoprene	0.20	0.15
2-Methylpentane	0.04	0.02
2-Methylpentenes	0.26	0.23
2,4- and 2,2-Dimethylpentane	0.10	0.31
C_7 Olefins	4.82	4.03
2,2,4-Trimethylpentenes	20.80	24.45
Cyclic olefins and paraffins	0.39	0.24
2,5-Dimethylhexenes and dienes	1.66	1.39
Toluene	0.57	0.84
p-Xylene	6.50	10.55
Carbonaceous material	1.25	1.25

[a] The feed hydrocarbon was of 99.9% purity.

[b] Cut 1 was taken during the first six minutes; cut 4, between 24 and 36 minutes of the experiment.

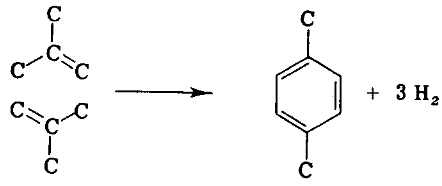
A mechanism similar to the one proposed by Cannings *et al.* (*5*) involving an adsorbed cyclopropane-type transition state explains both the formation of 2,5-dimethylhexane and *p*-xylene. Bond breakage occurred between the two most substituted carbon atoms of the cyclopropane ring.





There was no significant variation in product composition during the course of the experiment.

The major reaction occurring during the dehydrogenation of 2,2,4-trimethylpentane was cracking, which produced isobutane and isobutylene. Recombination of isobutylene could form *p*-xylene:



The equilibrium constant for this reaction at 527° was calculated to be 2.4×10^5 (*9*).

TABLE 2

Reaction of Isobutylene over Cr_2O_3–Al_2O_3 Catalyst at 525°

Cut number	1	2	3
Length of cuts (minutes)	6	6	12
Contact time (seconds)	1.6	1.6	2.6
Isobutylene reacted (mole %)	0.8	0.9	1.5
Composition of liquid reaction product (mole %)[a]			
Ethylene	3.0	3.3	1.7
Acetylene (?)	0.2	0.2	0.1
Propylene	6.0	9.0	12.9
Isobutane	32.0	40.0	49.0
2,2,4-Trimethylpentane	0.3	0.4	0.3
2,4,4-Trimethyl-1-pentene	2.0	2.3	1.2
2,4,4-Trimethyl-2-pentene	1.8	2.2	1.2
Benzene	2.5	2.3	1.3
Toluene	6.0	3.0	1.6
p-Xylene	44.0	35.4	28.0
m-Xylene	—	—	0.7
Ethylbenzene	—	—	0.7
Unknown C_8 paraffin	2.2	1.9	1.3

[a] 0.5% of the isobutylene feed was converted to carbonaceous materials.

The principal reactions of isobutylene over chromia-alumina were condensation to *p*-xylene and hydrogenation to isobutane (Table 2). The recombination mechanism could contribute to some extent to the formation of *p*-xylene in the aromatization of 2,2,4-trimethylpentane. However, the occurrence of nearly 50% of the radioactivity in the side chain of *p*-xylene in Cannings' experiments (*5*) eliminates this mechanism as an important one. Recombination would leave only 33% of the C^{14} in the side chains.

2,3,4-Trimethylpentane

The conditions of aromatization and the experimental results are summarized in Table 3. Four cuts were taken during the experiment (Table 3). The xylene fraction of the product of the first 6 minutes con-

TABLE 3

Dehydrogenation of 2,3,4-Trimethylpentane over Cr_2O_3–Al_2O_3 Catalyst at 523° and Contact Time of 3 Seconds[a]

Cut number	1	2	3	4
Length of cuts (minutes)	6	6	12	12
2,3,4-Trimethylpentane reacted (mole %)	36.3	34.6	31.3	25.6
Composition of reaction product (mole %)				
Methane	8.05	8.95	9.86	10.60
Carbon monoxide	0.33	0.35	0.37	0.38
Carbon dioxide	0.21	0.22	0.23	0.25
Ethane	0.80	0.90	0.98	1.06
Ethylene	0.40	0.45	0.49	0.53
Propane	8.83	10.35	12.50	13.62
Propylene	5.78	7.07	8.47	9.58
n-Butane	0.20	0.24	0.25	0.17
Isobutane	0.06	0.05	0.05	0.07
n-Butenes	1.02	1.52	2.28	2.32
Isobutylene	0.42	0.50	0.61	0.62
Butadiene	0.01	0.06	0.07	0.06
Isopentane	4.40	5.11	5.51	5.57
Methylbutenes	14.54	17.88	22.04	25.08
Isoprene	0.47	0.62	1.00	1.30
n-Pentenes	0.10	0.11	0.11	0.14
Methylpentenes and dimethylbutenes	0.85	1.02	0.86	0.87
2,3-Dimethylpentane + olefins	3.62	3.98	3.15	3.52
2,4-Dimethylpentane + olefins	0.57	0.66	0.53	0.57
2,3,4-Trimethylpentenes	26.60	22.15	17.30	13.15
Toluene	1.07	1.03	0.67	0.48
Ethylbenzene	0.11	0.10	0.08	0.02
o-Xylene	2.97	2.72	1.98	1.44
m-Xylene	7.42	3.52	1.31	0.54
p-Xylene	2.82	2.37	1.27	0.67
Unidentified diolefins and cyclic compounds	2.55	2.47	2.63	2.19
Carbonaceous material	5.80	5.60	5.40	5.20
Composition of the xylenes (%)				
o-Xylene	22.4	31.6	43.5	54.1
m-Xylene	56.2	40.8	28.7	20.2
p-Xylene	21.4	27.6	27.8	25.7

[a] The 2,3,4-trimethylpentane used in the reaction was of 99.9% purity.

tained mainly *m*-xylene. However, with time relatively less and less of this isomer was produced, and at the end of the aromatization cycle almost only *o*- and *p*-xylene were formed. Variations in the formation of the aromatic hydrocarbons during the dehydrogenation are summarized in Table 3 and illustrated in Fig. 1.

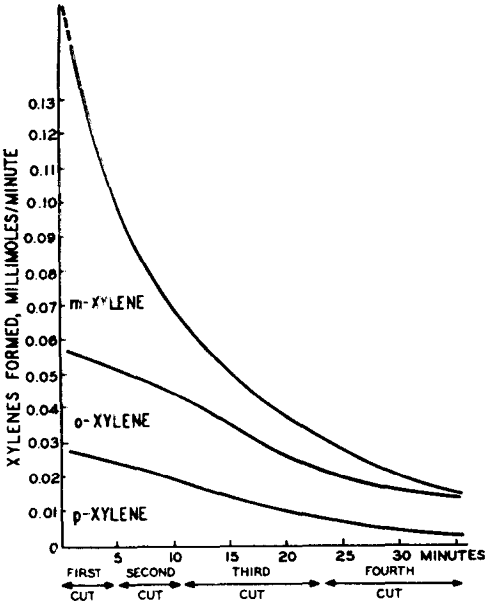
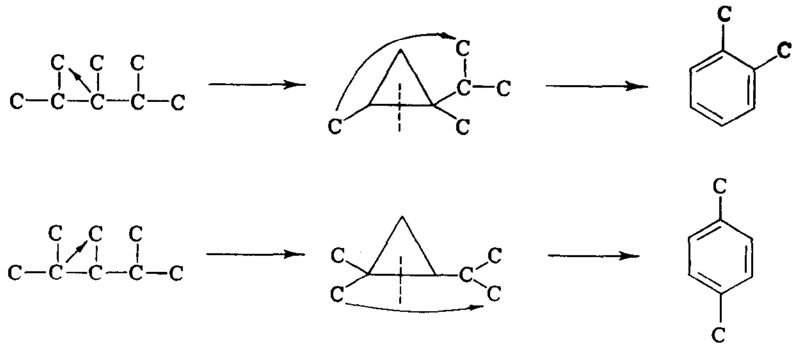


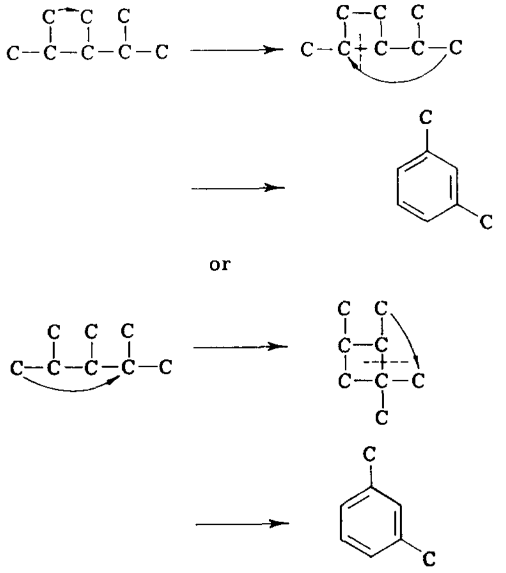
FIG. 1. Variation in the formation of xylenes in the dehydrogenation of 2,3,4-trimethylpentane over C_2O_3-Al_2O_3 catalyst as a function of time.

A small amount of toluene was also formed during the reaction.

A mechanism similar to the one proposed previously (*5*) would only explain the formation of *o*- and *p*-xylene:



The above mechanism would not explain the formation of the relatively large amount of *m*-xylene and small amount of ethylbenzene produced. For the formation of *m*-xylene it is necessary to assume the existence of an adsorbed transition state resembling substituted cyclobutane:



At the beginning of the cycle the reaction may proceed through the cyclobutane-type transition state, while later the relative contribution of the cyclopropane type becomes predominant.

Considerable cracking occurred during the dehydrogenation. The principle cracking products were propane, propylene, and methylbutenes. Recombination of these cracking products could produce all xylenes and ethylbenzene:

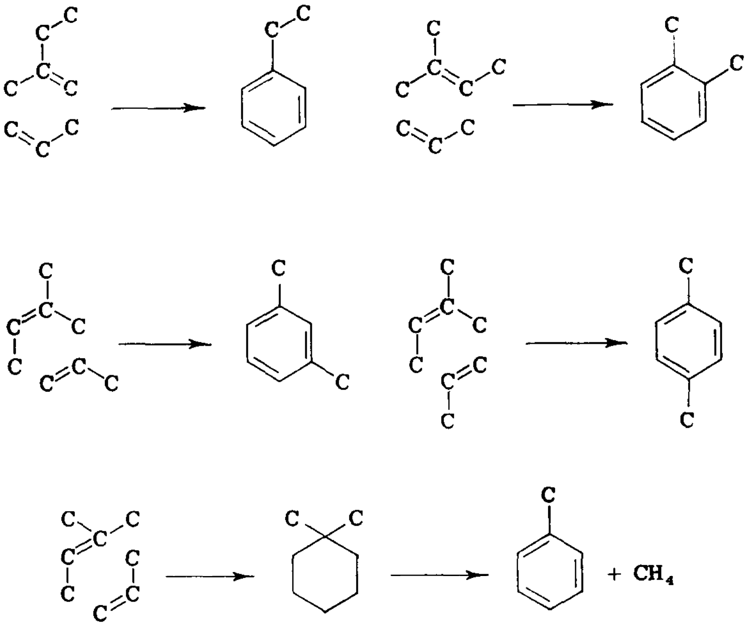


TABLE 4

REACTION OF 2-METHYL-2-BUTENE WITH PROPYLENE AND PROPANE OVER Cr_2O_3–Al_2O_3 CATALYST AT 527°

Cut number	1	2	3
Length of cuts (minutes)	10	10	10
Contact time (seconds)	2.1	0.9	1.5
2-Methyl-2-butene reacted (mole %)	14.2	10.8	9.6
Composition of reaction product (mole %)			
n-Butane	0.4	0.5	0.5
Isobutane	1.2	1.2	0.3
n-Butenes	3.2	2.3	1.3
Isobutylene	3.8	3.0	2.0
Butadiene	0.1	0.1	0.2
Isopentane	16.0	3.5	1.4
Isoprene	67.6	80.0	88.0
Toluene	2.1	2.8	2.0
Ethylbenzene	0.3	0.3	0.2
o-Xylene	1.7	2.1	1.3
m-Xylene	2.0	2.3	1.5
p-Xylene	1.6	1.9	1.3
Total C_7–C_8 aromatics formed based on mole % of reacted 2-methyl-2-butene	7.7	9.4	6.3
Composition of C_8 aromatics (mole %)			
Ethylbenzene	5	5	5
o-Xylene	30	32	30
m-Xylene	36	34	34
p-Xylene	29	29	31

The equilibrium constant for the reaction: Propylene + 2-Methyl-2-butene $\rightleftharpoons$ *m*-Xylene + $3H_2$ at 527°C is 5×10^5 (*9*).

To test the feasibility of such a mechanism, a mixture of 2-methyl-2-butene, propane, and propylene was reacted over chromia-alumina catalyst at 527°C (Table 4). The C_3/C_5 mole ratio was varied from 0.75 to 3.0 from cut to cut to study the reaction under different conditions. Considerable amounts of toluene and xylenes were formed. Contrary to the concentration variations observed in the case of 2,3,4-trimethylpentane, the relative concentrations of the C_8 aromatics remained constant through the experiment. Recombination of the cracking products may have an important contribution to the aromatization of 2,3,4-trimethylpentane. However, it does not explain the decrease of the relative concentration of *m*-xylene during the dehydrocyclization.

The possibility of *o*-xylene $\rightleftharpoons$ *m*-xylene isomerization was eliminated by an experiment in which *o*-xylene was passed over chromia-alumina at 544°. The experiment was performed under a moderate hydrogen partial pressure to simulate the conditions of the dehydrogenation experiments. Isomerizations to *m*- or *p*-xylenes were not observed. The only significant reaction was demethylation yielding toluene and methane.

TABLE 5

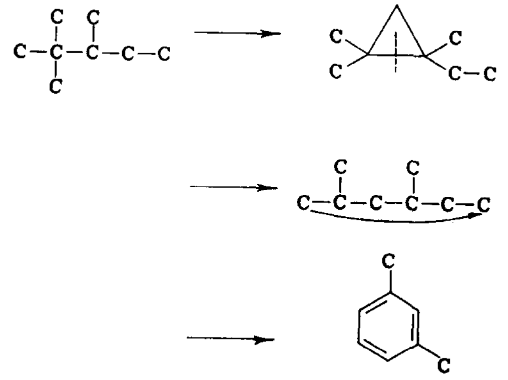
Dehydrogenation of 2,2,3-Trimethylpentane over Cr_2O_3–Al_2O_3 Catalyst at 533° and Contact Time of 3 Seconds

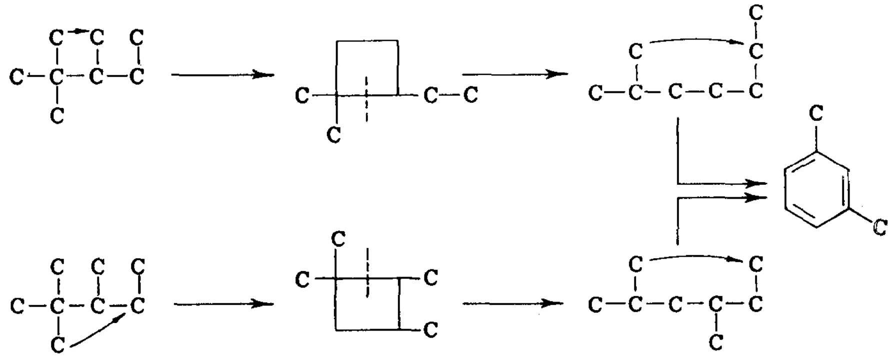
Cut number	1	2	3	4
Length of cuts (minutes)	6	6	20	12
2,2,3-Trimethylpentane reacted (mole %)	40	41.5	37	28.8
Composition of reaction product (mole %)				
Methane	11.08	11.09	11.50	11.80
Carbon monoxide	0.18	0.18	0.18	0.18
Carbon dioxide	0.02	0.02	0.02	0.02
Ethane	1.38	1.26	1.27	1.50
Ethylene	1.94	1.90	1.95	2.48
Propane	0.88	0.79	0.81	0.58
Propylene	4.82	4.26	3.62	2.88
n-Butane	7.25	7.00	7.15	6.50
Isobutane	6.04	6.30	6.53	4.90
n-Butenes	23.20	23.30	23.60	23.60
Isobutylene	28.30	28.60	29.20	27.00
Butadiene	1.15	1.17	1.04	0.90
n-Pentenes	0.06	0.07	0.06	0.07
Methylbutenes	1.64	1.55	1.40	1.80
2,2-Dimethylbutane	0.97	1.05	1.07	1.38
3,3-Dimethyl-1-butene	0.50	0.52	0.48	0.70
2-Methylpentenes	0.10	0.16	0.14	0.18
3-Methylpentenes	0.10	0.16	0.10	0.20
2,3-Dimethylbutenes	0.27	0.27	0.25	0.37
2,2,3-Trimethylbutane	0.19	0.33	0.29	0.39
2,3,3-Trimethyl-1-butene	0.60	0.60	0.60	0.50
2,2-Dimethylpentenes	0.34	0.34	0.30	0.20
2,3-Dimethylpentane	0.88	0.90	0.96	1.25
2,3-Dimethylpentenes	1.04	1.05	0.80	0.70
2,2,3-Trimethylpentenes	3.14	3.17	2.65	5.03
2,4-Dimethylhexenes	0.18	0.23	0.22	0.25
2-Methylheptenes	0.09	0.07	0.07	0.07
C_8 diolefins and cyclics	0.10	0.08	0.18	0.40
Benzene	0.06	0.05	0.05	0.05
Toluene	0.98	0.90	0.75	1.00
Ethylbenzene	0.06	0.04	0.03	0.06
o-Xylene	0.10	0.10	0.08	0.12
m-Xylene	0.80	0.95	1.08	1.33
p-Xylene	0.13	0.11	0.14	0.14
Higher aromatics	0.08	0.08	0.08	0.12
Carbonaceous material	1.35	1.35	1.35	1.35

2,2,3-Trimethylpentane

The experimental results are summarized in Table 5. Cracking was the main reaction. *m*-Xylene and toluene were the principal aromatic hydrocarbons produced and they were formed in nearly equal amounts. Ethylbenzene, *o*- and *p*-xylene and some C_9 aromatics were also present. Skeletal isomerization produced only 2,4-dimethylhexane and a very small amount of 2-methylheptane. The hydrogenated samples contained 0.4% methylcyclopentane and 0.01% trimethylcyclopropane.

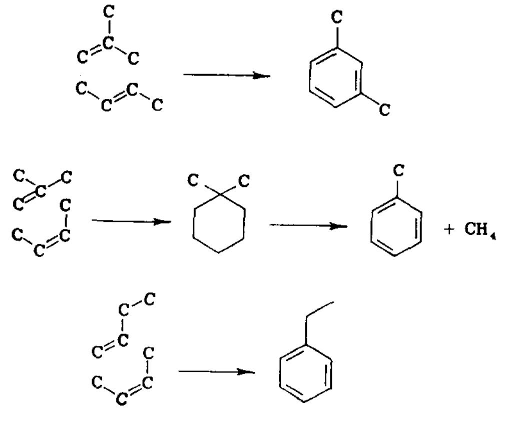
m-Xylene could be formed either through adsorbed cyclobutane- or cyclopropane-type species.

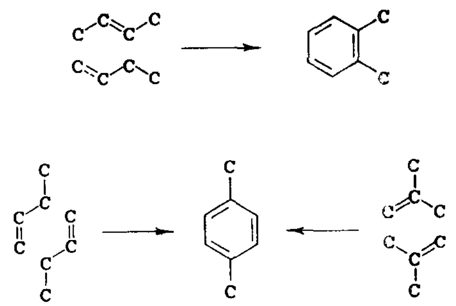




2,4-Dimethylhexane can be produced through both mechanisms. One of the cyclobutane-type intermediates can yield 2-methylheptane.

Cracking produced isobutane, isobutylene, *n*-butane, *n*-butenes, and butadiene. Recombinations should not only produce *m*-xylene and toluene, but also ethylbenzene, *o*-xylene, and *p*-xylene:





Recombination may explain the formation of the small amounts of ethylbenzene, *o*-xylene, and *p*-xylene, and may account for part of the *m*-xylene produced (see below).

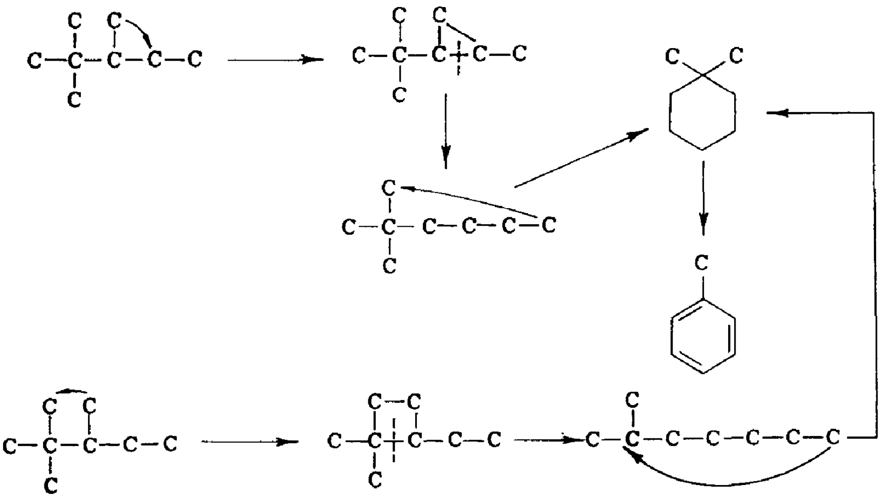
The formation of toluene could be explained by assuming cyclopropane and/or cyclobutane adsorbed species on the catalyst. (See scheme A, opposite page.)

A mechanism involving an alkylcyclopentane intermediate was considered; via this mechanism not only *m*-xylene and toluene but also *o*-xylene would be produced. (See scheme B, opposite page.)

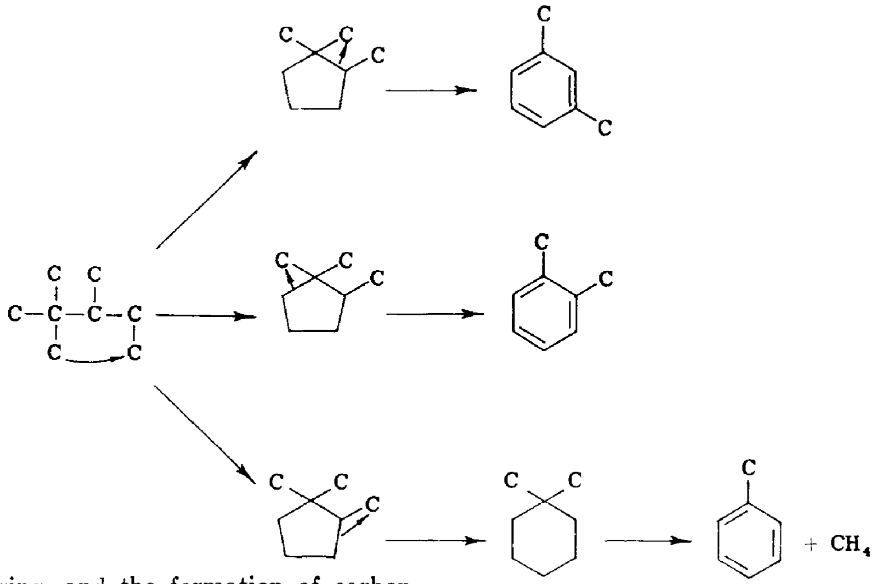
The involvement of alkylcyclopentanes as intermediates in the aromatization reaction is unlikely inasmuch as the amount of *o*-xylene produced in the aromatization of 2,2,3-trimethylpentane was less than one-tenth of that of *m*-xylene. Furthermore, this mechanism would not explain the formation of 2,4-dimethylhexane, *p*-xylene and ethylbenzene.

1-Methyl-2-ethylcyclopentanes

A mixture consisting of *cis*- and *trans*-1-methyl-2-ethylcyclopentane was dehydrogenated over chromia-alumina catalyst under the usual conditions (Table 6). The *cis*-isomer reacted faster than the *trans*. The principal reactions were dealkylation



A

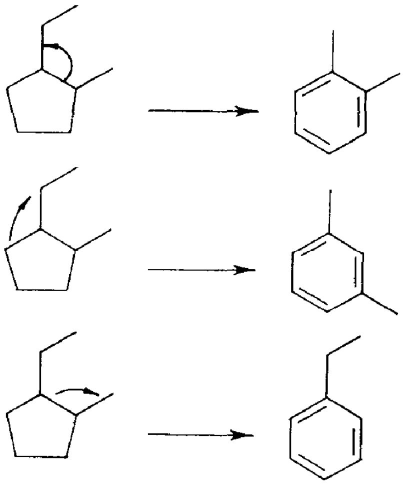


B

of the ring, and the formation of carbonaceous material. The latter was most probably produced by the condensation and dehydrogenation of cyclopentadienes formed. Small quantities of toluene, ethylbenzene, and xylenes were also produced. Less *m*- than *o*-xylene was formed and none of the *p*-xylene was found. Ring enlargement occurred at all available sites. (See scheme C.)

3-Ethylhexane

The main products of the aromatization were ethylbenzene and benzene which indicates that the 1,6-ring closure was the predominant reaction (Table 7). The reaction was accompanied by cracking with the



C

formation of C_2, C_3, and C_5 hydrocarbons. Very little 1,5-ring closure occurred, but products which could be interpreted by means of skeletal isomerization were practically absent.

TABLE 6

Dehydrogenation of 1-Methyl-2-Ethylcyclopentane[a] over Cr_2O_3–Al_2O_3 Catalyst at 522° and Contact Time of 3 Seconds

Cut number	1	3
Length of cuts (minutes)	6	6
trans reacted (mole %)	11.3	16.2
cis Reacted (mole %)	18.8	35.0
Total reacted (mole %)	11.9	17.7
Composition of reaction product (mole %)		
Methane	21.50	21.50
Carbon monoxide	1.44	1.44
Carbon dioxide	0.23	0.23
Ethane	12.28	11.30
Ethylene	2.84	2.70
Propane	0.70	0.40
Propylene	1.77	1.30
n-Butane	0.34	0.22
n-Butenes	2.06	1.32
Butadiene	0.04	0.04
Isobutylene	0.25	0.12
n-Pentane	0.25	0.16
n-Pentenes	1.68	0.95
Methylbutenes	0.10	0.07
Cyclopentane	0.04	0.05
Cyclopentene	0.38	0.26
Cyclopentadiene	0.65	0.51
n-Hexenes	0.20	0.25
2-Methylpentenes	0.11	0.14
3-Methylpentenes	0.09	0.11
Methylcyclopentane	1.96	0.60
Methylcyclopentenes	2.11	2.16
Methylcyclopentadienes	1.01	1.94
Ethylcyclopentane	0.91	0.32
Other C_7 cyclics	1.69	1.33
1-Methyl-2-ethylcyclopentenes	11.40	15.50
1-Methyl-2-ethylcyclopentadienes	0.78	3.06
Benzene	0.07	0.10
Toluene	1.67	1.30
Ethylbenzene	0.83	0.45
o-Xylene	1.32	1.00
m-Xylene	0.50	0.57
Carbonaceous material	28.80	28.60

[a] The hydrocarbons consisted of 91.8% *trans*- and 8.2% *cis*-isomer.

TABLE 7

Dehydrogenation of 3-Ethylhexane[a] over Cr_2O_3–Al_2O_3 Catalyst at 528° and Contact Time of 3 Seconds

Cut number	1	3
Length of cuts (minutes)[b]	8	12
3-Ethylhexane reacted (mole %)	29.6	36.7
Composition of reaction product (mole %)		
Methane	7.78	7.78
Carbon monoxide	0.29	0.29
Ethane and ethylene	15.05	14.00
Propane	5.90	4.80
Propylene	10.18	7.10
n-Butane	0.28	0.46
n-Butenes	3.90	3.24
Butadiene	0.14	0.10
n-Pentane	5.90	5.00
n-Pentenes	6.85	6.00
n-Pentadienes	2.40	2.30
Methylbutenes	0.20	0.12
Cyclopentane	0.03	0.06
Cyclopentadiene	0.03	0.02
n-Hexane	1.70	1.52
3-Methylpentane	0.11	0.13
n-Hexenes	4.50	3.60
2-Methylpentenes	0.20	0.15
3-Methylpentenes	1.30	1.00
Methylcyclopentenes	0.07	0.08
C_6 diolefins	0.10	0.12
3-Methylhexenes	0.40	0.50
3-Ethylpentenes	0.40	0.40
3-Ethylhexenes	7.11	8.00
3-Ethylhexadienes	0.80	1.00
Cyclic paraffins and olefins	0.54	0.47
Benzene	5.22	6.30
Toluene	1.03	1.35
Ethylbenzene	13.20	20.05
Styrene	2.03	1.70
o-Xylene	0.50	0.48
m-Xylene	0.21	0.22
C_9 aromatics	0.01	0.02
Carbonaceous material	1.64	1.64

[a] The hydrocarbon was of 99.4% purity.

[b] Cut 1 was taken during the first 8 minutes and cut 3 between 16 and 28 minutes of the experiment.

2,2-Dimethylbutane

The main reactions were the dehydrogenation of the title hydrocarbon to 3,3-dimethylbutene and the cracking to ethane, ethylene, isobutane, and isobutylene (Table 8). The only significant dehydroisomeriza-

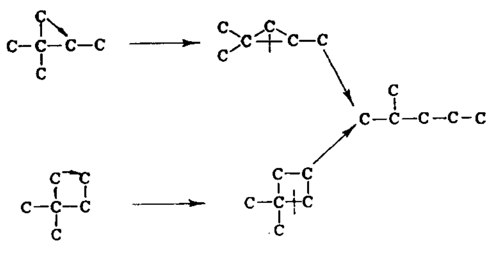
TABLE 8

DEHYDROGENATION OF 2,2-DIMETHYLBUTANE[a] OVER Cr_2O_3–Al_2O_3 CATALYST AT 528° AND CONTACT TIME OF 3 SECONDS

Cut number	1	2
Length of cuts (minutes)	12	15
2,2-Dimethylbutane reacted (mole %)	13.9	15.2
Composition of reaction product (mole %)		
Methane	9.50	9.50
Carbon monoxide	0.65	0.65
Carbon dioxide	0.06	0.06
Ethane	10.00	8.00
Ethylene	14.76	11.93
Propane	0.04	0.03
Propylene	0.02	0.02
Isobutane	6.14	5.50
Isobutylene	21.48	22.10
Neopentane	0.02	0.04
Isopentane	0.26	0.27
Methylbutenes	7.78	7.66
Isoprene	1.16	1.13
n-Pentenes	0.10	0.11
3,3-Dimethyl-1-butene	21.60	25.60
2-Methylpentenes	2.08	2.69
3-Methylpentenes	0.10	0.14
2,3-Dimethylbutenes	0.22	0.38
2-Methylpentadienes	2.88	2.94
2,3-Dimethylbutadiene	0.10	0.15
n-Hexenes	0.03	0.03
Methylcyclopentenes	0.08	0.08
1,1,2-Trimethylcyclopropane	0.09	0.16
Benzene	0.08	0.08
Toluene	0.08	0.07
p-Xylene	0.04	0.03
Carbonaceous material	0.65	0.65

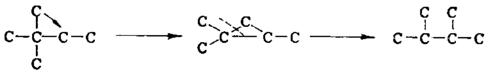
[a] The hydrocarbon was of 99.99% purity.

tion products formed were 2-methylpentenes and 2-methylpentadienes. The isomerization might have proceeded either through intermediates resembling adsorbed cyclopropane or cyclobutane species:



1,1,2-Trimethylcyclopropane in amounts of 0.09–0.16 mole % was found in the reaction product, which indicates that cyclopropane intermediates can desorb from the catalyst surface.

Only about 0.33–0.53% of the 2,2-dimethylbutane was converted to hydrocarbons having a 2,3-dimethylbutane skeleton, which could have been formed via cyclopropane adsorbed species.*



The 2-methylpentadiene/2-methylpentene ratio was 1.2–1.4. 2-Methylpentane was not formed in the reaction. The primary product of the dehydroisomerization could have been the diolefin, part of which was readsorbed and hydrogenated later to monoolefins.

2,3-Dimethylbutane

The main reactions consisted of the dehydrogenation of the 2,3-dimethylbutane to the corresponding olefins and diolefins and the cleavage to form propane and propylene (Table 9). Some demethanation also occurred with the resulting formation of methylbutenes. The products of the dehydroisomerization of 2,2-dimethylbutane consisted of 2- and 3-methylpentenes and pentadienes.

The 2-methylpentenes could be formed by the involvement of adsorbed cyclopropane-type intermediate, while the 3-methylpentenes could be formed through the involvement of cyclobutane-type. (See reaction scheme on next page.)

The ratio of 3-methylpentenes (and dienes) to 2-methylpentenes (and dienes) dropped from 2.1 to 0.4 from the beginning of the dehydrogenation cycle to its end. The reverse reactions, the isomerization of methylpentenes to 2,3-dimethylbutenes (and dienes), showed the same trend; the

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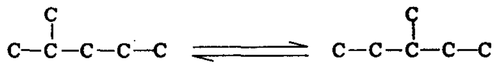
* W. Lorz, *et al.* (*10*) reported that 2,3-dimethylbutenes and butadienes were the main dehydroisomerization products. The authors failed to indicate the method of preparation of their chromia-alumina catalyst. From the results obtained it would seem that their catalyst contained acidic sites.

TABLE 9

Dehydrogenation of 2,3-Dimethylbutane over Cr_2O_3-Al_2O_3 Catalyst at 528° and Contact Time of 3 Seconds

Cut number	1	2	3
Length of cuts (minutes)	12	12	12
2,3-Dimethylbutane reacted (mole %)	28.0	31.3	33.0
Composition of reaction product (mole %)			
Methane	6.42	6.42	6.42
Carbon monoxide	0.38	0.38	0.38
Carbon dioxide	0.02	0.02	0.02
Ethane	0.20	0.25	0.22
Ethylene	0.13	0.13	0.11
Propane	11.22	10.42	9.16
Propylene	12.00	9.90	7.46
Isobutane	0.03	0.05	0.07
Isobutylene	0.32	0.32	0.30
n-Butenes	0.09	0.08	0.07
Isopentane	0.47	0.60	0.56
Methylbutenes	7.15	6.68	6.20
Isoprene	0.50	0.50	0.43
2,3-Dimethylbutenes	42.20	45.00	49.20
2,3-Dimethylbutadiene	8.30	8.40	8.68
2-Methylpentenes	2.10	2.71	3.61
2-Methylpentadienes	0.90	0.98	1.24
3-Methylpentenes	4.86	4.65	3.44
3-Methylpentadienes	0.71	0.44	0.46
Methylcyclopentenes	0.17	0.13	0.10
Benzene	0.16	0.23	0.22
Toluene	0.04	0.07	0.05
p-, *m*-Xylenes	0.04	0.04	0.03
o-Xylene	0.03	0.03	0.02
Higher aromatics	0.04	0.05	0.03
Carbonaceous material	1.52	1.52	1.52
Ratio of: $\frac{\text{2-Methylpentane skeleton}}{\text{3-Methylpentane skeleton}}$	1.85	1.38	0.80

dehydroisomerization of 3-methylpentane to 2,3-dimethylbutenes decreased with time while that of 2-methylpentane to 2,3-dimethylbutenes remained unchanged (*1*). Isomerization such as



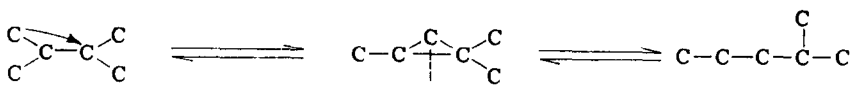
$$C-\overset{C}{\underset{}{C}}-C-C-C \rightleftharpoons C-C-\overset{C}{C}-C-C$$

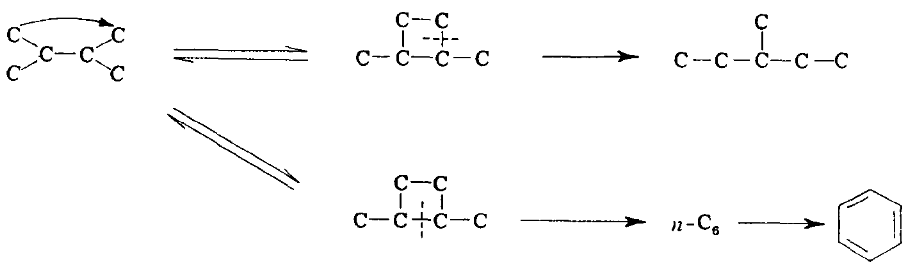
was found to be negligible under the same conditions.

The 2-methylpentadienes/2-methylpentenes ratio was approximately 0.4 while that of 2,3-dimethylbutadiene/2,3-dimethylbutenes was only 0.19, indicating again that the primary product of the cyclopropane-type isomerization seems to be a diolefin. The 3-methylpentadiene/3-methylpentene ratio varied between 0.1 and 0.14, and therefore the primary products of the cyclobutane-type isomerization seem to be olefins.

The 2,3-dimethylbutane ⇌ 3-methylpentane isomerization is similar to the dehydrocyclization of 2,3,4-trimethylpentane to *m*-xylene. Rates of both reactions change with the deactivation of the catalyst during each dehydrogenation cycle. The only mechanism which seems to explain these reactions proceeds through adsorbed cyclobutane-type intermediates, involving primary carbon atoms attached to vicinal tertiary carbons.

A small amount of benzene was also formed; this could have been produced through the adsorbed cyclobutane-type intermediate, or by recombination of propylene, the principal product of cracking.





Five-membered ring intermediates *cannot* be involved in the dehydroisomerization of the dimethylbutanes.

Neopentane

Isomerization was not observed when neopentane was reacted over chromia-alumina (Table 10). Apparently only hydrocarbons which can be dehydrogenated to olefins are able to form the adsorbed cyclopropane-type intermediates and undergo isomerization. Cracking to isobutylene and methane was the only important reaction of neopentane. "Recombination" of two isobutylene molecules yielded some *p*-xylene.

TABLE 10

DEHYDROGENATION OF NEOPENTANE OVER CHROMIA-ALUMINA CATALYST AT 537° AND CONTACT TIME OF 3 SECONDS

Length of experiment (minutes)	37
Neopentane reacted (mole %)	4
Composition of reaction product (mole %)	
Carbon monoxide	0.40
Carbon dioxide	0.30
Methane	48.00
Ethane and ethylene	0.30
Propane	0.06
Propylene	0.20
Isobutane	0.04
Isobutylene	49.80
Methylbutenes	0.10
Isoprene	0.10
Benzene	0.02
Toluene	0.06
p-Xylene	0.23
o-Xylene	0.03
Unknowns	0.36

CONCLUSIONS

A new type of isomerization of branched hydrocarbons occurs over nonacidic chromia-alumina catalyst. This isomerization might precede the aromatization of hydrocarbons with less than six carbon atoms in a chain. The reaction is not catalyzed by acids, and carbonium ion intermediates are not involved. Contrary to acid-catalyzed isomerizations, this reaction is selective, producing only certain distinct structures rather than a large number of skeletal isomers. This new type of isomerization may proceed through adsorbed alkylcyclopropane or alkylcyclobutane type intermediates. The relative contributions of each of the cyclic intermediates change with the deactivation of the catalysts during each dehydrogenation cycle.

The isomerization involving cyclobutane-type transition states decreases during a dehydrogenation cycle. Apparently the active sites responsible for this isomerization deactivate very rapidly. The cyclization occurs between two primary carbon atoms attached to tertiary carbons vicinal to each other. The primary products of this isomerization are monoolefins.

The isomerization involving adsorbed alkylcyclopropane-type intermediates is more general. The cyclopropane ring forms between a primary and a tertiary or secondary carbon atom. The alkylcyclopropane produced may desorb from the catalyst as such, or undergo ring-cleavage. The bond between the two most substituted carbon atoms breaks and a new molecule with a different carbon skeleton is produced. Apparently only hydrocarbons which can form olefins are able to form the cyclopropane intermediate and isomerize. The primary products of the isomerization are diolefins. The isomerization step may have to occur simultaneously with a dehydrogenation step. The active sites responsible for this isomerization do not deactivate as rapidly as those responsible for the cyclobutane-type isomerization.

Cyclobutane-type transition states are involved in the dehydroisomerization or dehydrocyclization of at least two hydrocarbons: 2,3-dimethylbutane and 2,3,4-trimethylpentane. The isomerization mechanism involving adsorbed alkylcyclopropane-type intermediates gives consistent and satisfactory explanations for all other dehydroisomerizations and aromatizations observed in our experiments.

Recombination of the products of cracking may contribute to the aromatization of some trimethylpentanes. In the case of 2,2,4-trimethylpentane recombination of isobutylene to form *p*-xylene is unimportant, as indicated by the C^{14} experiments of Cannings *et al.* (*5*). In the aromatization of 2,2,3-trimethylpentane the small quantities of ethylbenzene, *o*-xylene, and *p*-xylene were probably produced by recombination. Recombination of isobutylene and *n*-butenes may have contributed to some extent to the formation of the principal aromatic products, *m*-xylene and toluene.

An isomerization mechanism involving alkylcyclopentane intermediates cannot account for the aliphatic isomerization products. Five-membered ring intermediates cannot be formed from dimethylbutanes. Xylene distribution in the aromatization of the trimethylpentanes is inconsistent with the structures of the possible trimethylcyclopentane intermediates. Polyalkylcyclopentanes when reacted over nonacidic chromia-alumina produced xylenes in different distributions than expected if they were intermediates in dehydrocyclization reactions. In view of these facts a mechanism involving five-membered ring intermediates cannot be important in the dehydroisomerization and aromatization of branched hydrocarbons over nonacidic chromia-alumina catalyst.

The experimental results indicate the preferential involvement of primary carbon atoms in the reactions over the "nonacidic" chromia-alumina catalyst. This points to carbanion-type attachment to the catalyst during the initial stages of the reaction.

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