

Aromatization of Heptanes, Ethylcyclopentane, and Cycloheptane over "Nonacidic" Platinum-Alumina Catalyst. Comparison of the Mechanisms of Aromatization over Chromia-Alumina and over Platinum-Alumina Catalysts¹

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n-Heptane, 2- and 3-methylhexane, ethylcyclopentane, and cycloheptane were passed in the presence of hydrogen at 500°C over "nonacidic" platinum-alumina catalyst containing 3% by weight of platinum. The conversion ranged between 12 and 26%, depending on the interval of time the product was removed for analysis. In the case of cycloheptane, however, the conversion amounted to 98% during the first 30 min on stream and with time, during the approximate period between 2 and 3 h, it decreased to 69%. The products from the reaction contained besides toluene, also hydrocarbons resulting from a skeletal isomerization and dehydrocyclization of the original hydrocarbons, and to a smaller extent from a bond shift process, and a repetitive 1,5-ring closure followed by hydrogenolysis. Using 1,1-dimethylcyclohexane as a model compound, it was shown that the skeletal isomerization accompanying the aromatization of the seven-carbon hydrocarbons does not proceed through cationic intermediates. A survey of the literature relating to the mechanism of aromatization of hydrocarbon over "nonacidic" chromia-alumina and platinum-alumina catalysts is presented, and the differences between the two mechanisms are discussed.

INTRODUCTION

Chromia-Alumina

The aromatization of alkanes over chromia-alumina catalysts has been the subject of extensive studies in recent years. The mechanism of this reaction has been reviewed in 1965 by Pines and Goetschel (1), and in 1971 by Rozengart and Kazanskii (2). On the basis of extensive research made with a variety of radioactive-labeled

hydrocarbons, the mechanism of aromatization of normal and branched-chain heptanes and octanes, including trimethylpentanes and octanes, including trimethylpentanes, is now seemingly well understood.

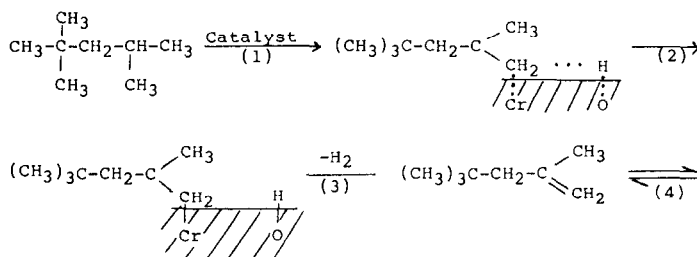
Three types of reactions participate in the aromatization of 2,2,4-trimethylpentane to *p*-xylene.

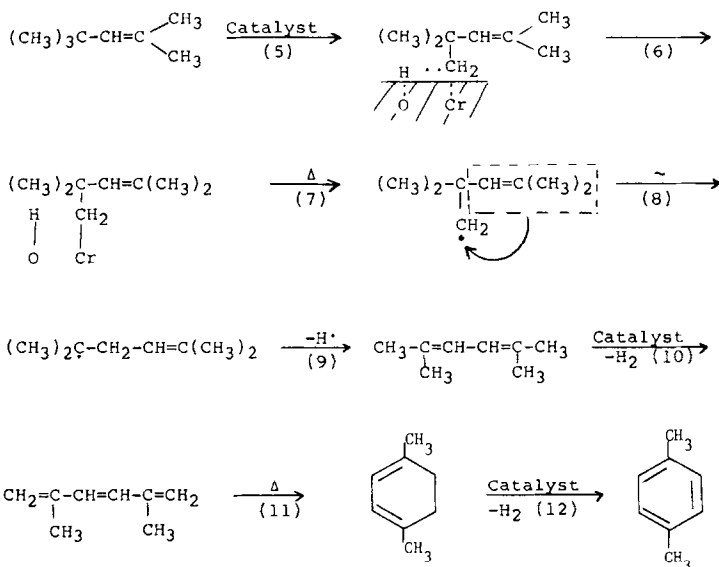
- a. Catalytic dehydrogenation with evolution of hydrogen.
- b. Free-radical skeletal isomerization of alkenes accompanied by vinyl migration.
- c. Thermal cyclization of hexatrienes to cyclohexadienes.

This mechanism can be adequately illustrated by the following equations (3):

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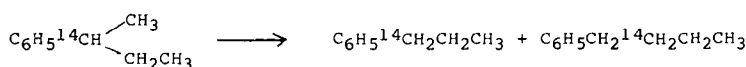


Steps 1–4, 10, and 12, involve catalytic dehydrogenation of hydrocarbons over chromia (4, 5). The homolytic rupture of the organometallic bond in step 7 (6) is followed in step 8 by vinyl migration, similar to a free-radical reaction induced by iodine (7).

Step 11 is a thermal reaction not requiring a catalyst. The triene undergoes a rapid cyclization via internal Diels–Alder reac-

tion (8), and this reaction has been studied extensively with heptatriene (2, 9–13).

The convincing diagnostic test that a radical intermediate participates in the rearrangement reaction was demonstrated by the dehydrogenation of *tert.*-butylbenzene to isobutenylbenzene and by the conversion of 2-[2-¹⁴C]phenylbutane to isotopic isomers of *n*-butylbenzene (14)



For a “nonacidic” chromia–alumina catalysts to act as a skeletal isomerizing catalyst of hydrocarbons, it is essential that the alkanes undergo a prior dehydrogenation reaction, or that they contain an aromatic ring as a substituent. Alkanes which cannot undergo dehydrogenation, such as neopentane (15) or 2,2,3,3-tetramethylbutane (16), do not undergo skeletal rearrangement.

The mechanism described above can also be applied to explain the results of aromatization of 2,2-dimethyl[3-*methyl*-¹⁴C]pentane in which 71% of the radioactivity in *m*-xylene formed was the methyl

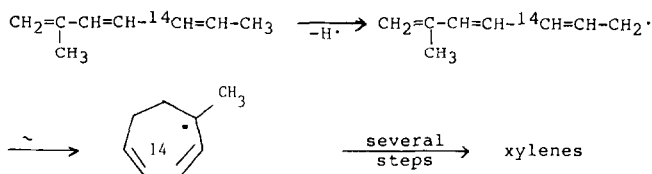
group, and the remainder in the benzene ring (17, 18).

The aromatization of 2,4-dimethyl[3-*methyl*-¹⁴C]pentane formed a mixture of xylenes of which *m*- and *p*-xylene contained about 95% of the radioactivity in the ring, while *o*-xylene contained 95% of ¹⁴C in the methyl groups (19). The formation of *o*- and *p*-xylene can also be explained by a free-radical-induced vinyl migration, while the presence of *m*-xylene could be interpreted by two vinyl migration steps (18).

The minor distribution of radioactivity in the ring of *o*-xylene and in the side chain of

p-xylene indicates that a portion of the xylenes was probably formed by seven-

carbon ring intermediates, via methylheptadiene intermediate (18):

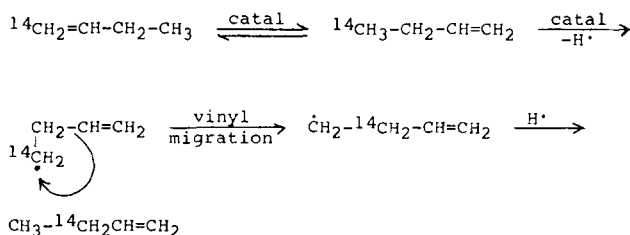


The intermediate formation of C₇-ring intermediates is also indicated by the fact that [1-¹⁴C]heptane produces toluene with less than 50% of radioactivity in the methyl group (20–23), and that [4-¹⁴C]heptane forms toluene with radioactivity in the methyl group (23, 24). This is a clear indication that 1,6-carbon ring closure is not the only mechanism by which toluene is produced. It was thus proposed that seven-carbon ring compounds must also participate in the reaction, which by ring contraction would then form toluene (25).

n-Octane on aromatization over nonacidic chromia–alumina produces besides ethylbenzene and *o*-xylene also *m*- and *p*-xylene and is an indication that in addition

to a direct 1,6-carbon ring closure, other cyclization reactions occur (26). From the study of aromatization of [1-¹⁴C]octane (27–29) it was proposed that 1,7- and 1,8-carbon ring closure must also participate in the aromatization. The observation that [4-¹⁴C]octane produced ethylbenzene with equal radioactivity on the α and β carbons of the ethyl group (29) reinforced our belief that an eight-membered ring intermediate participates in the aromatization reaction of octanes.

Free-radical mechanism as a suggested step in the skeletal isomerization of hydrocarbons in the presence of chromia–alumina, would also explain the rearrangement of [1-¹⁴C]butene to [2-¹⁴C]butenes (30)



Platinum–Alumina

Although the aromatization of alkanes over platinum catalysts was discovered in 1936 (31), the mechanism by which cyclization and skeletal isomerization accompanying this reaction occurs is still being disputed.

It was observed that skeletal isomerization and cyclization reaction are not re-

stricted to dual-function catalysts containing platinum and an acidic support. Skeletal isomerization may occur on evaporated platinum film and also on platinum deposited on an inert support, such as silica (32–34). Reviews of this subject have appeared (35a, b).

The hydrogenolysis of methylcyclopentane over the same catalysts has been studied and it was concluded that the isomeriza-

tion of hexanes and the hydrogenolysis of methylcyclopentane involve a common intermediate (34, 36).

Similar results were observed in the isomerization of heptane over platinum deposited on neutral silica gel (37).

"Nonacidic" platinum-supported catalysts also catalyze the conversion of hexanes and higher alkanes into aromatics. The aromatics are produced from alkanes which can undergo a direct 1,6-carbon ring closure, and from alkanes which have a chain length of five carbon atoms. It was reported that in the former case the aromatization produces virtually only those aromatics which can form by a direct 1,6-carbon ring closure (38, 39).

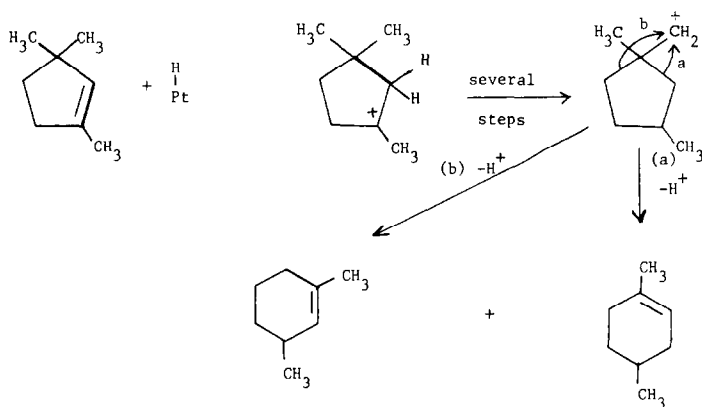
A similar conclusion has been reached from the study of aromatization of octanes and nonanes over 0.6% platinum catalyst supported on "nonacidic" alumina (40).

Open-chain olefins and diolefins are produced during aromatization of hexane (41). It was proposed that the cyclization to form aromatics proceeds through hexadiene or hexatriene intermediates (42).

In a separate study of the isomerization and dehydrocyclization of hexanes over platinum supported on nonacidic alumina and using low hydrogen partial pressures, it was found that five-membered ring structures are not involved in the conversion of *n*-hexane into benzene (43).

It was reported that platinum black shows different catalytic activities in the presence of helium and hydrogen (44). The main product from hexane in helium carrier gas was benzene, while in hydrogen methylpentanes and methylcyclopentane were among the products of the reaction, and their amounts were larger than that of benzene.

It was reported that 2,2,4-trimethylpentane and the corresponding alkenes, formed over nonacidic platinum-alumina catalysts 1,1,3-trimethylcyclopentane, and a mixture of *m*- and *p*-xylene (45). It was proposed that the reaction proceeds *via* a cationic ring expansion, platinum acting as an electron sink for adsorbed cyclopentenones.



It is difficult, however, to reconcile the above interpretation involving 1,3-hydride shift with the known behavior of carbonium ion chemistry, and with the absence of *o*-xylene in the reaction product.

The study with *n*-heptane has revealed that the cyclization activity of platinum-

alumina containing a small amount of halides increases linearly with the metal surface (46). The extrapolation of the data set to zero platinum surface led to a positive intercept indicating that the residual cyclization activity was due to ring closure of heptenes over alumina. *n*-Heptane was

also passed over platinum on silica, in which the residual acidity of the silica was neutralized by a small amount of lithium. From extrapolation of the data toward zero residence it was concluded that five-membered ring closure is responsible for at least 90% of the total conversion. The only cyclopentanes obtained were ethylcyclopentane and 1,2-dimethylcyclopentane. Since ethylcyclopentane isomerized nearly ten times as fast as dimethylcyclopentanes (47), it was concluded that toluene formed from the cyclization of heptane came from the dehydroisomerization of ethylcyclopentane.

From the study of the dehydrocyclization of *n*-heptane, having ^{14}C in the 1 and 4

positions over platinum on nonacidic alumina, Davis (48) has concluded that 89% or more of the toluene was formed by a direct six-carbon ring formation. The small amount of ^{14}C distribution in the toluene not allowed by a direct six-carbon ring formation, Davis considered to arise from isomerization of *n*-heptane to methylhexanes, prior to or during cyclization.

Platinum film or platinum deposited on inert supports can isomerize butanes in the presence of hydrogen (32, 49). This type of a nonionic skeletal isomerization was suggested to proceed *via* a C_3 cyclic reaction intermediate, and a mechanism for this reaction has been proposed (32, 35, 49, 50):



This type of reaction was named by bond shift isomerization, and more than one shift process can occur in one period of residence on the surface (22).

It was observed that the complexity of the reaction pathway is increased when alkanes large enough to form a C_5 or C_6 ring are passed over platinum metal catalyst. Thus hexane produced reversibly 2- and 3-methylpentane and methylcyclopentane (33, 34, 43). From the study of ^{13}C -labeled hexanes it was concluded that skeletal isomerization of hexanes may occur by two mechanisms: (a) hydrogenolysis of adsorbed methylcyclopentane and (b) bond shift process (51–53). The position of the labeling atom in most of the isomeric reaction products is consistent with the cyclic mechanism of isomerization involving cyclopentane-adsorbed species.

Platinum–alumina catalysts could be substantially improved by the addition of certain metals such as rhenium, tin, and germanium. The steady-state activity of these catalysts is superior to that of monometallic catalysts. The mechanism of bime-

tallic catalysts is still being disputed, and it is not certain whether the bimetallics function as “alloys” or “clusters.” It is assumed that in the presence of PtSn catalyst at temperatures above 500°C , hexatriene formed on the catalyst from hexane contributes to the production of benzene (54).

Davis reported that the ratio of *o*-xylene to ethylbenzene formed from octane increased with the decrease in platinum loading and the increase of Sn in the Pt/ Al_2O_3 catalyst. He also found the presence of *m*-xylene in the product (55).

From the concentration of ^{14}C in the methyl group of toluene derived from the aromatization of [1- ^{14}C]- and [4- ^{14}C]heptane over nonacidic Pt–Re/ Al_2O_3 catalyst, it is obvious that 1,6-ring closure cannot be the only way by which aromatization occurs (56).

Present Work—Its Scope

The survey of the literature on the aromatization and dehydrocyclization of alkanes over platinum-containing catalyst reveals controversial opinions regarding the

mechanism of aromatization. The main issue involved is whether 1,6-ring closure is the preferred step in the aromatization of *n*-heptane and methylhexanes, and to what extent a 1,5-ring closure competes with the direct aromatization reaction. Another issue under consideration is whether skeletal isomerization accompanying aromatization occurs *via* a bond shift process and/or through hydrogenolysis of alkylcyclopentanes produced in the reaction.

In order to determine some of the paths participating in or accompanying the aromatization of alkanes, the following hydrocarbons were passed over a "nonacidic" platinum-alumina catalyst: *n*-heptane, 2- and 3-methylhexane, ethylcyclopentane, and cycloheptane. The accompanying paper will describe the aromatization of [^{14}C]heptane to toluene, with the distribution of radioactivity in the individual ring positions of the toluene.

The "nonacidic" platinum-alumina catalyst was prepared by depositing 3% by weight of platinum in the form of diamino-platinum nitrite on 165-20 mesh alumina, which has been previously shown to contain very low intrinsic catalytic acidity (57).

The experiments were conducted in a modified flow system reaction developed by Steingaszner and Pines (58). For each set of experiments 400 mg of fresh catalyst was used. The hydrocarbons were passed over the catalyst at 50°C under hydrogen pressure of 5 atm, and the product was collected at intervals of time indicated in the respective Tables 1-5. The experiments were made at an hourly liquid space velocity of 7.3, and with a hydrogen-to-hydrocarbon mole ratio of 5.1. Instantaneous sampling of the product was performed at intervals by means of a pneumatically activated diaphragm sampling valve, and analyzed by vapor-phase chromatography.

TABLE 1
Dehydrocyclization of *n*-Heptane over Platinum-Alumina Catalyst^a at 500°C^b

Time on stream (min): Conversion:	Conversion product composition (mole%)			
	30	75	118	150
	20.3	18.5	13.6	11.7
Ethane	5.6	7.2	6.9	6.1
Propane	6.4	6.3	5.1	6.9
<i>n</i> -Butane	7.0	6.9	6.1	7.5
<i>n</i> -Pentane	7.1	6.5	5.3	5.9
2-Methylpentane	0.7	—	—	—
<i>n</i> -Hexane	6.8	5.4	6.2	4.5
2-Methylhexane ^c	6.4 (9.4)	7.4 (11.2)	7.1 (10.3)	7.7 (11.1)
3-Methylhexane	11.3 (18.3)	11.4 (17.2)	12.1 (17.5)	11.0 (15.9)
3-Ethylpentane	1.1 (1.7)	0.8 (1.2)	0.6 (0.9)	Traces
<i>trans</i> -1,2-Dimethylcyclopentane ^d	4.1 (6.4)	5.8 (8.8)	4.8 (6.9)	4.9 (7.1)
<i>cis</i> -1,2-Dimethylcyclopentane	1.1 (1.7)	1.8 (2.4)	1.3 (1.9)	1.4 (2.0)
Ethylcyclopentane	19.8 (30.8)	20.4 (30.8)	24.7 (35.7)	29.1 (42.1)
Toluene	20.5 (31.9)	18.6 (28.1)	18.6 (26.9)	15.0 (21.7)
Unidentified compounds	1.6	1.7 (2.6)	1.2 (1.7)	—

^a 400 mg of 3 wt% platinum on alumina.

^b The experiment was made at an hourly liquid space velocity of 7.3. The liquid hydrocarbon flow rate was 3.8 ml/hr and that of hydrogen 50 cm³ (STP)/min. The hydrogen-to-hydrocarbon mole ratio is 5.1

^c Composition of C-7 hydrocarbons given in parentheses.

^d Obtained by calculation assuming equilibrium between *trans*- and *cis*-1,2-dimethylcyclopentanes at 500°C. The ratio of *trans* to *cis* is 3.0 (API Research Project 44).

TABLE 2

Dehydrocyclization of 2-Methylhexane over Platinum-Alumina Catalyst^a at 500°C^b

Time on stream (min):	Conversion product composition (mole%)				
	30	70	110	155	215
Conversion:	26.3	20.7	18.3	15.6	15.0
Ethane	1.6	1.4	3.6	—	2.9
Propane	4.2	4.4	4.4	5.4	6.2
Isobutane	2.5	2.5	2.2	2.3	2.0
<i>n</i> -Butane	1.6	1.5	1.4	1.3	1.2
Isopentane	2.0	1.7	1.3	1.6	1.3
Pentane	0.1	—	—	—	—
2-Methylpentane	3.5	2.6	4.0	2.6	4.7
<i>n</i> -Hexane	2.7	2.8	2.8	2.1	2.3
2,4-Dimethylpentane ^c	4.6 (5.7)	3.9 (4.7)	2.8 (3.5)	3.4 (4.0)	1.9 (2.4)
3-Methylhexane	10.9 (13.4)	10.2 (12.4)	10.7 (13.4)	11.6 (13.8)	13.4 (16.9)
<i>n</i> -Heptane	23.5 (29.0)	26.2 (31.8)	30.2 (37.8)	28.5 (33.8)	31.7 (40.0)
Toluene	42.1 (51.9)	42.0 (51.1)	36.2 (45.3)	40.7 (48.3)	32.2 (40.7)
Unidentified compounds	0.7	0.8	0.4	0.5	0.2

^{a,b,c} See footnotes *a-c*, Table 1.EVALUATION OF THE INTRINSIC ACIDITY
OF THE CATALYST

In order to minimize isomerization reactions accompanying aromatization, which

may be due to a cationic process, it was necessary to establish the intrinsic acidity of the catalyst. It was found that only the respective xylenes with a small amount of toluene were obtained, when mixtures of

TABLE 3

Dehydrocyclization of 3-Methylhexane over Platinum-Alumina^a at 500°C^b

Time on stream (min):	Conversion product composition (mole%)				
	30	70	115	170	210
Conversion:	22.9	18.3	14.0	15.3	13.5
Ethane	4.9	4.9	4.2	4.2	5.0
Propane	2.8	3.2	2.6	2.8	2.6
<i>n</i> -Butane	2.8	3.0	2.7	2.2	3.6
Isopentane	2.4	2.0	2.1	1.9	2.0
Pentane	2.5	2.1	1.9	1.9	1.6
2-Methylpentane	4.4	4.0	2.7	2.8	1.8
3-Methylpentane	1.8	1.5	0.8	0.9	0.6
<i>n</i> -Hexane	1.8	1.4	0.9	1.1	0.5
2,4-Dimethylpentane ^{c,d}	0.9 (1.2)	0.7 (0.9)	0.4 (0.5)	—	—
2-Methylhexane	9.4 (13.0)	8.0 (10.8)	11.1 (14.1)	9.0 (11.3)	9.9 (12.2)
<i>n</i> -Heptane	31.6 (43.6)	34.5 (46.4)	35.8 (45.5)	26.7 (33.6)	24.5 (30.2)
<i>trans</i> -1,2-Dimethylcyclopentane ^d	Trace	Trace	Trace	7.3 (9.2)	7.2 (8.9)
<i>cis</i> -1,2-Dimethylcyclopentane ^d	—	—	—	2.0 (2.5)	2.0 (2.5)
Ethylcyclopentane	6.6 (9.1)	8.0 (10.8)	9.7 (12.3)	13.7 (17.2)	20.4 (25.2)
Toluene	23.9 (33.0)	23.1 (31.1)	21.7 (27.6)	20.2 (28.2)	17.0 (21.0)
Unidentified compounds	4.2	3.6	3.4	2.7	1.3

^{a,b,c,d} See footnotes *a-d*, Table 1.

TABLE 4

Dehydrocyclization of Ethylcyclopentane over Platinum–Alumina Catalyst^a at 500°C^b

Time on stream (min):	Conversion product composition (mole%)			
	30	80	140	175
Conversion:	26.1	19.7	16.4	16.6
Ethane	3.1	2.8	*	*
Propane	0.8	0.6	*	*
<i>n</i> -Butane	1.3	0.4	*	*
Isopentane	0.1	*	*	*
Pentane	1.8	0.8	*	*
2-Methylpentane	1.1	*	*	*
3-Methylpentane	1.4	3.2	*	*
<i>n</i> -Hexane	0.4	1.2	*	*
Unknown (I)	8.8	5.8	5.2	5.2
3-Methylhexane ^c	24.4 (30.1)	20.9 (24.8)	23.3 (24.6)	21.4 (22.8)
3-Ethylpentane	5.9 (7.3)	4.9 (5.8)	3.7 (3.9)	3.3 (3.5)
<i>n</i> -Heptane	17.9 (22.1)	7.3 (8.7)	1.7 (1.8)	3.4 (3.6)
<i>trans</i> -1,2-Dimethylcyclopentane ^d	4.0 (4.9)	10.2 (12.1)	14.8 (15.6)	11.3 (12.0)
<i>cis</i> -1,2-Dimethylcyclopentane	1.1 (1.4)	2.8 (3.3)	4.1 (4.3)	3.1 (3.3)
2- and 5-Ethylcyclopentadiene ^d	17.3 (21.9)	30.5 (36.2)	36.5 (38.5)	37.9 (40.4)
Toluene	10.4 (12.4)	7.6 (9.0)	10.7 (11.3)	14.4 (15.2)
Unidentified compounds	0.2	1.0	—	—

^{a,b,c} See footnotes *a–d*, Table 1.^d On hydrogenation these compounds formed ethylcyclopentane. Ultraviolet spectra of the dienes shows absorption maximum at 262 and 288 nm.

* Traces.

cis- and *trans*-1,2-, 1,3-, and 1,4-dimethylcyclohexane were passed over the catalyst. It was also found that the individual xylenes did not undergo isomerization when passed over the same catalyst under the described conditions.

Another “measuring stick” used in this laboratory for evaluating acidity of platinum–alumina catalysts consisted in passing over the catalyst, 1,1-dimethylcyclohexane, and determining the composition of the aromatics formed (59). By passing this hydrocarbon over our “nonacidic” platinum–alumina catalyst at 404°C, and using

the described experimental conditions, it was found that 82% of 1,1-dimethylcyclohexane underwent reaction. The liquid product obtained was composed of 86.6% toluene, 0.7% benzene, 0.5% ethylbenzene, 7.8% *o*-, 2.7% *m*-, and 1.0% *p*-xylene.

The major part of the reaction consisted on demethanation resulting in the formation of toluene. The presence of xylenes could be attributed to a cationic skeletal isomerization of 1,1-dimethylcyclohexene, the assumed intermediate of the main reaction:

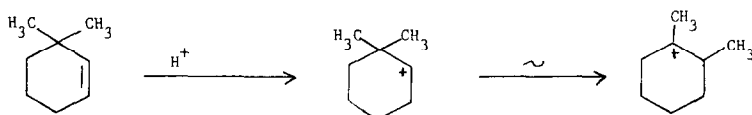


TABLE 5
Dehydrocyclization of Cycloheptane over
Platinum-Alumina^a at 500°C^b

Time on stream (min):	Conversion product composition (mole%)			
	30	70	110	165
Conversion:	98.4	91.5	78.7	68.8
Ethane	0.6	*	*	—
Propane	0.4	*	*	—
<i>n</i> -Butane	1.7	*	*	—
<i>n</i> -Pentane	0.1	*	*	—
3-Methylhexane	24.0	25.2	25.7	24.5
<i>n</i> -Heptane	9.4	11.2	7.5	7.8
1,2-Dimethylcyclopentanes	*	*	2.1	1.9
Ethylcyclopentane	1.2	0.9	1.0	1.0
Toluene	62.6	62.7	63.7	64.8

^{a,b} See footnotes *a* and *b*, Table 1.

* Traces.

This type of facile skeletal isomerization occurring on "nonacidic" alumina has been discussed previously (58). The cation once formed can undergo stepwise methyl migration, with an ultimate formation of *m*- and *p*-xylene.

The small amount of ethylbenzene formed could best be ascribed to a bond shift process. The rearrangement of 1,1-dimethylcyclohexane to ethylcyclohexane

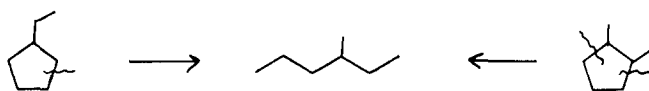
is similar to the rearrangement of neopentane to isopentane reported to occur over platinum film, and over platinum deposited on inert supports (32, 60-62).

Reactions of C₇ Hydrocarbons

The experimental results obtained from the conversion of C₇ alkanes and cyclanes are summarized in Tables 1-5.

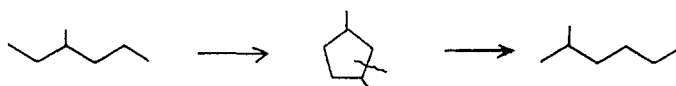
n-Heptane. One of the major products of the reaction is toluene, Table 1. Without a labeling technique it is, however, impossible to know whether the aromatization had occurred through a direct 1,6-ring closure of the original heptane, or from the products of the skeletal isomerization of the hydrocarbon.

1,2-Dimethylcyclopentanes and ethylcyclopentane were some of the products of reaction which resulted from a direct 1,5-ring closure of the original heptane. The total concentration of cyclopentanes in the C-7 fraction range from 34 to 50%, increasing with the time on stream, ethylcyclopentane being the predominant cyclopentane. The formation of 3-ethylpentane could best be explained by the hydrogenolysis of ethylcyclopentane, while 3-methylhexane could be produced from either ethyl- or 1,2-dimethylcyclopentane:



The formation of 2-methylhexane could be explained by a multiple 1,5-ring closure and opening involving an intermediate for-

mation of 1,3-dimethylcyclopentane from the closure of 3-methylhexane:



Such a path is, however, questionable because of the absence of 2,4-dimethylpentane and because only small traces of 1,3-

dimethylcyclopentane were detected in the reaction product. It is, however, possible that the formation of 2-methylhexane had

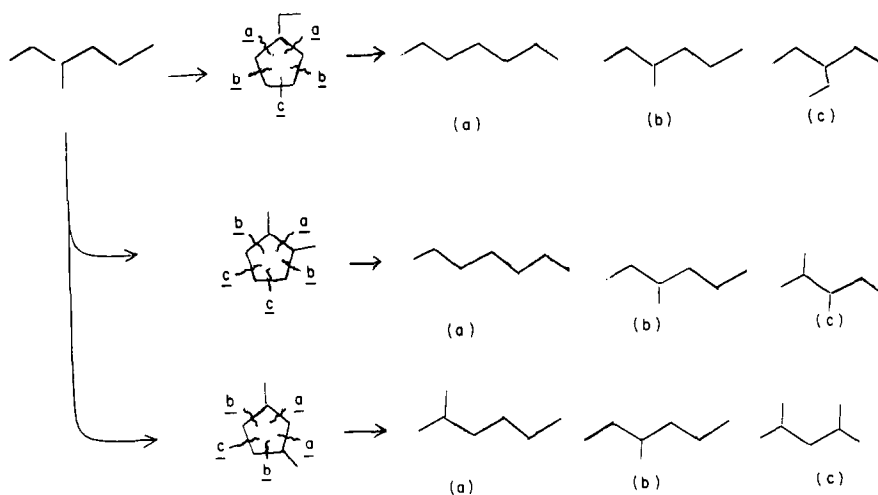
resulted from the isomerization of heptane through a bond shift process, similar to the reaction of butane to isobutane (32, 51, 63). This path is, however, also questionable on account of the results obtained with $[1-^{14}\text{C}]$ heptane (64).

The concentration of toluene in the C-7 fraction amounted to 31.9% initially and dropped to 21.7% with time on stream.

2-Methylhexane. Toluene was the major product of the conversion of the title hydrocarbon, Table 2. The presence of 2,4-dimethylpentane and 3-methylhexane could be explained from the cyclization of 2-methylhexane to 1,3-dimethylcyclopentane, followed by hydrogenolysis.

Cyclization of the 3-methylhexane to ethylcyclopentane, followed by hydrogenolysis, could explain the formation of *n*-heptane. However, the absence of ethylcyclopentane among the reaction products would strongly suggest that a bond shift process might be the principal path involved in the formation of both *n*-heptane and 2,4-dimethylpentane from the starting 2-methylhexane.

3-Methylhexane. The isomeric alkanes formed from 3-methylhexane could be explained as occurring *via* hydrogenolysis of the intermediate alkylcyclopentanes, produced by 1,5-carbon-carbon ring closure of the title hydrocarbon, Table 3.



Hydrogenolysis reaction may compete not only among the various alkylcyclopentanes which might have been formed in the reaction, but also among the various carbon-carbon bonds of the individual alkylcyclopentanes. Without further experimental data, using 1,2- and 1,3-dimethylcyclopentanes as a starting material, it is difficult to determine the origin of *n*-heptane, the main product of skeletal isomerization. The small amount of 2,4-dimethylpentane found in the product of the reaction is an indication that 1,3-dimethylcyclopentane might have partici-

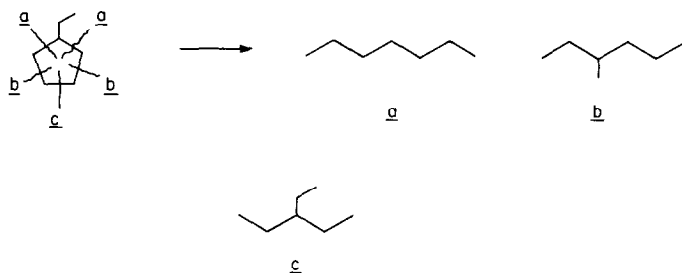
pated to a small extent only in the isomerization reaction.

Although ethylcyclopentane was one of the products of the reaction, it is surprising that 3-ethylpentane was not found among the reaction products. This may indicate that either the ethylcyclopentane produced did not undergo hydrogenolysis or that the hydrogenolysis of the ethylcyclopentane-adsorbed species on the catalyst occurs differently from that of a neutral ethylcyclopentane (Table 4).

Ethylcyclopentane. The alkanes formed from the reaction can be explained as oc-

curing by a direct hydrogenolysis of ethylcyclopentane, Table 4. It is assumed, based on Tables 1 and 3, that 1,2-dimethylcyclopentanes were produced mainly from the intermediate *n*-heptane formed by the

hydrogenolysis of the title compound. The ratio of the cleavage of each of the bonds in ethylcyclopentane can thus be estimated from the composition of the reaction products, e.g.,



The relative ratios of bonds a/b/c which underwent hydrogenolysis are about 4/4/1. Ethylcyclopentane yielded a large amount of isomeric conjugated dienes. A small amount of cycloheptane was also detected by means of a combination of gas chromatography and mass spectrometry.³

Cycloheptane. Of all the hydrocarbons studied cycloheptane was the most reactive, Table 5. The conversion amounted to 98.4 and 91.5%, during the time on stream of the first 30 min and 30–70 min. The main compound produced was toluene, amounting to about 64%, the remaining being 3-methylhexane and *n*-heptane in a ratio of 2.5 to 1.0. The presence of small amounts of ethylcyclopentane was also detected.

The facile formation of toluene could best be explained by a bond shift process to form methylcyclohexane which under the experimental conditions used undergoes quantitative conversion to toluene. It is attractive to explain the formation of the two hexanes which were produced through a direct conversion of a seven-membered ring to an adsorbed ethylcyclopentane species, which could then form 3-methylhexane and *n*-heptane by hydrogenolysis. The

absence, however, of 3-ethylpentane in the reaction product has yet to be explained.

EXPERIMENTAL PART

Preparation of Catalyst

The alumina (AL-0104 in T $\frac{1}{8}$ in. 480-005-45, 16–20 mesh, Harshaw Chemical Company, Cleveland, Ohio), which was used for the preparation of the catalyst, was calcined at 650°C for 4 h in a stream of a mixture of 2:1 nitrogen and oxygen. The 5.0 g of the alumina was added with vigorous stirring to a hot solution of 247 mg of diamino platinum dinitrite (Alfa Inorganics, Inc., Beverly, Mass.) in 2.5 ml of water. The excess of water was removed by evaporation with an infrared lamp. The platinum on alumina thus obtained, 3% Pt, was heated for 17 h at 400°C in a stream of a mixture of 2:1 nitrogen to oxygen, then in the presence of hydrogen at 350°C for 1 h, and then cooled at room temperature in the presence of nitrogen. The catalyst was screened to obtain 16–20 mesh particles.

Hydrocarbons

Cycloheptane, ethylcyclopentane, 2-, and 3-methylhexane were supplied by Aldrich Chemical Company, Inc., Milwaukee, Wis. *n*-Heptane was obtained from Phillips Petroleum Company, Bartlesville,

³ We wish to thank Arnaldo da Costa Faro, Jr., for the analysis.

Okla. 1,1-Dimethylcyclohexane was prepared by hydrogenation of 4,4-dimethylcyclohexene, which was synthesized by the method described previously (51, 63). All the hydrocarbons used in the reaction were over 99% pure, as tested by gas chromatography.

CONCLUSION

The mechanism of aromatization of heptanes over platinum–alumina catalyst proceeds differently from that occurring over chromia–alumina. With the latter catalyst skeletal isomerization accompanying aromatization occurs *via* a free-radical vinyl migration. There is very little if any 1,5-carbon–carbon ring closure and the 1,6-ring closure leading to aromatic hydrocarbons proceeds by a thermal cyclization of alkatrienes, followed by catalytic dehydrogenation to form aromatics.

In the case of platinum–alumina catalyst skeletal isomerization occurs by two competing processes: 1,5-carbon–carbon ring closure followed by hydrogenolysis, and to a smaller extent probably by a bond shift process. Cyclization *via* a direct 1,6-carbon ring closure over platinum–alumina catalyst seems to occur *via* cyclization of alkatrienes to cyclohexadienes.

There is evidence that alkylcyclopentane-adsorbed species, formed as intermediates in the reaction, undergo hydrogenolysis to alkanes, and the product of this reaction is not necessarily the same as that obtained when neutral alkylcyclopentanes are hydrogenolyzed.

The discovery of small amounts of cycloheptane in the product from the reaction of ethylcyclopentane is an indication that 1,7-ring closure might have also participated in the aromatization of the seven-carbon hydrocarbons. It is likely that cycloheptane has not been observed among the products of the reaction of heptanes because of the great ease with which it undergoes aromatization of toluene.

Contrary to suggestions proposed in the literature, experimental results obtained

with 1,1-dimethylcyclopentane indicate that ring expansion of cyclopentanes to cyclohexanes does not occur by a cationic mechanism.

Further research using carbon-labeled hydrocarbons and determining the position of the label in the recovered hydrocarbons would help to elucidate the mechanism of aromatization of alkanes over platinum-containing catalysts.

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