

resulting alcohol, and acetylation with acetyl chloride. 3-Methylhexane-5-C<sup>14</sup> was prepared in 94% yield by pyrolysis of 4-methylhexyl-2-C<sup>14</sup> 1-acetate at 560° and hydrogenation of the resulting olefin.

**3-Methyl-C<sup>14</sup>-hexane** was prepared in 16% over-all yield from propylmagnesium bromide by the procedure outlined in the text.

**Catalyst.**—The chromia-alumina catalyst was prepared according to the procedure described.<sup>4</sup> The alumina was precipitated from sodium aluminate and impregnated with chromic acid. The catalyst contained 13.8 wt. % of Cr<sub>2</sub>O<sub>3</sub>, its surface area was 89 m.<sup>2</sup>/g., and the average pellet weight was 0.022 g.

**Apparatus and Procedure. A. Aromatization.**—The apparatus and procedure for the aromatization were the same as those described earlier.<sup>11</sup>

**B. Separation of Aromatic Hydrocarbons from Reaction Product.**—The separation was accomplished using an F & M

Model 300 programmed-temperature gas chromatograph<sup>15</sup> with an 11 mm. × 2.4 m. preparative v.p.c. column filled with 5% 7,8-benzoquinoline on 30–60-mesh Chromosorb. The column temperature used was 75° with a helium flow rate of 105–114 cc./min. The liquid products obtained from radioactive compounds were before separation diluted with inactive toluene.

**C. Oxidation of Toluene.**—Toluene was oxidized to benzoic acid with alkaline potassium permanganate decarboxylated by heating in quinoline with copper oxide at 265° for 3 hr., and then both carbon dioxide and benzene were assayed for C<sup>14</sup> to obtain the isotope distribution.<sup>8</sup>

**D. Radiochemical Assay.**—The radiochemical assay of the benzoic acids and the decarboxylation products was the same that as previously described.<sup>16</sup>

(15) F & M Scientific Corp., Avondale, Pa.

(16) H. Pines and G. Benoy, *J. Am. Chem. Soc.*, **82**, 2483 (1960).

## Alumina: Catalyst and Support. XXVI.<sup>1</sup> Aromatization and Dehydroisomerization of Dimethylhexanes over Chromia-Alumina Catalyst. Contribution to the Mechanism of Aromatization<sup>2</sup>

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The aromatization and dehydroisomerization of the dimethylhexanes over nonacidic chromia-alumina-B catalyst was studied. Contrary to previous reports, the aromatization is preceded, to some degree, by skeletal isomerization. The isomerization reactions can be explained by assuming 1,2 and/or 1,3 methyl-carbon insertion reactions. However, in some cases it appears necessary to include cycloheptane- and/or cyclooctane-adsorbed species prior to aromatization. When cyclization to alkylcyclopentane derivatives is possible, the catalyst is deactivated more rapidly than when cyclopentane species cannot be formed. Formation of fulvene derivatives from the cyclopentanes followed by their facile polymerization would explain these results.

Studies on various trimethylpentanes in this and other laboratories<sup>3,5</sup> over nonacidic chromia-alumina catalyst have shown that considerable amounts of aromatic compounds have been formed, necessitating the involvement of skeletal isomerizations prior to ring closure. Since it has been shown that cationic isomerization cannot be involved over this catalyst,<sup>6</sup> it was proposed that 1,2 and 1,3 methyl-carbon insertions were involved during the isomerization steps. Later the picture was made even more complex when it was shown that C<sub>7</sub> and/or C<sub>8</sub> rings were formed from 2- and 3-methylhexane and 2,3,4-trimethylpentane prior to aromatization.<sup>1,7</sup>

It has been reported that the C<sub>8</sub> aromatics formed from 2,5-dimethylhexane consisted of 80% *p*-xylene and from 2,3-dimethylhexane, 90% *o*-xylene and 10% *p*-xylene.<sup>8</sup> Owing to the above described results it was felt that a reinvestigation of the aromatization of the various dimethylhexanes was necessary. Therefore 2,2-dimethylhexane (I), 3,3-dimethylhexane (II), 2,3-dimethylhexane (III), 3,4-dimethylhexane (IV), 2,4-dimethylhexane (V), and 2,5-dimethylhexane (VI) were synthesized and aromatized over nonacidic

chromia-alumina-B catalyst. If only 1,6 ring closure were operating to give the aromatic compounds, then each dimethylhexane would yield only one aromatic compound: namely, I and II, toluene; III and IV, *o*-xylene; V, *m*-xylene; and VI, *p*-xylene. If however, methyl-carbon insertion, *via* free-radical vinyl migration, occurs prior to ring closure, a combination of many of the aromatic compounds should be formed from each dimethylhexane.

**Procedure. A. Apparatus and Technique.**—The same apparatus was used as described previously.<sup>4</sup> The temperature of the catalyst was kept constant by an automatic temperature controller, while measured with thermocouples held inside and outside the catalyst bed. The amount of catalyst was 14.1 ml. (10.3 g.) mixed with 38.6 g. of glass beads of approximately the same dimension. All experiments were made at atmospheric pressure. The products were collected at Dry Ice-acetone temperature. In this manner, all the liquid and gaseous products were trapped with the exception of hydrogen and a small amount of methane; the latter was collected in a liquid nitrogen trap while the hydrogen was measured with a wet-test meter. Collecting the product at this low temperature simplified the analytical procedure since practically all of the gaseous products were dissolved in the liquid.

**B. Analytical Procedure.**—The products were analyzed by gas chromatography using an F & M Model 300 programmed-temperature gas chromatograph by a procedure previously described.<sup>4</sup>

**C. Catalyst.**—Nonacidic chromia-alumina catalyst was prepared as described previously.<sup>6</sup> The alumina was precipitated from potassium aluminate and im-

(1) For paper XXV of this series, see H. Pines and J. W. Dembinski, *J. Org. Chem.*, **30**, 3537 (1965).

(2) (a) Paper XV of the series "Aromatization of Hydrocarbons"; for paper XIV, see ref. 1. (b) This research was supported by the Atomic Energy Commission Contract AT(11-1)-1096.

(3) F. R. Cannings, A. Fisher, J. F. Ford, P. D. Holmes, and R. S. Smith, *Chem. Ind. (London)*, 228 (1960).

(4) H. Pines and S. M. Csicsery, *J. Catalysis*, **1**, 313 (1962).

(5) S. M. Csicsery and H. Pines, *J. Am. Chem. Soc.*, **84**, 3939 (1962).

(6) H. Pines and C. T. Chen, *ibid.*, **82**, 3562 (1960).

(7) C. T. Goetschel and H. Pines, *J. Org. Chem.*, **29**, 399 (1964).

(8) A. H. Steiner in "Catalysis," Vol. IV, P. H. Emmett, Ed., Reinhold Publishing Corp., New York, N. Y., 1956, pp. 529–560.

TABLE I  
PER CENT DISTRIBUTION OF AROMATIC PRODUCTS FROM THE DEHYDROCYCLIZATION OF VARIOUS HYDROCARBONS OVER CHROMIA-ALUMINA-B CATALYST

Aromatic compd.	2,2-Dimethylhexane			3,3-Dimethylhexane			2,3-Dimethylhexane			3,4-Dimethylhexane			2,4-Dimethylhexane			2,5-Dimethylhexane		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Benzene	5.7	7.9	12.7	13.9	12.8	13.8	31.0	25.7	6.8	6.5	16.8	17.8	29.6	12.1	11.4	...	...	...
Toluene	52.0	57.4	50.0	60.7	53.8	48.0	9.2	15.6	14.3	10.5	18.9	20.7	10.5	32.2	57.6	16.4	16.8	14.7
<i>o</i> -Xylene	11.1	8.5	11.5	3.8	2.1	Trace	47.3	36.3	49.6	62.4	22.4	17.9	1.1	1.2	...	2.9	1.9	Trace
<i>m</i> -Xylene	21.5	11.6	7.3	11.9	25.1	34.6	4.6	5.0	6.8	3.1	2.1	2.1	55.4	48.1	27.1	10.9	7.5	2.6
<i>p</i> -Xylene	6.1	8.8	12.1	6.2	4.1	3.6	4.1	1.7	1.5	10.9	27.9	29.3	2.3	4.1	3.8	69.8	73.8	82.7
Ethylbenzene	3.6	5.9	7.5	3.5	2.0	Trace	3.8	15.6	21.1	6.6	11.9	12.2	1.2	2.3	...	Trace	Trace	Trace
Styrene	...	...	...	...	...	...	...	...	...	Trace	Trace	Trace	...	...	...	...	...	...

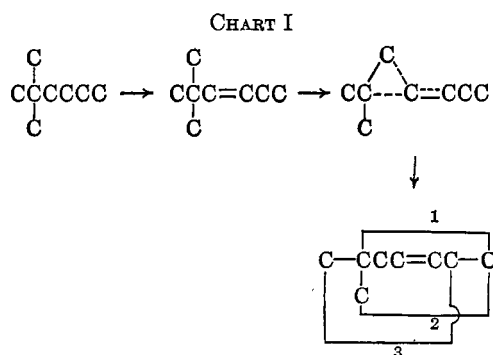
pregnated with chromic acid. Surface area, measured by the B.E.T. method, was 89 m.<sup>2</sup>/g. The average pellet weight was 0.022 g. and contained 13.8 wt. % chromia.

**D. Hydrocarbons.**—All the hydrocarbons were synthesized in greater than 99% purity as determined by v.p.c.

### Discussion of Results

The dimethylhexanes give aromatic products which cannot completely be explained by direct 1,6 ring closure. The methyl-carbon insertion, which has been proposed to explain the isomerization reactions of 3,3-dimethylbutane,<sup>9</sup> will also explain the aromatics produced in the present study. The 1,2 vinyl group migrations discussed by Slauch, *et al.*,<sup>10</sup> to explain the free-radical rearrangements of branched hydrocarbons with iodine at high temperatures appear to have application over chromia-alumina catalysts. Table I summarizes the aromatic distributions for the various dimethylhexanes over nonacidic chromia-alumina catalyst.

**2,2-Dimethylhexane.**—The conditions of dehydrogenation and experimental results are summarized in Table II. As observed, not just toluene was produced, but also benzene, ethylbenzene, and the xylenes. These latter products can only be explained by assuming a skeletal rearrangement prior to cyclization. Methyl-carbon insertion *via* 1,2 vinyl migration<sup>9,10</sup> would explain these rearrangements (Chart I). The 2-methylheptane species produced could give only toluene or *m*-xylene by 1,6 ring closure. However, 1,7 ring closure as shown previously<sup>7</sup> would yield methylcycloheptane which can give all of the aromatics produced.



1. toluene (1,6 ring closure)
2. methylcycloheptane (1,7 ring closure)  
toluene, *o*-, *m*-, *p*-xylene, and ethylbenzene
3. *m*-xylene (1,6 ring closure)

(9) H. Pines and C. T. Goetschel, *J. Org. Chem.*, **30**, 3530 (1965).

(10) L. H. Slauch, R. D. Mullineaux, and J. H. Raley, *J. Am. Chem. Soc.*, **85**, 3180 (1963), mechanism IV.

TABLE II  
DEHYDROGENATION OF 2,2-DIMETHYLHEXANE OVER CHROMIA-ALUMINA-B CATALYST AT 528° AND A CONTACT TIME OF 3 SEC.

Conversion products	Composition, mole % <sup>a</sup>			
	Cut (length in min.)			
	1 (5)	2 (7.5)	3 (10)	4 (18)
Methane	6.82	6.36	4.40	3.71
Ethane + ethylene	0.83	0.80	1.14	1.08
Propane + propylene	1.26	1.69	2.55	2.67
Isobutylene	2.93	0.71	1.41	0.21
Isobutane	0.92	0.59	0.48	0.15
<i>n</i> -Butenes	0.84	0.80	0.38	0.06
Neopentane + <i>n</i> -butane	0.55	0.43	0.34	0.09
<i>n</i> -Pentenes	0.06	0.06	0.03	0.02
Neohexene	0.30	0.37	0.25	0.03
Neohexane	0.38	0.31	0.18	0.02
<i>n</i> -Pentane	0.22	0.44	0.20	0.03
2-Methylhexane + olefins	1.19	1.76	1.04	1.19
3-Methylheptane + olefins	0.25	0.15	0.05	0.04
2-Methylheptane + olefins	0.41	0.26	0.09	0.05
2,2-Dimethylhexenes	6.65	3.93	2.18	2.23
2,2-Dimethylhexane	73.80	80.06	84.79	87.98
1,1-Dimethylcyclohexane + olefins	0.24	0.16	0.04	0.03
Methylcycloheptane + olefins	0.07	0.04	0.02	0.01
Benzene	0.08	0.08	0.05	0.05
Toluene	1.14	0.59	0.20	0.21
<i>o</i> -Xylene	0.28	0.10	0.05	0.02
<i>m</i> -Xylene	0.54	0.14	0.04	0.03
<i>p</i> -Xylene	0.15	0.10	0.05	0.05
Ethylbenzene	0.09	0.07	0.04	0.04
Total conversion of 2,2-dimethylhexane	26.2	19.9	15.2	12.0

<sup>a</sup> Total carbonaceous materials: 1.0%.

**3,3-Dimethylhexane.**—Aromatics other than toluene were produced from the aromatization of the title alkane (Table III). The 1,2 methyl-carbon insertion would explain the aromatics produced. As observed in Table I, the distribution of *m*-xylene is time dependent and it increases with the length of the experiment in the case of 3,3-dimethylhexane, owing to the possible formation of 4-methylheptane skeleton. Methylcycloheptene-adsorbed species seem to participate in the formation of the aromatics.

**2,3- and 3,4-Dimethylhexanes.**—Aromatic compounds other than the expected *o*-xylene were produced in considerable amounts from 2,3- and 3,4-dimethylhexane (Tables IV and V). In the case of a 1,2 methyl-carbon insertion, 2,3-dimethylhexane should yield predominately 2- and 4-methylheptene-adsorbed species producing *m*-xylene as the aromatic product. However, 3,4-dimethylhexane would give a 3-methylheptene-adsorbed species yielding ethylbenzene and *o*- and *p*-xylene (Chart IIa). In addition, cyclobutane-adsorbed species would create a *n*-octane-adsorbed

TABLE III  
DEHYDROGENATION AND DEHYDROCYCLIZATION OF  
3,3-DIMETHYLHEXANE OVER CHROMIA-ALUMINA-B AT 530°  
AND CONTACT TIME OF 3.0 SEC.

Conversion products	Composition, mole % <sup>a</sup>		
	Cut <sup>b</sup>		
	1	2	3
Methane	9.13	3.49	1.94
Ethane + ethylene	0.42	0.60	0.64
Propane	1.06	1.63	1.49
Propylene	2.59	3.35	3.70
Neopentane	0.16	0.19	0.30
Isopentane	2.41	2.06	2.06
Methylbutenes	7.21	7.82	8.46
2,2-Dimethylbutane	1.93	0.69	0.91
<i>gem</i> -Dimethylbutenes	3.07	3.41	4.08
2-Methylpentane	1.37	1.93	1.78
Isoprene	0.13	0.15	0.22
Methylpentenes	0.61	0.49	0.51
<i>gem</i> -Dimethylpentenes	1.73	1.60	1.85
3,3-Dimethylpentane	0.49	1.37	0.71
3,3-Dimethylhexane	62.48	67.63	69.37
3,3-Dimethylhexenes	4.32	2.75	1.42
3-Methylheptane (enes)	0.08	0.16	0.01
4-Methylheptane (enes)	0.38	0.35	0.30
1,1-Dimethylcyclohexane (enes)	0.09	0.06	0.06
Unknown	0.12	0.09	0.08
Cyclooctane (enes)	Trace	Trace	0.01
Benzene	0.06	0.02	0.01
Toluene	0.27	0.09	0.05
<i>o</i> -Xylene	0.02	0.01	Trace
<i>m</i> -Xylene	0.06	0.04	<0.04
<i>p</i> -Xylene	0.03	0.01	<0.01
Ethylbenzene	0.01	0.01	Trace
Total conversion of 3,3-dimethylhexane	38.0	22.5	30.7

<sup>a</sup> Total carbonaceous materials: 1.22%. <sup>b</sup> Length of cuts: 4.0 min.

TABLE IV  
DEHYDROGENATION AND DEHYDROCYCLIZATION OF  
2,3-DIMETHYLHEXANE OVER CHROMIA-ALUMINA-B AT 528°  
AND CONTACT TIME OF 3.0 SEC.

Conversion products	Composition, <sup>a</sup> mole %		
	Cut (length in min.)		
	1 (6.0)	2 (6.0)	3 (8.0)
Methane	0.21	0.05	0.07
Ethane + ethylene	0.13	0.18	0.20
Propane	0.76	0.86	0.94
Propylene	0.75	0.70	0.66
<i>n</i> -Butenes	0.91	0.62	0.56
Isopentane	0.14	0.07	0.09
<i>n</i> -Pentane	0.19	0.19	0.53
Methylbutenes	0.77	0.58	0.53
<i>n</i> -Pentenes	0.81	0.58	0.52
2,3-Dimethylbutane	0.42	0.29	0.27
Dimethylbutenes	0.29	0.14	0.14
Isoprene	0.04	0.02	...
1,3-Pentadienes	0.13	0.04	Trace
2,3-Dimethylhexane	85.95	92.67	93.67
2,3-Dimethylhexenes	6.40	2.83	2.02
Benzene	0.64	0.05	0.01
Toluene	0.19	0.03	0.02
<i>o</i> -Xylene	0.97	0.07	0.07
<i>m</i> -Xylene	0.10	0.01	0.01
<i>p</i> -Xylene	0.09	0.01	80.01
Ethylbenzene	0.08	0.03	0.03
1,2-Dimethylcyclohexane	0.03	0.02	0.01
Unknown	0.02	0.01	0.02
Cyclooctane	0.01	0.01	0.01
Total conversion of 2,3-dimethylhexane	14.1	7.3	6.3

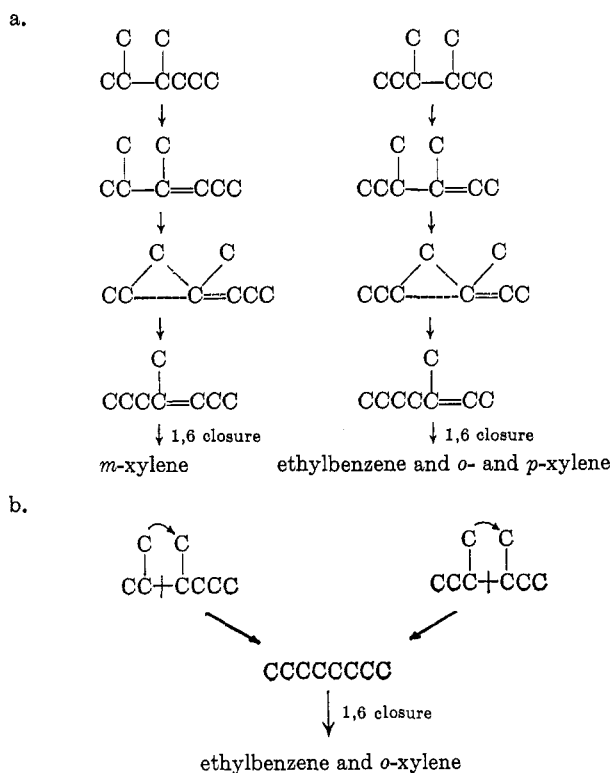
<sup>a</sup> Total carbonaceous materials: 1.92%.

TABLE V  
DEHYDROGENATION AND DEHYDROCYCLIZATION OF  
3,4-DIMETHYLHEXANE OVER CHROMIA-ALUMINA-B AT 526°

Conversion products	Composition, mole % <sup>a</sup>		
	Cut <sup>b</sup>		
	1	2	3
Methane	2.40	1.55	1.45
Ethane + ethylene	0.11	0.13	0.20
Propane	0.11	0.10	0.09
Propylene	0.30	0.04	0.36
Isobutane	0.02	0.02	0.01
<i>n</i> -Butane	1.65	0.89	0.73
Isobutylene	0.03	0.04	0.01
<i>n</i> -Butenes	2.87	2.25	1.82
Methylbutenes	0.12	0.09	0.09
1,3-Butadiene	0.09	0.10	0.08
2-Methylpentane	0.07	0.02	0.02
2,3-Dimethylbutane	0.26	0.20	0.17
3-Methylpentane	0.29	0.14	0.11
Methylpentenes	0.92	0.63	0.52
Dimethylbutenes	0.69	0.63	0.64
2,3-Dimethylpentane	0.11	0.08	0.04
2,3-Dimethylpentenes	0.68	0.48	0.47
3,4-Dimethylhexane	73.45	84.75	86.64
3,4-Dimethylhexenes	6.55	5.23	4.13
<i>n</i> -Octane (enes)	0.20	0.20	0.17
3-Ethylhexane (enes)	0.15	0.13	0.25
3-Methylheptane (enes)	0.76	0.26	0.25
Methylcycloheptane (enes)	0.34	0.47	0.50
Cyclooctane (enes)	0.02	0.03	0.04
Benzene	0.51	0.20	0.22
Toluene	0.82	0.23	0.25
<i>o</i> -Xylene	4.87	0.27	0.22
<i>m</i> -Xylene	0.24	0.03	0.03
<i>p</i> -Xylene	0.85	0.34	0.36
Ethylbenzene	0.51	0.14	0.15
Styrene	Trace	Trace	Trace
Total conversion of 3,4-dimethylhexane	24.6	15.3	13.4

<sup>a</sup> Total carbonaceous materials: 2.13%. <sup>b</sup> Length of cuts: 5.0 min.

CHART II



species in either case, thus leading to ethylbenzene and *o*-xylene via 1,6 ring closure (Chart IIb). The cyclo C<sub>7</sub>- and/or C<sub>8</sub>-adsorbed species would account for the *p*-xylene produced from 2,3-dimethylhexane and the *m*-xylene from 3,4-dimethylhexane. Indeed, small amounts of methylcycloheptane and cyclooctane were observed as reaction products, after selective hydrogenation. In all previous instances when cycloheptane and/or cyclooctane intermediates were proposed, they were time dependent, diminishing as the reaction proceeded. This is in agreement with the present data where the *p*- and *m*-xylenes diminish with time for 2,3- and 3,4-dimethylhexane, respectively.

**2,4- and 2,5-Dimethylhexanes.**—Direct 1,6 ring closure would yield *m*- and *p*-xylene for 2,4- and 2,5-dimethylhexane, respectively. However, such was not the case (Tables VI and VII), indicating that 1,2

TABLE VI  
DEHYDROGENATION AND DEHYDROCYCLIZATION OF  
2,4-DIMETHYLHEXANE OVER CHROMIA-ALUMINA-B AT 527°  
AND CONTACT TIME OF 3.0 SEC.

Conversion products	Composition, mole % <sup>a</sup>		
	Cut (length in min.)		
	1 (6.0)	2 (7.0)	3 (9.0)
Methane	0.20	0.16	0.06
Ethane + ethylene	0.09	0.12	0.11
Propane + propylene	2.01	0.62	0.63
Isobutane	1.37	1.39	1.23
<i>n</i> -Butane	1.01	0.08	0.52
Isobutylene	1.87	1.67	1.17
<i>n</i> -Butenes	0.65	0.98	0.96
1,3-Butadiene	0.01	0.02	0.04
Isopentenes	1.46	1.14	0.91
2-Methylpentane	0.04	0.16	0.07
2-Methylpentenes	0.27	0.68	0.62
2,4-Dimethylhexane	78.40	87.34	90.77
2,4-Dimethylhexenes	6.37	4.45	2.57
2-Methylheptane	0.16	0.11	0.08
3-Methylheptane	1.85	0.37	0.24
3-Ethylhexane	0.31	0.12	...
1,3-Dimethylcyclohexane	Trace	Trace	Trace
Benzene	1.17	0.07	<0.01
Toluene	0.41	0.20	<0.03
<i>o</i> -Xylene	0.04	0.01	...
<i>m</i> -Xylene	2.19	0.29	0.01
<i>p</i> -Xylene	0.09	0.03	<0.01
Ethylbenzene	0.05	0.01	...
Total conversion of 2,4-dimethylhexane	21.6	12.66	9.23

<sup>a</sup> Total carbonaceous materials: 1.04%.

methyl-carbon insertion processes were operating. Owing to the lack of vicinal methyl groups, the 1,3 methyl-carbon insertion process is not expected. However, 1,2 methyl-carbon insertions are possible yielding 2- and 3-methylheptene-adsorbed species from 2,4-dimethylhexane and 2-methylheptene species from 2,5-dimethylhexane (Chart III). Large-ring intermediates again would account for the aromatic compounds produced but not predicted by Chart III.

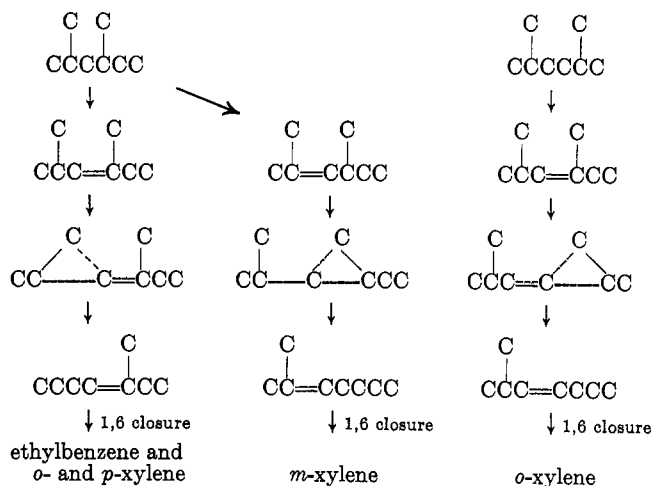
**Conclusion.**—The major products of aromatization are those derived from 1,6 ring closure. Skeletal isomerization prior to cyclization is found to be a large contributor during the dehydrogenation and dehydrocyclization of the dimethylhexanes. Methyl-carbon insertion reactions followed by 1,6, 1,7, and/or

TABLE VII  
DEHYDROGENATION AND DEHYDROCYCLIZATION OF  
2,5-DIMETHYLHEXANE OVER CHROMIA-ALUMINA-B AT 529°  
AND CONTACT TIME OF 3.0 SEC.

Conversion products	Composition, mole % <sup>a</sup>		
	Cut (length in min.)		
	1 (6.0)	2 (8.0)	3 (8.0)
Methane	0.09	0.04	0.05
Ethane + ethylene	0.06	0.12	0.14
Propane + propylene	2.47	1.89	2.41
<i>n</i> -Butane	0.06	0.03	0.04
Isobutane	2.94	2.62	2.99
Isobutylene	3.17	2.84	3.35
<i>n</i> -Butenes	0.15	0.09	0.14
Isopentane	0.85	0.37	0.37
Methylbutenes	3.66	3.08	3.11
2-Methylpentane + olefins	0.17	0.42	0.78
2-Methylheptane + olefins	1.55	2.02	1.87
2,5-Dimethylhexane	66.77	68.34	68.87
2,5-Dimethylhexenes	9.78	10.00	9.74
Toluene	1.36	1.37	0.90
<i>o</i> -Xylene	0.24	0.15	Trace
<i>m</i> -Xylene	0.90	0.61	0.16
<i>p</i> -Xylene	5.78	6.01	5.08
Ethylbenzene	Trace	Trace	Trace
Total conversion of 2,5-dimethylhexane	33.2	31.7	31.1

<sup>a</sup> Total carbonaceous materials: 0.20%.

CHART III



1,8 ring closure explain the composition of the aromatics produced.

### Experimental Section

**2,2-Dimethylhexane.**—A solution of 57.7 g. (0.80 mole) of *n*-butyraldehyde in 60 ml. of absolute ether was added to a Grignard solution prepared from 21.4 g. (0.88 g.-atom) of magnesium in 200 ml. of absolute ether and 74.1 g. (0.80 mole) of *t*-butyl chloride in 100 ml. of absolute ether. The alcohol, 2,2-dimethyl-3-hexanol (57.7 g., yield 44.4%), distilled at 142–144°; it was over 99% pure by gas chromatography. To a stirred solution of 48 ml. of dry pyridine and 26 g. (0.20 mole) of 2,2-dimethyl-3-hexanol cooled to 0° was added dropwise 27.3 g. (0.22 mole) of acetyl chloride. Following the addition, stirring was continued for 2 hr. at 0° followed by 3 hr. at room temperature. The mixture was then added to 18% aqueous hydrochloric acid solution (0.4 mole HCl) at 0° and stirred for 1 hr. The whole was extracted with four 50-ml. portions of ether. The combined ether extracts were washed with 10% sodium carbonate and water and dried over anhydrous sodium sulfate. The ether was removed by distillation, and the residue was vacuum distilled, yielding 31 g. (90%) of 2,2-dimethyl-3-hexyl acetate, b.p. 65–68°. The acetate, 31 g., was pyrolyzed by passing it dropwise over a vertical bed of glass beads 36 cm. long

at a temperature of approximately 550°. The product was collected in a 10% sodium carbonate solution to neutralize the acetate acid formed. The yield of 2,2-dimethyl-3-hexene was 16 g. (70%), and its purity was 98% by gas chromatography. The 2,2-dimethyl-3-hexene was hydrogenated using 5% palladium on charcoal in a Parr hydrogenation apparatus at an initial hydrogen pressure of 42 p.s.i. The 2,2-dimethylhexane obtained had a purity of 99%.

**3,3-Dimethylhexane.**—The coupling reaction between the Grignard reagent prepared from 57.0 g. (0.53 mole) of *t*-amyl chloride and 14.0 g. (0.58 g.-atom) of magnesium turnings with 24.2 g. (0.20 mole) of allyl bromide gave a crude product weighing 23 g. Chromatographing the crude product through silica gel yielded 7.0 g. (31.3%) of 4,4-dimethyl-1-hexene which had a purity of over 99%. Hydrogenation of 4,4-dimethyl-1-hexene in a Parr apparatus with platinum oxide catalyst and an initial hydrogen pressure of 45 p.s.i. yielded pure 3,3-dimethylhexane,  $n^{25}_D$  1.4028 (lit.<sup>12</sup>  $n^{25}_D$  1.4001).

**2,3-Dimethylhexane.**—The Grignard reaction of *n*-propylmagnesium bromide, prepared from 61.5 g. (0.50 mole) of 1-bromopropane and 13.2 g. (0.55 g.-atom) of magnesium turnings, with 34.4 g. (0.40 mole) of 3-methyl-2-butanone yielded a crude product weighing 43.5 g. Distillation yielded 33 g., 63%, of 2,3-dimethyl-3-hexanol, b.p. 78° (45 mm.),  $n^{25}_D$  1.4280. A mixture of 20 g. (0.15 mole) of 2,3-dimethyl-3-hexanol, 5.0 g. (0.06 mole) of dry pyridine, and 23.4 g. (0.20 mole) of phenyl isocyanate were heated together at 140° for 2 hr., then allowed to distil with the bath temperature raised to 205°. The distil-

(11) C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

(12) F. D. Rossini, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953, p. 103.

late was added to 5 ml. of water and shaken for 5 min. The solid material was filtered off, and the filtrate was washed with three 25-ml. portions of 10% aqueous acetic acid followed by 25 ml. of 10% aqueous sodium bicarbonate, and dried over anhydrous sodium carbonate. The 2,3-dimethylhexenes were then chromatographed using alumina and pentane, yielding 12.8 g. (74%). The olefinic mixture was hydrogenated as before using platinum oxide catalyst. The title alkane was over 99.9% pure, according to v.p.c.,  $n^{25}_D$  1.3983 (lit.<sup>12</sup>  $n^{25}_D$  1.3988).

**3,4-Dimethylhexane.**—A crude product of 22.1 g. of 3,4-dimethyl-3-hexanol was obtained from the Grignard reaction of 1 mole of 2-butyilmagnesium chloride with 1 mole of 2-butanone. The 22.1 g. (0.17 mole) of crude alcohol was dehydrated by the procedure described above using 4.86 g. of dry pyridine and 40.0 g. of phenyl isocyanate. The yield of 3,4-dimethylhexenes was 11 g. (58%). Hydrogenation of the olefinic mixture using platinum oxide yielded the title alkane of over 99% purity by v.p.c.

**2,4-Dimethylhexane.**—The reaction of 185 g. (1.7 moles) of ethyl bromide and 43.3 g. (1.8 g.-atoms) of magnesium turnings followed by 150 g. (1.5 moles) of methyl isobutyl ketone yielded 138 g., 71%, of pure 2,4-dimethyl-4-hexanol, b.p. 72° (38 mm.),  $n^{25}_D$  1.4241. The dehydration was accomplished as described before using 100 g. (0.77 mole) of 2,4-dimethyl-4-hexanol, 20 g. of dry pyridine, and 117 g. (0.98 mole) of phenyl isocyanate. The 2,4-dimethylhexenes obtained amounted to 75.3 g., yield 87%. Hydrogenation of the olefins using 5% palladium on charcoal gave the title paraffin which, by v.p.c., was 99% pure.

**2,5-Dimethylhexane.**—Hydrogenation of 2,5-dimethyl-1,5-hexadiene (Eastman Organic Chemicals No. 8778), using 5% palladium-on-charcoal catalyst, gave the desired paraffin of over 99% purity.

## Alumina: Catalyst and Support. XXVII.<sup>1</sup> Aromatization of Methylcycloheptane and Methyl-C<sup>14</sup>-cycloheptane over Chromia-Alumina Catalyst. Contribution to the Mechanism of Aromatization<sup>2</sup>

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The aromatization of methylcycloheptane and methyl-C<sup>14</sup>-cycloheptane was studied. The fact that fairly large amounts of methylheptenes and *n*-octenes were found in the reaction product and that some of the carbon-14 was distributed in the ring of the aromatics suggests that at least part of the aromatization occurred through a cleavage of the methylcycloheptane ring. The acyclic compounds once formed do not just cyclize to the aromatics but may rearrange *via* methyl-carbon insertion reactions and/or cyclooctane species.

During the many studies given to the aromatization reaction both from this laboratory and others,<sup>1,3-6</sup> methylcycloheptane has been proposed as a possible intermediate prior to aromatization. It was assumed all possible aromatics, C<sub>6</sub>-C<sub>8</sub>, could be formed from such an intermediate. However, a complete product analysis was not reported. Such an analysis would be helpful and possibly indicate a pathway between methylcycloheptane and the aromatic compounds. One postulated mechanism<sup>6</sup> was a direct collapse of the methylcycloheptane to the aromatic compounds. Such a mechanism would yield little acyclic compounds.

However, since cracking always accompanied the aromatization, the formation of acyclic compounds would not mean, necessarily, that the "collapse" mechanism is incorrect. Therefore, to examine more closely the mechanism of aromatic formation from methylcycloheptane, the methyl group was labeled with carbon-14. A direct collapse of the methylcycloheptane ring to the aromatic compounds would necessitate the carbon-14 to reside totally in the side chains. However, should the methylcycloheptane first open to acyclic compounds followed by closure to aromatics, the carbon-14 would be distributed partially in the ring (Chart I).<sup>7</sup>

**Procedure. A. Methylcycloheptane.**—This hydrocarbon was synthesized in over 99% purity and 69% over-all yield by dehydration of 1-methyl-1-cycloheptanol with phenylisocyanate and reducing the olefin with a platinum catalyst.

(1) For paper XXVI of this series, see H. Pines, C. T. Goetschel, and J. W. Dembinski, *J. Org. Chem.*, **30**, 3540 (1965).

(2) (a) Paper XVI of the series "Aromatization of Hydrocarbons"; for paper XV, see ref. 1. (b) This research was supported by the Atomic Energy Commission Contract AT (11-1)-1096.

(3) F. R. Cannings, A. Fisher, J. F. Ford, P. D. Holmes, and R. S. Smith, "Radioisotopes in the Physical Sciences and Industry," International Atomic Energy Agency, Vienna, 1962, pp. 205-216.

(4) H. Pines, C. T. Goetschel, and S. M. Csicsery, *J. Org. Chem.*, **28**, 2713 (1963).

(5) C. T. Goetschel and H. Pines, *ibid.*, **29**, 399 (1964).

(6) H. Pines and C. T. Chen, *J. Am. Chem. Soc.*, **82**, 3562 (1960).

(7) The exact attachment of the hydrocarbon to the catalyst, denoted by an asterisk (Chart Ia), is purely for illustrative purposes. Although the hydrocarbon must be adsorbed on the catalyst before any reaction will occur, the attachment may be other than that indicated.